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Preparation of high yield multi-walled carbon nanotubes by microwave plasma chemical vapor deposition at low temperature

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Vertically-aligned carbon nanotubes(CNTs) with multi-walled structure were successfully grown on a Fe-deposited Si substrate at low temperature below 330°C by using the microwave plasma chemical vapor deposition of methane and carbon dioxide gas mixture. This is apparently different from the conventional reaction in gas mixtures of hydrogen and methane, hydrogen and acetylene, and hydrogen and benzene . . . etc. High quality carbon nanotubes were grown at lower temperature with CO_2 and CH_4 gas mixture than those used by the previous. After deposition, the microstructure morphology of carbon nanotubes was observed with scanning electron microscope and high-resolution transmission electron microscope. The characteristics of carbon nanotubes were analyzed by laser Raman spectroscopy. The results showed the variation of the flow rate ratio of CH_4/CO_2 from 28.5 sccm/30 sccm to 30/30 sccm and the DC bias voltage from −150 V to −200 V, at 300 W microwave power, 1.3–2.0 kPa range of total gas pressure, and substrate temperatures between 300°C and 350°C. Vertically aligned carbon nanotubes with the diameter of about 15 nm and multi-walled structure were illustrated by SEM and HRTEM. However, the highest yield of carbon nanotubes of about 50% was obtained at low temperature below 330°C by MPCVD for the CH_4/CO_2 gas mixture with properly controlled parameters.

1. Introduction

Since carbon nanotubes (CNTs) were discovered, relevant researches have multiplied and the development of commercial applications such as hydrogen storage, atomic force microscope probe, microelectronic transistor, electrical field emitter of flat panel display and scanning tunneling microscope tip [1–5] have been stimulated tremendously. Recently, IBM successfully developed an integrated circuit (IC) by using carbon nanotubes to replace the conventional silicon.

High-quality and well-aligned carbon nanotubes are essential to the potential applications in the field of microelectronic industries. Many kinds of synthetic techniques have been developed, such as laser ablation, plasma-enhanced chemical vapor deposition, arc discharge, pyrolysis, thermal chemical vapor deposition [6–11]. In our previous studies [12–15], microwave plasma chemical vapor deposition was successfully used to grow the diamond film. In the present work well-aligned carbon nanotubes at low temperature below 330°C by using microwave plasma chemical vapor deposition (MPCVD) were synthesized successfully. On the other hand, the constituents of gas mixture are also key factors in the process of chemical vapor deposition. Gas mixtures of H_2—CH_4, H_2—C_2H_2, and H_2—C_6H_6 etc. [16–18] have also been used to grow the carbon nanotubes, but their processing temperatures are generally higher than 400°C to research the similar deterioration of quality of CNTs.

Major work of this study briefly depicted that high yield, well reproducible and vertically-alignment multi-walled carbon nanotubes on Fe-deposited Si substrate by MPCVD at low temperature below 300°C with CH_4 and CO_2 gas mixture have been achieved with success. Appeared in the scanning electron microscope (SEM) image is the mostly 50% yield of carbon nanotubes at various regions of the deposition substrate. Ratio variations of oxygen to CH_4/CO_2 gas mixture for carbon nanotubes growth were investigated by optical emission spectroscopy (to be discussed in a later publication). The microstructure morphology of bamboo-like and multi-walled carbon nanotubes was analyzed by high resolution transmission electron microscopy (HRTEM). The characterization analyses of CNTs were performed by laser Raman spectroscopy.

2. Experimental procedure

A thin Fe layer of 10 nm thickness was deposited on the n-type Si (100) wafer by sputtering, the 20 × 20 mm

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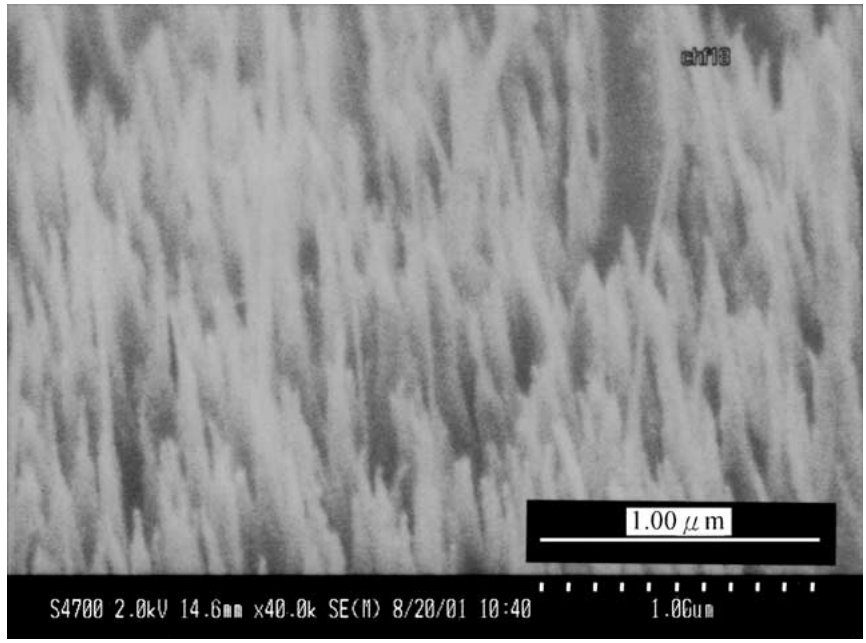
TABLE I Experiment condition for the growth reaction of CNTs

Experiment condition	Sample						
	A	B	C	D	E	F	G
Microwave power (W)	300	300	300	300	300	300	250
Pressure (kPa)	1.3	1.3	1.3	1.3	2.0	2.0	2.0
Substrate temp. (°C)	320	320	320	320	350	350	300
CH_4 flow rate (sccm)	25	28.5	29	29.5	30	30	30
CO_2 flow rate (sccm)	30	30	30	30	30	25	20
DC Bias (Volt)	−150	−150	−200	−200	−150	−150	−150
Quality	Poor	Good	Good	Good	Good	Fair	Poor
Deposition time (min)	20	20	20	20	20	20	20

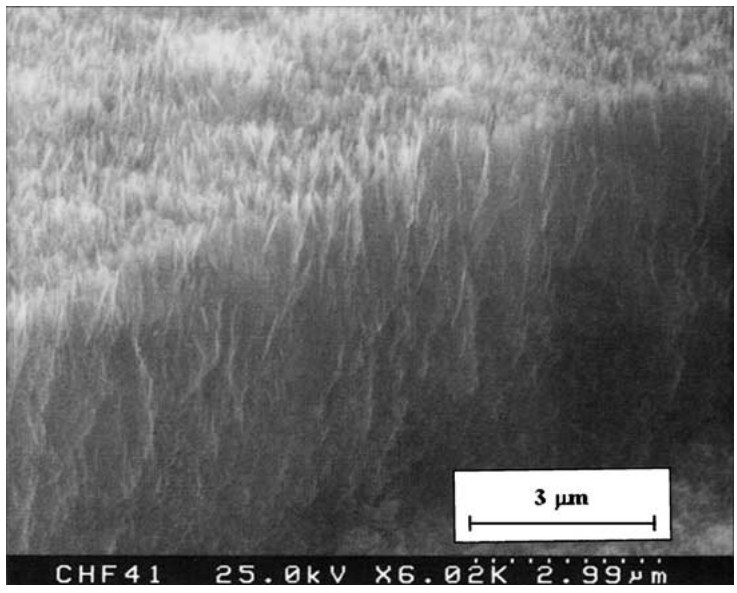
size Fe-deposited-substrate was loaded on a MPCVD. While the microwave power was set at 250–300 W, and the total gas pressure range was changed from 1.3 to 2.6 kPa, the optical pyrometer was used to monitor the substrate temperature maintained at about 300–350°C.

The CNTs were grown on Fe-deposited Si substrate by using CH_4 and CO_2 gas mixture and by changing the CH_4 flow rate from 20 to 30 sccm, and CO_2 from 20 to 30 sccm. DC bias adjusted from −100 V to −200 V was applied to align the carbon nanotubes. The detail growth conditions are shown in Table I.

Low temperature growth of CNTs was achieved by decreasing both the microwave power and total gas pressure. The substrate temperature was measured with an optical pyrometer and thermocuple in direct contact with substrate holder. The exact temperature of the substrate surface was identified by melting-point method, for example, lead (m.p = 335°C) and



(a)



(b)

Figure 1 (a) Low magnification of SEM image of dense carbon nanotubes (b) SEM image of vertically well-aligned carbon nanotubes which have closed end and encapsulated Fe particles tip.

Tin (m.p. = 243°C). the identification of true substrate temperature was reported detail in our previous research [12].

After deposition, a scanning electron microscope (Hitachi S-47001) was used to examine the morphology and to evaluate the yield of vertically-aligned carbon nanotubes. A high resolution transmission electron microscope (Philips Tecnai-20) was then used to investigate the microstructure of CNTs.

The characteristics of CNTs were determined by a Raman spectrometer (Renishaw system 200), driven with an argon-ion laser at $\lambda = 514.5$ nm.

3. Results and discussion

3.1. The effect of CH_4/CO_2 flow rate variation on CNTs growth

Table I shows various experiment conditions for the growth reaction of multi-walled CNTs. The effect of changing CH_4/CO_2 flow ratio was investigated by keeping power at 300 W and total gas pressure at 1.3 kPa. From sample A to D, the CH_4/CO_2 flow ratios were varied by changing CH_4 flow rate while at constant CH_4 flow rate of 30 sccm, the qualities of samples are rather good and the sample D gives the CNTs yield of about 50%. The maximun yield of CNTs of 50% resulted when CH_4 flow rate was increased to 29.5 sccm. The deposition time was 20 min for all cases. When the content of CH_4 flow rate is lower than 25 sccm, carbon nanotubes were not found, expect an amorphous carbon layer on the substrate.

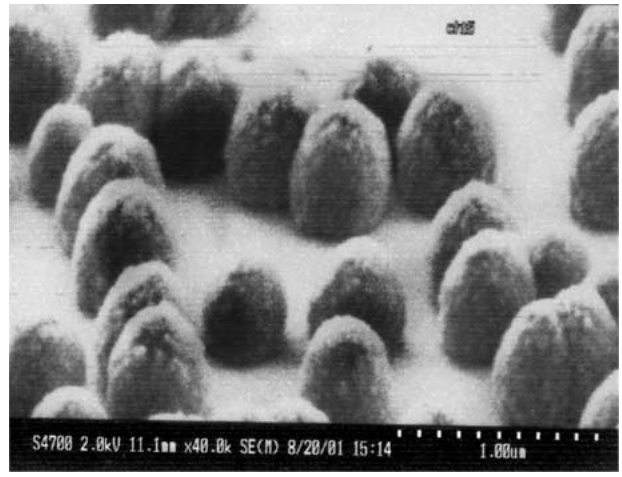
For samples E, F and G, increases of CO_2 flow rate at constant CH_4 flow rate of 30 sccm. as well as the deposition temperature promote the growth of CNTs to a maximum value up to 10% when CO_2 flow rate rise to 30 sccm under the same deposition time, DC bias voltage and CH_4 flow rate of 30 sccm, as the CO_2 flow rate increased up to near the flow rate of CH_4, better CNTs growth conditions would be expected. It shows that when the CH_4 flow rate was kept constant and the CO_2 flow rate was decreased from 30 sccm to 25 sccm and even 20 sccm, only granular ball-like graphite and sheet-like amorphous carbon appeared on the substrate when the reaction proceeded under low CO_2 concentration.

The best samples with 50% CNTs were formed at low temperature below 300°C, DC bias of −200 Volt, microwave power of 300 W, and the optimal CH_4 and CO_2 values of 29.5 sccm and 30 sccm total gas pressure of 1.3 kPa respectively. It shows that the relative variation of the ratio of CH_4 and CO_2 affects the growth condition of carbon nanotubes. Similar experiment results were also discovered in the formation of diamond film [12].

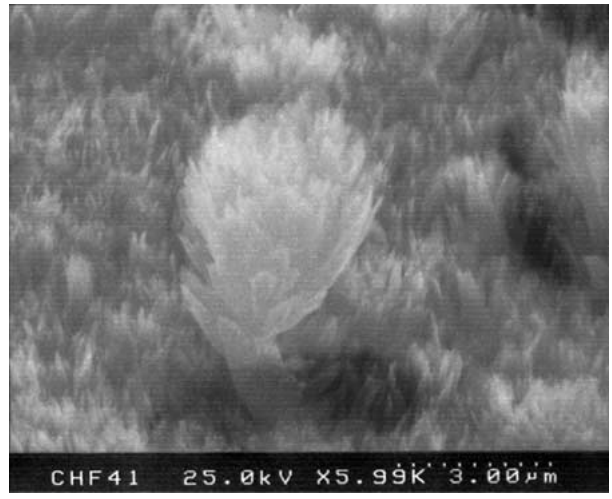
In the present study, we found that by substituting carbon dioxide for hydrogen in CO_2-CH_4 gas system, carbon nanotubes with high yield and good alignment could be obtained at lower temperature in the gas system.

3.2. The morphology of CNTs

Fig. 1 shows typical SEM morphology images of vertically aligned carbon nanotubes of the sample D. The lower magnification of SEM image is shown in Fig. 1a. It shows that the high density aligned carbon nanotubes with in a length about 4–5 μm were exhibited at various regions from right to left of the deposited substrates. Fig. 1b shows the SEM image of vertically well-aligned carbon nanotubes. These carbon nanotubes have closed end and encapsulated Fe particles tip, and the nanotube microstructure was identified by HRTEM, that will be described in more detail later.



(a)



(b)

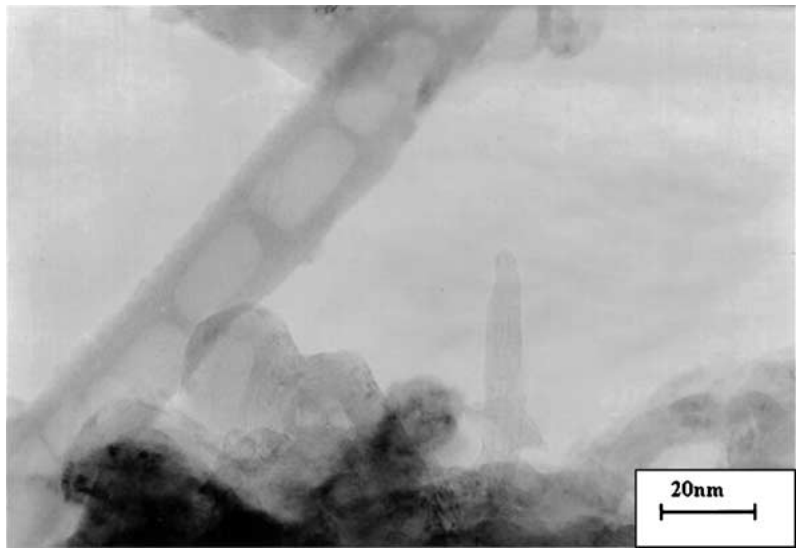
Figure 2 SEM morphology images of (a) granular ball-like amorphous carbon (b) plate-like amorphous carbon.

Fig. 2 show the SEM image of granular ball-like graphite and sheet-like amorphous carbon. This indicates that the growth of carbon nanotubes cannot be complete if carbon containing gas mixtures are not appropriately supplied.

3.3. HRTEM morphology images of CNTs

Further identification and analysis of CNTs growth mechanism still rely on the observation and studies of high-resolution transmission electron microscopy (HRTEM).

Fig. 3a shows the images of carbon nanotubes with bamboo-like microstructure observed by TEM. A hollow tube with compartment layers that appeared periodically, and connect with the wall. Fig. 3b is a HRTEM image for carbon nanotubes with multi-walled, arrow a shows the closed tip without any encapsulated Fe



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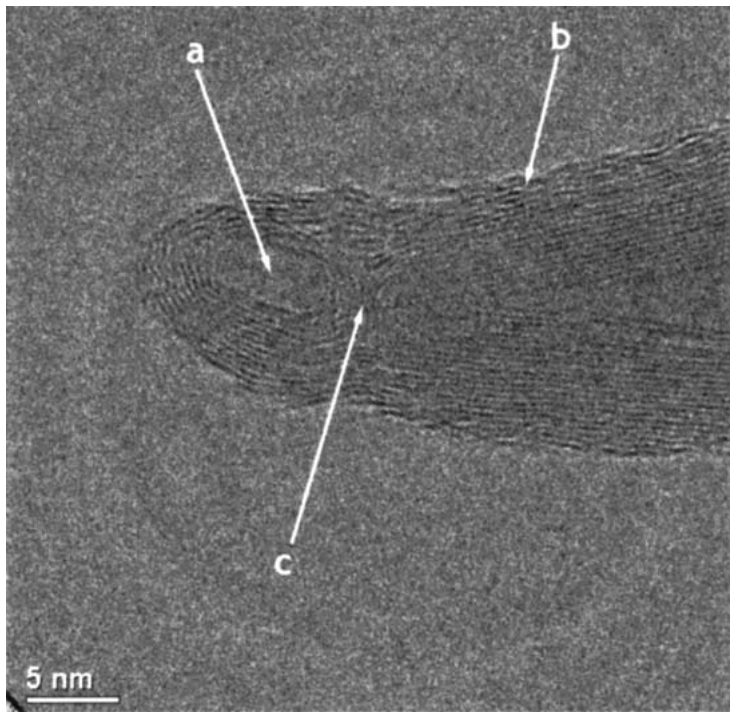


(b)

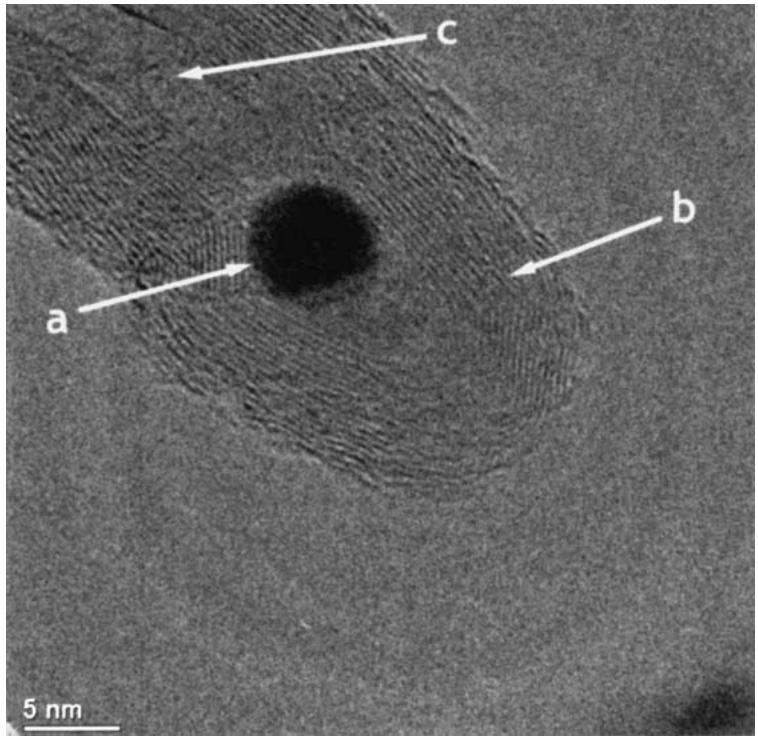
Figure 3 (a) TEM image of CNTs with multi-walled and bamboo-like microstructure, the wall connected with the compartment, being hollow core (b) HRTEM image of multi-walled CNT, indicating a Fe particle free tip.

particle with about 5 nm in tip diameter, arrow b indicates the nanotube diameter below the tip sized about 15–25 nm, the thickness of wall is about 6 nm. and A arrow c indicates the wall connecting with the compartment.

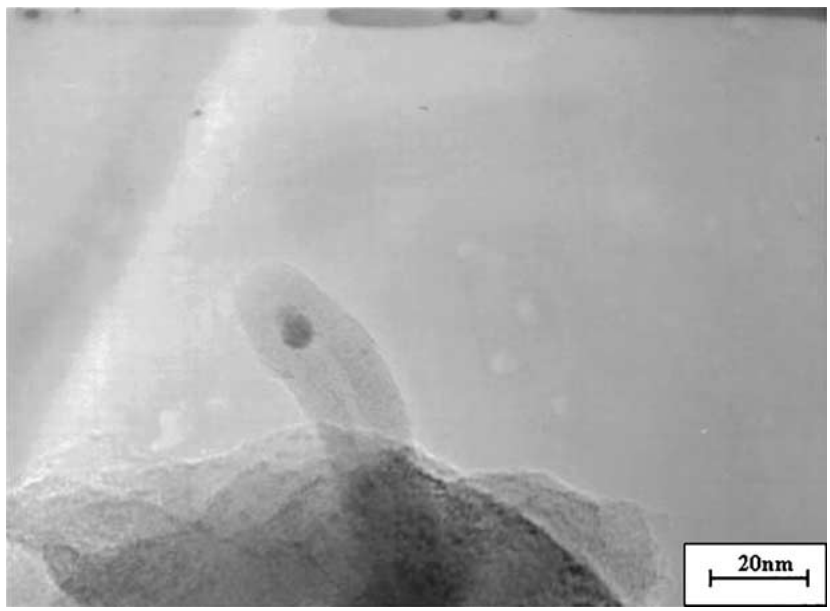
Fig. 4a is the HRTEM image for the multi-walled structure and exhibits the Fe particle encapsulated tip with the diameter of ∼6 nm indicated by arrow a. The diameter of CNTs is approximately 18 nm and thickness of CNTs wall is about 5 nm as shown by arrow b. A hollow tube with 3 nm diameter and next to a compartment layer is indicated by arrow c. The Fe particle that takes part in various reaction paths of decomposition, diffusion, growth and deposition finally results in the growth of CNTs vertically. The lower magnification of TEM image is shown in Fig. 4b

Fig. 5 shows HRTEM images of the nanostructure of multi-walled CNTs and multi-layers of graphitic carbon. Hollow core are evident. Arrow a indicates defective graphite sheets at the outside wall surface with the thickness of 2 nm and the wall thickness of the multi-wall CNTs shown in arrow b is about 4 nm. The diameter of the tube is about 1.5 nm. The surrounded graphite layer should be produced by the deposition of carbon-containing species and the incomplete reaction on the CNTs surface.

In fact, the appropriate increase of the concentration of CH_4 and CO_2 significantly improve the growth of carbon nanotubes in the vertical and lateral direction. Carbon nanotubes, grown vertically by the inducing effect of nanoparticle iron catalytic reaction and the extra carbon species, resulted from the decomposition



(a)



(b)

Figure 4 (a) HRTEM image for the multi-walled structure of CNT indicating an Fe-particle encapsulated tip (b) lower magnification TEM image of Fig. 4a.

of CH_4 and CO_2 during reaction, and were continously supplied or diffused into the growing CNTs. The CNTs in the lateral direction with multi-walled structure are significantly formed by the additional re-precipitation of carbon species, with mutual reaction and evaporization of hydrogen and oxygen. It finally resulted in the multi-walled CNTs. Although many various growth mechanism have been illustrated [19–22], reaction sequences of deposition, adsorption, decomposition, diffusion, growth and deposition vary according to the reaction conditions and species during plasma processing.

3.4. Characterization of MWCNTs

Fig. 6 shows a Raman shift of sample D in the region of 1000–4000 cm^{-1}. A typical graphite vibration mode G-band at 1582 cm^{-1} and a disordered carbon mode D-band at 1348 cm^{-1} appear in the Raman spectra. The 1582 cm^{-1} peak indicates that CNTs were formed during growth, the 1348 cm^{-1} peak is due to defects in the curved graphite sheet, tube ends and surviving impurities. Basca *et al*. attribute some of D-band scattering to curvature in the tube wall [23]. Additional two peaks are observed in the second order spectrum at 2707 $cm^{-1} \approx 2(1348\ cm^{-1})$ and 2959 $cm^{-1} \approx 2(1582\ cm^{-1})$.

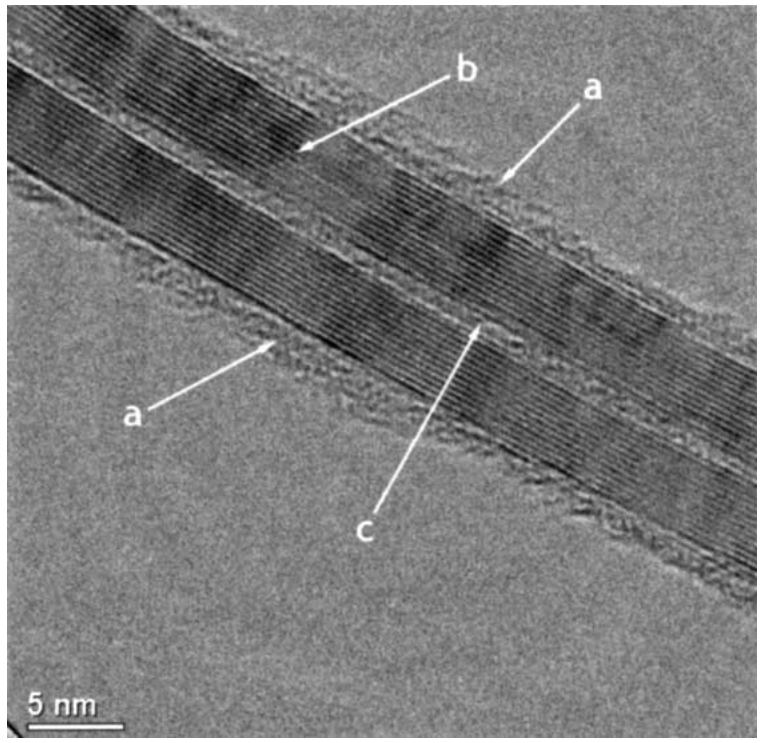


Figure 5 HRTEM image for the wall of a CNT indicating defective graphite sheets on the wall surface, vertically multi-walled with hollow core.

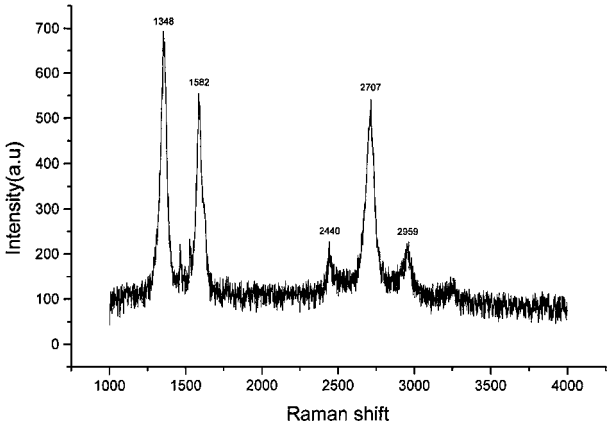


Figure 6 Raman spectra of multi-walled carbon nanotubes.

4. Conclusions

Carbon nanotubes were grown at low temperature below 330°C by microwave plasma chemical vapor deposition of CH_4–CO_2 gas mixture. The low temperature deposition conditions were achieved by adjusting both microwave power and total gas pressure. Vertically aligned and high yield carbon nanotubes were observed by SEM images. A diameter about 15–20 nm carbon nanotubes with multi-walled structure were analyzed by HRTEM.

In Summary, higher quality carbon nanotubes could be grow at lower temperature with CO_2–CH_4 gas mixture than those by H_2–C_2H_2, H_2–CH_4 and H_2–C_6H_6 gas mixtures. The results showed that the flow rate ratio of CH_4/CO_2 at 29.5 sccm/30 sccm, microwave power at 300 W, total gas pressure at 15 torr, DC bias voltage at −150 V, and substrate temperature at 330°C are essential to the high yield about 50% carbon nanotubes. It has be predicted here that high quality carbon nanotubes may possibly be grown by using CO_2–CH_4 gas mixture at temperature even lower than 300°C.

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References

1. S. J. CHANG, S. H. LIM, C. H. LEE and J. JANG, *Diamond Relat. Mater.* **10** (2001) 248.
2. D. L. CARRILL, P. REDLICH, P. M. AJAYAN, J. C. CHARLIER, X. BLASE, A. DEVITA and R. CAR, *Phys: Rev. Lett.* **78** (1997) 2811.
3. Q. H. WANG, T. D. CORRIGAN, J. Y. DAI, R. P. H. CHANG and A. R. KRAUSS, *Appl. Phys. Lett.* **70** (1997) 3308.
4. Y. CHEN, S. PATEL, Y. YE, D. T. SHAW and L. GUO, *ibid.* **73** (1998) 2119.
5. H. C. CHENG, W. K. HONG, F. G. TARNTAIR, K. J. CHEN, J. B. LIN, K. H. CHEN and L. C. CHEN, *Electrochemical and Solid-State Lett.* **4** (2001) 115.
6. R. STEVENS, C. NGUYEN, A. CASSELL, L. DELZEIT, M. MEYYAPPAN and J. HAN, *Appl. Phys. Lett.* **77** (2000) 3453.
7. X. K. WANG, X. W. LIN, V. P. DRAVID, J. B. KETTERSON and R. P. H. CHANG, *ibid.* **66** (1995) 2430.
8. L. C. QIN, D. ZHOU, A. R. KRAUSS and D. M. GRUEN, *ibid.* **72** (1998) 3437.
9. Z. SHI, Y. LIAN, X. ZHOU, Z. GU, Y. ZHANG, S. IIJIMA, L. ZHOU, K. T. YUE and S. ZHANG, *Carbon* **37** (1999) 1449.
10. Z. P. HUNG, J. W. XU, Z. F. REN, J. H. WANG, M. P. SIEGA and P. N. PROVENCIO, *Appl. Phys. Lett.* **73** (1998) 3845.
11. C. F. LEE and J. PARK, *Carbon* **39** (2001) 1891.
12. C. F. CHEN, S. H. CHEN, H. W. KO and S. E. HSU, *Diamond Relat. Mater.* **3** (1994) 443.

13. C. F. CHEN, S. H. CHEN, T. M. HONG, H. W. KO and S. E. SHEN, *Thin Solid Films* **236** (1993) 120.
14. C. F. CHEN, T. M. HONG and S. H. CHEN, *Scripta Metall. Mater.* **29** (1993) 317.
15. *Idem., J. Appl. Phys.* **74** (1993) 4483.
16. L. CI, J. WEI, B. WEI, J. LIANG, C. XU and D. WU, *Cabron* **39** (2001) 329.
17. Y. J. YOON and H. K. BAIK, *Diamond Relat. Mater.* **10** (2001) 1214.
18. J. H. HAN, W. S. YANG and J. B. YOO, *J. Appl. Phys.* **88** (2000) 7363.
19. Y. C. CHOI, Y. M. SHIN, S. C. LIM, D. J. BAE, Y. H. LEE and B. S. LEE, *Appl. Phys.* **88** (2000) 4898.
20. C. J. LEE and J. PARK, *Appl. Phys. Lett.* **77** (2000) 3397.
21. Y. SAITO and T. J. YOSHIKAWA, *Cryst. Growth* **71** (1993) 154.
22. M. JUNG, K. Y. EUN, J. K. LEE, Y. J. BAIK, K. R. LEE and J. W. PARK, *Diamond Relat. Mater.* **10** (2001) 1235.
23. W. S. BASCA, D. UGARTE, A. CHATELAIN and W. A. DE HEER, *Phys. Rev.* B **50** (1994) 15473.

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