27 July 2001

ELSEVIER

Chemical Physics Letters 343 (2001) 33–38

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Temperature effect on the growth of carbon nanotubes using thermal chemical vapor deposition

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Received 5 April 2001; in final form 22 May 2001

Abstract

Vertically aligned carbon nanotubes (CNTs) are grown on iron-deposited silicon oxide substrates by thermal chemical vapor deposition (CVD) of acetylene gas at the temperature range 750–950°C. As the growth temperature increases from 750°C to 950°C, the growth rate increases by four times and the average diameter also increases from 30 nm to 130 nm while the density decreases by a factor of about two. The relative amount of crystalline graphitic sheets increases progressively with the growth temperature and a higher degree of crystalline perfection can be achieved at 950°C. This result demonstrates that the growth rate, diameter, density, and crystallinity of CNT can be controlled with the growth temperature.

1. Introduction

As one of fascinating carbon materials carbon nanotubes (CNTs) have been considered for many different technological applications exploiting their unique electrical and mechanical properties [1–5]. Various synthetic methods have been developed for the production of CNTs, including arc discharge [6,7], laser vaporization [8], pyrolysis [9], and plasma-enhanced [10] or thermal chemical vapor deposition (CVD) [11,12]. The synthesis of multiwalled CNTs using CVD methods has attracted much attention because of many advantages that high purity, high yield, selective growth, and vertical alignment can be achieved [13–15].

It has been found that the structure of carbon materials is dependent on the growth parameters such as reaction temperature, catalyst, reaction gas, etc. A strict control of growth condition allows to design the structure of carbon materials in the nanometer regime [16–18]. Especially the growth temperature is crucial for selective and controlled growth of CNTs, which is necessary for many applications. A number of research groups reported that the growth of CNTs could be controlled by varying the growth parameters of CVD process [19–22]. However, there are not many systematic studies on the temperature-controlled growth of CNTs using thermal CVD.

This present work deals with the temperature effect on the growth of CNTs. The vertically aligned CNTs are synthesized on iron (Fe)-deposited silicon oxide (SiO_2) substrate by thermal CVD of acetylene gas at temperatures in the range

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0009-2614/01/$ - see front matter
PII: S0009-2614(01)00680-7

750–950°C. Configuration and structural characteristics of CNTs have been investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman spectroscopy. TEM is one of the most powerful methods for the evaluation of the crystallinity of nanostructured materials. Because of its very nature, however, TEM does not provide the overall information about the structure of entire specimen. We attempt to overcome this shortcoming by the use of TGA and Raman spectroscopy.

2. Experimental

20 mm × 30 mm sized p-type Si (1 0 0) substrates with a resistivity of 15 Ωcm were thermally oxidized. The thickness of silicon oxide (SiO_2) layer was estimated approximately as 300 nm. A 30 nm-thick Fe film was thermally deposited on SiO_2 layer using a thermal evaporator under a pressure of 10^{-6} Torr. The Fe-deposited substrates were loaded with face down direction on a quartz boat in quartz CVD reactor which was maintained in atmospheric pressure. The diameter of reactor tube is 550 mm. Argon (Ar) gas with a flow rate of 1000 sccm was supplied into the CVD reactor to prevent the oxidation of catalytic metal while raising the temperature. In order to form the catalytic particles in nanometer size, the substrates were pretreated by ammonia (NH_3) gas with a flow rate of 100 sccm for 20 min in the temperature range 750–950°C. The CNTs were grown on the substrate using C_2H_2 with a flow rate of 30 sccm for 10 min at the same temperature of NH_3 pretreatment in atmospheric pressure.

The CNTs were examined by SEM (Hitachi S-800, 30 kV) to measure the length, diameter, uniformity, and density. TEM (Philips, CM20T, 200 kV) was used to investigate the structure and crystallinity of CNTs. The CNTs are separated from the substrate and then dispersed on a carbon TEM microgrid. TGA (TA instrument TGA 2050) has been used for temperature-programmed oxidation at a constant heating rate of 10°C/min using air, in order to measure the degree of crystalline perfection. The weight loss of CNTs was recorded as a function of temperature and time. A Raman spectrometer (Renishaw micro-Raman 2000) was also used to identify the structure and the crystallinity of CNTs. The 632.8 nm line of a He–Ne laser was used for excitation.

3. Results and discussion

Fig. 1 shows SEM images for the CNTs grown on a Fe-deposited SiO_2 substrate at 750°C, 850°C, and 950°C. The edges are peeled off using a razor blade in order to visualize the configuration. The vertically well-aligned CNTs are homogeneously grown at all three temperatures. Fig. 1a shows uniformly grown 5 μm-long CNTs at 750°C. The CNTs have few carbonaceous particles at the surface. Fig. 1b shows uniformly grown 10 μm-long CNTs at 850°C. Fig. 1c is for the 20 μm-long CNTs grown at 950°C. The density of CNTs decreases from $\sim 4 \times 10^9/cm^2$ to $\sim 2 \times 10^9/cm^2$ as the temperature increases from 750°C to 950°C.

From several experimental runs, the averaged growth rate of CNTs at 750°C, 850°C, and 950°C is obtained as $0.5 \pm 0.05, 1.0 \pm 0.1$, and 2.0 ± 0.2 nm/min for 10 min, corresponding to four times increase for the temperature rise from 750 to 950°C. These data are plotted in Fig. 2. The diameters of CNTs are in the range 20–40, 40–80, 90–170 nm, respectively, at 750°C, 850°C, and 950°C. The respective average diameter of CNTs is found as $30 \pm 5, 60 \pm 10$, and 130 ± 20 nm. Fig. 2 also shows the average diameter of CNTs as a function of growth temperature. The result demonstrates that not only the growth rate of CNTs but also their diameter and density can be controlled by adjusting the growth temperature.

The increase of growth rate with increasing temperature is probably due to the enhanced diffusion and reaction rates of carbons. Further study is necessary in order to obtain quantitative kinetic information. As the temperature increases, the NH_3 etching rate of Fe particles increases, which can reduce the size. However, the migration rate of Fe particles on SiO_2 surface also increases to facilitate the agglomeration of Fe particles. As a result of more significant agglomeration at the higher temperature, larger size Fe particles are

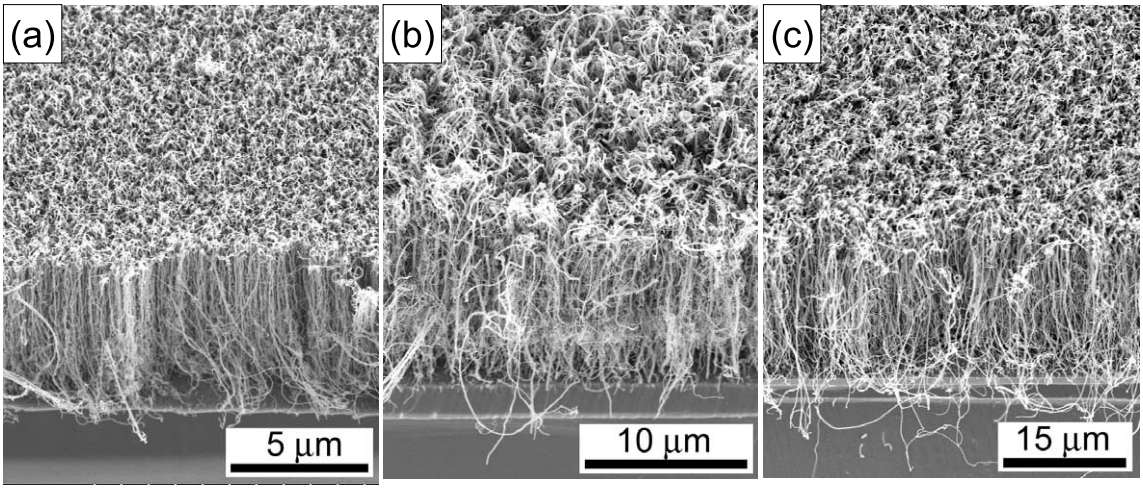

Fig. 1. SEM micrographs of vertically well-aligned CNTs on Fe-deposited SiO_2 substrate. (a) The 5 μm-long CNTs grown at 750°C. (b) The 10 μm-long CNTs grown at 850°C. (c) The 20 μm-long CNTs grown at 950°C.

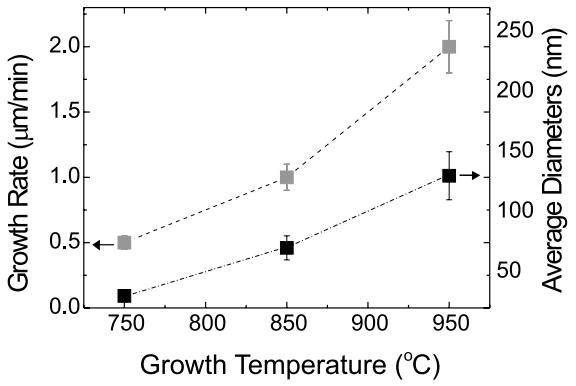

Fig. 2. The growth rate and diameter of CNTs as a function of the growth temperature.

formed with low density and broad diameter distribution. We found that the respective average diameter of Fe particles is as $40 \pm 10, 90 \pm 20$, and 150 ± 40 nm respectively, at 750°C, 850°C, and 950°C. The size of catalytic particles usually determines the diameter of CNTs in CVD growth [19]. Therefore, the CNTs with larger diameter and lower density can be grown by raising the growth temperature. There is the additional possibility of non-catalytic pyrolysis of acetylene on CNT sidewalls, leading to thickening of the tubes. We found that non-catalytic reaction of acetylene induces an increase of the tube diameter when the growth time is over 30 min in our test. But we could not find non-catalytic pyrolysis of acetylene on CNT sidewalls when CNTs are grown for 10 min.

We measured TEM images for the CNTs grown at all three temperatures. The CNTs exhibit exclusively a multiwalled bamboo-like structure. The closed tips are free of encapsulated catalytic particles and the curvature of compartment layers is oriented toward the closed tip, irrespective of the growth temperature [13–15]. The base growth mechanism is adequate to describe these results [23]. To verify the effect of growth temperature on the crystallinity of graphitic sheets, high-resolution TEM (HRTEM) images were obtained. Fig. 3 shows HRTEM images for about 25 graphitic sheets of the walls of CNTs grown at 750°C, 850°C, and 950°C. Left side of the image corresponds to the outside of the wall and the tip is directed towards the top. The outer graphitic sheets are usually less crystalline than the inner graphitic sheets. As illustrated in Fig. 3a, the graphitic sheets of CNTs grown at 750°C are waved over a short range. The graphitic sheets are tilted towards the tube axis with an angle of about 10°. The outer defective graphitic sheets vanish along the downward direction. Fig. 3b shows a HRTEM image of the CNTs grown at 850°C, revealing a

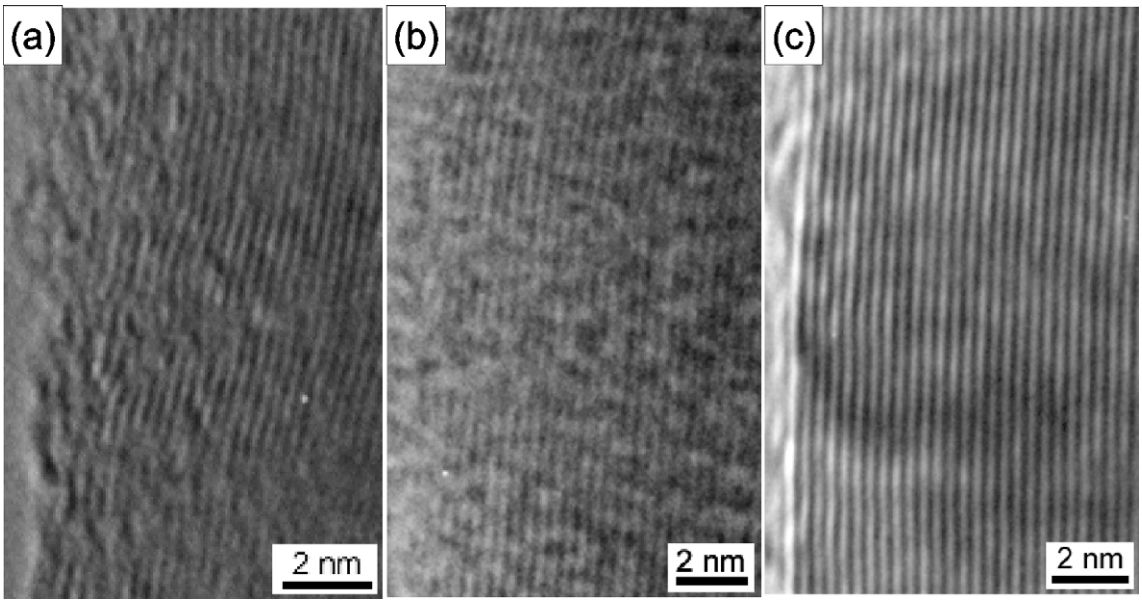

Fig. 3. HRTEM images for the CNT grown at (a) 750°C, (b) 850°C, and (c) 950°C.

good crystallinity compared to that of 750°C. The outer graphitic sheets are also less defective than that of CNTs grown at 750°C. Fig. 3c shows a highly ordered crystalline structure of CNTs grown at 950°C. The clear fringes of graphitic sheets are well separated by 0.34 nm and aligned with a tilted angle of about 2° toward the tube axis. The HRTEM images indicate that the long-range ordered crystalline structure improved with increasing growth temperature.

Temperature-programmed oxidation has routinely used to assess the crystallinity of carbons. In this method, the less-ordered structure reacts with the oxidant and loses weight because gasification occurs at a lower temperature. Fig. 4 is a plot for weight loss in percentage vs. oxidation temperature, measured by heating up the CNTs in a TGA. The percentage weight loss curve between 200°C and 800°C is plotted by adjusting 100% for the weight loss at 800°C which is presumably the weight of catalyst (usually 10% of total weight). The CNTs grown at 750°C, 850°C, and 950°C start to gasify at approximately 300°C, 400°C, and 550°C, respectively. The respective weight loss takes place over the range 300–600°C, 400–650°C, and 500–670°C for the CNTs grown at 750°C,

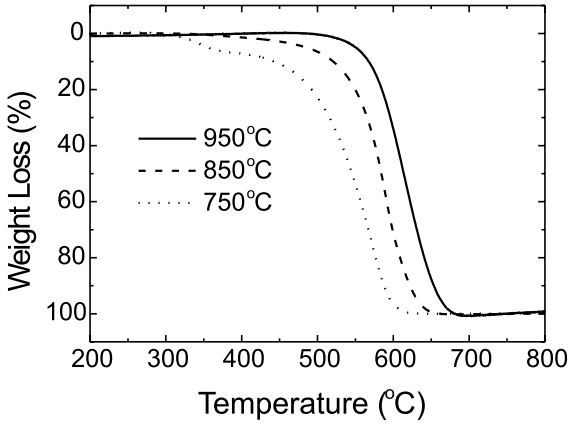

Fig. 4. TGA data of weight loss in percentage vs. oxidation temperature for the CNTs grown at 750°C, 850°C, and 950°C.

850°C, and 950°C, showing a narrow range for the higher temperature grown CNTs. The TGA data provide another strong evidence that the degree of crystalline perfection of CNTs becomes better as the growth temperature increases.

The first-order Raman spectra of as-grown CNTs at 750°C, 850°C, and 950°C are shown in Fig. 5. All spectra show mainly two Raman bands

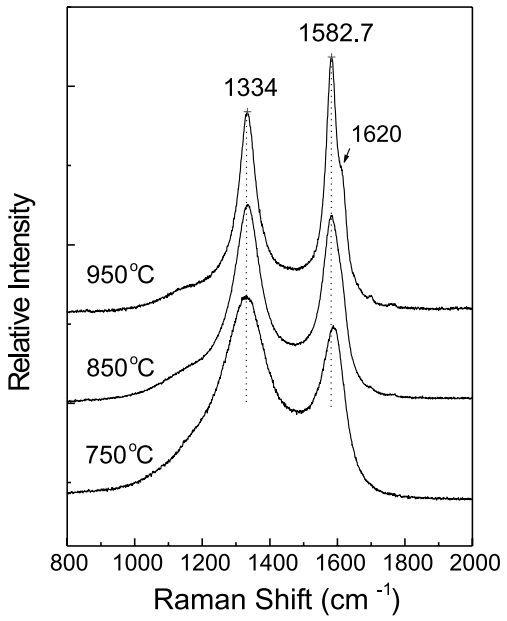

Fig. 5. Raman spectrum for the CNTs grown at 750°C, 850°C, and 950°C.

at $\sim$1335 cm^{-1} (D band) and $\sim$1580 cm^{-1} (G band). In the spectrum of CNTs grown at 950°C, the D′ band at $\sim$1620 cm^{-1} appears as a bump of G band. As the growth temperature decreases, D′ and D bands become stronger and broader. Thus D′ band is completely overlapping with the G band, resulting in a converged peak whose position is at a higher wavenumber than that of the G band by $\sim$10 cm^{-1}. The origin of D and D′ lines has been explained as disorder features of graphitic sheets [24,25]. In particular, Tuinstra and Koenig have noted a linear relation between the inverse of in-plane crystallite dimension and the intensity ratio of D and G bands (I(D)/I(G)) [24]. The value of I(D)/I(G) decreases from 1.2 to 0.8 with increasing the growth temperature. The results are very consistent with HRTEM image and TGA data in which the crystallinity of graphitic sheets improves progressively as the growth temperature increases.

In summary, we have successfully grown the vertically well-aligned CNTs on Fe-deposited SiO_2 substrate in the temperature range 750–950°C. The growth rate, the diameter, the density, and the crystallinity of CNTs can be controlled by adjusting the growth temperature. As the temperature increases from 750°C to 950°C, the growth rate enhances from 0.5 to 2.0 μm/min, corresponding to four times increase. The average diameter of CNTs also increases from 30 nm to 130 nm while the density of CNTs decreases from $\sim 4 \times 10^9/cm^2$ to $\sim 2 \times 10^9/cm^2$ by a factor of about 2. Bamboo-like structured CNTs are exclusively produced in this temperature range. The HRTEM images, TGA data, and Raman spectra reveal consistently that the degree of crystalline perfection increases progressively as the growth temperature increases.

Acknowledgements

This work was supported by the Brain Korea 21 Project of Kunsan National University and Directed Basic Research Program (Project No: KOSEF 2000-0-210-003-3). We acknowledge the support of this research by the Ministry of Science and Technology of Korea through the National Research Laboratory Program.

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