

Geometry variation for as-grown carbon coils under the minimized sulfur additive condition

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Abstract Carbon coils could be synthesized on nickel catalyst layer-deposited silicon oxide substrate using C_2H_2 and H_2 as source gases under thermal chemical vapor deposition system. By the incorporation of SF_6 additive in cyclic modulation manner, the dominant formation of the nanosized carbon coils could be achieved with maintaining the minimized sulfur additive amount. The geometry variation of the as-grown carbon coils, such as linear type, microsized coil type, wavelike nanosized coil type, and nanosized coil type, were investigated according to the different cyclic modulation manner of SF_6 flow. SF_6 gas incorporation develops the coil-type geometry. Furthermore, the higher flow rate of SF_6 gas increased the amount of the nanosized carbon coils. The slightly increased etching ability by SF_6 addition seems to be the cause for these results.

Key words Carbon coils, Minimized SF_6 amount, Geometry variation, Cyclic modulation process, Thermal chemical vapor deposition

1. Introduction

Due to the unique geometry, carbon coils have been noticed as the promising materials candidates for the electromagnetic wave absorbers in the GHz to THz regions, nano/microsized tactile sensors, actuators, resonators, mechanical springs, and so on [1-3]. Carbon coils have been occasionally found as a low-content byproducts of the vapor preparation of carbon fibers in microwave plasma-enhanced chemical vapor deposition or in thermal chemical vapor deposition (TCVD) [4-6]. Therefore the production yield of carbon coils should be preferentially enhanced for their practical application.

Recently, the reproducible synthesis of carbon coils was achieved by injecting additives to source gases during the catalytic pyrolysis of acetylene [7]. For the incorporated additives, meanwhile, the sulfur-incorporated chemical species were regarded as promising additives for the formation of carbon coils [7-9]. Hydrogen sulfide (H_2S) [10], carbon disulfide (CS_2) [11], and thiophene (C_4H_4S) as an impurity [8] were reported as effective catalytic materials.

Intrinsically, sulfur species are very hazardous for environment and human health. So, the use of sulfur

compound should be suppresses. In this work, we tried to synthesize carbon coils via minimizing the injection amount of SF_6 flow.

Among the various techniques for the production of carbon coils, the *in-situ* process would be more advantageous because *in-situ* technique might be combined with an *ex-situ* process such as the co-catalyst technique. Previously an *in-situ* cyclic on/off modulation process of C_2H_2/H_2 flow was introduced to enhance the formation yield of carbon nanofilaments [12-15]. It can be simply achieved by turning a source gas flow on or off during the initial reaction stage.

In this work, SF_6 flow was cyclic on/off manipulated as a function of the reaction time. In this way, carbon coils having a controlled geometry could be formed with minimizing SF_6 flow amount. According to the different reaction processes, the injection time of SF_6 flow as well as the flow rate of SF_6 was varied. The characteristics of the as-grown carbon coils were examined and discussed. Based on these results, we discussed the effect of the cyclic on/off modulation for SF_6 flow on the geometry of as-grown carbon coils with maintaining the used SF_6 amount as low as possible.

2. Experimental

SiO_2/Si substrates in this work were prepared by the

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thermal oxidation of the $2.0 \times 2.0 \text{ cm}^2$ p-type Si (100) substrates. The thickness of silicon oxide (SiO_2) layer on Si substrate was estimated about 300 nm. To form Ni catalyst layer, 0.1 mg of Ni powder (99.7 %) was evaporated for 1 minute on the substrate using thermal evaporator. The estimated Ni catalyst layer on the substrate was about 300 nm.

For carbon coils formation, TCVD system was employed. C_2H_2 and H_2 were used as source gases. SF_6 was injected

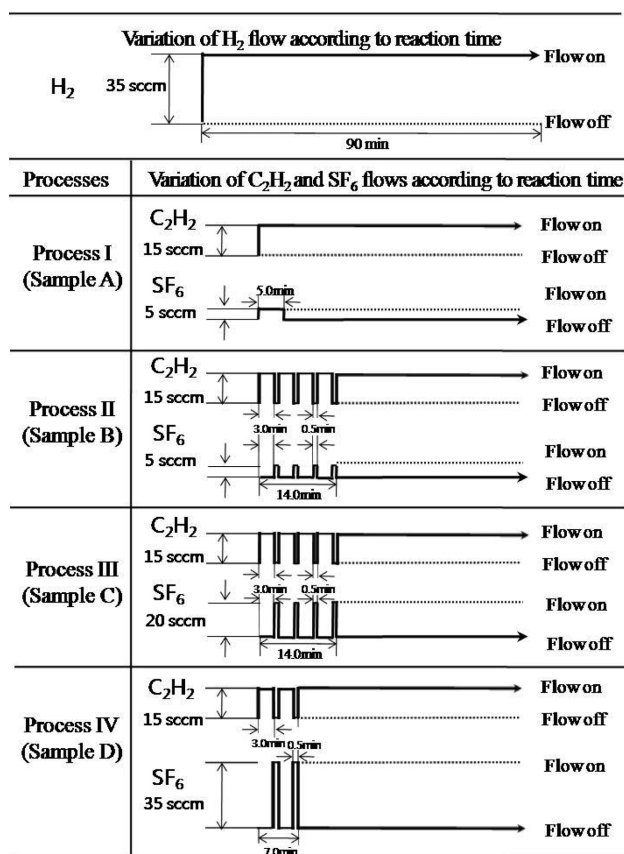


Fig. 1. Different reaction processes: process I (SF_6 flow rate = 5 sccm): $\text{H}_2 + \text{C}_2\text{H}_2 + \text{SF}_6$ flow for 5 minutes \rightarrow the continuous $\text{H}_2 + \text{C}_2\text{H}_2$ flow for 85 minutes, process II (SF_6 flow rate = 5 sccm): 4 times cyclic modulation of C_2H_2 flow on/off for 14 minutes \rightarrow the continuous $\text{H}_2 + \text{C}_2\text{H}_2$ flow for 76 minutes, process III: same process with process II except the higher SF_6 flow rate (20 sccm). process IV (SF_6 flow rate = 35 sccm): 2 times cyclic modulation of C_2H_2 flow on/off for 7 minutes \rightarrow the continuous $\text{H}_2 + \text{C}_2\text{H}_2$ flow for 83 minutes.

Table 1
Experimental conditions for the deposition of carbon coils on the substrates for samples A-D

Processes	Samples	C_2H_2 flow rate (sccm)	H_2 flow rate (sccm)	SF_6 flow rate (sccm)	Total pressure (Torr)	Total deposition time (min)	Source gases flow time (min)			Substrate temp. ($^{\circ}\text{C}$)
							C_2H_2	H_2	SF_6	
I	A	15	35	5	100	90	90	5	750	
II	B	15	35	5	100	90	88	90	2	750
III	C	15	35	20	100	90	88	90	2	750
IV	D	15	35	35	100	90	89	90	1	750

as an additive in a gas composition cycling manner. The in-situ cyclic modulation process was progressed by the variation of these gases flows during the initial deposition stage. Carbon species to form carbon coils are generated from $\text{H}_2 + \text{C}_2\text{H}_2$ flow (C_2H_2 flow on). On the contrary, H_2 flow or $\text{H}_2 + \text{SF}_6$ flow (C_2H_2 flow off) may etch carbon. 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. 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. The numbers of cycles were varied as 2 and 4 times. So, the total cyclic modulation time was varied as 7 and 14 minutes. According to the different reaction processes, SF_6 flow rate and injection time were varied as four kinds of the different procedures as shown in Fig. 1.

We fixed H_2 and C_2H_2 flow rates as 35 and 15 sccm, respectively. SF_6 flow rate was varied as 5, 20, and 35 sccm. The total reaction time was 90 min. 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. 2a shows FESEM image for the sample A under the 5 minutes SF_6 flow injection time and the minimized SF_6 flow rate (5 sccm) condition (process I). As shown in this figure, the embryo for carbon nanofilaments and the immature carbon nanofilaments, instead of carbon coils, could be observed. In four cyclic process of SF_6 flow at flow rate = 5 sccm (process II, sample B), we could observe various carbon geometries such as linear type and coil type as shown in Fig. 2b. In general, many types of carbon coils-related geometries could be formed on the substrate, which are usually classified into four geometrical categories, linear type

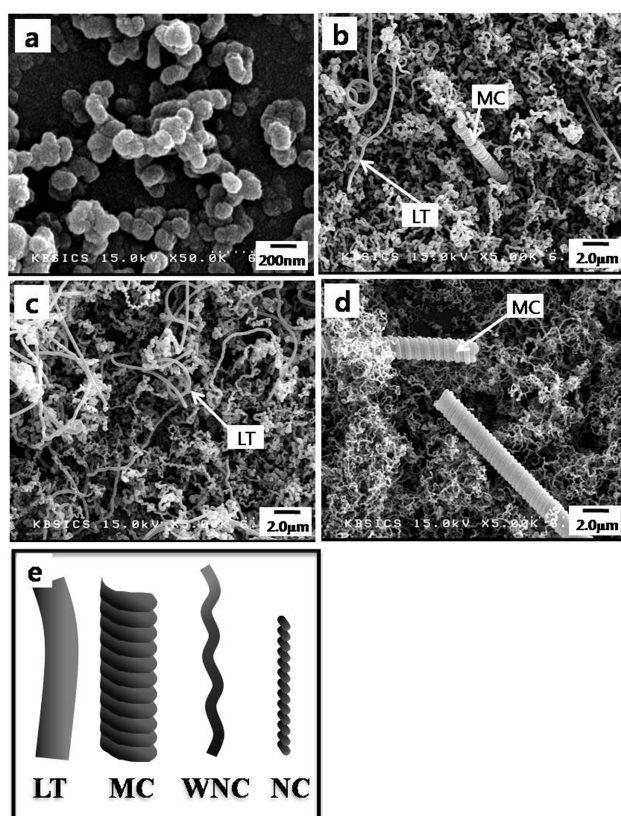


Fig. 2. FESEM images for as-grown carbon coils on (a) sample A, (b) sample B, (c) sample C, (d) sample D, and (e) schematic diagram showing various shapes of carbon coils-related geometries.

(LT), micro-sized coil type (MC), nanosized coil type (NC), and wave-like nanosized coil type (WNC) as shown in Fig. 2e. By increasing the SF_6 flow rate from 5 sccm to 20 sccm with maintaining four times cyclic process of SF_6 flow (process III, sample C), the number of geometry for LT seemed to be increased (compare Figs. 2c with b). The geometries for NC and WNC were mostly prevailing on the sample surface, while any existence of MC on the surface of sample C could not be observed. In case of two times cyclic process of SF_6 flow at highest SF_6 flow rate (process IV, sample D), however, the geometry for MC was reappeared as shown in Fig. 2d. NC and WNC, besides a few amount of MC, were mostly observed on this sample, while the geometry for LT couldn't be observed.

Using the square graph papers and FESEM images, we measured the average ratios of the occupied areas by the different-type carbon geometries, namely LT and MC from several 5,000 magnified FESEM images. Under the assumption of monolayer-grown carbon materials on the samples, the ratio of the occupied areas of carbon geometries were measured in equal-sized FESEM images.

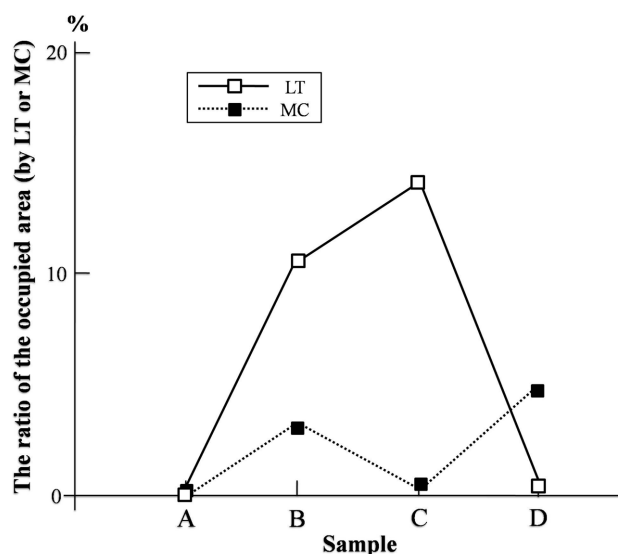


Fig. 3. The variation of the average ratios of the occupied areas in FESEM images by LT and MC as a function of the sample.

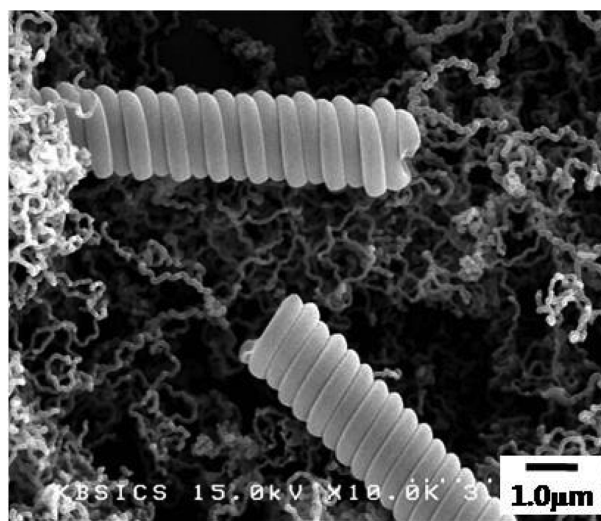


Fig. 4. High magnified FESEM image showing the micro-sized carbon coils for sample D.

Fig. 3 shows the variation of the average ratios of the occupied areas in FESEM images by LT and MC as a function of the sample. As mentioned in the discussion of Fig. 2, the occupied area by LT increased with increasing SF_6 flow rate from 5 (sample B) to 20 sccm (sample C), while that of MC decreased. However, sample D, namely two times cyclic process of SF_6 flow at the highest SF_6 flow rate (35 sccm), provides the most occupied area for MC in this work.

The details of micro-sized carbon coils were investigated by high-magnified FESEM image as shown in Fig. 4. Diameters of the micro-sized carbon coils are in the range of one micrometer to several micrometers. Their

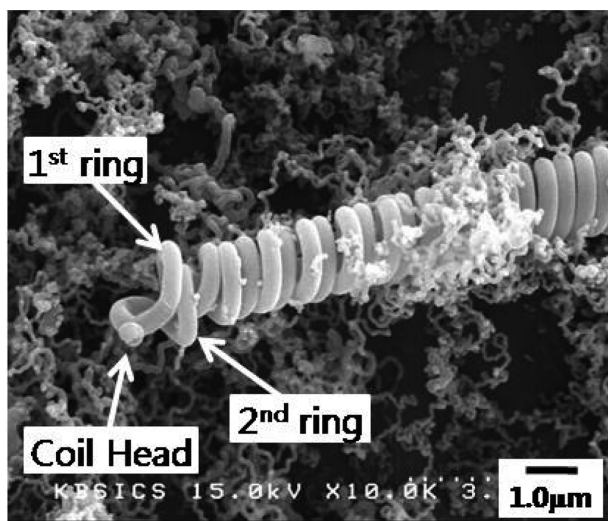


Fig. 5. The detailed image of the micro-sized carbon coil for sample D. The double helix structure and the ending points of the rings constituting the coils could be clearly observed.

individual carbon nanofilaments constituting the coils have the several submicrometer sized diameters. The length ranges of the coils are between a few micrometers and a few millimeters.

Fig. 5 shows the MC geometry for sample D indicating the well organized double helix structure. First and second ending points of the rings could be clearly observed. It indicates that the formation of MCs in our research follows a typical double-helix structure for the geometry. The shape of filament constituting the coils were mostly circular-type. For the shape of the rings constituting the coils, circular-type morphology instead of flat-type, could be well observed. Furthermore, the head of the coil could be clearly observed. As our previous report, the head of the coil seems to be the initiation point for two rings eventually forming the coils [16].

Fig. 6 shows FESEM images for the samples under the high magnified ($\times 50,000$) condition. Except sample A, all of the samples show WNC and NC formations. Interestingly, the changed turning direction of carbon nanofilaments constituting NC could be observed as shown in the dotted circle area of Fig. 6b. Using the square graph papers and high-magnified FESEM images, we also measured the average ratios of the occupied areas by the different-type carbon geometries, namely WNC and NC from several 50,000 magnified FESEM images. Fig. 7 shows the variation of the average ratios for the occupied areas by WNC or NC in FESEM images as a function of the sample. Negligible amounts of WNC and NC were observed in the continuous SF_6 gas flow

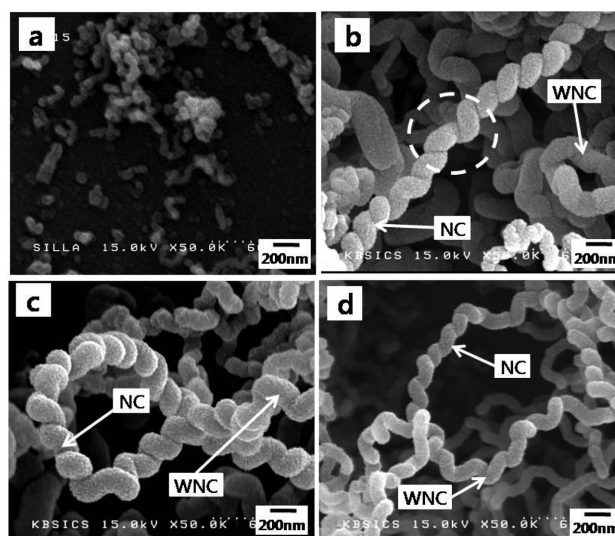


Fig. 6. High magnified (50 k) FESEM images for as-grown carbon coils on (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

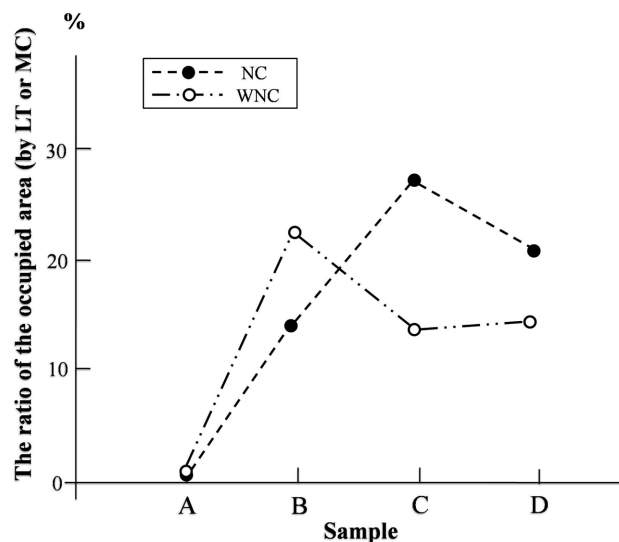


Fig. 7. The variation of the average ratios of the occupied areas in FESEM images by WNC and NC as a function of the sample.

injection without cyclic modulation manner (sample A). With the application of the cycling on/off process for $\text{C}_2\text{H}_2/\text{SF}_6$ flows, the ratios of the occupied areas by WNC or NC seemed to be drastically increased. Indeed, WNC was the major product for sample B and NC for sample C, respectively. The ratio of the occupied area of WNC to that of NC is more than one for sample B. On the other hand, this ratio is less than one for samples C and D. These results indicate that the amount of as-grown NC seemed to be higher than that of as-grown WNC under the condition of the higher SF_6 flow rate.

Based on the results, we propose that the incorpora-

tion of SF₆ in a cyclic modulation manner could develop the different-type carbon coils, namely, MC, WNC, and NC. The change of carbon nanofilament geometry from a conventional linear type to a coil type seems to be due to the sulfur role in SF₆ as previous reports [17, 18]. In addition, a higher flow rate of SF₆ gas in the cyclic modulation process could give rise to increase in the amount of as-grown NC. The cause for these results was considered to be due to the slightly increased etching ability by SF₆ addition to H₂ gas concentration during the etching time in the cyclic modulation process. Higher flow rate of SF₆ gas may preferentially etch away soft materials. Among the various geometries, NC seems to be a geometrically well-organized and hard materials characteristics. Therefore, NC would be survived even under the higher SF₆ flow rate.

4. Conclusions

The geometry development from conventional linear type to coil type could be achieved by the incorporation of SF₆ as a cyclic modulation manner. The micro-sized coil formation in this work follows a typical double-helix structure. The higher flow rate of SF₆ gas under the minimized SF₆ injection time in the cyclic modulation process could give rise to the increase in the amount of as-grown nanosized coil. The cause for these is considered to be due to the slightly increased etching ability by SF₆ addition and the geometrically well-organized structure for NC compared with other geometries. Finally, we could obtain the dominant NC geometry for as-grown carbon coils even under the minimized SF₆ additive condition

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