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Effect of mixture ratios and nitrogen carrier gas flow rates on the morphology of carbon nanotube structures grown by CVD

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Abstract We report on the growth of carbon nanotubes (CNTs) by thermal Chemical Vapor Deposition (CVD) and investigate the effects of nitrogen carrier gas flow rates and mixture ratios on the morphology of CNTs on a silicon substrate by vaporizing the camphor/ferrocene mixture at 750 °C in a nitrogen atmosphere. Carbon layers obtained after each CVD growth run of 15 min are characterized by scanning electron microscopy (SEM) and Raman spectroscopy. Growth of CNTs is found to occur on silicon substrates. The SEM micrographs helped better understand the nanotube growth morphology while Raman Spectroscopy was used to detect the presence of nanotubes and also identify their nature vizely semiconducting or metallic, single-walled or multi-walled. Raman Spectra was also useful to estimate the quality of the samples as a ratio of nanotube to non-nanotube content. The length and diameters of the aligned CNTs were found to depend on the pyrolysis temperatures, mixture ratio, and the nitrogen carrier gas flow rates.

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Introduction

The discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1] have proven to show great promise in a wide variety of applications such as fabrication of strong composite materials, nano-electronic devices, electrochemical devices, power devices, catalyst and adsorbents for gas separation or storage, etc. This is largely due to the fact that CNTs exhibit exceptional chemical and physical properties related to toughness (Young's Modulus $\geq$1 Tpa), chemical inertness, magnetism and electrical and thermal conductivity. Aligned CNTs have advantages over non-aligned CNTs in many applications. For example, when aligned, CNTs are ideal candidates for field emission devices in flat panel displays, so the controllable synthesis of aligned CNTs with good alignment and high purity is of great importance. Andrews et al. [2] obtained high-purity aligned CNTs on the inner wall of a quartz tube and on a quartz substrate using the catalytic decomposition of ferrocene-xylene at 675 °C with a growth rate of about 25 μm/h.

Carbon nanotubes are synthesized by several different processes, which include the arc discharge [3], the laser ablation [4] and the chemical vapor deposition (CVD) from catalytic decomposition of hydrocarbons on transition metals [5]. The CVD process has several advantages over the others and it is recognized as the most promising for industrial scale-up, due to the low growth temperature, high yields and purities that can be achieved. It has been found that the structure of carbon materials is dependent on

the growth parameters, such as reaction temperature, catalyst, reaction gas, etc.

The aim of the study was to grow vertically aligned CNTs using CVD on a silicon substrate by using an inexpensive carbon source. The effect of camphor/ferrocene mixture ratios as well as the effect of nitrogen carrier gas flow rates on the morphology of CNT structures was investigated.

Experimental details

Carbon nanotubes were grown on a silicon substrate by thermal CVD using about one gram of mixture of camphor and ferrocene in different ratios. Ferrocene was used as a catalyst source because it is a good precursor for the production of iron nanoparticles [6, 7]. Camphor was used as carbon source since it is inexpensive, non-toxic, and commercially available. Kumar et al. [8] showed that the hexagonal and pentagonal ring structures of camphor make it an ideal carbon precursor to produce nanotubes. The camphor/ferrocene mixture was heated at 250 °C to get the mixture in a gas phase. The vapors were carried to the 2nd furnace (high-temperature furnace) by a N_2 gas flow. In the 2nd furnace, which was set at temperatures, ≥750 °C pyrolysis of the vapors took place. After 15 min a deposit of carbon was found on the substrate and inside the tube walls in the high-temperature zone. The detailed experimental setup used for thermal CVD in this work is shown in Fig. 1. The effect of camphor/ferrocene mixture ratios and nitrogen carrier gas flow rates on CNT growth was studied using scanning electron microscopy (SEM) and Raman spectroscopy. A LEO 1525 Field emission scanning electron microscope with beam energy at 10 kV was used to investigate the sample morphology. The Raman model, Dilor XY–multi-channel spectroscopy was used to investigate structural properties of CNT. The measurements were conducted at room temperature with 514.5 nm Ar ion excitation laser. The power laser was set to 100 mW to reduce heating effects and degradation of the samples, and only probing about 100 nm of the sample surface.

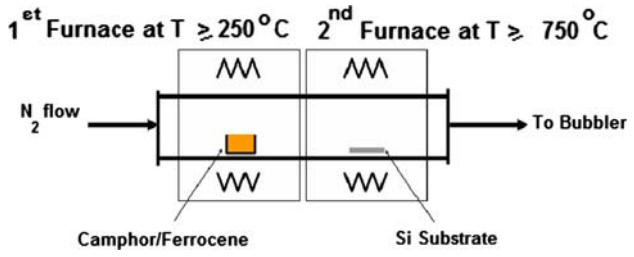

Fig. 1 Experimental set-up of the thermal CVD system

Results and discussion

The effect of nitrogen carrier gas flow in the CNTs growth was studied over the range of 50–200 standard cubic centimeters per minute (sccm), while maintaining the temperature constant at 750 °C and the camphor/ferrocene mixture ratio at 20:1, respectively. The SEM micrographs of the structures synthesized at the above conditions are shown in Fig. 2. A black film (carbon soot) could be observed on the Si substrate after it was exposed to the carbon precursor gas stream for at least 15 min with the substrate temperature at 750 °C. It was observed that all CNTs are randomly grown on the substrate surfaces. For a nitrogen flow of 50 sccm, CNTs with a diameter between 20 and 100 nm and some carbonaceous material are formed on the substrate. These diameter ranges are indicative of multi-walled CNTs. When a nitrogen flow rate of 150 sccm and a temperature of 750 °C are maintained, cleaner, densely packed CNTs with smaller diameters than those grown at lower nitrogen flow rates are observed (Fig. 2c). At a nitrogen carrier gas flow rate of 200 sccm a few localized tubes were grown and iron particles with diameters of about 0.05 μm were found attached to the substrate surface. This suggests that as the flow rate increases from 50 to 150 sccm, more vapors are carried to the 2nd furnace, resulting in an increase in CNT growth. However, as the flow rates exceed 150 sccm, vapors are carried out to the bubbler rapidly and do not have sufficient time for pyrolysis to occur, resulting in a decrease in CNT growth. The result demonstrates that the diameter, growth rate, and density of MWCNTs can be controlled by varying or adjusting the nitrogen carrier gas flow rates. Huczko [9] found that the CNTs diameters and the number of walls in the CNTs were mainly determined by the size of the catalysts. He also reported that higher temperatures (≥ 600 °C) enhance the full decomposition of ferrocene to produce fine Fe clusters, so there are more possibilities for the growth of aligned CNTs with smaller diameters. Therefore, the constant temperature at 750 °C and the higher carrier gas flow rates resulted in CNTs with smaller diameters.

During the deposition process most of the CNT growth took place inside the inner walls of the quartz tube. This is in agreement with results obtained by Musso et al. [10] who studied the growth of vertically aligned CNTs by CVD. They showed that it was not easy to quantify the yield of the deposition process. However, they showed that by rough estimations based on the values of the thickness of the film on the substrate and of the tube inner surface, and by assuming an average density of 1 g/cm^3 for all carbonaceous products; that the yield of the process is larger than 50% in weight, which means that the CVD process is efficient in converting the carbon source to soot.

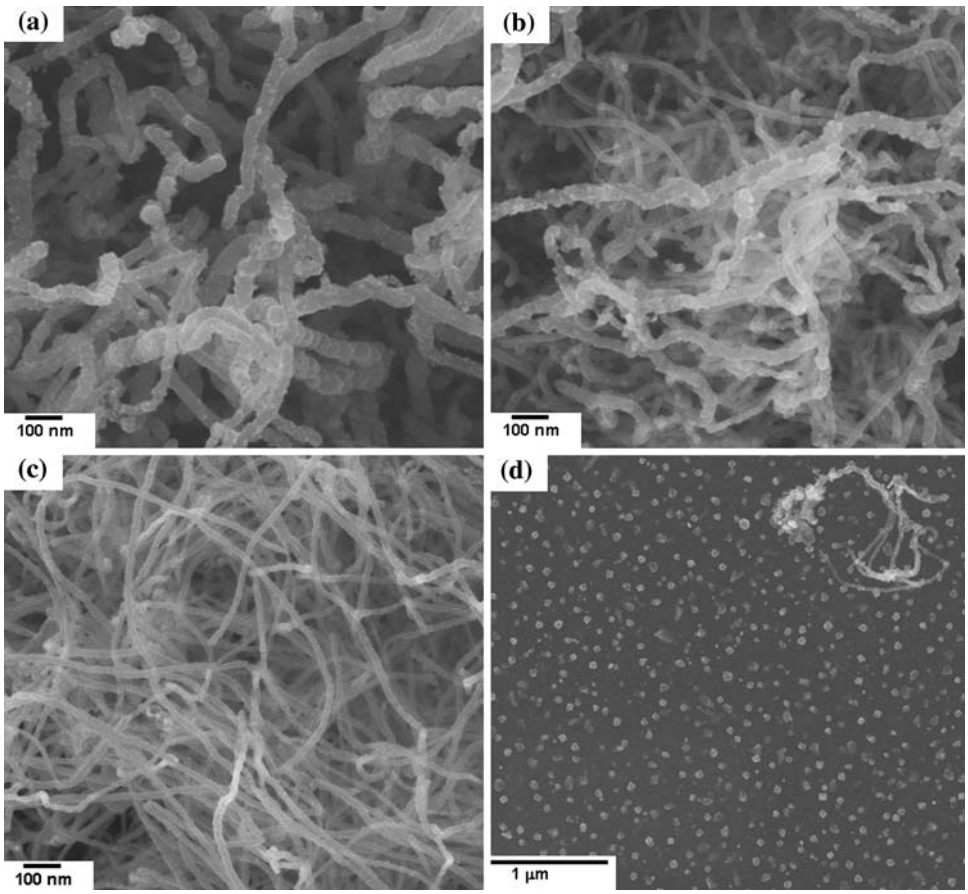

Fig. 2 SEM micrographs of CNT samples synthesized at 750 °C for 15 min at four different nitrogen carrier gas flow rates; (**a**) 50 sccm, (**b**) 92 sccm, (**c**) 150 sccm and (**d**) 200 sccm

A clear view of the length and alignment of as-grown CNT is shown in Fig. 3. Also shown in Fig. 3 is a block (densely packed) of aligned CNTs, peeled off from the Si substrate. Each vertical column consists of in numerous nanotubes self-organized into rope-like structure. It is interesting to note that very small growth is observed on the top surface of the substrate. The length of CNTs grown on silicon is found to be as long as 100 μm. A crack observed in the film may be either during the post-deposition sintering stage or while taking out from the quartz tube. The dense ordered packing of CNTs, coming from the effect of van der Waals interaction, results in the formation of CNT alignment [11, 12].

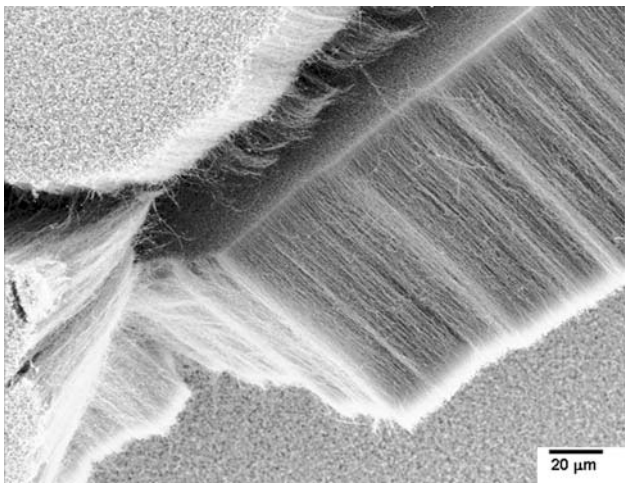

Fig. 3 SEM micrograph of aligned CNT sample grown at 750 °C for 15 min with a nitrogen carrier gas flow rate of 15 sccm

Raman spectroscopy is a non-destructive characterization tool that probes the structural bonding of CNTs [13]. A high and uniform crystallinity of the produced nanotubes is an important measure of the quality. The crystallinity/graphitization was analyzed with Raman spectroscopy, which has been shown to be a perfect tool to evaluate the crystallinity and the defects in sp^2-hybridized carbon structures. Figure 4 displays the first-order Raman spectra of CNTs synthesized at 750 °C for 15 min. during different nitrogen (N_2) carrier gas flow rates. The CNTs were excited by a 514.5 nm laser in the high-frequency (1,000–2,000 cm^{-1}) region. The effect of nitrogen flow rate on the structural changes is shown in the Raman spectra, Fig. 4. The strong band at $\sim$1,576 cm^{-1}, referred to as the G-band, is the Raman allowed phonon high frequency E_{2g} first-order mode. It is attributable to the movements of carbon atoms in opposite directions along the surface of the tube [14, 15]. The peak at $\sim$1,348 cm^{-1} (D-band)

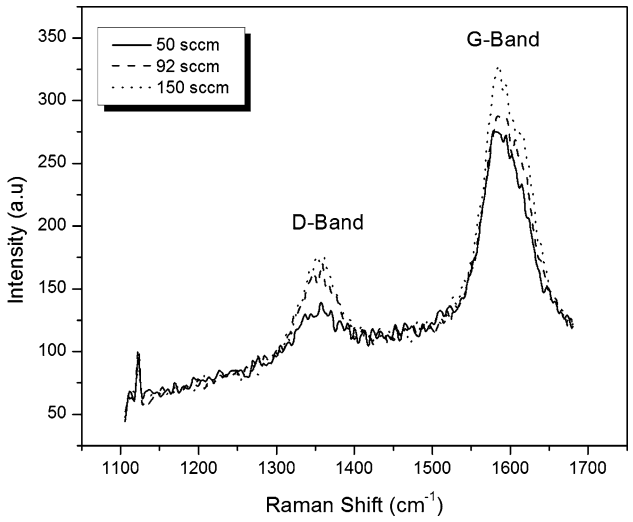

Fig. 4 First order Raman spectra of nanotubes synthesized at 750 °C for 15 min during different nitrogen gas flow rates. The high-frequency regions shows the disorder D and G bands

originates from defects in the curved graphene sheets, tube ends, or from the presence of carbon coating on the outside of the tubular bands [16, 17]. For flow rates between 50 and 150 sccm the peaks appear to be more or less at the same position. The common trend observed in our samples consists of a linear up-shift in Raman intensities for both the D- and G-band, with an increase in nitrogen (N_2) carrier gas flow. The intensity of both the D- and G-bands at a flow rate of 150 sccm is higher than that at a flow rate of 50 sccm. This indicates an increase in the amount of carbon as the flow rate increases, which is in agreement with SEM results. The increased intensity of the D-band (located at $\sim$1,348 cm^{-1}) with an increasing nitrogen carrier gas flow rate and a constant temperature (750 °C) is related to a large portion of defects caused by some types of structural transformation originated by the thermal energy suffered by the system. Moreover, a small bump appears on the high wavenumber side of the G-band, at 1,620 cm^{-1} which is again assigned to multi-wall nanotubes and is explained as a disorder-induced feature of graphitic sheets [18–21]. Thereupon, the results show that for all the experimental procedures which are presented in this article; the material produced is MWCNTs.

In order to evaluate the Raman parameters in detail (e.g., peak positions, relative intensities, and full width at half-maximum (FWHM)), curve fittings were carried out with a Lorentzian line-shape for all Raman spectra, as shown in Table 1. From the integrated area under the respective D-bands as well as the relative intensity ratios (I_D/I_G) in Table 1, it is concluded that an increase in the nitrogen carrier gas flow rate results in a decrease in the amount of defects (carbonaceous particles and impurities) of the deposited material. Furthermore, based on the decrease in the FWHM of the respective G-bands (in Table 1) with an increase in the nitrogen carrier gas flow rate, it is also concluded that the CNTs present in the deposited soot become more graphitic, i.e., has a greater degree of structural perfection.

Figure 5 shows SEM micrographs of CNTs grown at 750 °C, for 15 min by using five different camphor/ferrocene mixture ratios. It can be seen that at a camphor/ferrocene mixture ratio of 5:1 (higher ferrocene concentration) thick CNTs with a lot of carbonaceous particles are present on the Si substrate surface, Fig. 5(a). The micrographs show that as ferrocene concentration decreases from 0.16 g (5:1) to 0.02 g (40:1), the amount of carbonaceous particles also decreases. The diameters of aligned CNTs fabricated at lower ferrocene concentrations (Fig. 5c–e) are smaller ($\sim$10 nm) than those fabricated at higher concentrations ($\sim$100 nm) (Fig. 5a, b). Furthermore, the surfaces of the aligned CNTs synthesized at the lower ferrocene concentration are cleaner than those synthesized at higher ferrocene concentration because the higher ferrocene concentration results in more Fe clusters in the furnace that can adhere to the surfaces of the already grown aligned CNTs. This indicates that at higher ferrocene concentration more Fe particles decompose forming large clusters which inhibit CNT formation, resulting in the presence of more carbonaceous particles on the tube surface. Since the iron particles produced at lower concentrations are smaller than those produced at higher concentrations the CNTs catalyzed by lower ferrocene concentrations will have better crystal structures and smaller diameters than those catalyzed by higher ferrocene concentrations. Therefore, it can be concluded that lower ferrocene concentrations provide better conditions for the

Table 1 Raman factors for CNT samples synthesized at different nitrogen flow rates

N_2 flow rate (sccm)	D-band (cm^{-1})				G-band (cm^{-1})			
	Area	Peak position (cm^{-1})	FWHM	Intensity I_D	Area	Peak position (cm^{-1})	FWHM	Intensity I_G
50	14,879	1367.4	16.55	57.22	28,270	1592.6	89.06	202.08
92	12,773	1357.3	97.00	83.83	30,269	1594.5	88.70	217.24
150	12,244	1357.4	81.68	95.43	32,812	1593.9	84.66	246.73

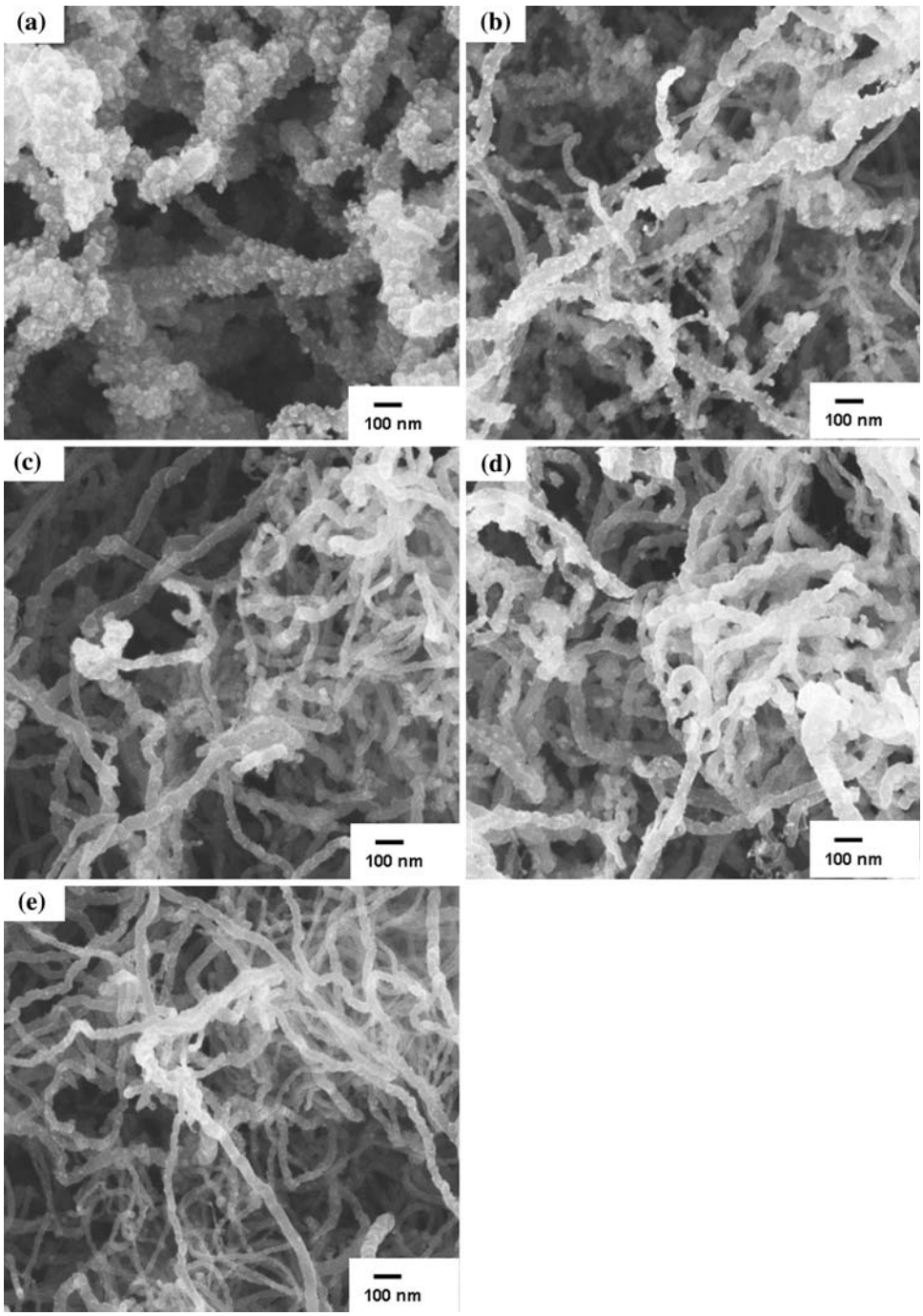

Fig. 5 SEM images of CNTs grown using different Camphor/Ferrocene mixture ratios/concentrations (**a**) 5:1, (**b**) 10:1, (**c**) 15:1, (**d**) 20:1 and (**e**) 40:1

growth of aligned single-walled CNTs with smaller diameters.

Conclusion

Vertically aligned MWCNTs were successfully grown on the surface of a silicon substrate using different mixture ratios of camphor and ferrocene under the flow of nitrogen carrier gas at a constant temperature of 750 °C. The substrate temperature, mixture ratios and nitrogen carrier gas flow rates are the most important factors for CNT growth. The data indicate that more defects (carbonaceous particles) are present when the nitrogen flow rates are high. The higher nitrogen carrier gas flow rates show MWCNTs with a higher degree of graphitization. The length of the aligned CNTs on the silicon substrate was about 100 μm. It is observed that temperatures below 750 °C and nitrogen carrier gas flow rates equal to and above 200 sccm is not suitable for CNT formation. The results show that the

diameter, density, and growth rate of MWCNTs can be controlled by adjusting the mixture ratios and nitrogen carrier gas flow rates. The optimum conditions for synthesizing vertically aligned MWCNTs with small diameters and minimal carbonaceous materials is a camphor/ferrocene mixture ratio between 20:1 and 40:1 with a nitrogen flow rate of 150 sccm.

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