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Research Article

Effect of Si and SiO_2 Substrates on the Geometries of As-Grown Carbon Coils

Semi Park,[1] Sung-Hoon Kim,[1] and Tae-Gyu Kim[2]

[1] *Department of Engineering in Energy and Applied Chemistry, Silla University, Busan 617-736, Republic of Korea*
[2] *Department of Nanomechatronics Engineering, Pusan National University, Kyungnam 627-706, Republic of Korea*

Correspondence should be addressed to Sung-Hoon Kim, shkim@silla.ac.kr

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Carbon coils could be synthesized using C_2H_2/H_2 as source gases and SF_6 as an incorporated additive gas under thermal chemical vapor deposition system. Si substrate, SiO_2 thin film deposited Si substrate (SiO_2 substrate), and quartz substrate were employed to elucidate the effect of substrate on the formation of carbon coils. The characteristics (formation densities, morphologies, and geometries) of the deposited carbon coils on the substrate were investigated. In case of Si substrate, the microsized carbon coils were dominant on the substrate surface. While, in case of SiO_2 substrate, the nanosized carbon coils were prevailing on the substrate surface. The surface morphologies of samples were investigated step by step during the reaction process. The cause for the different geometry formation of carbon coils according to the different substrates was discussed in association with the different thermal expansion coefficient values of Si and SiO_2 substrates and the different etched characteristics of Si and SiO_2 substrates by $SF_6 + H_2$ flow.

1. Introduction

Recently, carbon nano/microcoils were noticed for the promising materials to be used in electromagnetic absorbers, high sensitive nano/microsized detectors, effective reinforcing fillers for composites, essential building blocks for the fabrication of nanodevices, and so forth [1–5]. For the synthesis of carbon coils, chemical vapor deposition (CVD) method using metal catalyst is regarded as an effective technology due to its applicable feature. Up to the present, significant parameters in catalytic CVD system for the formation of carbon coils, such as the diverse combination of source gases and the various characteristics (shapes and compositions) for the used catalyst, have been deeply investigated [6–9].

Among the parameters, the characteristics of the used metal catalyst was known to be a decisive factor to determine the final growth geometry of as-grown carbon coils [10–16]. Supporting substrates seemed to be one of the significant parameters for the formation of carbon coils because the characteristics of the metal catalyst would be affected by the nature of supporting substrate. Consequently, the substrate-influenced metal catalyst could affect the geometry of the as-grown carbon coils.

In this respect, the research for the substrate effect on the characteristics of as-grown carbon coils is considered as a primary step for the carbon coils synthesis reaction. Bai obtained a more or less controlled morphology of carbon coils through the careful choice of alumina substrate pore size [17]. Huang et al. reported that the changed morphologies of Si substrate by corrosion would play an important role in the formation of carbon nanocoils [18]. Veziri et al. demonstrated that the morphology of carbon nanostructures grown by CVD on porous supports is strongly affected by the porosity and chemical composition of the supporting substrate [19]. They suggested that tuning of carbon morphology cannot only take place by changing the CVD conditions (carbon precursor, reaction temperature and time, gas flow rates, etc.) but also by appropriately modifying the supporting substrate, the catalyst, and the interaction between them. Despite these efforts, further investigation for the effect of the substrate on the formation of carbon coils is still required.

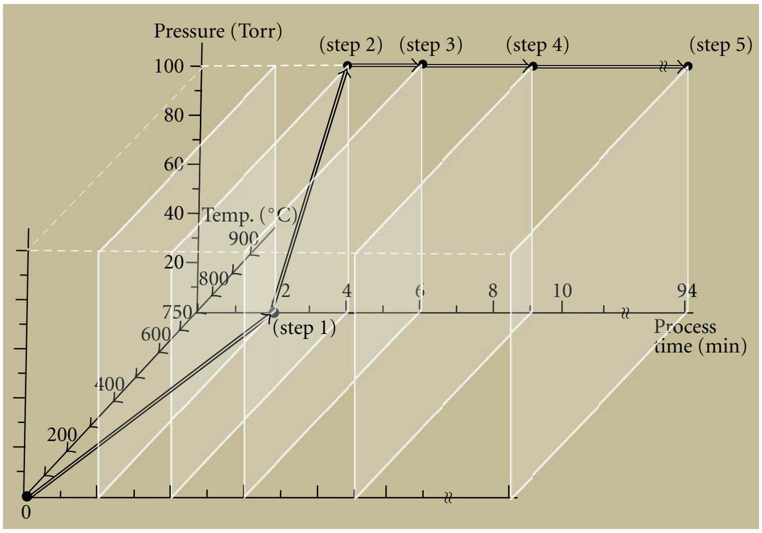


Figure 1: Step by step situations for the processes during the overall reaction.

In this work, different substrates, namely, Si substrate, SiO_2 thin film deposited Si substrate (SiO_2 substrate), and quartz substrate were employed to elucidate the effect of substrate on the formation of carbon coils. During the reaction process, the reaction was terminated step by step and the morphologies of as-grown sample surfaces were investigated according to the terminated step. Specifically silicon and its oxide substrates were chosen with keeping experimental conditions unchanged. Based on these results, the cause for this different geometry formation of carbon coils according to the different substrates was discussed.

2. Experimental Details

For silicon substrate, p-type Si (100) substrates were used. For its oxide substrate, SiO_2 layered Si substrates and quartz substrates were employed. SiO_2 layered Si substrates in this work were prepared by the thermal oxidation of $2.0 \times 2.0\,cm^2$ p-type Si (100) substrates. The thickness of silicon oxide (SiO_2) layer on Si substrate was estimated about 300 nm.

A 0.1 mg Ni powder (99.7%) was evaporated for 1 min to form Ni catalyst layer on the substrate using thermal evaporator. The estimated Ni catalyst layer on the substrate was about 100 nm.

For carbon coils deposition, thermal CVD system was employed. 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 initial reaction stage. The flow rate for C_2H_2, H_2, and $SF_6$was fixed at 15, 35, and 35 standard cm^3 per minute (sccm), respectively. According to the different reaction processes, the reaction processes were terminated by five steps. Figure 1 shows the step by step situations for the reaction processes during the overall reaction. The reaction conditions according to different processes were shown in Table 1. Detailed morphologies of carbon-coil-deposited substrates were investigated using field emission scanning electron microscopy (FESEM, Hitach 4500).

3. Results and Discussion

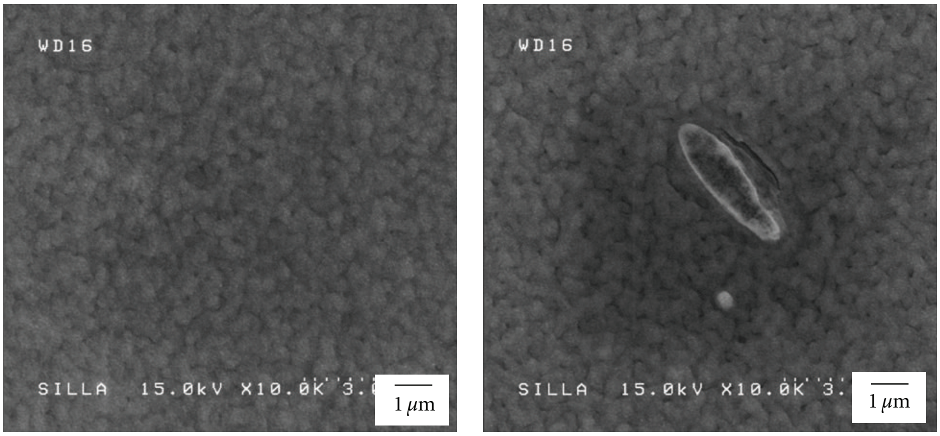
Ten samples (samples A–J) having the different substrates (Si and SiO_2 substrates) and the different reaction process steps (see Figure 1) were prepared. FESEM images showing the surface morphologies of the samples were measured after finishing the different reaction process steps. Indeed, the different substrates (Si and SiO_2 substrates) were simultaneously mounted into the reaction chamber. So, the carbon coils formation reaction on the different substrates could have a constant experimental condition.

After step (1), namely, finishing the substrate temperature set to 750°C, the Ni catalyst layer was converted to a lot of nanosized Ni grains and these grains were uniformly dispersed on the substrate as shown in Figure 2. The shapes and the densities of these grains for Si and SiO_2 substrates were almost similar (compare Figures 2(a) with 2(b)). Diameters of these grains were around a few hundred nanometers.

After step (2), namely, finishing the total pressure set to 100 Torr, both the nanosized (less than 100 nm in diameter) carbon nanofilaments (CNFs) and a few number of the microsized (more than 300 nm in diameter) CNFs were sparsely observed on Si substrate surface (sample C) as shown in Figures 3(a) and 3(b). The microsized CNFs were more frequently observed at the edge area of the substrate (see the inside of the oval in Figure 3(b)). The nanosized CNFs were usually gathered around the tip area of the microsized CNFs as shown in Figures 3(c) and 3(d). For SiO_2 substrate, the developed CNFs seemed to be more uniformly dispersed, compared with those of Si substrate (compare Figures 3(e) with 3(a)). Instead of the microsized CNFs, the nanosized CNFs were mostly observed as shown in Figure 3(f). In some position on the substrate the microsized CNFs could be observed as shown in Figure 3(g). Indeed, most of the microsized CNFs were observed as a form of linear-type sticking two similar-shaped carbon nanofilaments as shown in the inside of oval area in Figure 3(h).

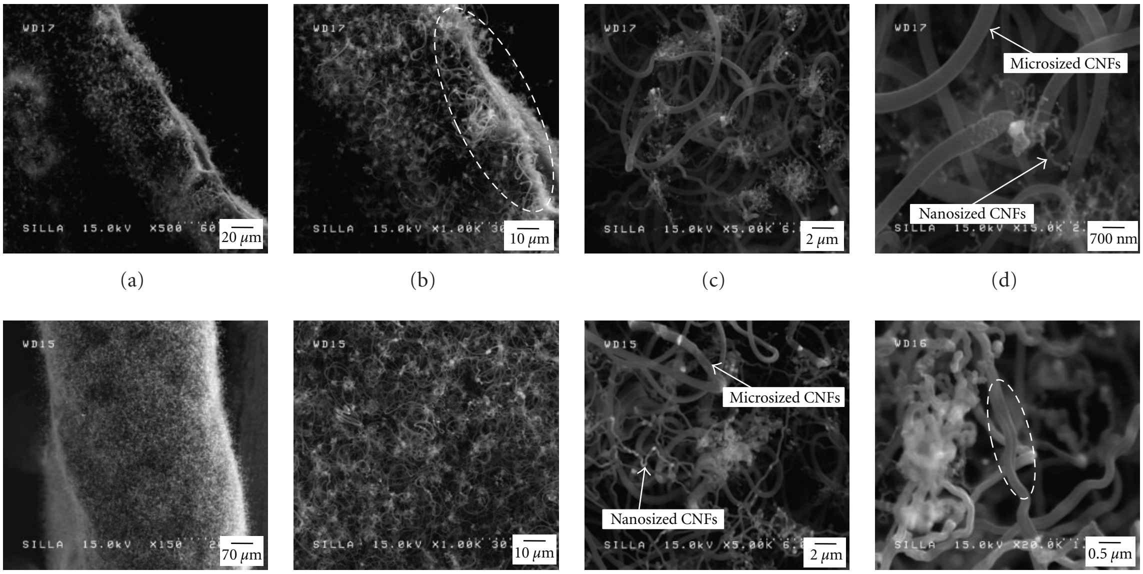
Table 1: Experimental conditions of the deposition of carbon coils for the different samples.

Process steps	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 kinds and temp. (°C)
							C_2H_2	H_2	SF_6	
(1)	A	—	—	—		—	—	—	—	Si, 25 ~ 750
(1)	B	—	—	—		—	—	—	—	SiO_2, 25 ~ 750
(2)	C	15	35	35	0 ~ 100	—	—	—	—	Si, 750
(2)	D	15	35	35	0 ~ 100	—	—	—	—	SiO_2, 750
(3)	E	15	35	35	100	2	2	2	2	Si, 750
(3)	F	15	35	35	100	2	2	2	2	SiO_2, 750
(4)	G	15	35	35	100	5	5	5	5	Si, 750
(4)	H	15	35	35	100	5	5	5	5	SiO_2, 750
(5)	I	15	35	35	100	90	90	90	5	Si, 750
(5)	J	15	35	35	100	90	90	90	5	SiO_2, 750



(a) (b)

Figure 2: FESEM images for (a) sample A and (b) sample B after process step (1).



(a) (b) (c) (d)

(e) (f) (g) (h)

Figure 3: FESEM images for sample C under the magnification of (a) 500, (b) 1,000, (c) 5,000, and (d) 15,000 and for sample D under the magnification of (e) 150, (f) 1,000, (g) 5,000, and (h) 20,000.

Step (3): after 2.0 minutes reaction, the length of CNFs on the Si substrate seems to be much longer than those on SiO_2 substrate (compare Figures 4(b) with 4(f)). As shown in Figures 4(d) and 4(h), two individual CNFs seemed to independently come out from Ni grains (see white dots in the circle of Figures 4(d) and 4(h)) and then grow to the opposite direction with each other, irrespectively of the substrate.

After 5.0 minutes deposition reaction, in case of Si substrate, the initiation of carbon coils geometry formation could be observed on sample G as shown in Figures 5(a)–5(c). In this case not only the microsized carbon coils but also the nanosized carbon coils could be observed on the substrate. Around the tip area of the microsized carbon coils, the nanosized CNFs were mainly gathered (see Figure 5(c)). In SiO_2 substrate case, however, the nanosized carbon coils were mostly formed on the surface of the substrate as shown in Figures 5(d)–5(f). The formation of the microsized carbon coils is rare, and they are usually buried among a lot of the nanosized carbon coils as shown in Figure 5(f). Indeed, the initial reaction stage with SF_6 would be responsible for the geometries of as-grown carbon coils. After initial reaction, the proceeded reaction times, such as 10, 30, and 60, did not seem to give any distinctive variation for the geometries of carbon coils [6]. So we investigated the morphologies of the samples after finishing the deposition reaction.

After finishing the deposition reaction (90 min), in case of Si substrate the well-developed microsized carbon coils were mostly observed on the surface of the substrate as shown in Figure 6(a). The length of the microsized carbon coils is more than ten micrometers (see Figure 6(b)). The

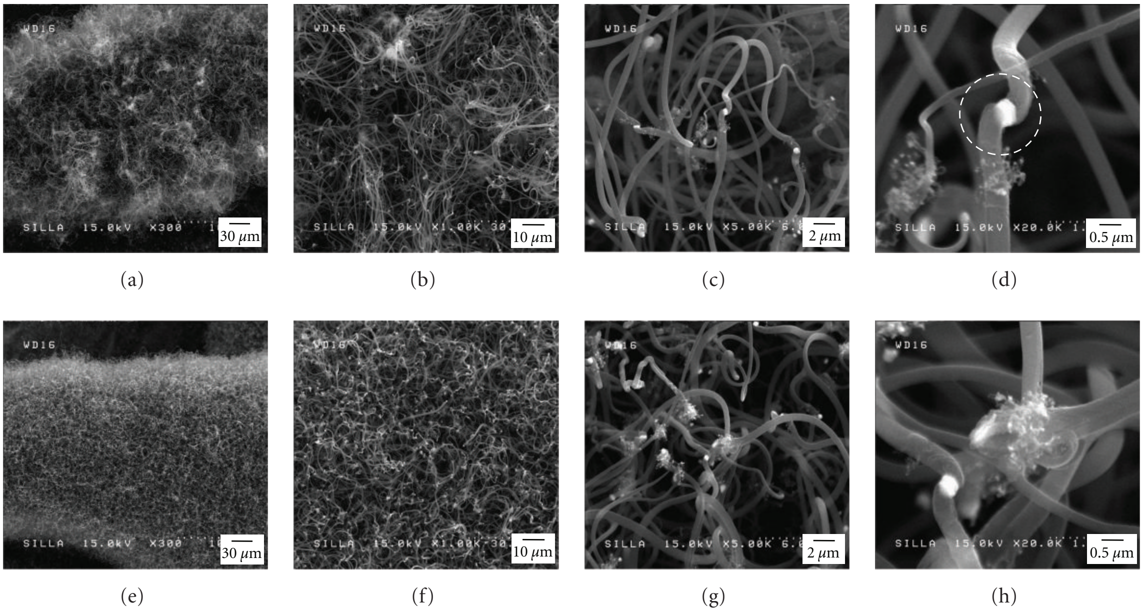


Figure 4: FESEM images for sample E under the magnification of (a) 300, (b) 1,000, (c) 5,000, and (d) 20,000 and for sample F under the magnification of (e) 300, (f) 1,000, (g) 5,000, and (h) 20,000.

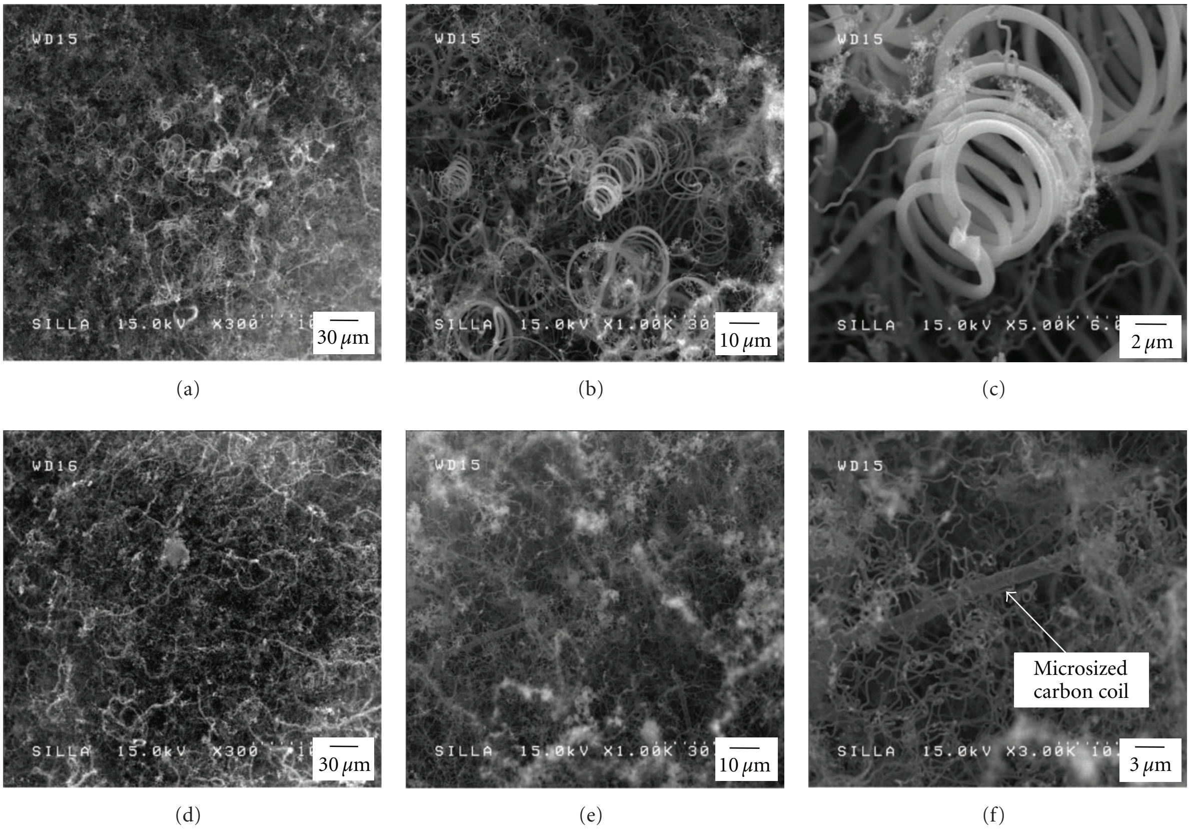
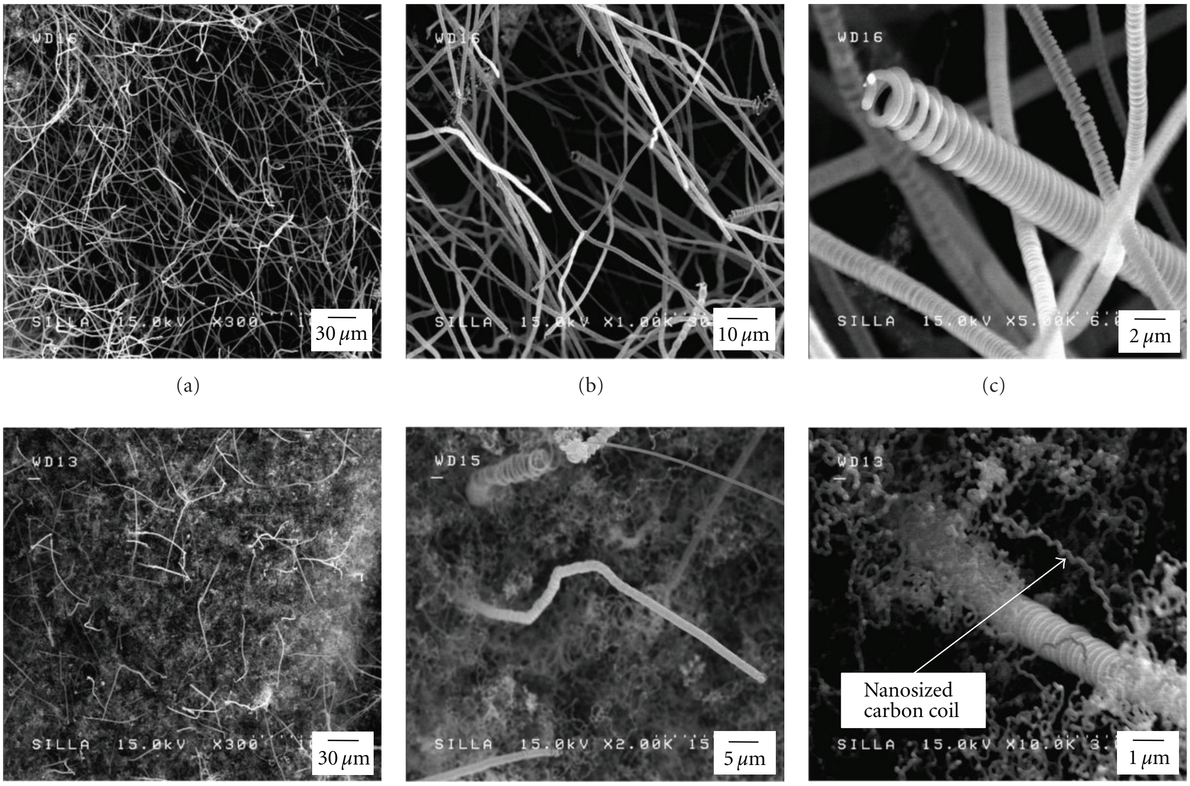


Figure 5: FESEM images for sample G under the magnification of (a) 300, (b) 1,000, and (c) 5,000 and for sample H under the magnification of (d) 300, (e) 1,000, and (f) 3,000.



(a) (b) (c)

(d) (e) (f)

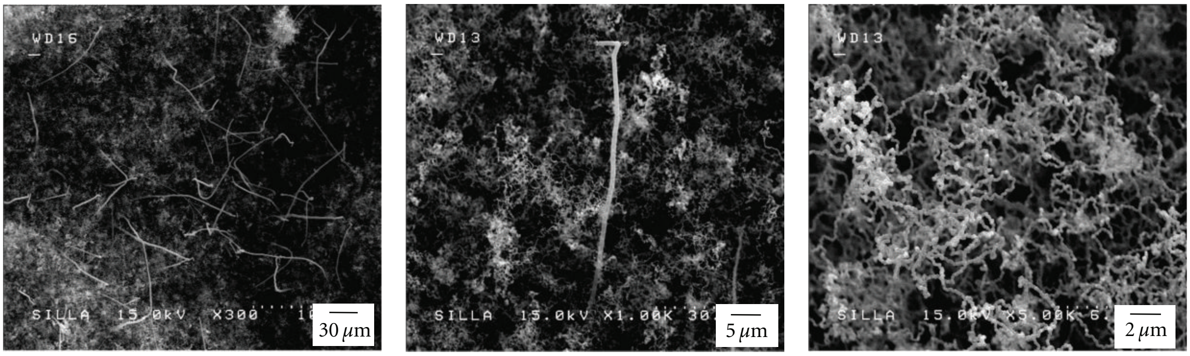
Figure 6: FESEM images for sample I under the magnification of (a) 300, (b) 1,000, and (c) 5,000 and for sample J under the magnification of (d) 300, (e) 2,000, and (f) 10,000.

diameters of the microsized carbon coils are in the range of a few tens nanometers to a few micrometers as shown in Figure 6(c). In case of SiO_2 substrate, however, the nanosized carbon coils were dominant on the surface of the substrate as shown in Figure 6(d). Occasionally, the microsized carbon coils were protruded among a lot of the nanosized carbon coils (see Figure 6(e)). As shown in Figure 6(f), several nanosized carbon coils were attached along the side of the microsized carbon coils.

The combined results of Figures 2–6 confirm that Si substrate favors the microsized type for the main geometry of as-grown carbon coils. In SiO_2 substrate case, however, the nanosized carbon coils were mostly developed on the substrate surface even under the same experimental condition. It may indicate the occurrence for the geometry change of carbon coils from the microsized type to the nanosized one simply by using the oxygen incorporated Si substrate. This result was also confirmed by the dominant formation of the microsized carbon coils on quartz substrate under the same experimental condition as shown in Figure 7.

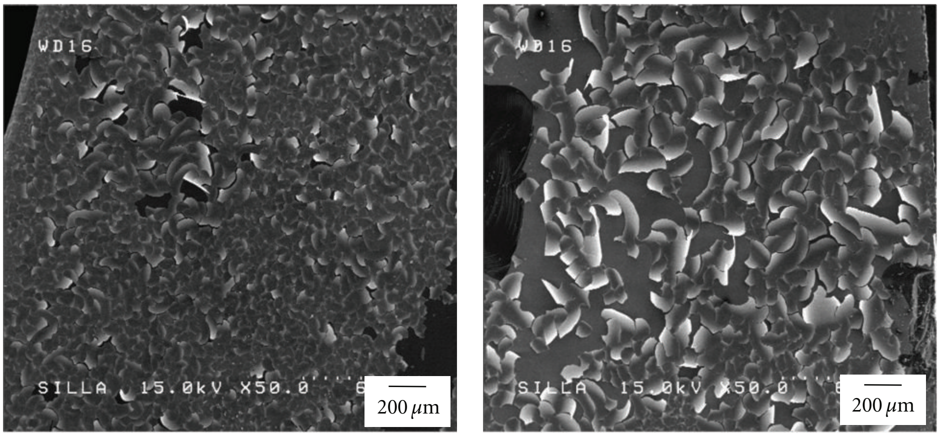
The different thermal expansion coefficient between the Ni catalyst layer and the different substrates was proposed as the main cause for the geometry change of carbon coils according to the different substrates (Si or SiO_2). The difference of thermal expansion coefficient value between Ni catalyst layer and the different substrates was known to be higher in case of SiO_2 substrate compared with that in case of Si substrate [20, 21]. The higher difference of thermal expansion coefficient between the metal layer and the substrate may induce the higher stress between them. Consequently, the metal layer will be more easily peeled off and eventually will be broken into very tiny nanosized pieces and scattered in surrounding area. Basically, the mechanism of carbon coils growth was based on the metal size and shape [10, 22]. So, the peeled-off tiny nanosized Ni pieces could be the seed of the nanosized carbon coils. Consequently, the as-grown nanosized carbon coils from the nanosized Ni pieces would deposit on the whole surface of the substrate. This is the reason why the density of the nanosized carbon coils from SiO_2 substrate is higher than that from Si substrate. Figure 8 shows FESEM images indicating the different situation of the peeled-off Ni layers from Si substrate (Figure 8(a)) and from SiO_2 substrate (Figure 8(b)) after cooling down the substrate from 750°C under vacuum. As shown in these images, SiO_2 substrate gives rise to the more readily peeled-off Ni layer, which may form the nanosized geometry for as-grown carbon coils.

In addition, the different etched characteristics of Si or SiO_2 substrate by SF_6 + H_2 flow was believed to be another cause for the geometry change of carbon coils according to the different substrates (Si or SiO_2). Figure 9 shows FESEM images indicating the different etched situation for Si substrate (Figure 9(a)) and SiO_2 substrate (Figure 9(b)) by $SF_6 + H_2$ flow for 1 minute under the condition of 100



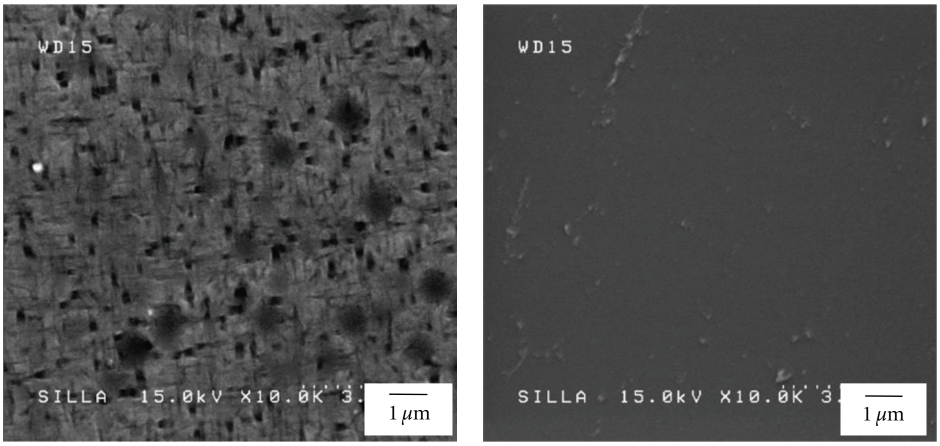
(a) (b) (c)

Figure 7: FESEM images for as-grown carbon coils on quartz substrate under the magnification of (a) 300, (b) 1,000, and (c) 5,000.



(a) (b)

Figure 8: FESEM images for the peeled-Ni layers from (a) Si substrate and (b) SiO_2 substrate after cooling down the substrate from 750°C under vacuum.



(a) (b)

Figure 9: FESEM images for the etched surface of (a) Si substrate and (b) SiO_2 substrate by SF_6 + H_2 flow.

Torr and room temperature. As shown in these images, Si substrate would be more effectively etched by SF_6 flow, and the porous morphology would be formed on Si substrate. The porosity of the substrate was known to foster the coils geometry [19]. Previously, the microsized carbon coils were known to be come out by the joining of several nanosized coils [23]. Therefore, the well developing atmosphere of carbon coils by the porous morphology of Si substrate may eventually lead to the microsized geometry for as-grown carbon coils.

4. Conclusions

By exchanging the substrate from Si to SiO_2, the geometry of carbon coils was changed from the microsized type to the nanosized one even under the same experimental condition. The difference of thermal expansion coefficient values between Ni catalyst layer and the substrates was believed to be a main cause for this geometry change. In addition, the different etched characteristics for Si and SiO_2 substrates by $SF_6 + H_2$ flow during the reaction was suggested as another cause for the geometry change of as-grown carbon coils.

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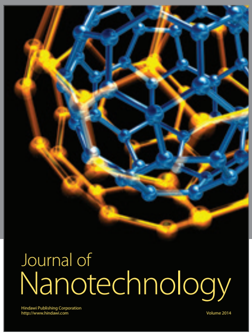
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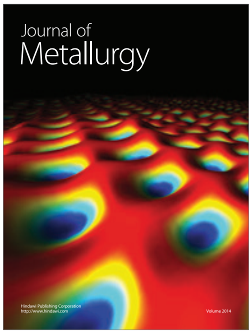
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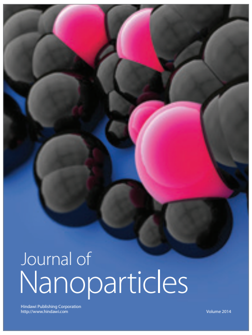
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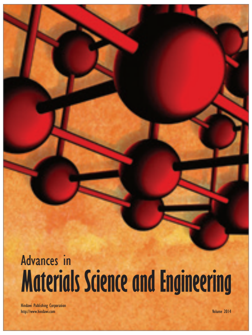
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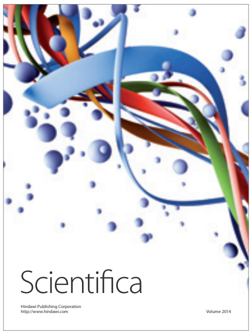
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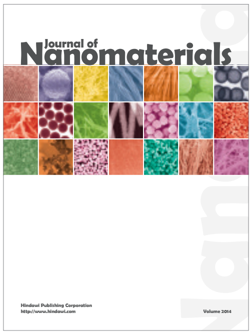
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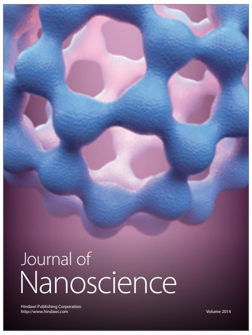
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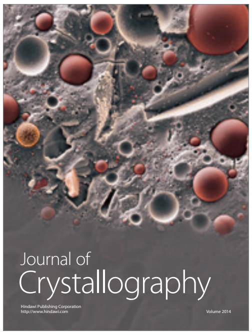
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