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Atomic force microscopy of bamboo-shaped multiwalled carbon nanotube structures

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Abstract

Atomic force microscopy (AFM) was employed for the morphology measurements of bamboo-shaped multiwalled carbon nanotubes (BS-MWNTs) grown by thermal chemical vapor deposition on Fe catalyst deposited SiO_2/Ti substrates. Greater diameters and compartment distances of the bamboo structures were observed for the BS-MWNTs grown at 950 °C than for those grown at 850 °C.

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1. Introduction

Carbon nanotubes (CNTs) are of great interest because of their fascinating electronic, chemical, and mechanical properties [1–4]. The CNTs have electrical properties dependent on the structure such as the diameter and the chirality [5–7]. Therefore, structure control of the CNTs is a very important subject in the field. Different methods have been used to synthesize the CNTs, including arc discharge [8], laser ablation [9], pylosis [10], organometallic precursor pyrolysis [11], plasma enhanced thermal chemical vapor deposition (CVD) [12], and thermal CVD [13]. Because the CVD method has many controllable parameters for the growth of the CNTs, such as the plasma intensity, composition of precursors, and the catalyst particle size [12,14–17], a number of groups have employed the CVD methods for the purpose of structure control. Recently bamboo-shaped multiwalled carbon nanotubes (BS-MWNTs), synthesized by thermal CVD on catalytic film deposited substrates, were reported [13]. The BS-MWNTs have compartment structures and discontinuous graphitic sheet regions exist near the compartments [18]. For their structural uniqueness, the BS-MWNTs are expected to be applied in various cases. For example, adhesion of particles at the discontinuous sheet region can be useful for gas sensor and storage applications, and improved mechanical stability is expected from the bamboo structure. Furthermore, the discontinuous graphitic sheet regions may be employed as gate electrodes for sub-μm size 1-D transistors.

In this work, the bamboo structures of BS-MWNTs were studied by atomic force microscopy (AFM). While transmission electron microscopy (TEM) only gives information on the intrinsic structures of the CNTs, with AFM one is able to not only observe the structures of the CNTs [19] but also measure their electrical properties [20] and manipulate them [21,22]. Thus, the AFM applications on the investigation of the bamboo structures of the BS-MWNTs are very important as a pre-process of the electrical measurements of the BS-MWNTs by modified AFM.

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2. Experiments

For the growth of the BS-MWNTs, 20 mm × 30 mm size p-type Si (100) substrates with a resistivity of 15 Ωcm were thermally oxidized. The thickness of the silicon oxide (SiO_2) layer was estimated to be approximately 300 nm. A 1 μm-thick Ti film, used as electrode for bulk resistivity measurements [23], was thermally deposited on the SiO_2 substrate, and a 100-nm-thick Fe film was thermally deposited on a SiO_2/Ti layer. The Fe-deposited SiO_2/Ti substrates were dipped in a diluted HF solution and then loaded with face-down direction on a quartz boat placed in a quartz CVD reactor. The deposited Fe film was pretreated at 850 and 950 °C by NH_3 gas in order to form the Fe particles in nanometer size. The CNTs were grown on the Fe particles using C_2H_2 gas with a flow rate of 30 sccm for 10 min at the same temperature of NH_3 pretreatment in atmospheric pressure [24].

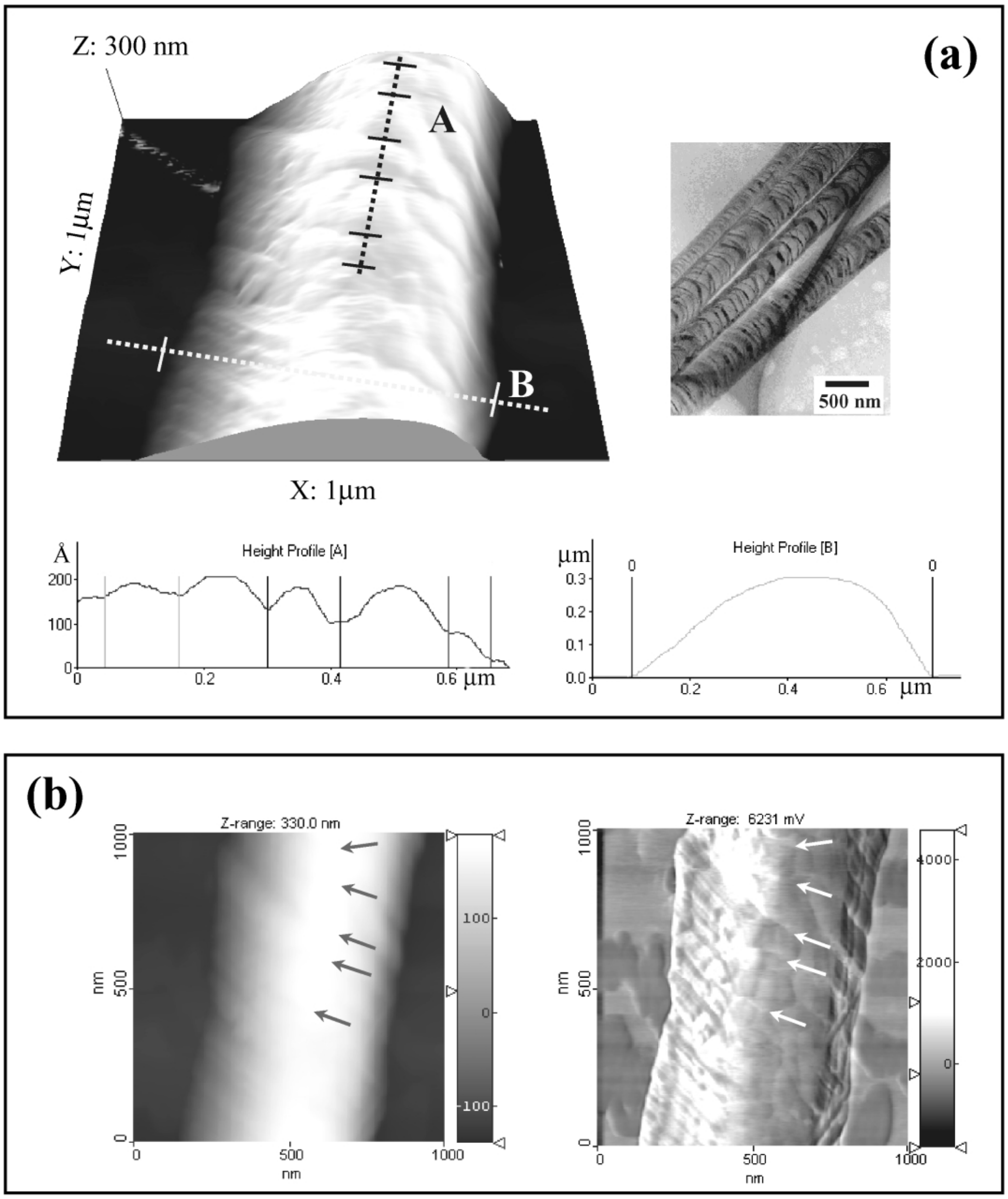

Fig. 1. (a) 3-D AFM image of BS-MWNTs grown on Fe deposited SiO_2/Ti substrates at 950 °C and the profiles of the compartment distance (*A*) and the diameter (*B*) of the BS-MWNTs. Upper right: TEM image. (b) AFM and LFM images of the same BS-MWNTs. Arrows represent the compartment boundaries.

The AFM measurements were carried out using a 'Park Scientific Instruments (PSI) AutoProbe CP' operated at room temperature in ambient conditions, using a pyramidal tip (TM Microlevers, spring constant 0.05 N/m). For the measurements the BS-MWNTs were sonicated in acetone for an hour, and then were dropped on cleaned Si substrates. Two groups of the BS-MWNT samples, grown on Fe catalyst deposited SiO_2/Ti substrates at 850 and 950 °C, respectively, were prepared for the measurements of the diameters and the compartment distances. For more accurate results, the measurements were carried out on several samples for each group.

3. Results and discussions

Fig. 1(a) displays a 3D AFM image of the BS-MWNTs. The compartment structures are clearly visible, as confirmed by the TEM image. The diameter and the compartment profiles are also shown in Fig. 1(a). For reliable measurements, the compartment distances were only taken at the top of the BS-MWNTs image. Fig. 1(b) displays the AFM and lateral force microscopy (LFM) images for the same BS-MWNTs sample. It is shown that the LFM image provides a much better detailed view of the morphology of the BS-MWNTs than the AFM image does. The LFM images were simultaneously taken while taking the AFM images. Because of different surface conditions near the compartments of the BS-MWNTs, the bamboo-structure was more distinctly observed by LFM than by AFM [25]. The LFM images were used for defining correct compartment positions.

Fig. 2 shows the relationships between the diameter and the compartment distance of the BS-MWNTs grown at 850 and 950 °C. Each point represents a single nanotube, and 10 compartments were measured for each nanotube. The error bars indicate the distribution of compartment lengths and diameters. It is found in Fig. 2, which displays the change of distribution of compartment lengths with growth temperature, that the diameters and the compartment distances are greater for the samples grown at 950 °C than for those grown at 850 °C. This is in good agreement with the result of our previous work that the average diameter, the growth rate, and electrical property of CNTs increase at higher growth temperatures [24,26,27]. It is also shown in Fig. 2 that the compartment distance generally increases with increasing diameter for the BS-MWNTs.

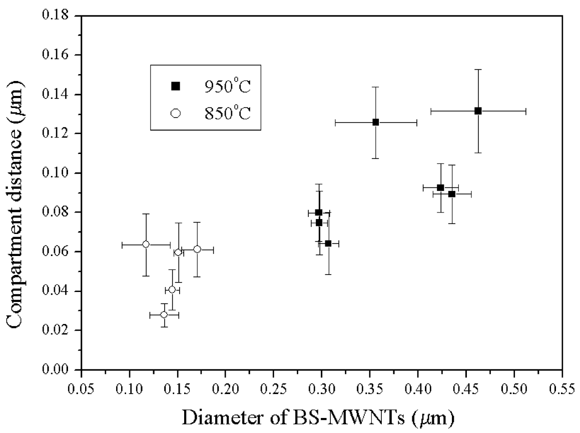

Fig. 2. Relationships between the diameter and the compartment distance for the BS-MWNTs grown on Fe catalyst deposited SiO_2/Ti substrates.

According to the base growth model [18], the carbons diffuse via the surface and/or bulk of the metal particles, forming graphite sheets as a cap on the catalytic particles. The vertical graphitic sheets are grown by surface diffusion of carbons, and the compartment graphitic sheets are grown by bulk diffusion of carbons [18]. As the carbons are continuously added to the edge of cap, the cap of graphite sheets lifts off the catalytic particle. Then a closed tip with the inside hollow is formed. The motive force of lift-off of the cap at the catalytic particle may be the stress accumulated under the graphite cap. When the carbons are supplied continuously under steady-state condition, the higher growth rate of BS-MWNTs gives rise to more active growth of the vertical graphitic sheets by surface diffusion than that of the compartment graphitic sheets by bulk diffusion. At higher growth temperature, the diffusion of carbons with higher kinetic energy may accelerate into the reaction zone of the catalytic particle, giving rise to greater surface and bulk diffusion. However, increase of surface diffusion with increasing temperature is generally considered to be greater than that of bulk diffusion. In other word, accelerated diffusion of carbons with increasing growth temperature acts more on the growth of vertical graphitic sheets at the edge of the catalytic particle than that of the compartment graphitic sheets by bulk diffusion at the inner surface of the catalytic particle. As a consequence, the higher growth rate of BS-MWNTs at higher growth temperatures results in the longer compartment distances. While higher growth temperatures result in larger diameters as well as larger compartment distances, the mechanism of larger diameters at higher temperatures is known to be distinct from that of larger compartment distances at higher temperatures. In other words, as the temperature increases, the migration rate of the Fe particles on the surface of the substrates increases to facilitate the agglomeration of the Fe particles. As a consequence, the larger size Fe particles give rise to larger diameters of the BS-MWNTs at higher temperatures [24,28].

In summary, AFM measurements were employed in order to observe the bamboo structure morphologies of BS-MWNTs grown at the temperatures of 850 and 950 °C by thermal CVD. The BS-MWNTs grown at the higher temperature 950 °C were found to have greater diameters and longer compartment distances. It is noteworthy that AFM can be used as good tools for the observation of morphologies of the BS-MWNTs.

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