Journal of Korean Vacuum Science & Technology; JKVST
Vol. 4, No. 2, June 2000, pp. 55~60

Effects of Input Gases on the Growth Characteristics of Vertically Aligned Carbon Nanotubes in Plasma Enhanced Hot Filament Chemical Vapor Deposition

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(Received May 18, 2000)

Abstract – Vertically aligned carbon nanotubes on nickel coated glass substrates were obtained at low temperatures below 600°C by plasma enhanced hot filament chemical vapor deposition where acetylene gas was used as the carbon source and ammonia gas was used as the dilution gas and catalyst. The diameters of the nanotubes decreased from 96 nm to 41 nm as NH_3/C_2H_2 ratio increased from 2:1 to 5:1. Total flow rate of input gases with constant NH_3/C_2H_2 ratio did not change the diameter of carbon nanotubes. No growth of the carbon nanotubes was observed with only C_2H_2 nor N_2 instead of NH_3. G line and D line in Raman spectra were observed, which implies that there were many structural defects in carbon nanotubes.

I. Introduction

Carbon nanotubes (CNTs) have received considerable attention since the first discovery of the carbon nanotube in 1991 [1] because the CNTs offer the prospect of both new fundamental science and many technological applications including electron emitter for field emission display, hydrogen storage, gas sensors and nano electronic devies. CNTs are an especially promising candidate for the cold cathode field emitters because of their unique electrical properties, their high aspect ratios and small radii of curvature at their tips. Numerous papers have been reported on the growth characteristics and the properties of the CNTs [2-5]. For applications such as flat panel displays and vacuum microelectronics, large area films of the nanotubes producing uniform field emissions are required. Particularly, controllability of alignment, diameter and density of CNTs is important to the application. The growth of vertically well-aligned CNTs on nickel-coated glass over areas up to several square centimeters below 660°C has been reported using plasma enhanced hot filament chemical vapor deposition (PEHFCVD) with a gas mixture of ammonia and acetylene [16,17]. But there are few reports on the effects of growth parameters on the CNTs growth using PEHFCVD. Especially, effects of NH_3 and a composition of input gas on the growth characteristics of the CNTs have not been reported yet.

In this study, we report the growth of vertically aligned, multiwalled CNTs on nickel coated substrates at low temperatures (<600°C) using PEHFCVD. We investigate the effect of growth parameters such as the gas composition and flow rate on the growth characteristics of the CNTs focusing on the role of NH_3 in the CNTs growth in PEHFCVD. Microstructure and morphology of the CNT grown by PEHFCVD was analyzed using Raman spectroscopy and scanning electron microscopy respectively.

II. Experiments

The experiments were carried out in a plasma enhanced hot filament chemical vapor deposition (PEHFCVD) system (Model: MST-CNT2000). A schematic diagram of the PEHFCVD system was shown in Figure 1. A detailed information on reactor system was previously published elsewhere [17,18]. Acetylene (C_2H_2) gas was used as the carbon source and ammonia (NH_3) gas was used as a catalyst and dilution gas. The typical flow rate of acetylene was

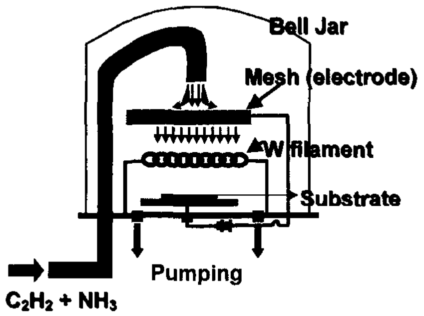

Fig. 1. Schematic diagram of plasma enhanced hot filament chemical vapor deposition system for carbon nanotube growth.

80 sccm and that of ammonia was 160 sccm. A dc plasma was employed in this work to grow vertically aligned CNTs. A thin nickel layer was deposited on glass by dc magnetron sputtering. The thickness of nickel film was 300 Å. Prior to CNTs growth, the substrate was cleaned in Trichloroethylene, Acetone, Methanol for 10 min., and rinsed in deionized water to remove organic contaminants. The substrate was transferred to the vacuum chamber and pumped down below 2×10^{-5} Torr by a mechanical and a diffusion pump. After the chamber pressure reached 2×10^{-5} Torr, NH_3 was introduced into the chamber in order to maintain a working pressure of 1 to 5 Torr. After the working pressure had been stabilized, the power to the tungsten filament coil and to the dc power supply were turned on to generate heat and plasma. The filament current changed from 5 ampere to 15 ampere. The bias voltage for plasma generation changed from 480 to 600 volts. The pre-treatment (surface etching) was conducted by NH_3 plasma for 1 to 5 min.. Then C_2H_2 was introduced into the chamber for the CNTs growth. The effect of input gas composition and flow rate on the characteristics of the CNTs growth was investigated by changing the flow rate and ratio of input gases under the same plasma condition.

The grown CNTs were characterized by scanning electron microscopy (SEM) to investigate the effect of growth parameters on their morphology. Raman spectroscopy was employed for the chemical analysis of CNTs.

III. Results and Discussion

Growth of vertically well-aligned CNTs has been reported using PEHFCVD, where C_2H_2 gas was used as the carbon source and NH_3 gas was used as

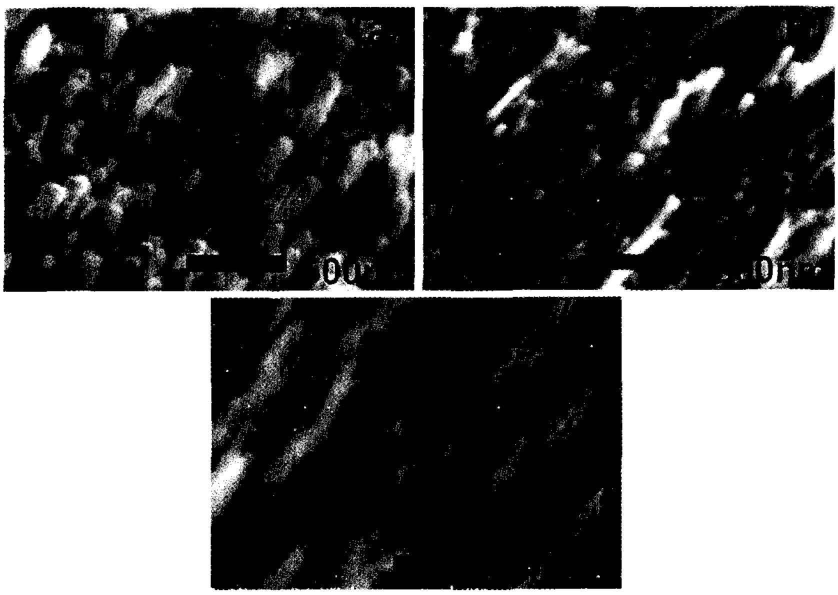

Fig. 2. Effects of NH_3 flow rate on the growth characteristics of CNTs : (a) 60 sccm, (b) 120 sccm, and (c)180 sccm with C_2H_2 flow rate of 30 sccm.

the catalyst and dilution gas. But the role of NH_3 gas and input gas composition in the growth of CNTs was not clearly understood at the moment. The effect of NH_3 gas on the characteristics of the CNTs growth was investigated by changing the flow rate of NH_3 gas. The flow rate of C_2H_2 gas was kept constant at 30 sccm and that of NH_3 gas varied from 60 sccm to 180 sccm. The chamber pressure was 3.2 Torr and the time for Ni surface pre-etching by NH_3 plasma was 1 min.. The filament current was 14 A and the plasma intensity was kept about 81 watts (580 V/0.14 A), and the growth time of the CNTs was 14 min.. As shown in Figure 2, as the flow rate of NH_3 increased from 60 sccm to 180 sccm, the mean diameter of the CNTs decreased from about 75 nm to 20 nm and the length of CNTs increased. As shown in Figure 2(c), at the high ratio of NH_3/C_2H_2 the diameter of the each CNT became very thin and each CNTs seemed to form bundles. In the Figure 2(c), the upper-rightward growth directions of the CNTs were due to the tilt view of SEM image at 45 degree. We reported that an increase in the pre-etching of Ni surface by NH_3 plasma increased the roughness of Ni surface, resulting in the decrease in the diameter of CNTs and CNTs growth required the incubation time for nucleation [17,18]. The increase in the flow rate of NH_3 increased the Ni surface etching during the incubation time for nuclei formation, resulting in the decrease in the diameter of nuclei and the CNTs. It may be also expected that increase in the flow rate of NH_3 enhanced the dissociation rate of C_2H_2 through catalyst reaction.

In order to identify the role of NH_3 gas, the effect of the NH_3/C_2H_2 ratio on the CNT growth was studied under the constant total flow rate of input gases (240 sccm). As shown in Figure 3, increase in the NH_3/C_2H_2 ratio from 2:1 to 5:1 decreased the diameter of the CNTs from 96 nm to 41 nm. This indicated that the relative flow rate of NH_3 to that of C_2H_2 was important in the growth of the CNTs. Dependence of diameter of CNTs on the NH_3/C_2H_2 ratio in this work was opposite to that of Rens group [16], where diameter of CNTs increased with increase in the NH_3/C_2H_2 ratio. It may be attributed to the difference in other experimental conditions such as plasma intensity but it needs further study on the growth characteristics. The effect of the total flow rate on the CNTs growth was investigated under the constant NH_3/C_2H_2 ratio of 4:1. The total flow rate of input gases was varied from 100 sccm to 240 sccm. Even though the flow rate of NH_3 increased as the total flow rate increased, the diameter of CNTs

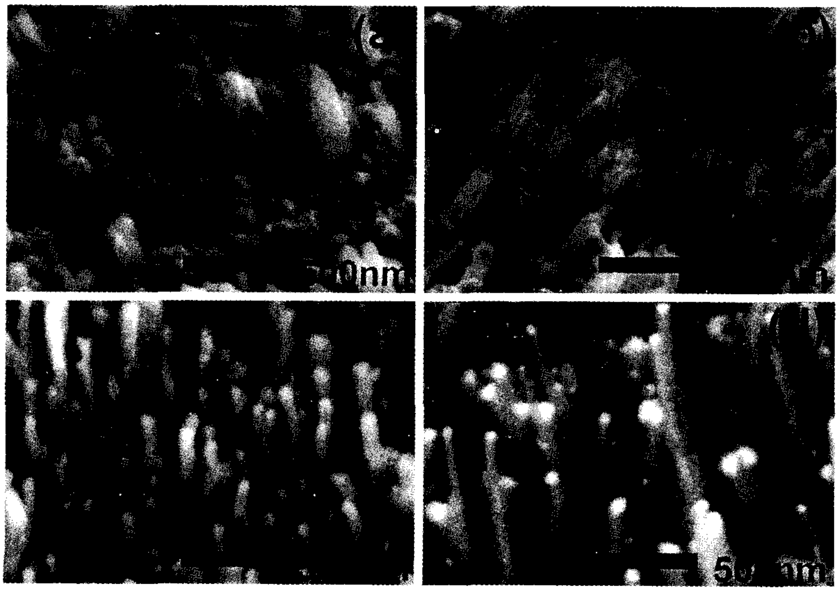

Fig. 3. Effect of NH_3/C_2H_2 ratio on the carbon nanotubes growth with constant total flow rate of 240 sccm: (a) 2:1, (b) 3:1, (c) 4:1, and (d) 5:1.

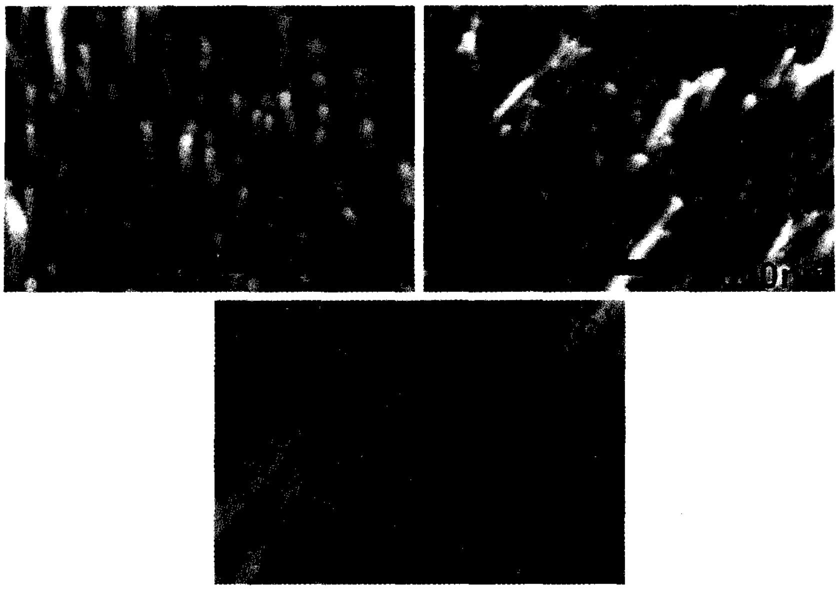

Fig. 4. Effect of total gas flow rate on the carbon nanotubes growth with constant NH_3/C_2H_2 ratio of 4:1. (a) 240 sccm, (b) 150 sccm, and (c) 100 sccm.

remained almost the same about 52 nm (shown in the Figure 4). As the total flow rate of input gases decreased, alignment of the CNTs improved as the crooked-shape CNTs were reduced. It may be due to the effect of growth temperature. As the growth temperature increased, the structural defects, such as pentagons or heptagons decreased, resulting in the improvement of alignment of the CNT. Namely, as the total flow rate of input gases decreased, velocity of the input gas reduced and the growth temperature

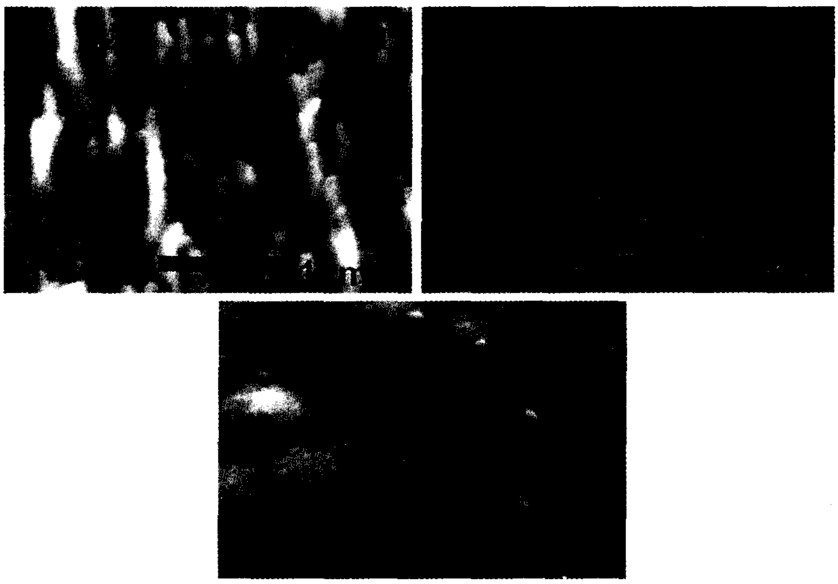

Fig. 5. Surface morphology of carbon nanotubes with and without NH_3. (a) with NH_3 (C_2H_2: 30 sccm, NH_3: 120 sccm, plasma intensity: 580 V/0.14 A) (b) without NH_3 (C_2H_2: 80 sccm, plasma intensity: 700V/0.04A), (c) with N_2 (C_2H_2: 80 sccm, N_2: 160 sccm, plasma intensity: 580 V/0.14 A) at constant filament current of 11.1 A.

increased, leading to the improvement of alignment of the CNTs.

Based on these results shown in Figure 3 and 4, it may be concluded that NH_3 made effects on the diameter and length of the CNT through the etching of Ni surface as well as the catalytic reaction in the growth of the CNTs. It was also suggested that the ratio of NH_3 to C_2H_2 is more important factor in the CNTs growth than the total flow rate of NH_3. To clarify the effect of NH_3 on the CNTs growth, the growth of the CNTs was performed with only C_2H_2 and with N_2 instead of NH_3. Ni surface was first pre-etched with NH_3 in 4 min., and then the growth of the CNTs was performed with only C_2H_2. As shown in Figure 5(b), the thick amorphous carbon layer was immediately deposited and no CNTs were observed without NH_3. Instead of NH_3 gas, N_2 was used during the etching and growth stage of the CNTs, but the CNTs were not observed neither. These results are consistent with previous results and agreed with Ren *et al.*s result [16]. It can be concluded that NH_3 is the very important catalytic gas in the growth of the CNTs in PEHFCVD method.

Raman characterization is known to be very sensitive to the breakdown in translational symmetry of carbon and can provide detailed information on microstructure. Micro-Raman spectra were obtained using Ar laser with wavelength of 514.5 nm (Model: Renishaw-3000) and shown in Figure 6. It is reported that in the high frequency region of the first-order Raman spectra, the tangential C-C stretching mode (G) is located at 1572 and 1591 cm^{-1}. These multiply split peaks originated from the vibrational modes of phonon in graphite. Peak at 1592 cm^{-1} in Figure 6 corresponds to the mode of longitudinal optical component (LO) in G mode. Peak at

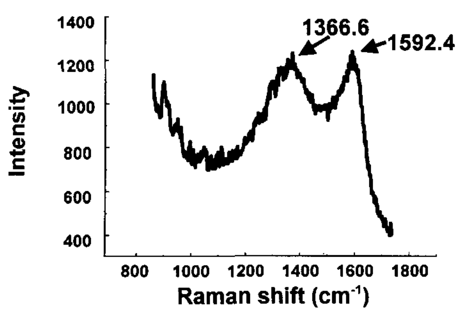

Fig. 6. Raman spectra of carbon nanotubes.

the 1336 cm^{-1} (D line) was also found. D line of the CNT can be interpreted as being due to (1) the finite size of the crystalline domains or lattice distortions and (2) the high density of the aligned tubes. Raman spectra indicate that the CNTs grown by HFPECVD contain many impurities and disorder. Incorporation of impurities and defects in CNTs may be attributed to the low temperature PECVD process, which needs further improvement.

IV. Conclusion

Vertically aligned CNTs on nickel-coated glass substrates were obtained at low temperatures below 600°C by plasma enhanced hot filament chemical vapor deposition using acetylene gas as the carbon source and ammonia gas as the dilution gas and catalyst. The ratio of NH_3 to C_2H_2 is more important factor in the CNTs growth than the total flow rate of NH_3. A control of the flow rate of input gases determines the morphology of the CNTs. No CNTs were obtained without NH_3 gas nor with N_2 instead of NH_3. G line and D line in Raman spectra were observed, which indicated that there were many defects in the CNTs.

Acknowledgement

This work is partially supported by the Ministry of industry and commerce through the project, "Development of advanced nanocomposite materials".

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