

# The geometry change of carbon nanofilaments by SF<sub>6</sub> incorporation in a thermal chemical vapor deposition system

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**Abstract** Carbon nanofilaments (CNFs) could be synthesized on nickel catalyst layer-deposited silicon oxide substrate using C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> as source gases under thermal chemical vapor deposition system. By the incorporation of SF<sub>6</sub> as a cyclic modulation manner, the geometries of carbon coils-related materials, such as nano-sized coil and wave-like nano-sized coil could be observed on the substrate. The characteristics (formation density and morphology) of as-grown CNFs with or without SF<sub>6</sub> incorporation were investigated. Diameter size reduction for the individual CNFs-related shape and the enhancement of the formation density of CNFs-related material could be achieved by the incorporation of SF<sub>6</sub> as a cyclic modulation manner. The cause for these results was discussed in association with the slightly increased etching ability by SF<sub>6</sub> addition and the sulfur role in SF<sub>6</sub> for the geometry change.

**Key words** Carbon nanofilaments, Carbon coil, SF<sub>6</sub>, Geometry, Cyclic modulation process, Thermal chemical vapor deposition

## 1. Introduction

Carbon nanofilaments (CNFs), called carbon nanotubes if hollow and carbon nanofibers if filled, would be useful for the elements of nanoelectronic devices due to their fascinating shape of the micrometer scale length and the nanometer scale diameter [1, 2]. Helical carbon coils, as an eccentric shape of carbon nanofilaments, were also regarded to have promising materials characteristics [3, 4]. Basically, helically coiled carbon nanotubes were known to be constructed by periodically inserting heptagonal and pentagonal rings into hexagonal network [5]. The electrical properties of CNFs or helically coiled carbon nanotubes may be metallic, semiconducting or semi-metallic depending on their geometry including diameter and the pentagonal and heptagonal rings placement in carbon coils [6]. Therefore the controlled geometry of CNFs would be essential to achieve the controlled electrical properties of CNFs.

For the synthesis techniques of carbon nanofilaments, various methods have been introduced, such as arc-discharge [7], pyrolysis [8], laser ablation [9], plasma or thermal chemical vapor deposition methods [10, 11], and so forth. Among these techniques, thermal chemical vapor deposition (TCVD) technique using the metal catalyst has

been more noticed because of its relative inexpensive and applicable feature. In addition, the enhancement of carbon nanofilaments having the controlled-geometry (diameter, shape, and so on) would be indispensable for the practical application of carbon nanofilaments. Recently, we have introduced an in-situ cyclic on/off modulation process of C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> flow to enhance the formation yield of CNFs [12]. It can be simply achieved by turning a source gas flow rate in a reaction system on or off during the initial deposition stage. For the metal catalyst used in TCVD, iron family (Fe, Co, Ni), especially Ni, were known to be effective catalysts for the formation of carbon nanofilaments [13, 14].

This work presents the variation of carbon filaments geometries by the incorporation of SF<sub>6</sub> in source gases (C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub>) during the initial deposition stage. To enhance the formation yield of carbon nanofilaments, we applied the gas composition cycling technique for C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub> and SF<sub>6</sub>. The variation of the as-grown CNFs characteristics according to the different catalysts, namely the formation density and the geometry, was examined and discussed.

## 2. Experimental

The SiO<sub>2</sub> substrates in this work were prepared by the thermal oxidation of the 2.0 × 2.0 cm<sup>2</sup> p-type Si (100) substrates. The thickness of silicon oxide (SiO<sub>2</sub>) layer on Si substrate was estimated about 300 nm. To form Ni

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catalyst layer, a 0.1 mg Ni powder (99.7 %) was evaporated for 1 min on the substrate using thermal evaporator. The estimated Ni catalyst layer on the substrate was about 400 nm.

For CNFs deposition, thermal chemical vapor deposition system was employed.  $C_2H_2$  and  $H_2$  were used as source gases.  $SF_6$  was injected as an additive in a gas composition cycling manner. Total flow rate was fixed at 50 standard  $cm^3$  per minute (sccm). The in-situ cyclic modulation process was progressed by the modulation of these gases flows during the initial deposition stage. According to the different reaction processes, the flows of source gases were the continual  $H_2 + C_2H_2$  flow and the iterative orders of the procedures. Namely,

Process I: Continual  $H_2 + C_2H_2$  flow

Process II:  $H_2 + C_2H_2$  flow  $\rightarrow H_2 + SF_6$  flow  
 $\rightarrow H_2 + C_2H_2$  flow  $\rightarrow H_2 + SF_6$  flow  
 $\rightarrow H_2 + C_2H_2$  flow.

Carbon species to form CNFs are generated from  $H_2$

+  $C_2H_2$  flow ( $C_2H_2$  flow on). On the contrary, the solely  $H_2$  flow or  $H_2 + SF_6$  flow ( $C_2H_2$  flow off) may etch carbon components. The cycle was defined as the source gases were fluctuated as  $C_2H_2$  flow on plus  $C_2H_2$  flow off. The interval time for one cycle was defined as the time for  $C_2H_2$  flow on plus the time for  $C_2H_2$  flow off. Fig. 1 shows the detailed manipulation of these gases flows according to the processes.

We fixed  $H_2$  flow rate,  $C_2H_2$  flow rate,  $SF_6$  flow rate and total reaction time as 35 sccm, 15 sccm, 35 sccm and 90 min, respectively. The  $C_2H_2$  flow on/off time ratio was set as 180/30 s. So, the interval time for one cyclic was 3.5 minutes and the numbers of cycles were 2 times. The total cyclic modulation time was 7 minutes. The detailed reaction conditions according to the different processes with samples were shown in Table 1.

Detailed morphologies of CNFs-deposited substrates were investigated by using field emission scanning electron microscopy (FESEM).

### 3. Results and Discussion

Fig. 2 shows FESEM images showing the surface morphologies for sample A (without  $SF_6$  incorporation case). To compare the formation density of CNFs, the outermost side (Figs. 2a and c) and center (Figs. 2b and d) positions on the samples were chosen for investigation using FESEM. As shown in Fig. 2, CNFs-related materials including embryos could be well-developed irrespective of the position on the sample. Furthermore, the CNFs formation density seems to be not much different according to the position on the sample. As shown in high-magnified FESEM images (Figs. 2c and d), the embryo for CNFs formation and the immature CNFs could be observed.

Fig. 3 shows FESEM images showing the surface morphologies for sample B (with  $SF_6$  incorporation case). The CNFs formation aspect and density according to the position on the sample are not much different from the case of Fig. 2. In this case, however, the change of CNFs geometry from a conventional linear type to a nano-sized coil-like type could be clearly observed by the incorpo-

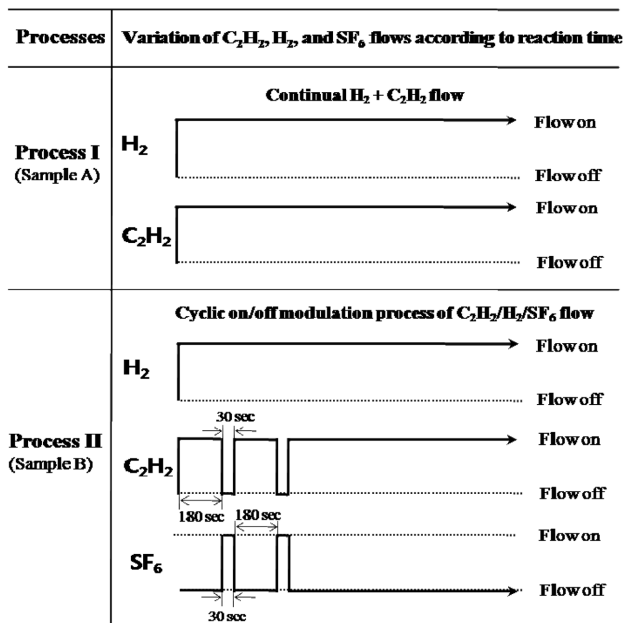


Fig. 1. Different reaction processes: the steady process (process I: sample A) and the cyclic process having  $SF_6 + H_2$  as etching components (process II: sample B).

Table 1  
Experimental conditions for the deposition of CNFs on the substrates for samples A and B

| Processes | Samples  | Conditions | Cyclic on/off modulation of source gases flow (sec) |       |        | Total deposition time (min) | Total pressure (Torr) | Number of cycles (No.) | Total cyclic process time (min) | Substrate temperature ( $^{\circ}C$ ) |   |     |
|-----------|----------|------------|---|-------|--------|-----------------------------|-----------------------|------------------------|---------------------------------|---------------------------------------|---|-----|
|           |          |            | $C_2H_2$  | $H_2$ | $SF_6$ |                             |                       |                        |                                 |                                       |   |     |
| I         | Sample A | 35         | 15  | 0     | 125    | 90                          | -                     | -                      | 0                               | 750                                   |   |     |
| II        | Sample B | 35         | 15  | 35    | 125    | 90                          | 180/30                | -                      | 30/180                          | 2                                     | 7 | 750 |

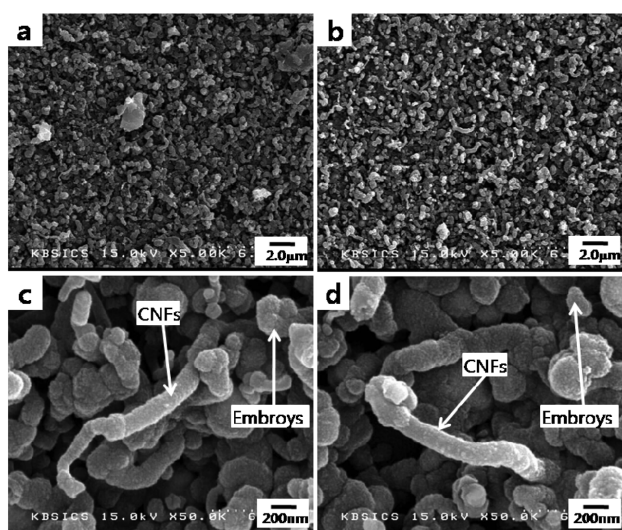


Fig. 2. FESEM images of CNFs-deposited substrate for sample A (a) at the outermost side and (b) center positions on the substrate and their magnified images (c) at the outermost side and (d) center positions on the substrate.

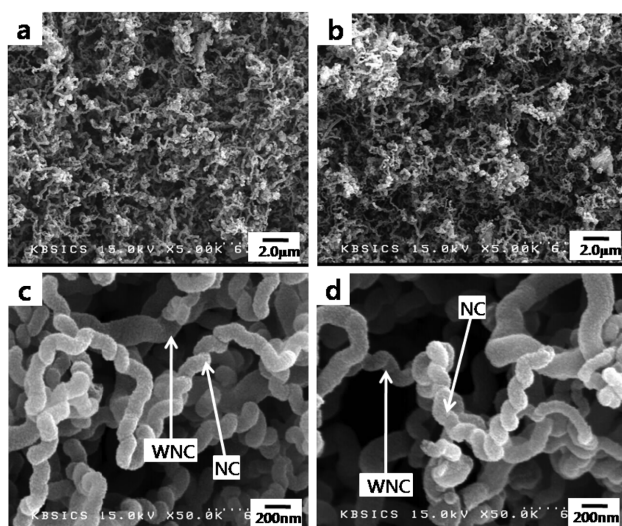


Fig. 3. FESEM images of CNFs-deposited substrate for sample B (a) at the outermost side and (b) center positions on the substrate and their magnified images (c) at the outermost side and (d) center positions on the substrate.

ration of SF<sub>6</sub> as a cyclic modulation manner (compare Figs. 2 with 3). In general, many types of carbon coils-related geometries could be observed on sample surfaces, so they could be usually classified into four geometrical categories, namely linear tub (LT), micro-sized coil (MC), nano-sized coil (NC), and wave-like nano-sized coil (WNC) (see Fig. 4). In this case, nano-sized coil (NC) and wave-like nano-sized coil (WNC) could be mostly observed as shown in high-magnified FESEM images (see Fig. 3).

Carbon coils formation densities were mainly measured using several 50k magnified FESEM images. For objec-

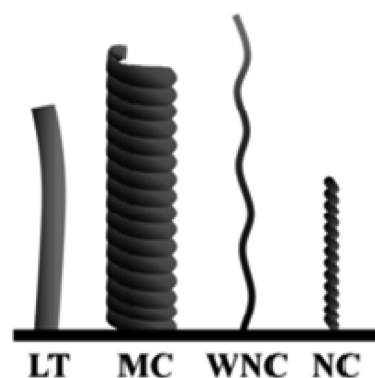


Fig. 4. Various shapes of carbon coils-related geometries. In generally, many types of carbon coils-related geometries could be mainly classified into four geometrical categories, namely linear tub (LT), micro-sized coil (MC), nano-sized coil (NC), and wave-like nano-sized coil (WNC).

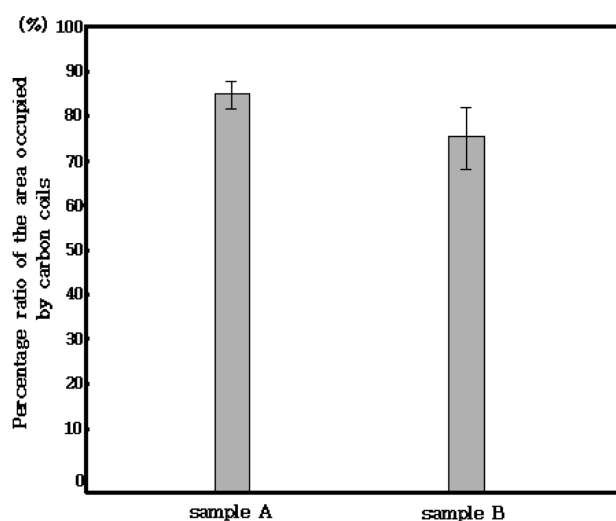


Fig. 5. The occupied areas by various type carbon coils with (sample A) or without (sample B) SF<sub>6</sub> incorporation as a cyclic modulation manner. It was measured under the assumption of monolayer-grown carbon coils formation on the substrate.

tively measuring carbon coils formation density, image analyzing method has been developed by placing square-graphed transparent paper onto the enlarged copies of FESEM images. Under the assumption of monolayer-grown carbon coils formation on the substrate, the occupied areas by various type carbon coils including embryos with or without the incorporation of SF<sub>6</sub> as a cyclic modulation manner were measured as shown in Fig. 5. The y-axis represents the percentage ratio of the area occupied by carbon coils. The analysis showed that the average occupied area of carbon coils with SF<sub>6</sub> incorporation was about 113% for that without SF<sub>6</sub> incorporation. In addition, the incorporation of SF<sub>6</sub> as a cyclic modulation manner in the source gases seems to reduce the diameter size of the individual CNFs (comparing

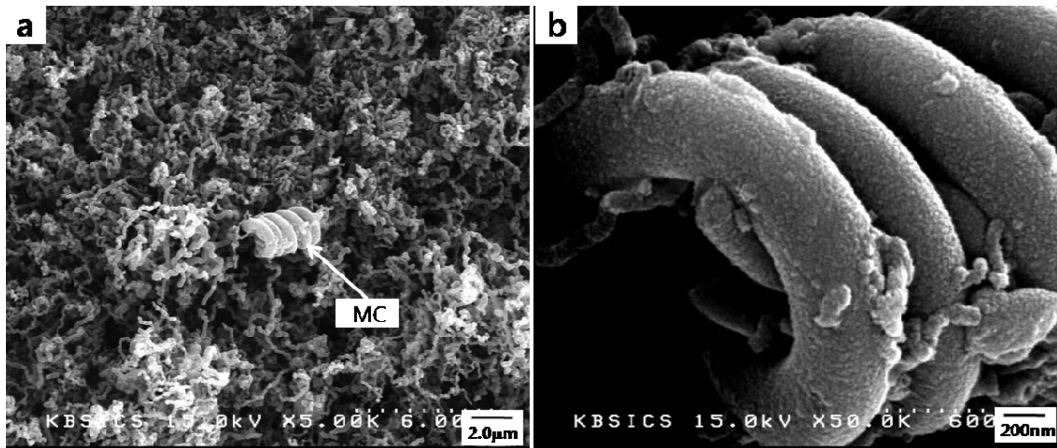


Fig. 6. FESEM images of the CNFs-deposited substrate for sample B (a) at the center position on the substrate and (b) its magnified image. Occasionally, a couple of micro-sized carbon coils could be observed on the surface of the substrate.

CNFs-related shape images of Figs. 2 with 3). Consequently, the number density of the individual CNFs would be much higher at sample B.

Occasionally, a couple of micro-sized carbon coils could be observed on the surface of the substrate as shown in Fig. 6. Diameters of the micro-sized carbon coils and the composed carbon nanofilaments are in the range of several micrometers and a few hundred nanometers, respectively. The length range of the coil are in the range between a few micrometers and a few tens micrometers.

Based on the results shown in Figs. 2~6, we propose that the incorporation of  $\text{SF}_6$  as a cyclic modulation manner could give rise to the change of CNFs geometry from a conventional linear type to a nano-sized coil-like type. In addition, a reduction of the diameter size of the individual CNFs as well as the enhancement of CNFs-related materials formation density could be achieved by the incorporation of  $\text{SF}_6$  as a cyclic modulation manner.

The cause for these results was considered to be due to the slightly increased etching ability by  $\text{SF}_6$  addition to  $\text{H}_2$  gas concentration during the etching time in the cyclic modulation process. It may facilitate the suitable CNFs nucleation sites. Furthermore, it may etch away the superfluous materials of the as-grown CNFs. Consequently the diameter size of the as-grown CNFs would be reduced by  $\text{SF}_6$  addition. The change of CNFs geometry from a conventional linear type to a nano-sized wave-like coil type seems to be due to the sulfur role in  $\text{SF}_6$  as previous reports [15, 16].

#### 4. Conclusions

The CNFs geometry change from conventional linear

type to nano-sized coil-like type could be achieved by the incorporation of  $\text{SF}_6$  as a cyclic modulation manner. Diameter size for the individual CNFs-related shape could be reduced by the cyclic on/off modulation process of  $\text{C}_2\text{H}_2/\text{H}_2$  flow. In addition, the  $\text{SF}_6$  incorporation in the cyclic process could promote the formation density of CNFs-related material. The cause for these results was considered to be due to the slightly increased etching ability by  $\text{SF}_6$  addition to  $\text{H}_2$  gas concentration during the etching time in the cyclic modulation process. The change of CNFs geometry from a conventional linear type to a nano-sized coil-like type seems to be due to the sulfur role in  $\text{SF}_6$ .

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