The Role of C\textsubscript{2} 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/O\textsubscript{2} DC plasma without any catalyst materials. At the optimum oxygen concentration of O\textsubscript{2}/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 C\textsubscript{2} molecules in the present CNFs growth process, the correlations among emission intensities of C and C\textsubscript{2} and CNFs growth rates have been evaluated for various O\textsubscript{2}/CO ratio. Although the emission intensity of C atom spectra was not influenced by the addition of oxygen, the emission intensity of C\textsubscript{2} 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 C\textsubscript{2} 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 C\textsubscript{2} high-pressure bands emission intensity show a good correlation toward O\textsubscript{2}/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 CH\textsubscript{4} (Boskovic et al., 2002), DC discharge of C\textsubscript{2}H\textsubscript{2}/NH\textsubscript{3} (Hofmann et al., 2003), AC discharge of C\textsubscript{2}H\textsubscript{2}/NH\textsubscript{3}/N\textsubscript{2}/He (Kyung et al., 2006), and microwave discharge of CH\textsubscript{4}/H\textsubscript{2} (Liao and Ting, 2006). To our knowledge, few attempts at low-temperature plasma CVD 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 CO + CO \rightarrow CO\textsubscript{2} + C is thermodynamically favorable at low temperature; (3) vibrationally excited molecules are formed and enhance reactions at low temperature, such as CO(v) + CO(v) \rightarrow CO\textsubscript{2} + 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/O\textsubscript{2} 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/O\textsubscript{2} 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 C\textsubscript{2} high-pressure bands and CNFs growth. In the discharge plasma of CO, C\textsubscript{2} molecules are known...
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
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$^\circ$C.

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 Dorthe, 1994).

Figure 4 shows the influence of oxygen fraction on the emission intensities of CO*, C$_2$*, and C* as a function of O$_2$/CO ratio. 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 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 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.

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
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\textsubscript{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\textsubscript{2} molecule formation is still high, i.e. even if the etching ability is low, the suppression of C\textsubscript{2} molecule formation may result in the disappearance of fibrous structure. Therefore, it is reasonable to assume that, instead of C atoms, C\textsubscript{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\textsubscript{2} plasma. The dissociation and excitation of CO (CO\textsuperscript{2+}) by the electron impacts initiate the following gas-phase reactions:

\[
\begin{align*}
C + CO + M &\rightarrow C_2O + M \quad (1) \\
O + CO + M &\rightarrow CO_2 + M \quad (2) \\
C + C + M &\rightarrow C_2 + M \quad (3) \\
O + O + M &\rightarrow O_2 + M \quad (4) \\
C + O + M &\rightarrow CO + M \quad (5) \\
C + C_2O &\rightarrow C_2 + CO \quad (6) \\
O + C_2O &\rightarrow 2CO \quad (7) \\
C + O_2 &\rightarrow CO + O \quad (8) \\
C + CO_2 &\rightarrow 2CO \quad (9) \\
CO + CO^* &\rightarrow C + CO_2 \quad (10)
\end{align*}
\]

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, C\textsuperscript{*} = C(3\textsuperscript{s1}P), C\textsubscript{2}, C\textsubscript{2}\textsuperscript{*} = C\textsubscript{2}(d\textsuperscript{3}Π\textsubscript{g}, ν = 6) and CO radicals are given by

\[
[C^2\textsubscript{2}] = \frac{\beta k_4[C][C_2O]}{k_{E_2C_2^*} + k_{Q_2C_2^*}[M] + k_{D_2C_2^*}} \quad (11)
\]

\[
[C^*] = \frac{k_{e_2}[C]}{k_{E_2C^*} + k_{Q_2C^*}[M] + k_{D_2C^*}} \quad (12)
\]

\[
[C_2O] = \frac{k_{6}[C][CO][M]}{k_6[C] + k_7[O] + k_{dis_2C_2O}[k_{D_2C_2O}]} \quad (13)
\]

\[
[C] = \frac{(k_{dis_2CO}[e] + k_{10}[CO^*][CO])}{k_{1}[CO][M] + k_b[C_2O] + k_{8}[O_2] + k_{D_2C}} \quad (14)
\]

where \(k_1, k_b, k_7, k_8\) and \(k_{10}\) are the rate constants of reactions (1), (6), (7), (8) and (10), \(k_{D_2A}\) is the rate constants for the diffusion loss of molecules A, \(k_{dis_2A}\) is the rate constants of dissociation reaction of molecule A by the electron impact, \(k_{E_2A}\) and \(k_{Q_2A}\) are the rate constants for the deactivation reaction of A\textsuperscript{*}. This is also explained by the fact that when O\textsubscript{2}/CO = 1/1000, the reaction rate of Eq. (7) due to increasing in [O] is thought to be the reason for the reduction in C\textsubscript{2} emission intensity. From Eq. (13), [C\textsubscript{2}O] density is reduced by only the increment in [O] density when O\textsubscript{2} is increased. Therefore, the acceleration of the reaction rate of Eq. (7) due to increasing in [O] is thought to be the reason for the reduction of C\textsubscript{2}. This is also explained by the fact that when O\textsubscript{2}/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\textsubscript{2}O as shown in Table 1, and emission intensity of C\textsubscript{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 $k_d[O_2]$ can be partially compensated by the decrease in $k_d[C_2O]$ 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 (Morid 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 graphic 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 carbon 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]
- $k_{\text{D},A}$ = the rate constant for the diffusion loss of molecules A [1/s]
- $k_{\text{diss},A}$ = the rate constant of dissociation reaction of molecule A by the electron impact [cm$^3$/s]
- $k_{\text{E},A}$ = the rate constant for the deactivation reaction of A$^*$ due to the photon emission [1/s]
- $k_{\text{ex}}$ = the rate constant of the electron impact excitation of atomic carbon, C + e → C(3s$^1\Pi_g$) + e [cm$^3$/s]
- $k_i$ = the rate constant of reaction (i) [cm$^3$/s or cm$^6$/s]
- $k_{\text{Q},A}$ = 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]
- $\beta$ = the fraction of C2 produced in the level $\Delta^1\Pi_g (v = 6)$ by the C + C2O reactions [—]
Literature Cited


