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Effect of Injection Stage of SF_6 Gas Incorporation on the Limitation of Carbon Coils Geometries

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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 according to the injection stage of SF_6 gas incorporation were investigated. A continuous injecting of SF_6 gas flow could give rise to many types of carbon coils-related geometries, namely linear tub, micro-sized coil, nano-sized coil, and wave-like nano-sized coil. However, the limitation of the geometry as the nano-sized geometries of carbon coils could be achieved by the incorporation of SF_6 in a short time (1 min) during the initial deposition stage. A delayed injection of a short time SF_6 gas flow can deteriorate the limitation of the geometries. It confirms that the injection time and its starting point of SF_6 gas flow would be very important to determine the geometries of carbon coils.

Keywords : Carbon coil, SF_6, Geometry, Injection stage, Thermal chemical vapor deposition

I. Introduction

Carbon coils have been occasionally found as the low-content byproducts of the vapor preparation of the carbon fibers in microwave plasma-enhanced chemical vapor deposition or in thermal chemical vapor deposition [1,2]. Because of the unique shape, they were predicted to have promising materials characteristics [3,4]. Microscopically, helically coiled carbon nanotubes were known to be constructed by periodically inserting heptagonal and pentagonal rings into hexagonal network [5]. Double helix shaped carbon coils geometry may induce an electrical current and consequently generate a magnetic field. So, electrical, magnetic and mechanical properties of carbon coils are more attractive for nanoelectro-magnetism than straight ones [6]. The electrical properties of carbon nanofilaments 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 [7-9]. Therefore the controlled geometry of carbon coils would be essential to achieve the controlled electrical properties of carbon coils. Indeed, carbon coils devices or sensors were supposed to show the femto-scaled sensitivity and ultra-high resolution [10,11]. Furthermore, the coiled structure seemed to avoid the covalent functionalization problem in the graphite network of the reinforced carbon nanotube [12].

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Among the various techniques to synthesize carbon coils, thermal chemical vapor deposition (TCVD) technique using the metal catalyst has been more noticed because of its relative inexpensive and applicable feature. The mainly used metal-based catalysts for carbon coils in TCVD were Fe, Co, Ni or their organic compounds [13-15]. For incorporated additives, meanwhile, a trace of sulfur-related species [16-18] was regarded as promising additives for the formation of carbon coils. In general sulfur-related species are very hazardous for environment and inevitably damage the health of the people in surroundings. So, it should be indispensible to reduce the use of these materials in the synthesis of carbon coils as possible as one can.

To do this, in this work, we chose SF_6 as a sulfur species because it was known as a relatively safe material among the materials containing sulfur species. Furthermore, we tried to reduce the amount of the used SF_6 gas by shortening the injection time as low as 1 min. In this work, therefore, we varied the injection starting point of a short time (1 min) SF_6 gas flow (1 min-SF_6 flow). The variation of the as-grown carbon coils characteristics, namely the formation density and the geometry, according to the injection starting point of a 1 min-SF_6 flow was examined and discussed.

II. Experiments

The SiO_2 substrates in this work were prepared by the thermal oxidation of the 2.0×2.0 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 min 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

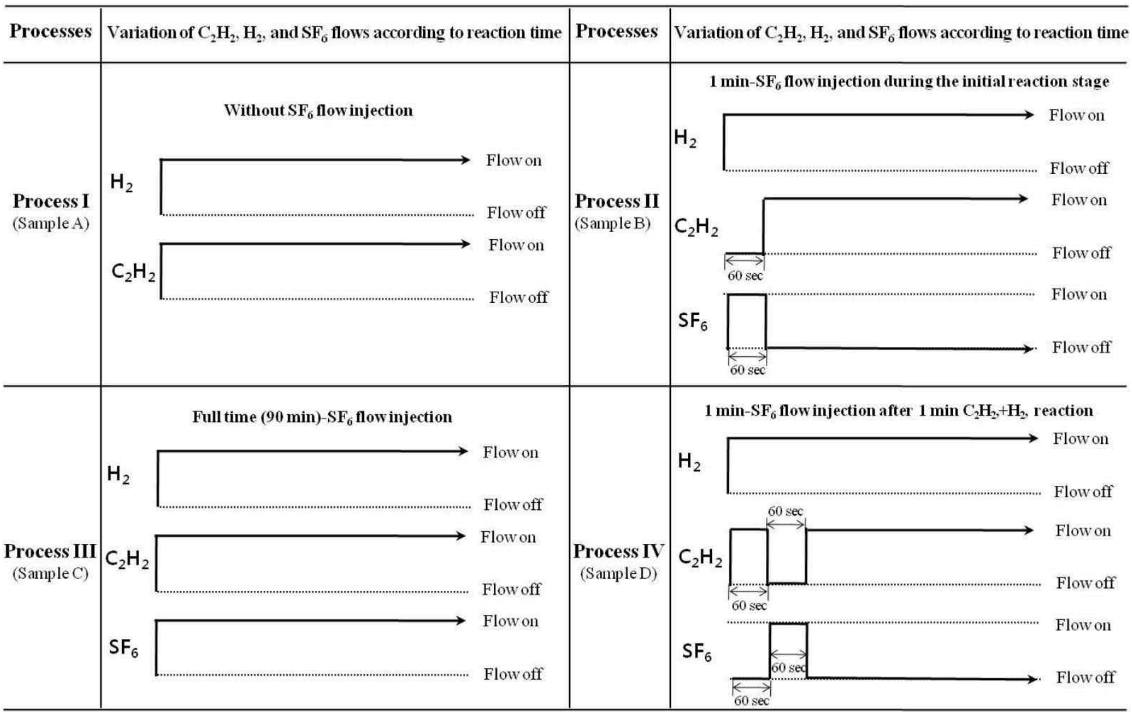

Figure 1. Different reaction processes: process I (sample A): continual H_2+C_2H_2 flow (90 min), process II (sample B): H_2+SF_6 flow (1 min)→H_2+C_2H_2 flow (89 min), process III (sample C): continual H_2+C_2H_2+SF_6 flow (90 min), process IV (sample D): H_2+C_2H_2 flow (1 min)→H_2+SF_6 flow (1 min)→H_2+C_2H_2 flow (88 min).

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

Processes	Conditions \ Sample	C_2H_2 flow rate (sccm)	H_2 flow rate (sccm)	SF_6 flow rate (sccm)	Total pressure (Torr)	Total deposition time (min)	Injection starting point duration			Substrate temperature (℃)
							C_2H_2	H_2	SF_6	
I	Sample A	15	35	0	100	90	Initial, 90 min	Initial, 90 min	–	750
II	Sample B	15	35	35	100	90	After 1 min, *89 min	Initial, 90 min	Initial, 1 min	750
III	Sample C	15	35	35	100	90	Initial, 90 min	Initial 90 min	Initial, 90 min	750
IV	Sample D	15	35	35	100	90	Initial, *89 min	Initial, 90 min	After 1 min, 1 min	750

*In process IV (sample D) case, C_2H_2 flow was intermitted for 1 min after 1 min C_2H_2+H_2 reaction.

deposition system was employed. C_2H_2 and H_2 were used as source gases. SF_6 was injected for a relatively short time (1 min). 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: continual H_2+C_2H_2 flow (90 min),

process II: H_2+SF_6 flow (1 min) → H_2+C_2H_2 flow (89 min),

process III: continual H_2+C_2H_2 flow+SF_6 flow (90 min),

process IV: H_2+C_2H_2 flow (1 min) → H_2+SF_6 flow (1 min) → H_2+C_2H_2 flow (88 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 compo-nents. 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 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 showing the surface morphologies of samples according to the processes (processes I~IV, samples A~D). As shown in Fig. 2(a), 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 well observed as shown in high-magnified FESEM images (Fig. 3(a)).

Fig. 2(b) shows FESEM images showing the surface morphology for sample with 1 min-SF_6 flow injection during the initial reaction stage case (sample B). In this case, however, the dominant formation of nano-sized wave-like coil types could be clearly observed (compare Fig. 3(a) with 3(b)). Occasionally, a couple of micro-sized carbon coils such as linear tub (LT), micro-sized coil (MC) could be well observed around the center position of sample B as shown in Fig. 4(a) and 4(b). Diameters of the micro-sized carbon coils and the individual carbon nano-filaments 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. In general, many types of carbon coils-related geometries could be formed, 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) as shown in Fig. 4(c). Among many types of carbon coils-related geometries, wave-like nano-sized coil (WNC) could be mostly observed on sample B as shown in Fig. 3(b).

To figure out the difference between a 1 min-SF_6 flow case and a full time (90 min) SF_6 flow case, the morphologies of sample (process III, sample C) completing full time (90 min) incorporation of SF_6 flow were examined. As shown in Fig. 2(c) and 3(c), various types of carbon coils-related geometries such as LT, MC, NC and WNC could be well observed. This result reveals that a full time SF_6 flow injection can't limit the geometries of carbon coils related materials.

To know the effect of injecton starting point of 1 min-SF_6 flow, we set back the injecting of 1 min-SF_6 flow by 1 min carbon coils synthesis reaction like process IV (sample D), namely H_2+C_2H_2 flow (1 min) → H_2+SF_6 flow (1 min) → H_2+C_2H_2 flow (88 min). As shown in Fig. 3(d), various types of carbon coils-related geometries such as LT, MC, NC and WNC could be well observed like a full time (90 min) SF_6 flow case (process III, sample C). Based on the results

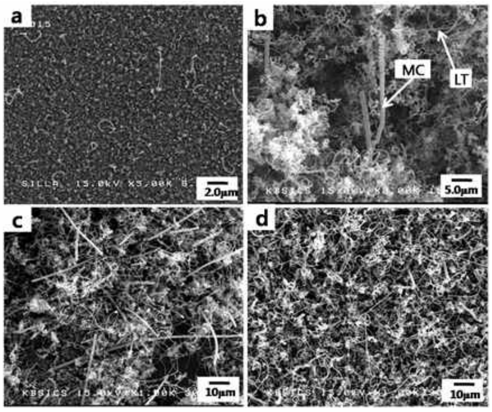

Figure 2. FESEM images of carbon coils-related materials-deposited substrates for (a) sample A, (b) sample B, (c) sample C and (d) sample D.

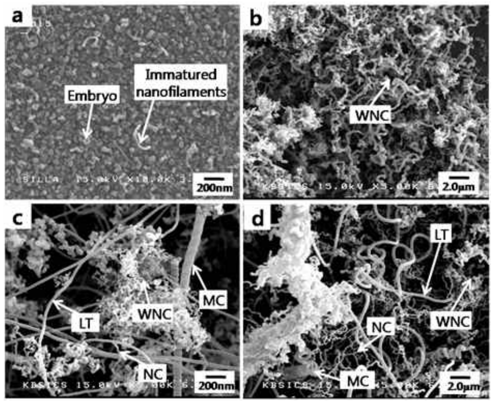

Figure 3. High-magnified FESEM images of carbon coils-related materials-deposited substrates for (a) sample A, (b) sample B, (c) sample C and (d) sample D.

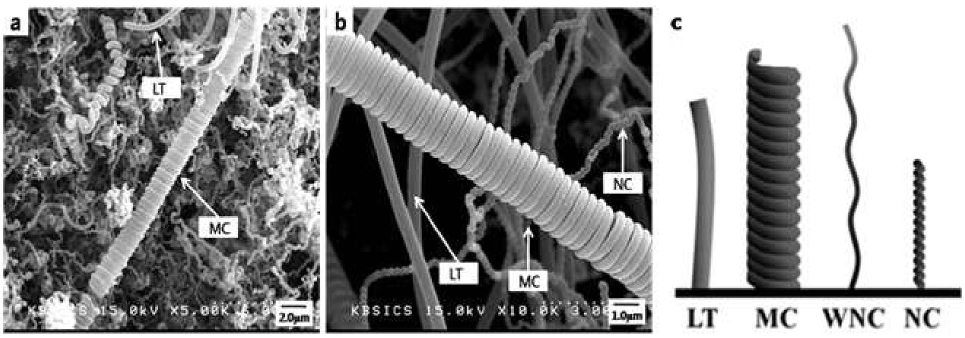

Figure 4. FESEM images of the carbon coils-deposited substrate for sample B (a) around the center position on the substrate and (b) its magnified image. Occasionally, a couple of micro-sized carbon coils could be observed on the surface of the substrate. Fig. 4(c) shows the generally accepted four geometrical categories of carbon coils, namely linear tub (LT), micro-sized coil (MC), nano-sized coil (NC), and wave-like nano-sized coil (WNC).

from Fig. 2 and 3, we confirm that even a short time (1-min) SF_6 flow injection could change the geometry of carbon-coils related materials. Furthermore, the injection starting point of 1 min-SF_6 flow would be very important to limit the geometries of carbon coils related materials.

Carbon coils formation densities were mainly measured using several 10 k magnified FESEM images. For objectively 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 according to the processes were measured as shown in Fig. 5. The y-axis represents the percentage ratio of the area occupied by carbon coils-related materials. The analysis showed that the average occupied area by carbon coils-related materials of process II is higher than that of any other process.

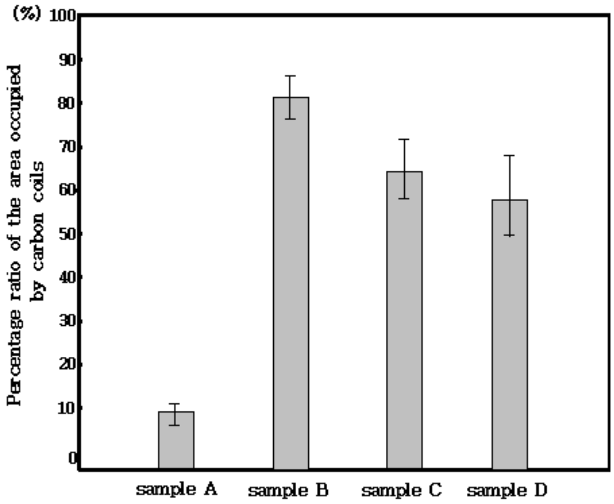

Figure 5. The occupied areas by various types carbon coils according to the (a) process I (sample A), (b) process II (sample B), (c) process III (sample C) and (d) process IV (sample D). It was measured under the assumption of monolayer-grown carbon coils formation on the substrate.

Based on the results shown in Fig. 2～5, we propose that 1 min-SF_6 flow injection during the initial reaction stage (process II, sample B) could give rise to the limitation of the geometry for a dominant WNC type as well as the enhancement of carbon coils-related materials formation density. However, a continuous injecting of SF_6 gas flow or a delayed injecting of SF_6 gas flow can deteriorate the limitation of the geometries. The study on the exact causes and the detailed mechanism for developing the controlled-geometry carbon coils by 1 min-SF_6 flow injection during the initial reaction stage is underway.

IV. Conclusions

The carbon coils geometry limitation from various types to the dominant formation of nano-sized coil-like type could be achieved by 1 min-SF_6 flow injection during the initial reaction. In addition, the SF_6 incorporation during the initial reaction could promote the formation density of carbon coils-related materials. It confirms that even a short time (1-min) SF_6 flow injection could change the geometry of carbon-coils related materials. Furthermore, the injection starting point of 1 min-SF_6 flow would be very important to limit the carbon coils related geometries.

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육불화황 기체의 주입단계에 따른 탄소코일 기하구조의 제약

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(2011년 5월 31일 받음, 2011년 8월 13일 수정, 2011년 8월 23일 확정)

니켈촉매 막을 증착시킨 산화규산 기판위에 아세틸렌기체와 수소기체를 원료로 육불화황기체를 첨가기체로 탄소코일을 증착하였다. 육불화황이 투입되는 단계에 따라 성장된 탄소코일의 특성(형성 밀도, 형상)을 조사하였다. 육불화황을 연속적으로 주입하였을 경우 선형, 마이크로크기 코일, 나노크기 코일, 그리고 파동형 나노크기 코일 등 다양한 형태의 탄소코일들이 성장하였다. 하지만, 탄소코일 초기 증착단계에서 1분정도의 짧은시간 동안 육불화황을 주입한 경우 나노크기의 탄소코일 형상만을 대부분 얻을 수 있었다. 탄소코일 합성반응시간이 1분 정도 지체된 후의 단계에서 짧은시간 동안의 육불화황 주입은 코일형상 제어를 저해하였다. 따라서, 육불화황의 주입 시간과 주입단계가 탄소 코일의 형상을 결정하는 중요한 요인임을 알 수 있었다.

주제어 : 탄소코일, 육불화황, 기하구조, 주입단계, 열화학기상증착

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