

Synthesis of Carbon Nanofibers Using Carbon Monoxide DC Plasma at Room Temperature

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A low temperature synthesis of carbon nanofibers was demonstrated by a plasma-enhanced chemical vapor deposition (PECVD). A low temperature CO/Ar DC plasma was used in this study. Carbon films deposited on glass substrate during PECVD were characterized by scanning electron microscopy and Raman spectroscopy. The effect of discharge current and substrate location on the CNFs formation has been investigated. The results show that vertically aligned carbon nanofibers can be synthesized at even room temperature with optimum discharge conditions when the substrate is placed on the cathode.

Key words: Carbon nanofiber, CO plasma, Room temperature synthesis, DC glow discharge, PECVD

1. 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 supercapacitors. 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 [1-5]. For example, Hofmann et al. demonstrated the low temperature synthesis of CNFs using a DC glow discharge plasma of C_2H_2 and NH_3 and vertically aligned CNFs were successfully grown on a polyimide substrate at 200 °C [6]. In the present study, we performed the low temperature synthesis of CNFs using CO plasma because a CO plasma has a attracting characteristic for low temperature CVD that disproportionation reaction of CO is enhanced by the vibrational excitation of CO caused by the vibrational energy pumping of CO in plasma at a low translational temperature condition [7-9].

2. EXPERIMENTAL

Figure 1 shows the schematic diagram of experimental apparatus. The quartz discharge tube has a 10 mm inner diameter, and there are two electrodes which are spaced 5 cm apart and connected to the DC power supply in the discharge tube; one of them is stainless steel sample stage with a diameter of 6 mm and the other is stainless steel rod with a diameter of 1.5 mm. In this study, borosilicate glass substrates (4 mm x 4 mm x 0.2 mm) with a thin Fe catalyst layer were used as substrates. The Fe catalyst layer was prepared using wet coating of the solution of Fe acetate. The solution was prepared by dissolving Fe acetate into ethanol so that the concentration of Fe was 0.01 wt% and then 0.1 ml

solution was dropped onto the substrates and dried in the atmosphere. The catalyst layer was pretreated by H_2/Ar plasma for 5 minutes before CNFs synthesis and then a CO/Ar glow discharge plasma was generated for the CNFs deposition. The detailed parameters for the deposition process are listed in Table I and shown below: CO flow rate: 10 sccm, Ar flow rate: 10 sccm, pressure: 800 Pa. The substrate temperature, T_s , was monitored by a thermocouple placed below the substrate. The plasma emission was monitored by a spectrometer (Ocean Optics, HR4000). Carbon deposits grown on the substrates were observed by scanning electron microscopy (KEYENCE, VE-8800) and analyzed by Raman spectroscopy (JASCO, NRS-2100).

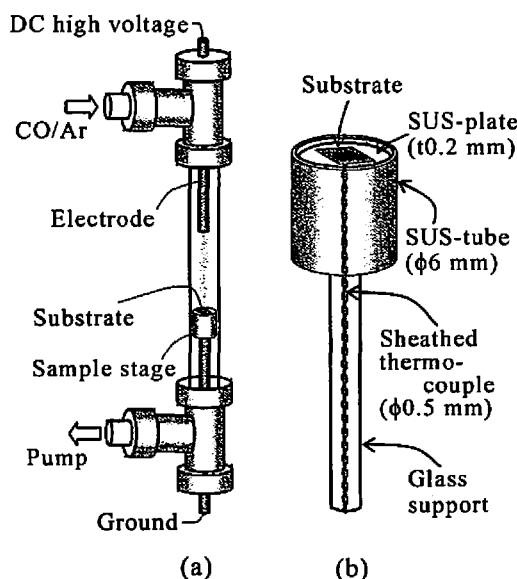


Fig.1 Schematic diagram of experimental apparatus: (a) Plasma reactor and (b) Sample stage.

Table I Experimental conditions and results

	Discharge Current (mA)	Discharge Voltage (kV)	Deposition Time (min)	Sample Temperature (°C)	Sample position	CNF formation
Sample (1)	0.2	1.10	120	28	Cathode	○
Sample (2)	2.0	0.75	60	92	Cathode	○
Sample (3)	4.0	0.72	30	138	Cathode	×
Sample (4)	5.0	0.70	30	182	Cathode	×
Sample (5)	2.0	0.75	60	39	Anode ^(a)	×
Sample (6)	2.0	0.75	60	44	Positive Column ^(b)	×

(a) The substrate was placed on the sample stage but the polarity of electrodes was changed.

(b) The substrate was attached on the inner surface of discharge tube at positive column area and the substrate temperature was measured by a thermo-couple placed on the outer surface of discharge tube.

3. RESULTS AND DISCUSSION

Figure 2 shows the SEM images of carbon deposits after 30-120 minutes deposition time with different discharge current. When the discharge current was lower than 2.0 mA, aligned carbon nanofibers were able to be synthesized. However, for higher discharge current conditions, the fibrous structure disappeared. Although the deposition rate of sample (3) seems to be lower than

that of sample (2), the density and total carbon amount deposited in sample (3) would be higher than that in sample (2). As shown in Table I, the substrate was heated up by the discharge itself. However, the temperature of sample (1) increased very slightly and kept almost room temperature.

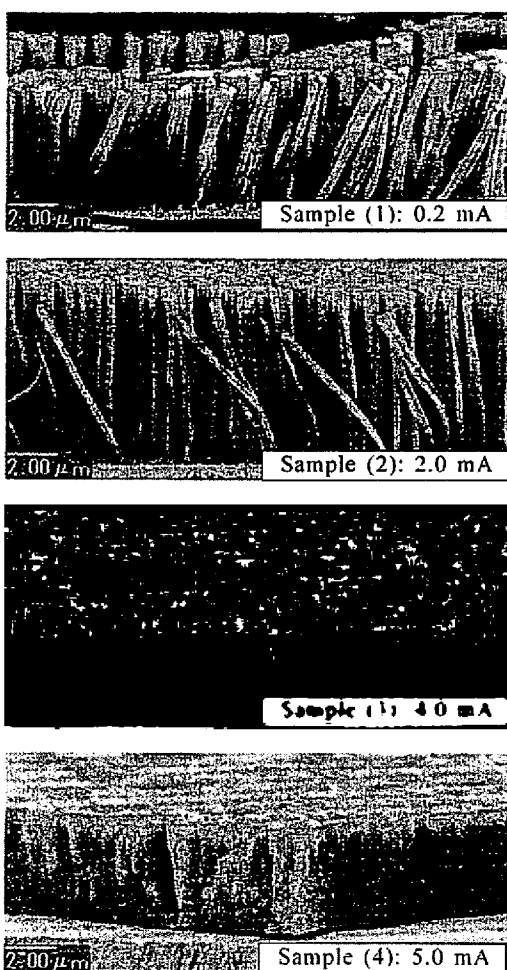


Fig.2 SEM images of samples (1) to (4).

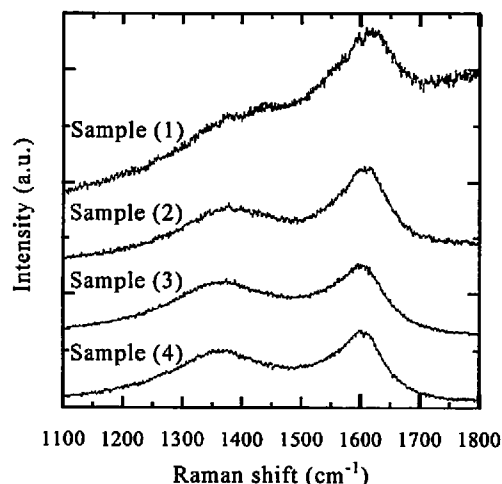


Fig.3 Raman spectra of samples (1) to (4) with same exposure time.

Figure 3 shows Raman spectra of the carbon materials formed on the glass substrates. The spectra for all samples present two peaks of carbon materials: the rather sharp G-band peak at approximately 1590 cm^{-1} which indicates crystalline graphene layers and the broad D-band peak at 1350 cm^{-1} which indicates the existence of defective graphene layers such as amorphous carbon layers. The intensity ratio of G-band and D-band signifies the degree of graphitization of CNFs. As shown in Fig. 3, the G/D ratio decreases with increasing current density. It means that for higher discharge current conditions, amorphous carbon deposits increased and it would be the reason for the disappearance of fibrous structure.

In this study, the effect of substrate position has also been investigated. The experimental conditions for samples (2), (5), and (6) were same but the positions of

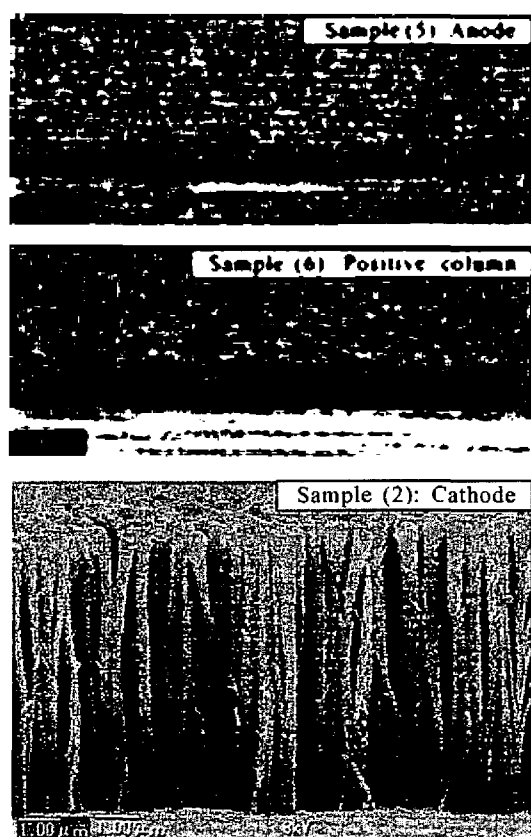


Fig.4 SEM images of samples (5), (6), and (2).

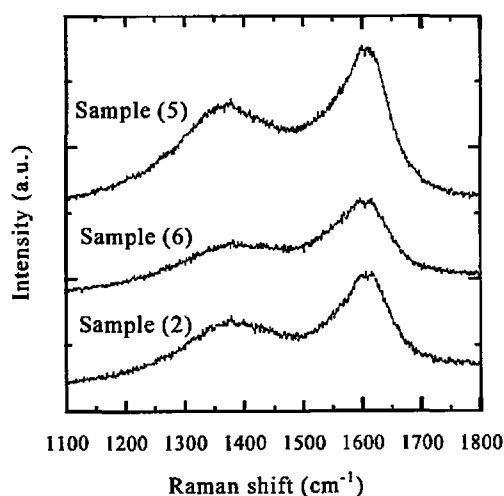


Fig.5 Raman spectra of samples (5), (6), and (2) with same exposure time.

substrates were different: Samples (2), (5), and (6) were placed in the cathode, anode, and positive column area, respectively. SEM images and Raman spectra of samples (2), (5), and (6) are shown in Fig. 4 and Fig. 5, respectively. Among three samples, the intensity of Raman spectra for sample (2) indicates medium value and the G/D ratios are almost same for three samples. However, CNFs are not observed for samples (5) and (6).

The substrate biasing to the negative potential would be essential for low temperature synthesis of CNFs using CO plasma.

Figure 6 shows a typical emission spectrum from CO/Ar plasma. The strong CO Angstrom band spectra around 500 nm and weak C₂ swan band spectra at 563.6 nm and C atom spectra at 247.9 nm have been observed. The emission intensity of C₂ and C and C/C₂ intensity ratio are plotted for different discharge current and sample position in Fig. 7 and 8, respectively.

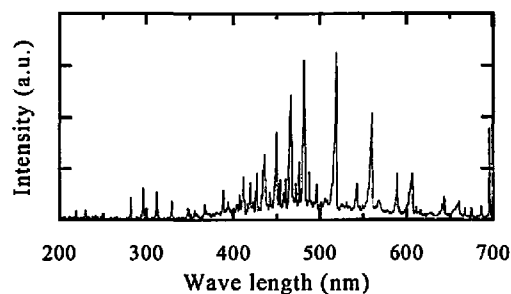
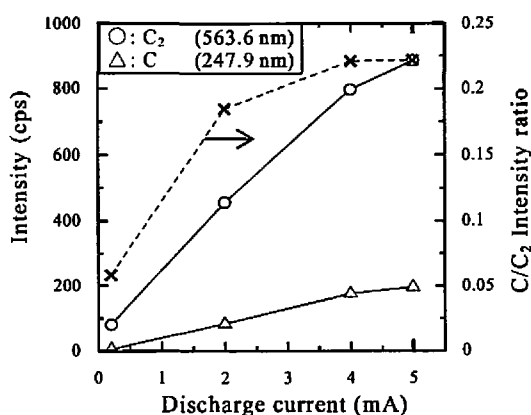
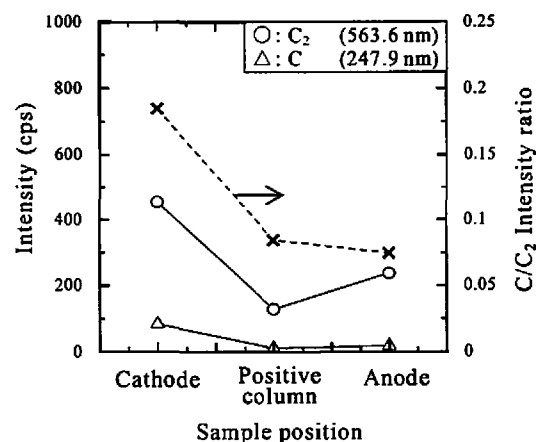


Fig.6 Typical emission spectra of CO/Ar plasma with 2.0 mA discharge current.

Fig.7 Emission intensity of C and C₂ from CO/Ar plasma.Fig.8 Emission intensity of C and C₂ from CO/Ar plasma.

It is presumed from Fig. 7 that the excess C_2 and C formation, especially atomic carbon formation, was enhanced by the increased discharge current and would result in the formation of amorphous carbon deposits. On the other hand, as shown in Fig. 8, although the C and C_2 intensity from positive column and anode are not higher than that from cathode and the C/ C_2 intensity ratio is almost constant for the different positions, CNFs were able to be synthesized only at cathode. Therefore, the disappearance of fibrous structure in the positive column and anode are mainly attributed to their inadequate substrate biasing.

As for a low temperature growth model for PECVD of CNFs, Hofmann et al. suggested [10] that the rate-determining step is not diffusion of carbon through the catalyst particle bulk which was proposed by Baker et al. [11] and is generally well accepted at high temperature conditions, but diffusion of carbon on the catalyst surface. In this surface diffusion model, carbon atoms adsorbed at the top surface of the metal particle can diffuse along the surface, where their motion is much faster than bulk diffusion and then segregates at the bottom of the particle, forming graphitic planes. These graphitic basal planes are parallel to the metal surface and the orientation angle between the graphite basal planes and the tube axis is not zero, which results in the disappearance of tubular structure of CNFs. From this point we might go on to characterize the morphology of CNFs synthesized with various growth temperatures using transmission electron microscopy.

CONCLUSION

A low temperature synthesis of carbon nanofibers was performed by a plasma-enhanced chemical vapor deposition using a low temperature CO/Ar DC plasma. The carbon films deposited on glass substrate during PECVD were characterized by scanning electron microscopy and Raman spectroscopy. The results show that vertically aligned carbon nanofibers can be synthesized at even room temperature conditions with the smallest discharge current, 0.2 mA, in the present study when the substrate is placed on the cathode.

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