The Role of C₂ in Low Temperature Growth of Carbon Nanofibers

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The synthesis of carbon nanofibers at low temperature was performed by plasma-enhanced chemical vapor deposition using a low-temperature CO/Ar/O₂ DC plasma without any catalyst materials. At the optimum oxygen concentration of O₂/CO = 0.002–0.005, vertically aligned CNFs can be synthesized at temperature as low as 90°C. In order to clarify the importance of C₂ molecules in the present CNFs growth process, the correlations among emission intensities of C and C₂ and CNFs growth rates have been evaluated for various O₂/CO ratio. Although the emission intensity of C atom spectra was not influenced by the addition of oxygen, the emission intensity of C₂ HP band decreased drastically with increasing additional oxygen fraction. From the comparison of growth rates of CNFs and optical emission spectroscopic results, it was concluded that C₂ molecules play an important role as the main precursors of CNFs synthesis process in this system because the reduction tendencies of CNFs growth rates and C₂ high-pressure bands emission intensity show a good correlation toward O₂/CO ratio.

Introduction

Carbon nanofibers (CNFs) as well as carbon nanotubes (CNTs) are the most promising materials as field emitters in flat panel display due to their low turn-on voltage and good current stability with chemical inertness and mechanical strength. Their high surface area makes CNTs/CNFs also attractive for applications such as electrochemistry, electrodes for fuel cells, and super capacitors. For practical applications of CNTs/CNFs, a method for their synthesis at low temperatures is essential to allow direct deposition of CNTs/CNFs on various substrates involving materials with low melting points, and a large number of studies on low temperature synthesis of CNFs/CNTs have been reported with various discharge systems, such as radio frequency discharge of CH₄ (Boskovic *et al.*, 2002), DC discharge of C₂H₂/NH₃ (Hofmann *et al.*, 2003), AC discharge of C₂H₂/NH₃/N₂/He (Kyung *et al.*, 2006), and microwave discharge of CH₄/H₂ (Liao and Ting, 2006). To our knowledge, few attempts at low-temperature plasma-enhanced chemical vapor deposition (PECVD) of CNFs/CNTs using CO as the carbon source have been made (Han *et al.*, 2002; Plönjes *et al.*, 2002). In general, the advantages of low-temperature plasma CVD using CO instead of hydrocarbons as the carbon source gas are as follows: (1) the deposition of amorphous carbon is suppressed even at low temperatures (Muranaka *et al.*,

1991; Stiegler *et al.*, 1996); (2) the CO disproportionation reaction $\text{CO} + \text{CO} \rightarrow \text{CO}_2 + \text{C}$ is thermodynamically favorable at low temperature; (3) vibrationally excited molecules are formed and enhance reactions at low temperature, such as $\text{CO}(v) + \text{CO}(v) \rightarrow \text{CO}_2 + \text{C}$ (Capitelli *et al.*, 1986; Mori *et al.*, 2001; Plönjes *et al.*, 2002). In the previous study, we have reported that the vertically aligned CNFs were able to be synthesized at temperature as low as 90°C using low temperature CO/Ar/O₂ plasma system (Mori *et al.*, 2007; Mori and Suzuki, 2008). In the subsequent study on the importance of catalyst particle, we have found that the CNFs growth process is not controlled by the catalyst particle and the CNFs can be grown surprisingly even if no catalyst is used in our CO/Ar/O₂ plasma system.

As for the CNF growth model for PECVD at such a low temperature, Hofmann *et al.* (2003) have suggested that the rate-determining step is not the diffusion of carbon through the catalyst particle bulk, as was proposed by Baker and Harris (1978) and is generally accepted for high-temperature conditions, but the diffusion of atomic carbon on the catalyst surface. In this surface diffusion model, carbon atoms adsorbed at the top surface of the metal particles diffuse along the surface, where their motion is much faster than bulk diffusion, and then segregate at the bottom of the particles, forming graphitic planes. However, that model is not applicable to our catalyst-free CNFs synthesis process and different growth model has to be introduced. In the previous report, spectroscopic study has revealed that there is a steady correlation between C₂ high-pressure bands and CNFs growth. In the discharge plasma of CO, C₂ molecules are known

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Fig. 1 SEM images of carbon deposits with different additional O_2 flow rates: $O_2/CO =$ (a) 0 (1 h); (b) 0.001 (2 h); (c) 0.004 (2 h); (d) 0.007 (2 h).

Fig. 2 Growth rates of CNFs as a function of O_2/CO ratio

to be formed through the $C + C_2O \rightarrow C_2 + CO$ reaction effectively with C_2O molecules formed in the process $C + CO + M \rightarrow C_2O + M$ where M is a collision partner (Caubet and Dorthe, 1994). Therefore, there is a possibility that C_2 molecules could play an important role as the precursors of CNFs growth in CO plasma CVD system. In this study, we try to clarify the role of C_2 molecules in low temperature growth of CNFs.

1. Experimental

The CNFs were grown using a DC PECVD system in a quartz discharge tube with a 10 mm inner diameter (Mori *et al.*, 2007; Mori and Suzuki, 2008). In this study, borosilicate glass substrates (4 mm × 4 mm × 0.2 mm) were used as substrates and the substrate is placed on the cathode. At the beginning of our CNFs synthesis study, we prepared the Fe catalyst layer on the substrates using wet coating method. However, we have found that even if no catalyst layer is prepared on the substrate, we can synthesize the CNFs which have same morphology as those with Fe catalyst. Therefore, for simplicity, we do not use any catalysts in this study. The parameters for the CNTs/CNFs deposition process are as follows: CO flow rate: 20 sccm, Ar flow rate: 20 sccm, O_2 flow rate: 0–1.0 sccm, total pressure: 800 Pa, discharge current: 2 mA. The substrate temperature, T_s , was monitored by a thermocouple placed below the substrate. The plasma emission was monitored by a spectrometer (HR4000, Ocean Optics Inc.). In the previous study, we could not detect any emission lines from the atomic carbon (Mori and Suzuki, 2008). In this study, in order to observe the weak ultraviolet emission of atomic carbon from cathode region, a quartz lens whose focal length is 10 mm was used. Carbon deposits grown on the substrate were observed by scanning electron microscopy (S-4500, Hitachi Ltd.). In this study, growth rate is determined by the length of CNFs at the edge of substrates using SEM images. The growth rate is not uniform for the different position on

Fig. 3 Typical emission spectra of CO/Ar Plasma from the cathode region ($O_2/CO = 0$)

the substrate; it is very low in the central area and higher at the edge.

2. Results and Discussion

Figure 1 shows SEM images of the carbon deposits after 1–2 h deposition with different additional O_2 gas compositions. Without an addition of oxygen, pillar-like carbon films were formed. When a small amount of O_2 was added to the CO plasma, the morphology of carbon films changed to cauliflower-like structure ($O_2/CO \sim 1/1000$) and fibrous structure ($O_2/CO = 2/1000$ – $5/1000$). At higher O_2 flow rates, however, the deposition rate decreased and more smooth carbon films are deposited. Although the substrate was heated up by the discharge, the temperature of all the samples shown in **Figure 1** remained as low as 90°C . **Figure 2** shows the growth rates of carbon fibers. The growth rate of CNFs is decreased with increasing oxygen fraction monotonously.

Figure 3 shows the typical emission spectra from CO/Ar/ O_2 plasma. A strong C_2 high-pressure band and CO Ångström bands ($B^1\Sigma^+ \rightarrow A^1\Pi$) and also a weak C atom spectrum at 247.9 nm can be seen. Interestingly, instead of C_2 sawn bands ($d^3\Pi_g \rightarrow a^3\Pi_u$), which are well known as the most prominent bands of C_2 in hydrocarbon discharge and combustion flames, C_2 high-pressure bands ($d^3\Pi_g, v = 6 \rightarrow a^3\Pi_u$) were observed in our system, which are known to be predominant compared to other C_2 band systems under certain CO discharge conditions (Caubet and Dorthé, 1994).

Figure 4 shows the influence of oxygen fraction on the emission intensities of CO Ångström band, C_2 HP band, and C atom spectra. From this figure, the contribution of C_2 molecules to the CNF synthesis is suggested, because it is only C_2 molecules that the emission intensity shows a substantial change when the amount of oxygen increases. As for atomic carbon, the emission intensity is not influenced by the addition of oxygen and it is thought

Fig. 4 Emission intensity of CO^* , C_2^* , and C^* as a function of O_2/CO ratio

Fig. 5 Normalized growth rates of CNFs and emission intensities of C_2^* and C^* as a function of O_2/CO ratio (In this figure, growth rates and emission intensities are normalized using their values at $O_2/CO = 0$)

that there is no substantial change in the amount of C atom concentration.

It is more clearly suggested from **Figure 5** in which the normalized growth rate of CNFs and emission intensity of CO, C and C_2 by those without oxygen addition are plotted as a function of oxygen fraction. Although the normalized emission intensity of C atom spectra are not influenced by the addition of oxygen, that of C_2 HP band and normalized growth rates decrease drastically with increasing additional oxygen fraction and show a good correlation between them.

In general, the change in the precursor density and the increase in the etching ability are thought to be the reasons why CNFs disappears as the amount of oxygen increases. However, as shown in the previous study, it cannot be thought that an increase in the etching ability is the reason for the disappearance of the CNFs in our

Table 1 Rate constants and reaction characteristic time for atomic carbon consumption paths

Reaction number	Rate constants	Characteristic time [s]	References
(1)	$1.5 \times 10^{-31} \text{ cm}^6/\text{s}$ ($M = \text{CO}$)	$3 \times 10^{-4} (1/k_1[\text{CO}][M])$	Gosse <i>et al.</i> (1972)
(3)	$1.2 \times 10^{-32} \text{ cm}^6/\text{s}$	$\sim 4 \times 10^1 (1/k_3[\text{C}][M])^a$	Martinotti <i>et al.</i> (1968)
(5)	$4.8 \times 10^{-33} \text{ cm}^6/\text{s}$ (300 K)	$> 5 (1/k_5[\text{O}][M])^b$	Brown and Bell (1974)
(6)	$3 \times 10^{-10} \text{ cm}^3/\text{s}$ (300–400 K)	$\sim 6 \times 10^{-4} (1/k_6[\text{C}_2\text{O}])^c$	Ionikh <i>et al.</i> (1994)
(8)	$2.5 \times 10^{-11} \text{ cm}^3/\text{s}$ (300 K)	$3 \times 10^{-4} (1/k_8[\text{O}_2])$	Bergeat <i>et al.</i> (1999)
(9)	$< 1 \times 10^{-14} \text{ cm}^3/\text{s}$ (300 K)	$> 1 (1/k_9[\text{CO}_2])$	Husain and Kirsch (1971)
Diffusion loss	$3.1 \times 10^4 \text{ Pa cm}^2/\text{s}$ (D in CO at 400 K)	$1 \times 10^{-4} (L^2/D)^d$	Ito <i>et al.</i> (2000)

^a $[\text{C}] \sim [\text{C}_2\text{O}]$ is assumed for the simplicity.

^b $(1/2)[\text{O}] < [\text{O}_2] = 1/1000 [\text{CO}]$ is assumed.

^c $[\text{C}_2\text{O}] \sim k_1[\text{CO}][M]/2k_6 = 1 \times 10^{13} \text{ cm}^{-3}$ is used (Caubet and Dorthe, 1994).

^d L is determined to be 0.5 mm from the thickness of negative glow region.

system. When we added the small amount of hydrogen to the CO/Ar plasma, the CNFs disappear but the carbon deposits are not removed. As for the change in the spectrum, it is only C_2 molecules that the emission intensity shows a substantial change when the amount of hydrogen increases. It means that, in the case of hydrogen addition, the carbon etching ability of hydrogen is much lower than that of oxygen (Mucha *et al.*, 1989), but the suppression ability of C_2 molecule formation is still high, i.e. even if the etching ability is low, the suppression of C_2 molecule formation may result in the disappearance of fibrous structure. Therefore, it is reasonable to assume that, instead of C atoms, C_2 molecules play an important role as the main precursors of CNF synthesis in this system.

Here, let us consider the reaction mechanism in CO/Ar/ O_2 plasma. The dissociation and excitation of CO (CO^*) by the electron impacts initiate the following gas-phase reactions:

When the sequence of the above reactions has proceeded to an extent where the steady-state approximation is verified, the concentrations of the species C, $\text{C}^* = \text{C}(3s^1\text{P})$, C_2 , $\text{C}_2^* = \text{C}_2(d^3\Pi_g, v = 6)$ and C_2O radicals are given

by

$$[\text{C}_2^*] = \frac{\beta k_6[\text{C}][\text{C}_2\text{O}]}{k_{\text{E-C}_2^*} + k_{\text{Q-C}_2^*}[\text{M}] + k_{\text{D-C}_2^*}} \quad (11)$$

$$[\text{C}^*] = \frac{k_{\text{ex}}[\text{e}][\text{C}]}{k_{\text{E-C}^*} + k_{\text{Q-C}^*}[\text{M}] + k_{\text{D-C}^*}} \quad (12)$$

$$[\text{C}_2\text{O}] = \frac{k_1[\text{C}][\text{CO}][\text{M}]}{k_6[\text{C}] + k_7[\text{O}] + k_{\text{dis-C}_2\text{O}}[\text{e}]k_{\text{D-C}_2\text{O}}} \quad (13)$$

$$[\text{C}] = \frac{(k_{\text{dis-CO}}[\text{e}] + k_{10}[\text{CO}^*])[\text{CO}]}{k_1[\text{CO}][\text{M}] + k_6[\text{C}_2\text{O}] + k_8[\text{O}_2] + k_{\text{D-C}}} \quad (14)$$

where k_1 , k_6 , k_7 , k_8 and k_{10} are the rate constants of reactions (1), (6), (7), (8) and (10), $k_{\text{D-A}}$ is the rate constants for the diffusion loss of molecules A, $k_{\text{dis-A}}$ is the rate constants of dissociation reaction of molecule A by the electron impact, $k_{\text{E-A}}$ and $k_{\text{Q-A}}$ are the rate constants for the deactivation reaction of A^* due to the photon emission and collisional quenching, k_{ex} is rate constants of the electron impact excitation of atomic carbon, $\text{C} + \text{e} \rightarrow \text{C}(3s^1\text{P}) + \text{e}$, and β is the fraction of C_2 produced in the level $d^3\Pi_g$ ($v = 6$) by the $\text{C} + \text{C}_2\text{O}$ reactions, respectively.

Although emission intensity of C atom is unchanged by increasing O_2 concentration, the emission intensity of C_2 molecule is decreased with increasing O_2 concentration in our experiments. From Eq. (11), the reduction in $[\text{C}_2\text{O}]$ is thought to be the reason for the reduction in C_2 emission intensity. From Eq. (13), $[\text{C}_2\text{O}]$ density is reduced by only the increment in $[\text{O}]$ density when O_2 is increased. Therefore, the acceleration of the reaction rate of Eq. (7) due to increasing in $[\text{O}]$ is thought to be the reason for the reduction of C_2 . This is also explained by the fact that when $\text{O}_2/\text{CO} = 1/1000$, the reaction rate of Eq. (8) corresponds to that of (1), i.e. generation rate of O atom is equivalent to that of C_2O as shown in **Table 1**, and emission intensity of C_2 starts to be reduced.

The reason for the independence of C* emission from O₂ concentration is explained by Eqs. (12) and (14). The density of C* is proportional to the [C] as indicated in Eq. (12) and the influence of [O₂] on the [C] can be evaluated by the denominator of the right hand side of Eq. (14). In the denominator, the increment in $k_8[\text{O}_2]$ can be partially compensated by the decrease in $k_6[\text{C}_2\text{O}]$ up to low O₂/CO ratio. However, for higher [O₂], compensation by the [C₂O] reduction would not be enough to sustain the [C]. Therefore, it would be reasonable to think about the existence of much faster reducing path for [C] and that is found to be the diffusion loss from the comparison among the characteristic times in Table 1.

Although the reason for the formation of fibrous structure without catalyst metal particles has not been clearly understood yet, we believe that the nucleation and island growth process is the key and the dispersed nuclei play the role of growth site for the CNFs. This is because that CNFs grown on the polycarbonate has different morphology (Mori and Suzuki, 2009). The diameter of CNF grown on the polycarbonate is increased and fiber bundling arises and the length of fiber is diminished. The large affinity between precursor species and organic materials would result in the formation of large nuclei on the substrates and result in the growth of CNFs with large diameter.

From the above-mentioned results, we may derive the following model for the non-catalytic CNFs growth mechanism. At first, precursor species such as C and C₂ appear mainly in the negative glow area, in which strong emission from C₂ molecules are observed, and diffuse to the substrate. Then, the Volmer–Weber island growth occurs on the substrate. During this nucleation and growth process, the precursor species deposited on the substrate are etched by the oxygen selectively, and only the crystallized carbons on the nuclei remain (Muranaka *et al.*, 1991; Stiegler *et al.*, 1996). However, without addition of oxygen, both amorphous and graphitic carbon deposit. Although partially the fibrous structure is created by the C₂ molecules, C atom leads to the fiber bundling and inhibit the formation of the fibrous structure. After some growth of the nuclei, the local deposition of precursor species occurs around the tip area, which leads the anisotropic growth. This is because the sticking probability of the precursor species onto the CNF surface is so high (Traskelin *et al.*, 2008) that almost all of the precursor species are deposited around the tip area and rarely reach the lower fiber surface. In this anisotropic growth process, if the O₂/CO ratio is optimal, the diameter of CNFs does not increase as the fiber grows, and a fibrous structure can be achieved. However, if the O₂/CO ratio is slightly lower than its optimum value, the diameter of the CNFs increases as the fiber grows and the CNFs attach to adjacent fibers, which finally extinguishes the fibrous structure. On the other hand, if the O₂/CO ratio is slightly higher than its optimum value, the additional oxygen leads not only to amorphous carbon etching but

also to the suppression of C₂ molecules formation by scavenging C₂O radicals, which results in the disappearance of the fibrous structure and suppression of the carbon deposition. This optimum O₂/CO window is so narrow that this phenomenon would not have been observed until now.

Conclusions

The low temperature synthesis of carbon nanofibers was performed by plasma-enhanced chemical vapor deposition using a low-temperature CO/Ar/O₂ DC plasma without any catalyst materials and the role of C₂ molecules in the growth process was evaluated.

The morphology of carbon deposits is strongly affected by the O₂/CO ratio and the growth rate of carbon deposits is decreased with increasing oxygen fraction monotonously. Without an addition of oxygen, pillar-like carbon films were formed. However, when a small amount of O₂ was added to the CO plasma, the cauliflower-like structure (O₂/CO ~ 1/1000) and fibrous structure (O₂/CO = 2/1000 to 5/1000) appeared. At higher O₂ flow rates, the deposition rate decreased and fibrous structure disappeared and finally no carbon materials deposited.

Although the emission intensity of CO Ångström band and C atom spectra are not influenced by the addition of oxygen, the emission intensity of C₂ HP band decreased drastically with increasing additional oxygen fraction.

From the comparison of growth rates of CNFs and optical emission spectroscopic results, it is concluded that C₂ molecules play an important role as the main precursors of CNF synthesis in the present CO/Ar/O₂ PECVD system because the influence of O₂ concentration on CNFs growth rates and emission intensity of C₂ HP band show a good correlation.

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Nomenclature

D	=	the diffusion constant of C in CO	[cm ² /s]
k_{D-A}	=	the rate constant for the diffusion loss of molecules A	[1/s]
k_{dis-A}	=	the rate constant of dissociation reaction of molecule A by the electron impact	[cm ³ /s]
k_{E-A}	=	the rate constant for the deactivation reaction of A* due to the photon emission	[1/s]
k_{ex}	=	the rate constant of the electron impact excitation of atomic carbon, $C + e \rightarrow C(3s^1P) + e$	[cm ³ /s]
k_i	=	the rate constant of reaction (i)	[cm ³ /s or cm ⁶ /s]
k_{Q-A}	=	the rate constant for the deactivation reaction of A* due to the collisional quenching	[cm ³ /s]
L	=	the thickness of the negative glow region	[cm]
β	=	the fraction of C ₂ produced in the level $d^3\Pi_g (v = 6)$ by the $C + C_2O$ reactions	[—]

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