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Growth of carbon nanotubes by microwave plasma chemical vapor deposition using CH_4 and CO_2 gas mixture

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Abstract

Carbon nanotubes (CNTs) were grown vertically and aligned on Fe catalytic nanoparticles which were deposited on a Si substrate at low temperature using CH_4 and CO_2 gas mixtures. A dynamic form of optical emission spectroscopy was used to detect the species in the plasma. These data show the dominant species in gas phase reaction. The composition of plasma significantly affects the reaction mechanism of CNTs growth and diamond film synthesis. The growth quality of CNTs is better than a conventional reaction in a gas mixture of hydrogen and hydrocarbons. However, the highest yield of CNTs of approximately 70% was obtained by microwave plasma chemical vapor deposition for CH_4–CO_2 gas mixture at a flow rate of CH_4/CO_2 at 96%, power supply of 300 W, reaction time of 20 min and bias voltage of 150 V. In summary, the oxygen containing in the CH_4–CO_2 gas system can increase the amount of C_2. In the C_2-rich plasma the excited C_2 emission at a higher intensity is beneficial to graphite deposition, which enhances CNTs synthesis on catalyst-deposited surface quality.

Keywords: Carbon nanotubes; Chemical vapor deposition; Diamond film

1. Introduction

Since carbon nanotubes(CNTs) were discovered by Iijima [1], several researches have investigated the physical, chemical and mechanical properties. Numerous investigators have reported CNTs, its 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 [2–6] have been stimulated tremendously. It has been well established that high quality CNTs may be grown by a variety of deposition schemes. Microwave plasma chemical vapor deposition (MPCVD) had been regarded as the potential method due to its yield, purity, and controlled alignment. In microwave plasma deposition of CNTs, many reactions are involved in plasma and on substrate surfaces in order to obtain a described composition and microstructure. It is important to understand the plasma species that dominantly controlled the CNTs formation. In order to understand the formation and decomposition of the reaction species in the gas phase, optical emission spectroscopy (OES) should be well suited for the investigation.

Previously, several researchers have studied the OES for diamond film deposition [7–9]. We have investigated diamond film nucleation and growth in the MPCVD system with OES [10,11]. Some results on carbon plasma characteristics during CNTs and fullerene growth have been published [12,13].

In this study, a method using MPCVD with a CH_4–CO_2 gas mixture was performed to grow the CNTs. Typically, catalytic metal used for the growth of CNTs are iron. A DC bias was used to align the CNTs. Growth of CNTs were in a higher quality in the CH_4–CO_2 gas mixture made by MPCVD. There may be more activity of the oxygen contained in the plasma species. It is reasonable to say that reaction mechanism of CNTs growth in the CH_4–CO_2 system is different from H_2–CH_4. OES was used to detect the species in the plasma during the CNTs deposition in the continuous mode. We found that the compositions of plasma significantly affect the reaction mechanism in CNTs growth and it was also compared with diamond film synthesis. In this report, CNT growth characterization and plasma emission spectroscopy are used to study the relationship between growth features and plasma species. The results

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Table 1
Conditions of experiments

Substrate	n-Si(1 0 0)
Microwave power	250–400 W
Total gas pressure	1.3–2.6 kPa (10–20 Torr)
Reaction time	10, 15, 20 min
Gas flow rate ratio	CH_4/CO_2: 50–150%
Flow rate of CO_2	30 $cm^3\,min^{-1}$

may help us to comprehend the CNTs growth mechanism in the CH_4–CO_2 system.

2. Experimental procedure

A thin iron layer of 10 nm was deposited on the n-type Si(1 0 0) wafer by sputtering, the 20×20 mm^2 size Fe-deposited-substrate was loaded on a MPCVD. The microwave power was set at 250–400 W, the total gas pressure range was changed from 1.3 kPa (10 Torr) to 2.6 kPa (20 Torr), the optical pyrometer was used to monitor the substrate temperature.

The CNTs were grown on Fe-deposited Si substrate by using CH_4 and CO_2 gas mixture. The flow rate of CO_2 was set at 30 $cm^3\,min^{-1}$ and the flow rate (by volume) ratio of CH_4/CO_2 was adjusted from 50 to 150%. A DC bias was performed to align the CNTs, which was adjusted from -100 to -200 V. The detail growth conditions are shown in Table 1.

After deposition, a scanning electron microscope (Hitachi S-4700I) was used to examine the morphology. The yield of CNTs were evaluated by scanning the deposited substrate at various regions from right to left. A high resolution transmission electron microscope (Philips Tecnai-20) was then used to investigate the microstructure of CNTs.

The OES was used to detect the species in the plasma during the CNTs growth process. Plasma emission actinometry (Ar, 4 $m^3\,min^{-1}$) was used to exhibit the change of electron energy distribution and the complementary excitation efficiency in CH_4 and CO_2 gas mixture. The analysis equipment used for OES experiments was SOFIE instrument SD 20 system. The optical emissions were transferred from the plasma center near the deposition surface to monochrometer through the optical fiber after being focused by a quartz lens. The scanning wavelength was set between 200 and 600 nm to record the emission intensities.

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

3. Results and discussion

3.1. The morphology of CNTs

Fig. 1a shows a lower magnification of SEM micrograph of aligned CNTs. It can be seen that the CNTs are well aligned. The highly densed and well-aligned CNTs have a length approximately ranging from 5 to 7 μm. It was observed in a CH_4–CO_2 gas mixture with the flow rate of CH_4/CO_2 at 96% (basis on CO_2 gas flow rate is 30 sccm), a power supply of 300 W, a reaction time of 20 min and a bias voltage of 150 V in which condition the CNTs were of good quality ($\sim$70% yield). Fig. 1b shows the SEM image of vertically well-aligned CNTs have a closed end and encapsulated iron particles tip. The SEM image was used to examine the yield of vertically aligned CNTs at various regions from the right to left of the deposited substrate. Fig. 2a shows HRTEM image of the nanostructure of multi-walled CNTs. It is indicated that the closed tip without any encapsulated catalyst particle was approximately 15 nm in tip diameter, the nanotube diameter below the tip size was approximately 15–20 nm, the thickness of wall was

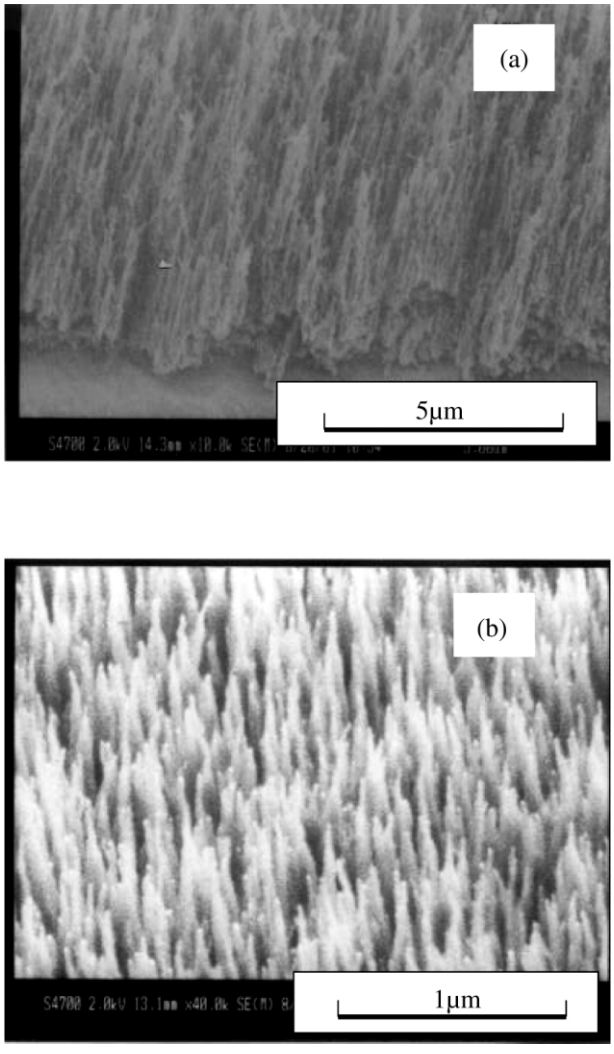

Fig. 1. (a) The lower magnification of SEM morphology image of CNTs in a CO_2–CH_4 gas mixture with flow rate ratio of CH_4/CO_2 is 96%. (b) SEM morphology image of aligned CNTs observed in the flow rate of CH_4/CO_2 at 96%.

approximately 6 nm and the defective graphite sheets at the outside wall surface had a thickness of 2 nm. Fig. 2b is the HRTEM image for the multi-walled structure and exhibits the Fe particle encapsulated tip with a diameter of approximately 9 nm. The diameter of CNTs is approximately 12 nm and the thickness of the CNTs wall is approximately 5 nm. The wall thickness of the multi-wall CNTs is 4 nm and a hollow tube is 3 nm in diameter.

3.2. Optical emission spectra

Fig. 3a shows the OES from a microwave plasma observed in a CH_4–CO_2 gas mixtures with a flow rate of CH_4/CO_2 at 96%, reaction time of 20 min and bias voltage of 150 V, that resulted in good quality CNTs (~70% yield). The identification of plasma species in this work are according to Ref. [14]. Species identified in this work includes:

- CO: the positive and 5B bands system and the Ångstrom system
- OH: 3064 Å system, 306 and 308.9 nm
- CH: 387.1 and 431.4 nm
- C_2: Swan band, 516.5 and 563.5 nm
- Atom oxygen: 533 nm
- Excited O_2: 592.5 nm
- Atom hydrogen H_β: 486.1 nm

The OES measurements show that the primary difference between the plasma of the gas mixture was in the intensities of excited O_2, OH, C_2, CH, and CO radicals. Under high quality CNTs growth conditions, the C_2 and CO emission from the CH_4–CO_2 plasma were clearly more intense than the CH, C_2, H corresponding emission.

The C_2 radical facilitated the formation of amorphous or graphite carbon. Optical emission measurement indicated that because of an abundance of C_2 radicals in the CO plasma graphite formed on the Si substrate [15].

The high C_2 radicals concentration in the microwave plasma benefits the quality of CNTs. When the flow ratio of CH_4/CO_2 is approximately 100%, i.e. the atomic ratio of H/O is 2/1, the atomic O and H are formed into OH radical, and then the most of the remaining carbon is decomposed, precipitated and deposited onto the substrate surface from the CH_4 and CO_2 gas mixture.

Fig. 3b shows the typical OES from the microwave plasma observed in the CH_4–CO_2 gas system with a flow rate ratio of CH_4/CO_2 at 70.7%. The OES in Fig. 3b is apparently different from Fig. 3a. In this gas system, OH, CH, CO, excited O_2, and C_2 radicals are present. A large amount of CH and CH^+ is decomposed from the CH_4 and CO_2 plasma. We have previously investigated diamond film growth in a PECVD system with OES [10,11]. The high concentrations of CH and CH^+ are beneficial to increasing diamond nucleation density but they are harmful to the growth of diamond film [16].

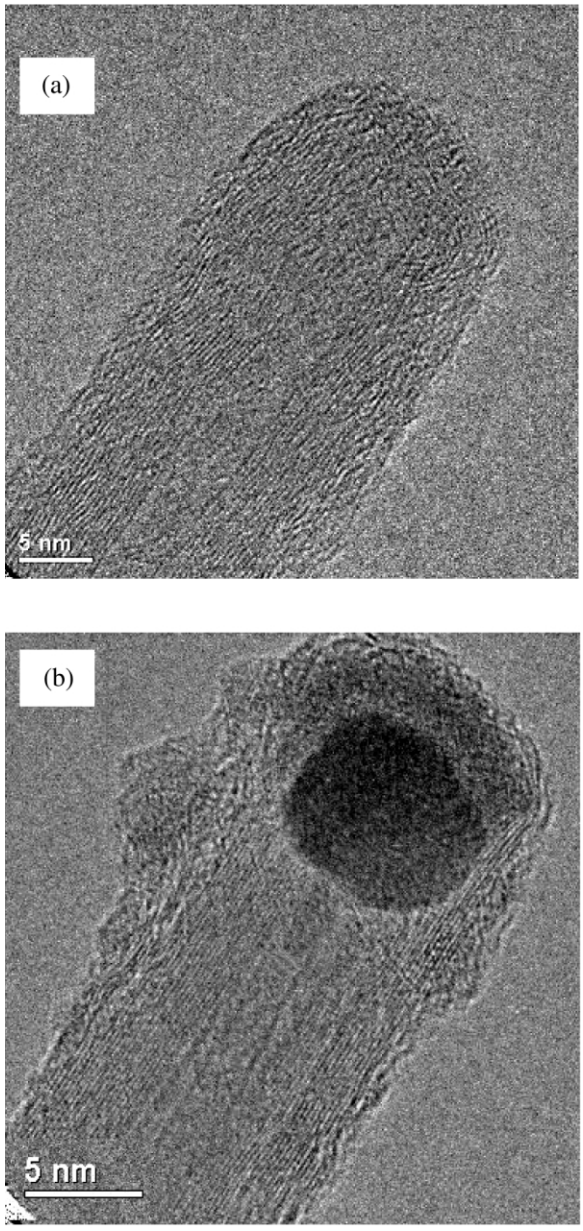

Fig. 2. (a) HRTEM image of multi-walled CNTs indicating the closed tip without any encapsulated a Fe particle. (b) HRTEM image for the multi-walled structure of CNTs indicating an Fe-particle encapsulated tip.

According to the present results, we suggest that the excited C_2 emission in higher intensity will be beneficial to graphite or carbon amorphous deposition, which was discussed in several studies [17–21] of diamond film synthesis gas system.

In fact, the appropriate increase of the concentration of CH_4 and CO_2 significantly improve the growth of CNTs in the vertical and lateral direction. CNTs were grown vertically by the inducing effect of nanoparticle

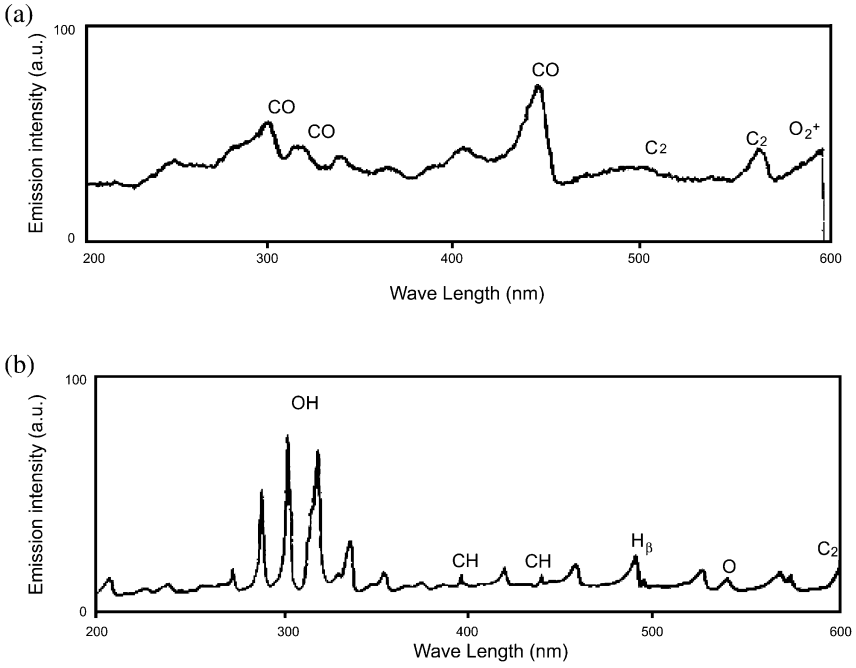

Fig. 3. (a) Emission spectra of growth CNTs from microwave plasma observed in a CO_2–CH_4 gas mixture with flow rate ratio of CH_4/CO_2 at 96%. (b) Emission spectra of diamond synthesis from the microwave plasma observed in a CO_2–CH_4 gas mixture with flow rate ratio of CH_4/CO_2 at 70.7%.

iron catalytic reaction and the extra carbon species, resulted from the decomposition of CH_4 and CO_2 during reaction, and were continuously supplied or diffused into the growing CNTs. The CNTs in the lateral direction with a multi-walled structure are formed significantly by the additional reprecipitation of carbon species, with mutual reaction and evaporization of hydrogen and oxygen. It finally resulted in the multi-walled CNTs. However, many various growth mechanisms have been illustrated [22–24]. The reaction sequences of deposition, adsorption, decomposition, diffusion, growth and deposition vary according to the reaction conditions and species during plasma processing.

3.3. Characterization of MWCNTs

Fig. 4 shows a Raman shift of multi-walled CNTs in the region of 1000–4000 cm^{-1}. A typical graphite vibration mode G-band at 1583 cm^{-1} and a disordered carbon mode D-band at 1355 cm^{-1} appear in the Raman spectra. The 1583 cm^{-1} peak indicates that CNTs were formed during growth, the 1355 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 [25]. An additional two peaks are observed in the second order spectrum at 2710 $cm^{-1} \approx 2$ (1355 cm^{-1}) and 2965 $cm^{-1} \approx 2$ (1583 cm^{-1}).

4. Conclusion

Growth of CNTs were produced in a higher quality in CH_4–CO_2 gas mixture made by MPCVD. This may be due to the activation of the oxygen contained in the plasma species. It is reasonable to say that reaction mechanism of CNTs growth in the CH_4–CO_2 system is different from H_2–CH_4. Our results indicate that the characteristics of multi-walled CNTs synthesized during deposition by MPCVD depend on the plasma species. Hence, the oxygen contained in the CH_4–CO_2 gas

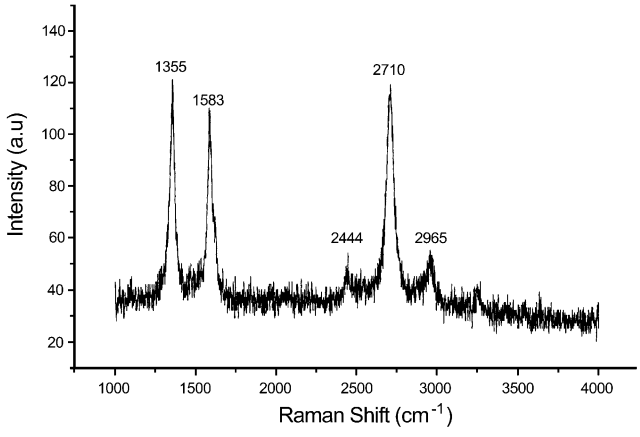

Fig. 4. Raman spectra of multi-walled CNTs.

system can increase the amount of C_2. In the C_2-rich plasma the excited C_2 emission is higher intensity and is beneficial to graphite deposition, which enhance CNTs synthesis on catalyst-deposited surface quality. Therefore, the highest yield of CNTs of approximately 70% was obtained by MPCVD for the CH_4–CO_2 gas mixture with a flow rate of CH_4/CO_2 at 96%, power supply of 300 W, reaction time of 20 min and bias voltage of 150 V.

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