

Effect of Reaction Temperature on the Geometry of Carbon Coils Formed by SF₆ Flow Incorporation in C₂H₂ and H₂ Source Gases

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Carbon coils could be synthesized on nickel catalyst layer-deposited silicon oxide substrate using C₂H₂ and H₂ as source gases and SF₆ as an additive gas under thermal chemical vapor deposition system. The geometries of as-grown carbon materials were investigated with increasing the reaction temperature as the increment of 25°C from 650°C up to 800°C. At 650°C, the embryos for carbon coils were formed. With increasing the reaction temperature to 700°C, the coil-type geometries were developed. Further increasing the reaction temperature to 775°C, the development of wave-like nano-sized coils, instead of nano-sized coils, and occasional appearance of micro-sized carbon coils could be observed. Fluorine in SF₆ additive may shrink the micro-sized coil diameter via the reduction of Ni catalyst size by fluorine's etching role. Finally, the preparation of the micro-sized carbon coils having the smaller coil diameters, compared with the previously reported ones, could be possible using SF₆ additive.

Keywords : Carbon coil, SF₆, Geometry, Reaction temperature, Thermal chemical vapor deposition

I. Introduction

Since the first report by Davis et al. carbon coils have been noticed because of their unique shape [1]. Carbon coils have spring-like helix-shaped geometry. Therefore they may induce an electrical current and consequently generate a magnetic field. So, electrical, magnetic and mechanical properties of carbon coils are more attractive for electromagnetism than straight ones [2]. Their predicted electrical, magnetic and mechanical properties might be attractive to use as nano/micro-sized tactile sensors, actuators, resonators, mechanical springs, and so on [3-6].

Coils-type geometries were also reported using SiC [7,8] and Si₃N₄ [9-12]. However, the production of coils-type geometry was accidental and lack of reproducibility. Furthermore, the electrical properties of helically coiled geometry may have metallic, semiconducting or semi-metallic depending on their geometry including diameter [13]. Therefore the controlled geometry of carbon coils would be the problem to be addressed in order to achieve the controlled electrical properties of carbon coils.

For the catalyst, In and Sn were known to play an important role for the formation of carbon coils [14-16]. Co-silica or Fe-silica catalysts have been

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served as substrates for the preparation of carbon coils by catalytic pyrolysis of acetylene [17]. In general, iron-family catalysts (Fe, Co, and Ni) were noticed for use in the synthesis of carbon coils. Among them, especially Ni was known as an effective catalyst for the formation of the super elastic carbon coils [18].

Motojima et al. first reported the regularly micro-coiled carbon fibers with high reproducibility by the catalytic pyrolysis of acetylene containing a small amount of sulfur impurity, and reported the preparation conditions and morphologies [19–21]. Sulfur impurities were mostly incorporated in the form of hydrogen sulfide (H₂S), carbon disulfide (CS₂), and thiophene (C₄H₄S) [22–26]. Sulfur-related species are very hazardous for environment and inevitably damage the health of the people in surroundings. So, their use should be reduced in the synthesis of carbon coils as possible as one can.

In our previous work, we chose SF₆ as a relatively

safe sulfur impurity and reduced the amount of the incorporated SF₆ gas by minimizing the injection time [27]. In this work, we varied the reaction temperature and examined the growth patterns and morphologies of the carbon coils formed by 5 min-SF₆ flow incorporation in C₂H₂ and H₂ source gases.

II. Experimental

The SiO₂ substrates in this work were prepared by the thermal oxidation of the 2.0×2.0 cm² p-type Si (100) substrates. The thickness of silicon oxide (SiO₂) layer on Si substrate was estimated about 300 nm. A 0.1 mg Ni powder (99.7%) was evaporated for 1 min to form the Ni catalyst layer on the substrate using thermal evaporator as shown in Fig. 1a.

Prior to carbon coils deposition, Ni-coated substrate was placed in the plasma enhanced chemical

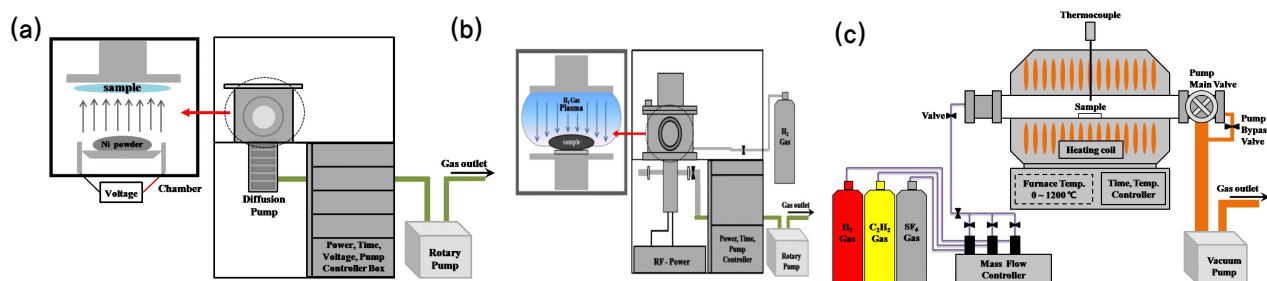


Figure 1. Schematic diagram of experimental setup of (a) thermal evaporator system, (b) plasma enhanced chemical vapor deposition system, and (c) thermal chemical vapor deposition system.

Table 1. Experimental conditions for the deposition of carbon coils on the substrates for sample A ~ G.

Processes	Samples	C ₂ H ₂ flow rate (sccm)	H ₂ flow rate (sccm)	SF ₆ flow rate (sccm)	Total pressure (Torr)	Total deposition time (min)	Source flow time (min)			Substrate temp. (°C)
							C ₂ H ₂	H ₂	SF ₆	
I	A	15	35	35	100	90	90	90	5	650
II	B	15	35	35	100	90	90	90	5	675
III	C	15	35	35	100	90	90	90	5	700
IV	D	15	35	35	100	90	90	90	5	725
V	E	15	35	35	100	90	90	90	5	750
VI	F	15	35	35	100	90	90	90	5	775
VII	G	15	35	25	100	90	90	90	5	800

vapor deposition (PECVD) system as shown in Fig. 1b. H_2 gas was introduced into PECVD chamber and then the substrate was pre-cleaned for 5 minutes using H_2 plasma. After H_2 plasma reaction, the thickness of Ni catalyst layer was measured about 100 nm by investigating the cross section of Ni catalyst layer de-

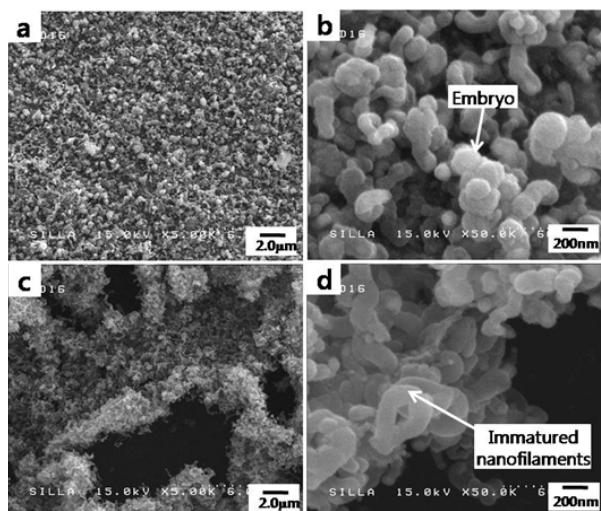


Figure 2. (a) FESEM images for sample A, (b) the high-magnified FESEM images for sample A, (c) FESEM images for sample B, and (d) the high-magnified FESEM images for sample B.

posited substrate using field emission scanning electron microscopy (FESEM).

For carbon coils deposition, thermal chemical vapor deposition (TCVD) system was employed as shown in Fig. 1c. C_2H_2 and H_2 were used as source gases. SF_6 , as an incorporated additive gas, was injected into the reactor during the reaction. The flow rate for C_2H_2 and H_2 were fixed at 15 and 35 standard cm^3 per minute (sccm), respectively. SF_6 flow rate and injection time were set as 35 and 5 minutes, respectively. According to the different reaction processes, the reaction temperatures were varied as the increment of $25^\circ C$ from $650^\circ C$ up to $800^\circ C$. The detailed reaction conditions were shown in Table 1. Morphologies of carbon coils-deposited samples were investigated using FESEM.

III. Results and discussion

Fig. 2 shows FESEM images showing the surface morphologies of samples A and B at the reaction

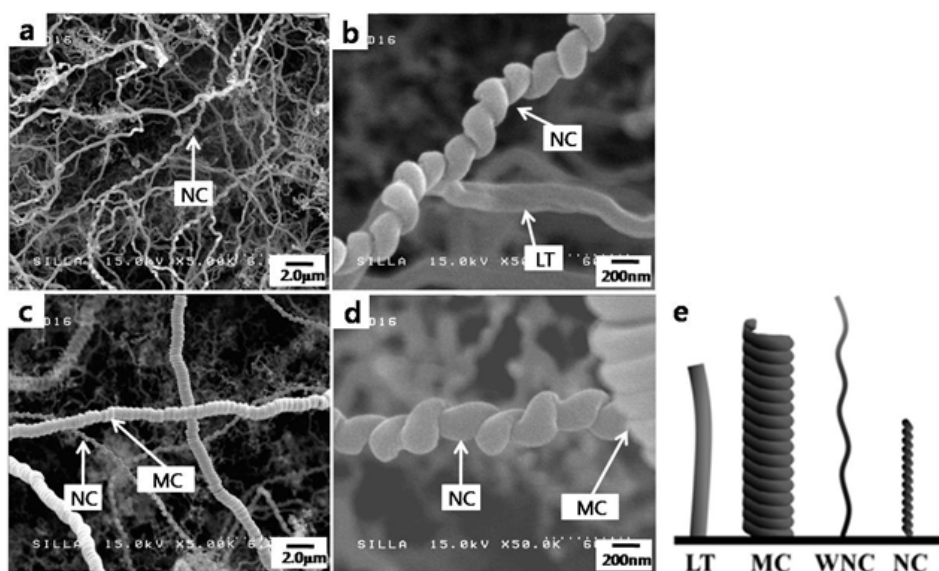


Figure 3. (a) FESEM images for sample C, (b) the high-magnified FESEM images for sample C, (c) FESEM images for sample D, and (d) the high-magnified FESEM images for sample D, and (e) the generally accepted four geometrical categories of carbon coils, namely linear tub (LT), micro-sized coil (MC), nano-sized coil (NC), and wave-like nano-sized coil (WNC).

temperature of 650°C and 675°C, respectively. Indeed, the CNFs formation density seems to be not much different according to the position on the sample. It reveals the uniformly distributed CNFs in whole area for the sample. The uniformly distribution phenomena of carbon materials formation according to the samples A~G could be clearly and repeatedly observed. The high-magnified FESEM images reveal

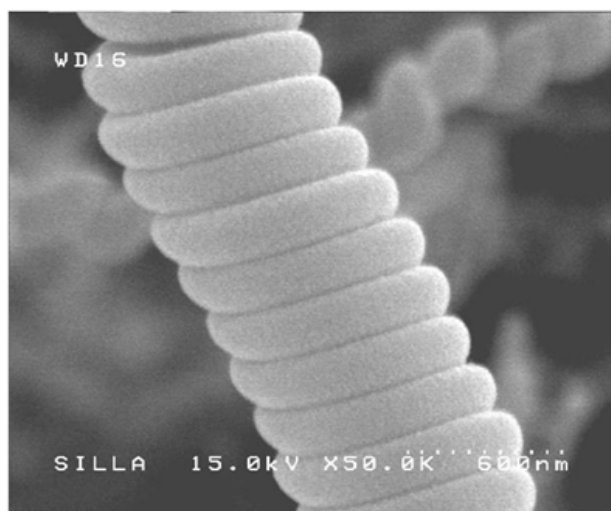


Figure 4. Representative FESEM image of the regular micro-sized coil (MC) obtained at 725°C.

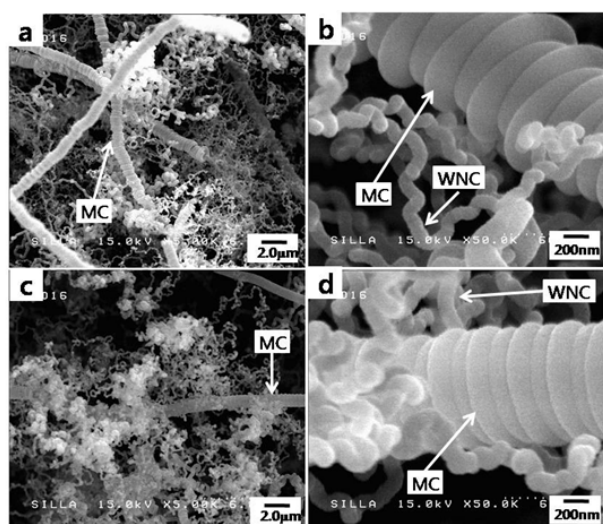


Figure 5. (a) FESEM images for sample E, (b) the high-magnified FESEM images for sample E, (c) FESEM images for sample F, and (d) the high-magnified FESEM images for sample F.

the embryo for CNFs formation on sample A (Fig. 2b) and the immature CNFs on sample B (Fig. 2d).

Fig. 3 shows FESEM images showing the surface morphologies of samples C and D at the reaction temperature of 700°C and 725°C, respectively. In this case, the CNFs geometry having conventional linear type and nano-sized coil-type could be clearly observed at 700°C (Fig. 3b). 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 type (LT), micro-sized coil (MC), nano-sized coil (NC), and wave-like nano-sized coil (WNC) (Fig. 3e). At 725°C, NC could be mostly observed and the occasional appearance of MC could be also observed as shown in Figs. 3c and d. This result reveals the occurrence of geometry change from NC and LT to NC and MC with increasing the reaction temperature from 700°C to 725°C. Representative FESEM image of the regular MC obtained at 725°C are shown in Fig. 4. This regular carbon coil has constant coil pitch of $\sim 0.2 \mu\text{m}$ without any coil gap and have coil diameter of $\sim 0.8 \mu\text{m}$. In some reports [24], the carbon filaments in the carbon coils have a flat type edge shape. However, our case the edge shape was a circular type as shown in Fig. 4.

Further increasing the reaction temperature up to 775°C, the appearance of WNC and the occasional development of MC could be clearly observed as shown in Fig. 5. Indeed, the number density of MC was highest at 750°C. Indeed WNC type geometries, in-

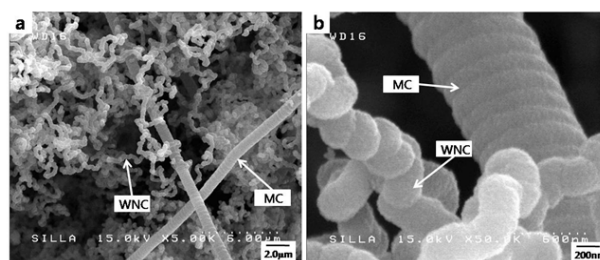


Figure 6. (a) FESEM images for sample G and (b) the high-magnified FESEM images for sample G.

stead of NC, were mostly observed in this temperature range. At the highest reaction temperature (800°C) in this work, we could find WNC as the prevalent coil structure with the occasional appearance of MC as shown in Fig. 6a. Comparing the images between Fig. 5d with Fig. 6b, the diameters of WNC was increased from ~150 nm to ~250 nm. Based on above results, we suggest the geometry development of carbon coils as embryos \rightarrow NC \rightarrow NC with MC \rightarrow WNC with MC with increasing the reaction temperature from 650°C up to 800°C.

In this work, diameters of the micro-sized carbon coils and the composed carbon nanofilaments are on average 10 μ m and 0.2 μ m, respectively. The length of the coil are in the range between a few micrometers and a few tens micrometers. The dependence of the coil diameters of micro-sized carbon coils on the reaction temperature is negligible. However, the diameter of carbon nanofilaments seems to be increased at the highest temperature (800°C) in this work. Compared with the previous result by Chen and Motojima [24], this results show slightly different phenomena. Chen reported about 10 μ m and 0.5 μ m sizes of micro-sized coil diameter and coil pitch, respectively in thiophene additive and C₂H₂/H₂ source gases system. In addition, they showed the strong dependence of the micro-sized coil diameter and morphologies on the reaction temperature from 700°C to 870°C. At this time, we understood the dependence difference of the micro-sized coil diameter with the temperature, compared with Chen's result, may be due to the different reaction temperature range with different additive and injection time. Meanwhile, the size difference of the micro coils seems to be due to the fluorine's etching ability in SF₆ additive. It was reported that the growth mechanism of the micro-sized carbon coils in which the driving force of the coiling of the carbon nanofilaments to form the micro-sized carbon coils is an anisotropic deposition on the carbons from the respective Ni catalyst faces

[28]. Therefore fluorine in SF₆ additive may shrink the micro-sized coil diameter via the reduction of Ni catalyst size by fluorine's etching role. Although the exact causes and the detailed mechanism for the difference of micro-sized coils diameter for our results, compared with the previous reported ones, couldn't be fully understood at this time, we could reduce the micro-sized coil diameter by incorporation SF₆ additive. Consequently this work may provide the preparation of the micro-sized carbon coils having the smaller coil diameters, compare with the previously reported ones.

IV. Conclusion

The geometry of carbon coils were developed as embryos \rightarrow NC \rightarrow NC with MC \rightarrow WNC with MC with increasing the reaction temperature from 650°C up to 800°C. Fluorine in SF₆ additive may shrink the micro-sized coil diameter via the reduction of Ni catalyst size by fluorine's etching role. Finally, the preparation of the carbon micro coils having the smaller coil diameters, compared with the previously reported ones, could be possible using SF₆ additive.

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SF₆-C₂H₂-H₂ 기체에 의해 생성된 탄소 코일 기하구조의 반응온도 효과

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니켈촉매 막을 증착시킨 산화규소 기판위에 아세틸렌기체와 수소기체를 원료로, 육불화황기체를 첨가기체로 열화학기상증착 시스템하에서 탄소코일을 증착하였다. 반응온도를 650°C에서 800°C까지 증가시키면서 증착된 탄소 코일의 기하구조를 조사하였다. 650°C에서는 주로 탄소나노필라멘트 형성의 전단계가 나타났으며, 반응온도가 증가하자(700°C) 나노 크기의 코일들이 나타났다. 775°C로 반응온도를 더욱 증가시키자, 파도물결과 같은 나노 코일들이 성장되었으며, 간혹 마이크로 크기의 코일들도 나타났다. 육불화황에 첨가된 불소의 에칭효과로 니켈 촉매의 크기를 줄일 수 있을 것으로 여겨지며, 따라서 육불화황 첨가 기체의 사용으로 기존에 보고된 것보다 작은 크기의 직경을 갖는 마이크로 탄소 코일을 얻을 수 있었다.

주제어 : 탄소 코일, 육불화황, 기하구조, 반응온도, 열화학기상증착

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