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Different formation of carbon nanofilaments as a function of the gap between the substrate and the microwave plasma

Sung-Hoon Kim†

Department of Nano Materials Science & Engineering, Silla University, Busan 617-736, Korea

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Abstract Iridium-catalyzed carbon nanofilaments were formed on MgO substrate as a function of the gap between the substrate and the plasma using microwave plasma-enhanced chemical vapor deposition method. Under the remote plasma condition, carbon nanofibers were formed on the substrate. Under the adjacent plasma condition, on the other hand, carbon nanotubes-like materials instead of carbon nanofibers could be formed. When the substrate immersed into the plasma, any carbon nanofilaments formation couldn't be observed. During the reaction, the substrate temperatures were measured as a function of the gap. Based on these results, the cause for the different carbon nanofilaments formation according to the gap was discussed.

Key words Carbon nanofibers, Carbon nanotubes-like materials, Microwave plasma, The gap between the substrate and the plasma

1. Introduction

Due to the unique shape and characteristics, carbon nanofilaments which were classified as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been regarded as the promising material candidates for the diverse nanoelectronic application, such as the nanowiring to the nanoelectronic devices and the field emission display [1-6].

To apply CNTs to the nanowiring, the formation of CNTs having entirely single electrical properties is preferential, because the electrical properties of CNTs were known to be varied as metallic, insulating, or semiconductor characteristics according to their diameter, wrapping angle, or post-growth treatment [7, 8]. Therefore the practical application of CNTs to the nanowiring still needs a long way to launch on. On the other hand, the electron emitter, especially for the field emission display (FED), has been noted for the practical application of CNTs.

CNFs, a tip-type shape like CNTs, have been also noted for the electron emitter of FED [4]. However, the field emitter characteristics of CNFs seemed to be lower than those of CNTs [6]. The different characteristics seemed to be due to the different crystal structure for CNTs and CNFs. For the crystal structure point of view, CNFs basically has a vertical stacking lattice structure to the principal axis of the nanofiber [9]. On the other hand, CNTs shows a parallel lattice structure to the principal axis of the nanotube [4, 10]. It seems that the parallel lattice structure to the principal axis of the nanotube provides an effective way for the electron transportation.

A few reports regarding the structural transformations between CNTs and CNFs are known as follows; CNTs transform into CNFs by the sonication [11]. A structural transformation from CNFs into CNTs-like morphology by the thermal annealing was also known [12, 13]. Recently, we reported the competitive formation between CNTs and CNFs by the applied bias voltage during the plasma reaction [14]. We confirmed the initiation of bamboo-like CNTs by the application of the negative high bias voltage.

In this work, we presented the different carbon nanofilaments formation as a function of the gap between the substrate and the plasma. Based on the substrate temperature measurement results, the cause for the different carbon nanofilaments formation according to the gap was suggested.

2. Experimental

Iridium coated $1.0 \times 1.0\ cm^2$ MgO substrate was prepared by iridium coating on a MgO substrate using a radio frequency (RF) sputtering. In RF-sputtering experi-

†Corresponding author
Tel: +82-51-999-5619
Fax: +82-51-999-5176
E-mail: shkim@silla.ac.kr

Table 1
Experimental condition for the iridium catalyst layer deposition

Radio Frequency power	Injection gas	Flow rate of injection gas	Substrate Temperature	Total Pressure	Reaction time
20 W	Ar	10 sccm	25°C	30 mTorr	5 min

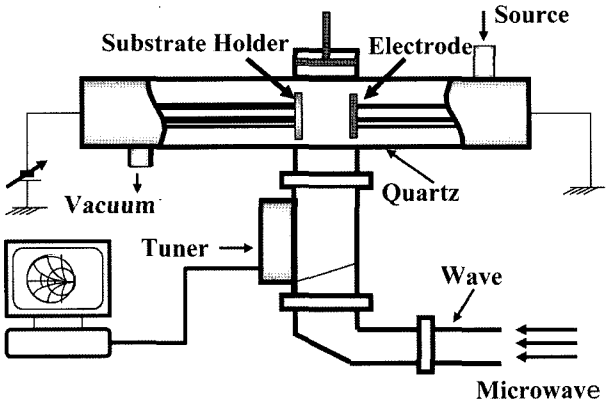

Fig. 1. Systematic diagram of a horizontal-type microwave plasma-enhanced chemical vapor deposition (MPECVD) system.

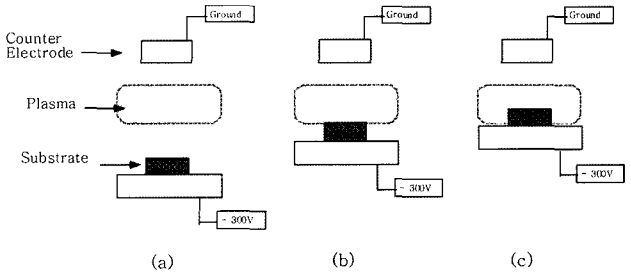

Fig. 2. Positions between the substrate and the plasma according to (a) the remote plasma, (b) the adjacent plasma, and (c) the immersed plasma.

ment, we used Ar gas with 30 mTorr total pressure under 20 W RF power condition. Detailed experimental condition for the iridium catalyst coating was shown in Table 1.

Before the carbon nanofilaments deposition reaction, we pre-cleaned the substrate with H_2 plasma for a few minutes. For carbon nanofilaments deposition, 5 % CH_4 and 95 % H_2 were introduced to the deposition system after pre-cleaning the substrate. The substrate temperature was measured by a back-side-touching K-type chromel-alumel thermocouple. Negative bias voltage applied microwave plasma-enhanced chemical vapor deposition (MPECVD) system was employed for the formation of carbon nanofilaments as shown in Fig. 1. Table 2 shows the detailed experimental condition for carbon nanofilaments deposition.

The morphologies of carbon nanostructures were investigated using field emission scanning electron microscopy (FESEM) and the compositions of carbon nanostructures were analyzed by electron probe micro-analysis (EPMA). The samples for TEM were prepared by dispersing CNTs and CNFs using acetone in an ultrasonic bath. A drop of suspension was placed onto a carbon film supported by a Cu grid; then, Cu grid was placed into TEM chamber and the detailed morphologies of CNTs and CNFs were investigated via transmission electron microscopy (TEM) study.

3. Results and Discussion

We investigated the surface images of CNTs or CNFs deposited substrates under the remote plasma condition. Remote plasma from the substrate could be achieved by leaving the spacing about 3 cm between the plasma and the substrate as shown in Fig. 2a. Figure 3a shows FESEM images of the synthesized carbon nanofilaments on the iridium-coated MgO substrates after deposition reaction under −300 V bias voltage condition. Figures 3b and c show the magnified images of Figs. 3a and b, respectively. As shown in Fig. 3a, the formation of the carbon nanofilaments could not be observed on the smooth plane area of the substrate surface. However, on the side area of the substrate, the growth of the carbon nanofilaments could be well-observed (see Fig. 3a). Compared with the substrate surface area, the side area has rough surface morphologies. Thus we suggest that the growth of the iridium-catalyzed carbon nanofilaments favors the rough surface morphologies [14]. In this work, the roughness at the side area was assumed above 100 nm. Based on these results, we confirmed that the iridium

Table 2
Experimental conditions of carbon nanofilaments formation

Microwave power	Source gases	Flow rates of source gases	Reaction time	Total Pressure	Bias voltage
600 W	CH_4, H_2	CH_4 : 2.5 sccm H_2 : 47.5 sccm	5 min	60 Torr	−300 V

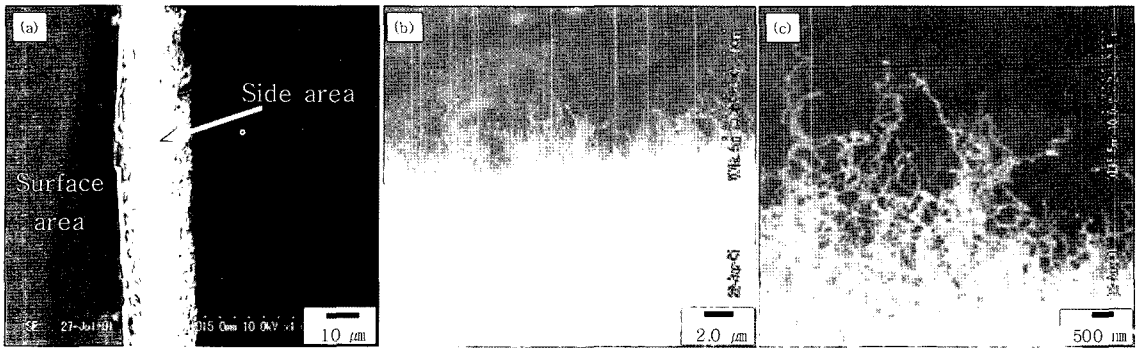

Fig. 3. (a) FESEM image of the carbon nanofilaments on the surface and the side area of the substrate under the remote plasma condition. (b) The magnified FESEM image of Fig. 3a and (c) the magnified FESEM image of Fig. 3b.

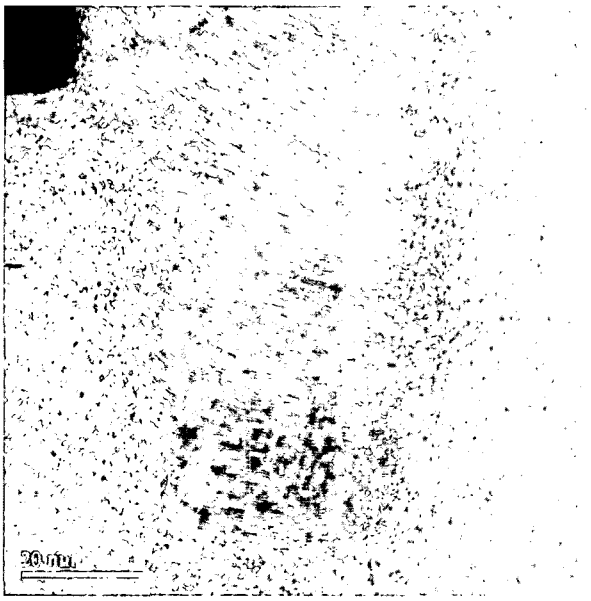

Fig. 4. TEM image for one of CNFs under the remote plasma condition.

catalyst could give rise to the selectivity for the formation of the carbon filaments according to the surface morphologies, as the previous report [15]. To identify the detailed nanostructures of the carbon nanofilaments, we carried out TEM study. Figure 4 shows the stacking lattices, the protrusions of the lattices to the outside of the nanostructure and the filled image at the inside of the nanostructure. These results confirmed that this material would follow the nanostructure of CNFs [3, 13].

By moving the substrate to the plasma, we could make the adjacent plasma condition to the substrate as shown in Fig. 2b. Figure 5a shows FESEM images of the carbon nanofilaments deposited on the iridium-coated MgO substrates under the adjacent plasma condition. Figures 5b and c show the magnified images of Figs. 5a and b, respectively. As the remote plasma case, the formation of the carbon nanofilaments could not be observed on the smooth plane area of the substrate surface (see Fig. 5a). However, on the side area of the substrate, the growth of the carbon nanofilaments could be well-observed as shown in Fig. 5a. We also investigated the detailed nanostructures of these carbon nanofilaments using TEM. Figure 6 shows the parallel-developed lattice structure at the wall of the nanostructure. These results reveal that these carbon nanofilaments would follow the nanostructure of the CNTs-like materials. Consequently, we could suggest that the CNTs-like materials, instead of the carbon nanofibers, were more pronounced

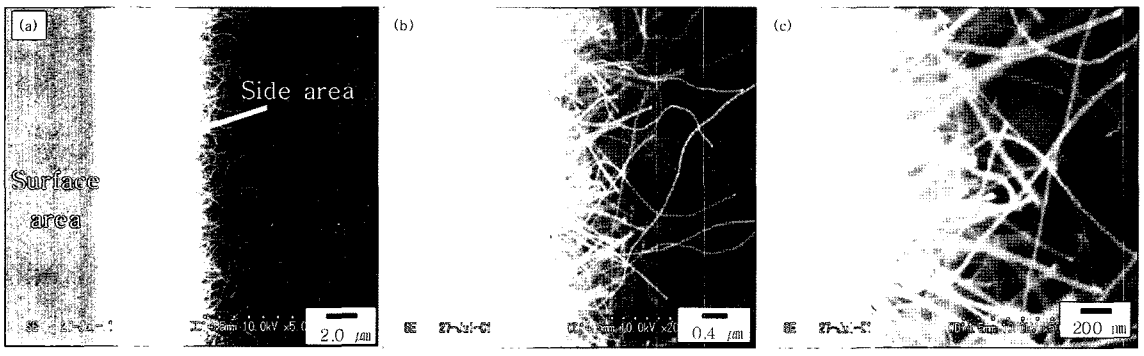

Fig. 5. (a) FESEM image of the carbon nanofilaments on the surface and the side area of the substrate under the adjacent plasma condition. (b) The magnified FESEM image of Fig. 5a and (c) the magnified FESEM image of Fig. 5b.

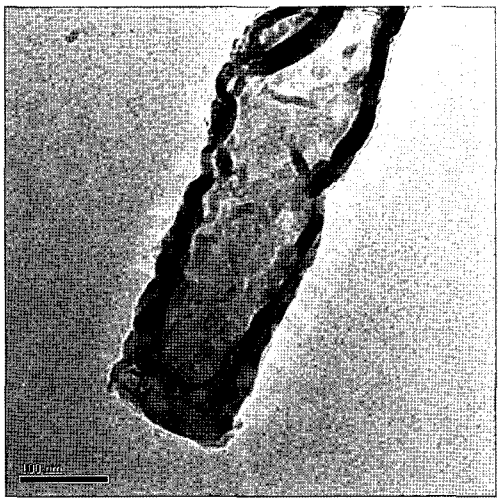

Fig. 6. TEM image for one of CNTs-like materials under the adjacent plasma condition.

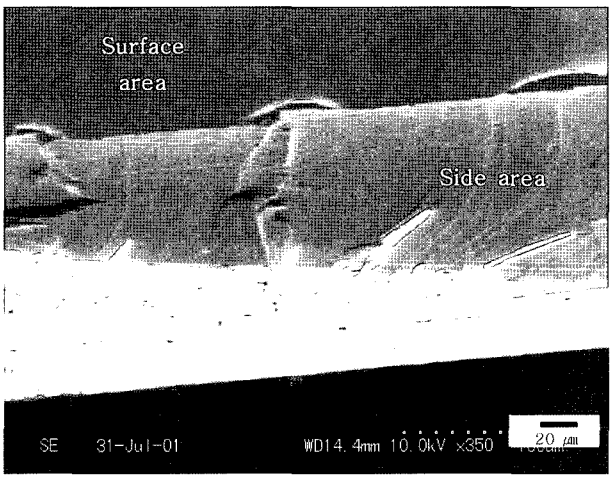

Fig. 7. FESEM image of the carbon nanofilaments on the surface and the side area of the substrate under the immersed plasma condition.

under the adjacent plasma condition.

When the substrate immersed into the plasma (see Fig. 2c), the carbon nanofilaments seemed hardly formed on the substrate. As shown in Fig. 7, the formation of the carbon nanofilaments couldn't be observed on any area of the substrate. Atomic hydrogen can readily etch away carbon species [16]. In the middle of the plasma, the amount of the atomic hydrogen is considerable. Therefore, the carbon species for the formation of the carbon nanofilaments seemed to be readily etched away by the abundant amount of the atomic hydrogen under the immersed plasma condition.

The cause for the different formation of carbon nanofilaments may be attributed to the variation of the induced temperature of the substrate as a function of the gap between the substrate and the microwave plasma (see Table 3). Although the exact temperature at the region of the carbon nanofilaments formation couldn't be measured, the adjacent plasma condition seemed to induce a relative higher temperature of the substrate surface. Previously, it was reported that a new structural transformation from CNFs into CNTs-like morphology was developed by the high temperature thermal annealing [12, 13]. So, we could suggest that the formation of CNTs-like materials seems to favor a relative higher temperature of the substrate surface, namely the adjacent plasma condition rather than the remote plasma condition.

Table 3
The substrate temperature according to the different plasma condition

Plasma conditions	Substrate temp.
Remote plasma	950 °C
Adjacent plasma	~1050 °C
Immersed plasma	>1200 °C

4. Conclusions

Under the remote plasma condition, the formation of CNFs could be obtained on the side area of the iridium-coated MgO substrate. On the other hand, CNTs-like materials, instead of CNFs, could be produced under the adjacent plasma condition. The different formation of the carbon nanofilaments as a function of the remote or the adjacent plasma condition seemed to be due to the different induced substrate temperature according to the gap between the substrate and the microwave plasma.

Acknowledgements

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