Effect of Gas Phase Cycling Modulation of C_2H_2/SF_6 Flows on the Formation of Carbon Coils

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Carbon coils could be synthesized on nickel catalyst layer-deposited silicon oxide substrate using C_2H_2 and H_2 as source gases and SF_6 as an additive gas under thermal chemical vapor deposition system. The characteristics (formation density and morphology) of as-grown carbon coils were investigated as functions of additive gas flow rate and the cycling on/off modulation of C_2H_2/SF_6 flows. Even in the lowest SF_6 flow rate (5 sccm) in this work, the cycling on/off modulation injection of SF_6 flow for 2 minutes could give rise to the formation of nanosized carbon coils, whereas the continuous injection of SF_6 flow for 5 minutes could not give rise to the carbon coils formation. With increasing SF_6 flow rates from 5 to 30 sccm, the cycling on/off modulation injection of SF_6 flow confines the geometry for the carbon coils to the nanosized ones. Fluorine's role of SF_6 during the reaction was regarded as the main cause for the confinement of carbon coils geometries to the nano-sized ones.

Keywords : Carbon coil, SF_6 , Geometry, The cycling modulation, Thermal chemical vapor deposition

I. Introduction

The study of carbon nanomaterials with a helical morphology, so called carbon coils, has been the particular interest to recent scientists because carbon coils could be predicted to have the particular properties such as high elasticity, low electrical resistance, chirality, and high specific surface area [1–4]. Up to the present, the control over the synthesis of a specific type of helical carbon nanomaterial has been met with only limited success [5–8]. So, for the practical application of these materials, the controlled-characteristics for coil morphology and ge-

ometry (diameter, pitch, length, and turning direction) should be preferentially achieved. In addition, the electrical properties of carbon nanofilaments or helically coiled carbon nanotubes may be metallic, semiconducting or semimetallic depending on their geometry including diameter and the pentagonal and heptagonal rings placement in carbon coils [9]. Therefore the controlled geometry of carbon coils would be essential to achieve the controlled electrical properties of carbon coils.

Among the various techniques to synthesize carbon coils, the incorporated additives, a trace of the sulfur-related species [10–15], was regarded as the

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promising method for the formation of carbon coils. Carbon coils were reported to be well-synthesized by adding a trace of hydrogen sulfide (H_2S) [10], carbon disulfide (CS_2) [13], thiophene (C_4H_4S) as an impurity [14] or using WS_2 as a catalytic material [15]. In general sulfur-incorporated species are very hazardous for the environment and inevitably damage the health of the people in surroundings. So, it should be indispensable to use these materials as small as possible. It was also known that the addition of fluorine species was known to enhance the rate of hydrogen abstraction, thereby opening more nucleation sites of carbon materials for possible interaction with growth species even in the low temperature case [16]. In this respect of sulfur and fluorine, we chose SF_6 and tried to reduce the amount of the used SF_6 gas by shortening the injection time [17]. In this work, the flow rate and the injection time of SF_6 were manipulated to obtain the controlled geometry of carbon coils. The variation of the as-grown carbon coils characteristics, namely the formation density and the geometry, according to the additive gas (SF_6) flow rate and the cycling modulation of C_2H_2/SF_6 flows was examined and discussed.

II. Experimental

The SiO_2 substrates in this work were prepared by the 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, a 0.1 mg 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 400 nm.

For carbon coils deposition, thermal chemical vapor deposition system was employed. C_2H_2 and H_2 were used as source gases. The injection time for C_2H_2 and H_2 was almost 90 minutes, whereas that for SF_6 was

less than 5 minutes. Total flow rate was fixed at 50 standard cm^3 per minute (sccm). According to the different reaction processes, the flows of source gases were as follows, namely

process I: $H_2 + C_2H_2$ (90 min),

processes II and III: $H_2 + C_2H_2 + SF_6$ flow (5 min)

$\rightarrow H_2 + C_2H_2$ flow (85 min), and

processes IV, V, and VI: $H_2 + C_2H_2$ flow (3 min)

$\rightarrow H_2 + SF_6$ flow (0.5 min) $\rightarrow \rightarrow \rightarrow$

$H_2 + C_2H_2$ flow (3 min) $\rightarrow H_2 + SF_6$ flow (0.5 min)

$\rightarrow H_2 + C_2H_2$ flow (76 min).

Carbon species to form carbon coils are generated from $H_2 + C_2H_2$ flow (C_2H_2 flow on). On the contrary, $H_2 + SF_6$ flow (C_2H_2 flow off) may etch carbon components. Fig. 1 shows the detailed manipulation of these gases flows according to the processes. The detailed reaction conditions according to the different processes with samples were shown in Table 1.

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

III. Results and Discussion

Fig. 2 shows FESEM images indicating the surface morphologies of sample at process I. As shown in Fig. 2, carbon nanofilaments-related materials could be developed on the surface of sample without SF_6 incorporation case (sample A). The embryo for carbon nanofilaments formation and the immatured carbon nanofilaments could be observed as shown in high-magnified FESEM images (Fig. 2b).

To prevent the very hazardous problem in the use of sulfur-incorporated species, we limited SF_6 flow injection time less than 5 minutes. Furthermore, SF_6 flow injection carried out merely during the initial reaction stage. Fig. 3(a) show FESEM image showing the surface morphology of as-grown sample (sample B) in case of 5 sccm SF_6 flow for continuous 5 minutes

Figure 1. Different reaction processes.

Table 1. Experimental conditions for the deposition of carbon coils on the substrates for samples A~F.

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. ($^{\circ}C$)
							C_2H_2	H_2	SF_6	
I	A	15	35	—	100	90	90	90	—	750
II	B	15	35	5	100	90	90	90	5	750
III	C	15	35	25	100	90	90	90	5	750
IV	D	15	35	5	100	90	88	90	2	750
V	E	15	35	10	100	90	88	90	2	750
VI	F	15	35	30	100	90	88	90	2	750

Figure 2. FESEM images for (a) as-grown sample A and (b) high magnified image of Fig. 2(a).

injection (process II). In this case the geometries like carbon coils could not be developed. Meanwhile, the embryos of carbon nanofilaments morphologies could

be observed as shown in 50 k magnified FESEM images (Fig. 4). In case of 25 sccm SF_6 flow for continuous 5 minutes injection (process III), the surface

Figure 3. FESEM images for as-grown (a) sample B, (b) sample C, and (c) sample D.

Figure 4. High magnified image of Fig. 3(a).

morphology of as-grown sample (sample C) was also investigated. In this case the formation of carbon nanofilaments (designated by arrow in Fig. 3b) could be well observed. Most of them were observed as somewhat bent and twisted geometries instead of the conventional coil type geometry. Diameters of them are in the range of a few hundred nanometers.

Fig. 3(c) shows the FESEM image indicating the surface morphology of as-grown sample (sample D) in case of 5 sccm SF_6 flow for 4 times on/off manipulating (see process IV in Fig. 1). Applying the cycling on/off modulation process for C_2H_2/SF_6 flows could give rise to a couple of micro-sized carbon coils as shown in the designated position by arrow in Fig 3(c).

In general, many types of carbon coils-related geometries could be formed, so they could be usually classified into four geometrical categories, namely linear type (LT), micro-sized coil (MC), nanosized coil (NC), and wave-like nanosized coil (WNC) [18]. Among many types of carbon coils-related geometries, WNC could be mostly observed on sample D as shown in Fig. 3(c). Diameters of LT are in the range of a few hundred nanometers. In addition, diameters of MC and the individual carbon nanofilaments are in the range of several micrometers and a few hundred nanometers, respectively. The length range of MC are in the range from a few micrometers to a few tens micrometers.

The effect of the cycling on/off modulation process for C_2H_2/SF_6 flows on the geometries was also investigated as a function of SF_6 flow rate. With increasing SF_6 flow rate from 5 to 30 sccm, the geometry for the carbon coils gradually confined to WNC as shown in Fig. 5. At 30 sccm SF_6 flow rates, indeed, MC could not be observed on the whole surface of the sample. Even in case of LT, a few numbers of them could be found on the whole surface of the sample. This result reveals that the increased SF_6 flow rate from 5 to 30 sccm can confine the geometries of carbon coils-related materials to WNC formation. High-magnified FESEM images could give the well-developed MC for sample D (see arrow in Fig. 6a) and the undeveloped MC for sample E (see arrow in Fig. 6b). This result

Figure 5. FESEM images for as-grown (a) sample D, (b) sample E, and (c) sample F.

Figure 6. High-magnified FESEM images for as-grown (a) sample D, (b) sample E, and (c) sample F.

reveals that the well-developed MC favors a relatively small amount of SF_6 flow.

Based on the results from Fig. 1 to 6, we confirm that even a short time (2 minutes) SF_6 flow injection case, the geometries of carbon coils-related materials could be developed by the application of the cycling on/off modulation process for $\text{C}_2\text{H}_2/\text{SF}_6$ flows. Furthermore, the geometries of the carbon coils gradually confined to WNC geometries with increasing SF_6 flow rate from 5 to 30 sccm.

IV. Conclusions

Even in the case of the small amount of SF_6 flow injection (5 sccm for flow rate and 2 minutes for injection time), the carbon coils formation could be obtained by the application of the cycling on/off modulation

process for $\text{C}_2\text{H}_2/\text{SF}_6$ flows during the initial reaction stage. Furthermore, the geometries of the carbon coils could be gradually confined to WNC type by increasing SF_6 flow rate. Finally, we could obtain the geometrically controlled carbon coils using sulfur-incorporated chemical species as small as possible.

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탄소 코일 생성에 대한 C_2H_2/SF_6 기체유량의 싸이클릭 변조 효과

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니켈촉매 막을 증착시킨 산화규산 기판 위에 아세틸렌기체와 수소기체를 원료기체로 육불화황기체를 첨가기체로 사용하여 열화학기상증착 방법으로 탄소코일을 합성하였다. 첨가기체의 유량과 아세틸렌/육불화황 기체들의 싸이클릭 on/off 유량 변조에 따라 성장된 탄소코일의 특성(형성 밀도, 형상)을 조사하였다. 육불화황의 기체 유량이 가장 낮은 경우(5 sccm)에서, 2분 동안 육불화황을 주입하여 아세틸렌/육불화황 기체를 싸이클릭 on/off 유량 변조시킴에 따라 탄소코일을 형성시켰다. 반면 육불화황을 5분 동안 연속적으로 주입한 경우에는 탄소나노필라멘트 형상이 나타나지 않았다. 육불화황의 유량이 5 sccm에서 30 sccm으로 증가함에 따라 아세틸렌/육불화황 기체들의 싸이클릭 on/off 유량 변조는 탄소코일의 형상을 나노크기의 형태로만 제한시켰다. 육불화황 기체의 플로린 종에 의한 에칭 특성이 이러한 효과를 주게 하는 것으로 이해되었다.

주제어 : 탄소 코일, 육불화황, 기하구조, 싸이클릭 변조, 열화학기상증착

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