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Research Article

Effect of the on/off Cycling Modulation Time Ratio of C_2H_2/SF_6 Flows on the Formation of Geometrically Controlled Carbon Coils

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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. Nickel catalyst layer deposition and then hydrogen plasma pretreatment were performed prior to the carbon coils deposition reaction. To obtain the geometrically controlled carbon coils, the cycling on/off modulation process for C_2H_2/SF_6 flows was introduced during the initial reaction. According to the different reaction processes, the different cycling on/off ratio and the different cycling numbers for C_2H_2/SF_6 flows were carried out. The characteristics (formation density, morphology, and geometry) of the deposited carbon coils on the substrate were investigated. Microsized coils as well as nanosized coils could be existed under the higher growing/etching time ratio (180/30 s) condition. On the other hand, the formation of nanosized coils could be mainly observed under the lower growing/etching time ratio (30/180 s) condition. With increasing the numbers of cycles, the diameters of carbon nanofilaments composed the coils decreased. The enhanced etching ability by the fluorine species was considered the main cause to control the geometry of carbon coils according to the growing/etching time ratio of the cycling on/off modulation process for C_2H_2/SF_6 flows.

1. Introduction

Although the unique springlike geometry of carbon coils have been noticed as the promising material candidate for the micro/nanoelectronic devices, some problems should be solved for their practical applications [1–4]. The most urgent problems to solve would be the achievement of the geometrically controlled carbon coils as well as the mass production of carbon coils [5]. In general, the carbon coils at as-grown state had a randomly shaped geometry. Carbon coils having a randomly shaped geometry could give rise to unpredictable electrical characteristics, because the electrical properties of carbon coils were supposed to be varied according to their geometries including diameter [6]. Therefore, the controlled characteristics of carbon coils, resulting from the controlled coil morphology and geometry (diameter, pitch, length, and turning direction), are indispensable for their practical application in micro/nanoelectronic devices.

Thermal chemical vapor deposition (TCVD) technique using the metal catalyst has been noticed for the practical synthesis techniques of carbon coils because of its relative inexpensive and applicable features [7–9]. However, due to the low yield of carbon coils, normal TCVD process is not suitable for the scaled-up production of carbon coils. Therefore, it is desired to explore a more efficient and reliable TCVD method for the growth of carbon coils.

Recently, an *in situ* cycling on/off modulation process of C_2H_2/H_2 flow has been introduced to enhance the formation density of carbon nanofilaments (CNFs) [10]. It can be simply achieved by turning a source gas flow rate in a reaction system on or off during an initial deposition stage. It seems that the *in situ* process is more advantageous than *ex situ* process because one can combine an *in situ* process and an *ex situ* process without altering the detailed reaction condition. In this work, an *in situ* cycling on/off modulation process of C_2H_2/SF_6 flow has been adopted.

Meanwhile, a trace of sulfur species [11–14] was usually incorporated as an additive to readily form carbon coils. In this paper, a trace of sulfur species was incorporated as an SF_6 form. Fluorine species, as an SF_6 form, was intentionally introduced in this work in order to take the advantage for fluorine species characteristics regarding the enhancement of the nucleation sites of carbon coils. For the diamond, as an allotrope of carbon coils, it was known that the addition of fluorine would enhance the rate of hydrogen abstraction, thereby opening more nucleation sites for possible interaction with growth species even in the low-temperature case [15–17]. Like the diamond film deposition case, fluorine species in this work was expected to play a role for enhancing nucleation sites of carbon coils by hydrogen abstraction.

Therefore, in this work, the injection of fluorine species, as an SF_6 form, was combined with an *in situ* cyclic on/off modulation process of C_2H_2/SF_6 flow. The investigation on the influence of C_2H_2/SF_6 flow on/off ratio on the characteristics of carbon coils was focused. According to the different reaction processes, the different cycling on/off ratio and the different cycling numbers for C_2H_2/SF_6 flows were carried out. In this process, the relative concentrations of hydrogen and fluorine species during the reaction could be varied by the cycling on and off control of C_2H_2 and SF_6 flows. Finally, we could achieve the large-scale production of the geometrically controlled carbon coils merely by adjusting the cycling on/off ratio for C_2H_2/SF_6 flows. Characteristics of as-grown carbon coils, namely, the formation density and the geometry were examined and discussed.

2. Experimental Details

The SiO_2 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 estimated about 100 nm.

Prior to carbon coils deposition, Ni-coated substrate was placed in plasma-enhanced chemical vapor deposition (PECVD) system. H_2 gas was introduced into PECVD chamber, and then the substrate was precleaned for 5 minutes using H_2 plasma.

For carbon coils deposition, thermal chemical vapor deposition (TCVD) 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 reaction. The flow rate for C_2H_2, H_2, and SF_6 were fixed at 15, 35, and 35 standard cm^3 per minute (sccm), respectively.

The *in situ* cyclic modulation process of the source gas flow in this work was merely carried out by the on/off control of C_2H_2 flow and simultaneously off/on control of SF_6 flow. According to the reaction processes, the sequence of source gas flow was the iterative order of procedures, $C_2H_2 + H_2$ flow (C_2H_2 flow on and SF_6 flow off) and then $SF_6 + H_2$ flow (C_2H_2 flow off and SF_6 flow on). The cyclic modulation period was defined as the time the source gas was composed of H_2 and C_2H_2 plus the time the source gas was H_2 and SF_6. In this manner, carbon species to form carbon coils are generated from the $C_2H_2 + H_2$ flow (C_2H_2 flow on and SF_6 flow off). This is termed as the growing time. On the other hand, the $SF_6 + H_2$ flow (C_2H_2 flow off and SF_6 flow on) may etch carbon components. Therefore, the $SF_6 + H_2$ flow time is termed as the etching time. We defined the time ratio of C_2H_2 flow on/off (SF_6 flow off/on) as the growing/etching time ratio.

For objectively examining the effect of the growing/etching time ratio on the characteristics of carbon coils, we first fixed H_2 flow rate as 35 sccm. C_2H_2 flow on and off times (SF_6 flow off and on times) were varied as two kinds of C_2H_2 flow on/off time ratio, namely, 180/30 s and 30/180 s. So the time for one cyclic was 7.0 min. The numbers of cycles for these experiments were 2 and 16 times. For the steady process, we deposited carbon coils for 90 min without incorporating the cyclic modulation process. Namely, continuous $C_2H_2 + H_2$ flow or $C_2H_2 + SF_6 + H_2$ flow was introduced for 90 min.

To elucidate the effect of the growing/etching time ratio on the characteristics of carbon coils, six samples having the different reaction processes were prepared. Sample A is the steady process of $C_2H_2 + H_2$ flow. For sample B, the cyclic modulation process was applied during the initial deposition stage at the number of cycles = 2. The growing/etching time ratio of this sample was 180/30 s (higher growing/etching time ratio). For sample C, the cyclic modulation process was also applied during the initial deposition stage at the number of cycles = 2. However, the growing/etching time ratio of this sample was 30/180 s (lower growing/etching time ratio). For sample D, the cyclic modulation process having the higher growing/etching time ratio (180/30 s) was applied during the initial deposition stage at the number of cycles = 16. For sample E, the cyclic modulation process having the lower growing/etching time ratio (30/180 s) was applied during the initial deposition stage at the number of cycles = 16. Sample F is the steady process of $C_2H_2 + SF_6 + H_2$ flow. Figure 1 shows the detailed manipulation processes for these gases flows. The reaction conditions according to different processes were shown in Table 1. Detailed morphologies of carbon coils-deposited substrates were investigated using field emission scanning electron microscopy (FESEM).

3. Results and Discussion

Figure 2 shows FESEM images showing the surface morphologies of the samples A~C. These images indicate the formation of carbon coils for the cyclic process having the higher growing/etching time ratio (180/30 s) (see Figure 2(b)) and for the cyclic process having the lower growing/etching time ratio (30/180 s) (see Figure 2(c)). Without SF_6 gas flow injection, we could merely observe the embryos for carbon nanofilaments (CNFs) as shown in Figure 2(a). Any geometry related with carbon coils-type could not be observed. Therefore, it is clear that the incorporation of SF_6 even for a few minutes would play a significant role for the formation of the carbon coils-related geometry.

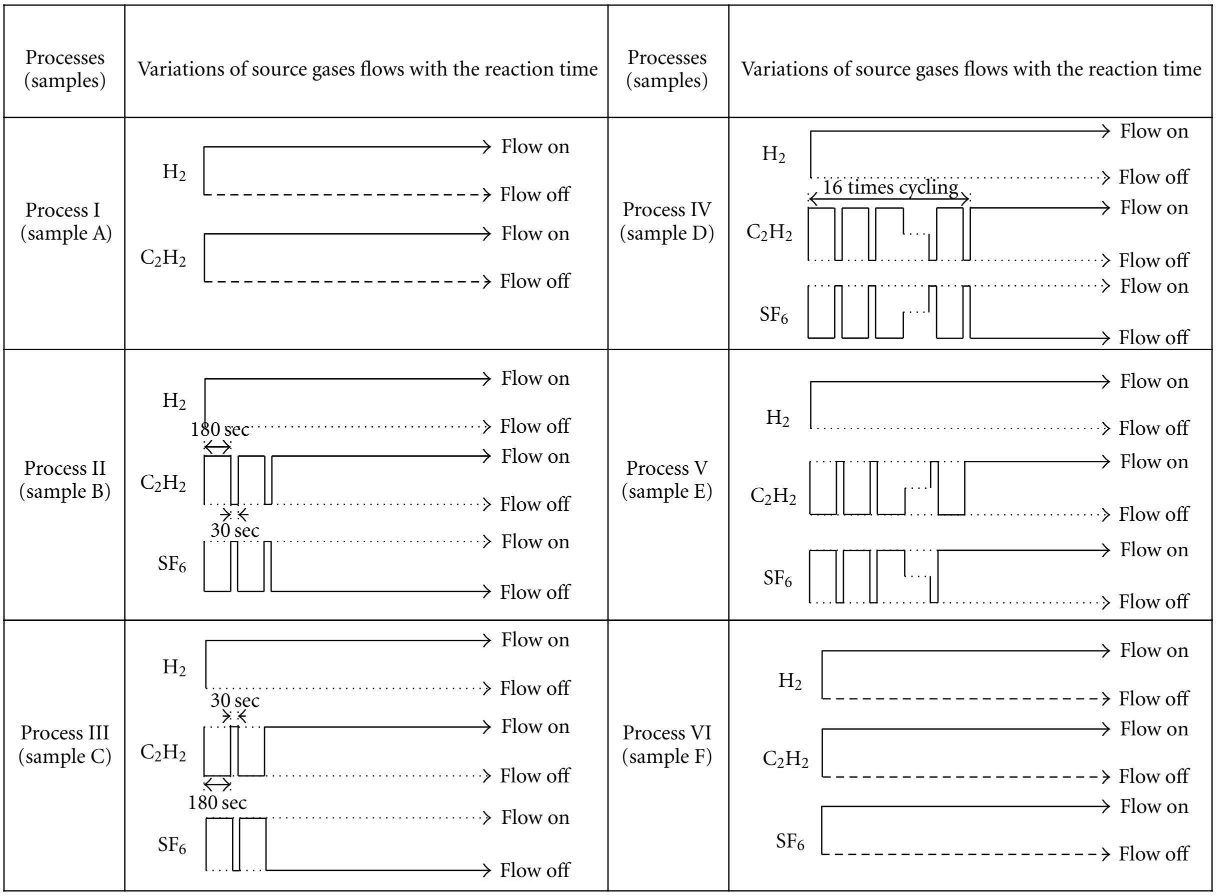


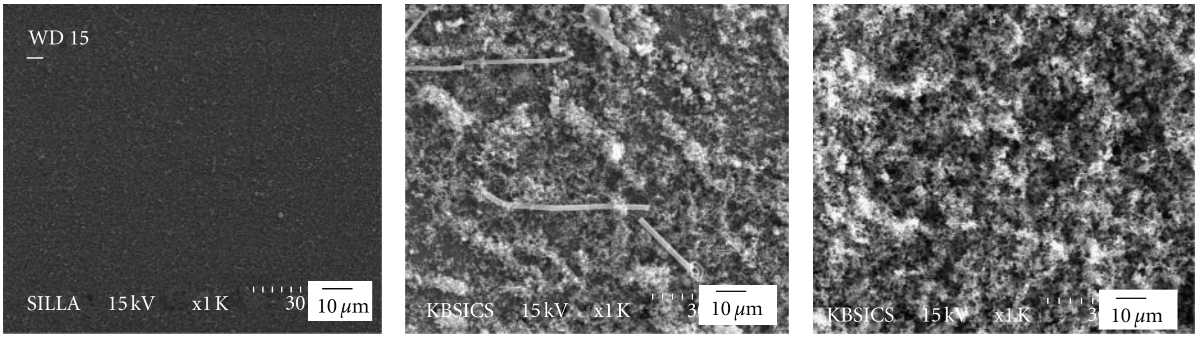
Figure 1: Different reaction processes: the steady injection process without incorporating the cycling modulation process for C_2H_2 + H_2 flows (process I, sample A) and C_2H_2+ H_2 + SF_6 flows (process VI, sample F), the cycling on/off modulation of C_2H_2/SF_6 flows having the higher growing/etching time ratio (180/30 s) for two cycles (process II, sample B) and for sixteen cycles (process IV, sample D), the cycling on/off modulation of C_2H_2/SF_6 flows having the lower growing/etching time ratio (30/180 s) for two cycles (process III, sample C) and for sixteen cycles (process V, sample E).

Table 1: Experimental conditions for the deposition of carbon coils on the substrates for samples A, B, C, D, E, and 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. (°C)
							C_2H_2	H_2	SF_6	
I	A	15	35	—	100	90	90	90	—	750
II	B	15	35	35	100	90	89	90	1	750
III	C	15	35	35	100	90	84	90	6	750
IV	D	15	35	35	100	90	82	90	8	750
V	E	15	35	35	100	90	42	90	48	750
VI	F	15	35	35	100	90	90	90	90	750

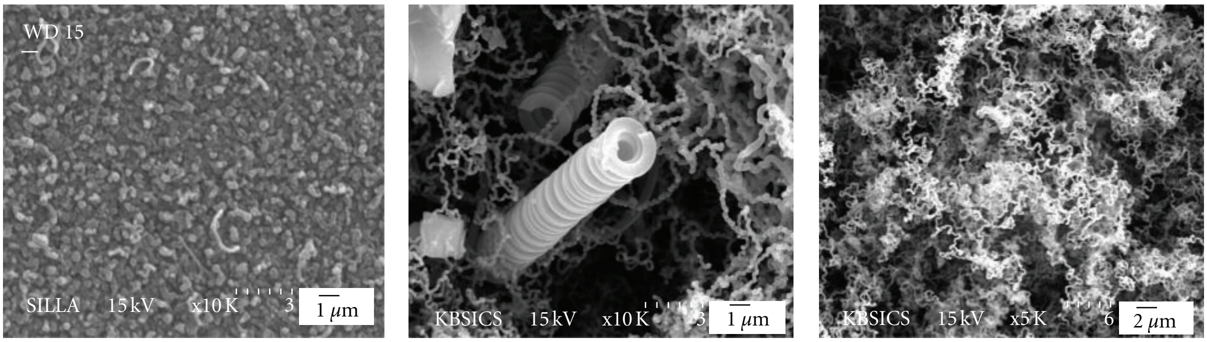
Figure 3(a), the magnified image of sample A, clearly shows merely the embryos formation for the carbon nanofilaments under the C_2H_2 + H_2 flow steady process condition. Figure 3(b), the magnified image of sample B, shows the existence of microsized coils as well as nanosized coils under the higher growing/etching time ratio (180/30 s) condition. On the other hand, the dominant formation of the nanosized coils could be observed under the lower growing/etching time ratio (30/180 s) condition as shown in the magnified image of sample C (see Figure 3(c)). The highest magnified (×50,000) image of the nanosized coils area of samples B (Figure 4(a)) and the highest magnified image of sample C (Figure 4(b)) show the existence of the tangled geometries in some parts of the coils. The diameters sizes of the individual carbon nanofilaments composed the coils seemed to be invariant even by the change of growing/etching time ratio in the cyclic modulation process.

Figure 5 shows FESEM images showing the surface morphologies of the samples D and E. At number of cycles = 16, a few number of the carbon coils having the microsized



(a) (b) (c)

Figure 2: FESEM images showing the surface morphologies for (a) sample A, (b) sample B, and (c) sample C.



(a) (b) (c)

Figure 3: The magnified FESEM images showing the surface morphologies for (a) sample A, (b) sample B, and (c) sample C.

diameter of carbon nanofilaments composed the coils could be still observed under the higher growing/etching time ratio (180/30 s) condition (see the arrow position in Figure 5(a)). However, any geometry related with microsized carbon nanofilaments composed the coils could not be observed under the lower growing/etching time ratio (30/180 s) condition as shown in Figure 5(c). At 50,000-high magnified FESEM images, the existence of the tangled geometries seemed to be prevalent under the lower growing/etching time ratio (30/180 s) condition as shown in Figure 5(d). The diameter sizes of the carbon nanofilaments composed the coils seemed to be about 100 nm under the higher growing/etching time ratio (180/30 s). However, their sizes seemed to be less than 100 nm under the lower growing/etching time ratio (30/180 s) condition (compare the diameter sizes of carbon nanofilaments of Figure 5(b) with those of Figure 5(d)). Furthermore, the comparing results of the images for Figures 4 and 5 give rise to the information for the decrease in the diameter sizes with increasing the number of cycles under the lower growing/etching time ratio (30/180 s) condition.

Carbon coils deposition reaction in a steady flow process with SF_6 incorporation was also carried out. Dominant formation of the coil geometries having the microsized diameters of carbon nanofilaments composed the coils could be observed on as-grown sample surface as shown in Figure 6. For the nanosized ones, indeed, a relatively a small amount of the coil geometries could be observed.

Considering fluorine's characteristics for etching other materials or enhancing nucleation sites, we propose that the increased SF_6 incorporation in the reaction with decreasing the cycling on/off modulation time ratio of C_2H_2/SF_6 flows could etch away the relatively soft microsized carbon coils-related materials due to fluorine species' etching capability. In addition, the increase in the etching amount of fluorine + hydrogen species under the lower growing/etching time ratio (30/180 s) may facilitate the decrease in the diameter sizes with increasing the number of cycles. Meanwhile, the existence of the tangled geometries, instead of spring-like-coiled geometries, seemed to be more prevalent under the lower growing/etching time ratio (30/180 s) condition with increasing the number of cycles. Therefore, the increase in the etching gases amount of fluorine + hydrogen species seemed to deteriorate the formation of the coiled geometry. However, the continuous supply of fluorine species with carbon source gas, as $C_2H_2 + SF_6 + H_2$ flow in this work, may develop the microsized geometry formation of carbon coils. In this case, the fluorine species with carbon source gas seems to work as a promoter for the formation of the microsized carbon coils. Finally, we could obtain the

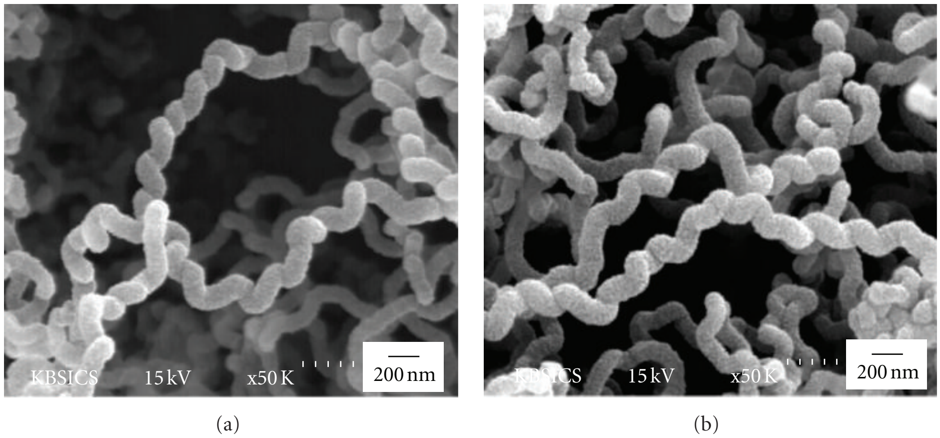


Figure 4: The high-magnified images for (a) the nanosized coils area of sample B and (b) the randomly chosen area of sample C.

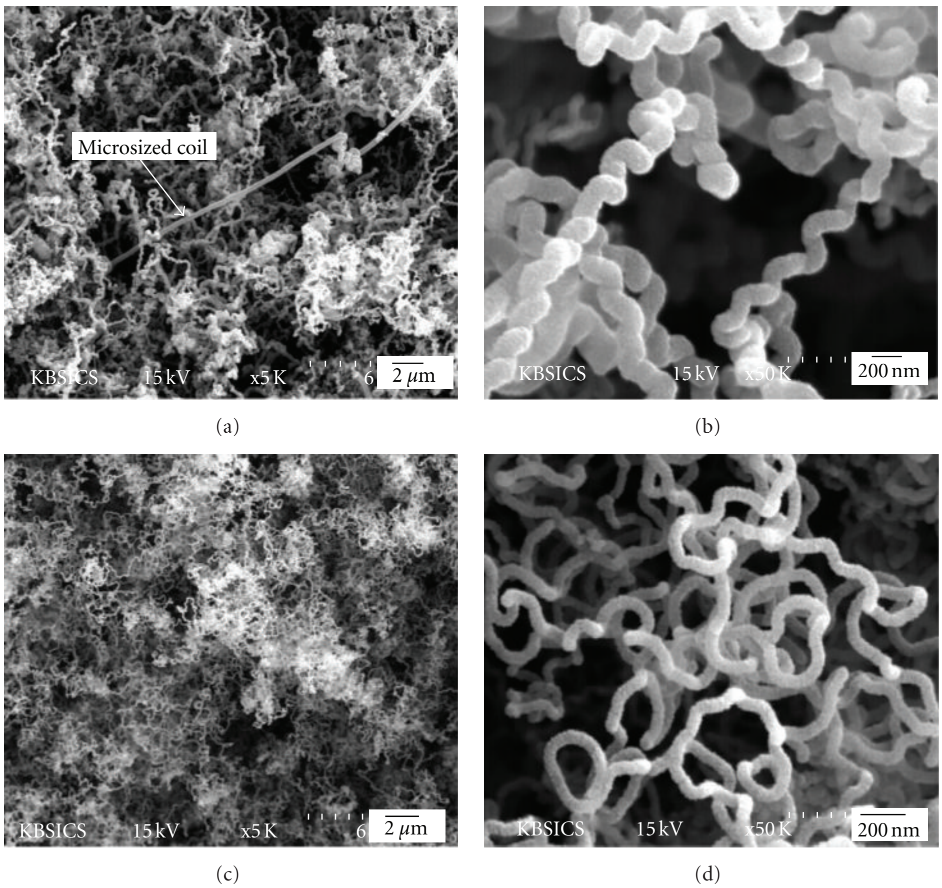
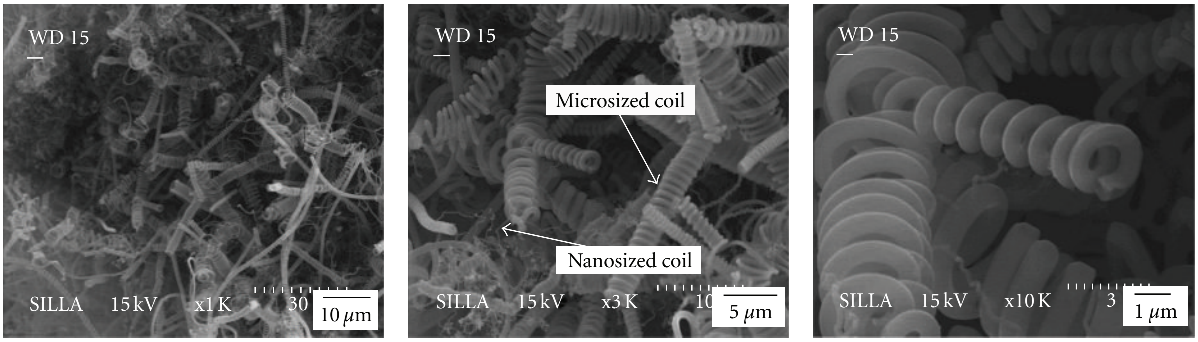


Figure 5: FESEM images showing the surface morphologies for (a) sample D and (c) sample E and the high-magnified FESEM images for (b) the nanosized coils area of sample D and (d) the randomly chosen area of sample E.

dominant geometry, namely, nanostructured geometry, by simply decreasing the cycling on/off modulation time ratio of C_2H_2/SF_6 flows in the reaction. However, the increase in the number of cycles at this condition may deteriorate the formation of the coiled geometry.

4. Conclusion

By SF_6 gas flow injection during the reaction, micro- and/or nanosized carbon coils could be formed on the samples surfaces. The microsized carbon coils were suppressed with



(a) (b) (c)

Figure 6: (a) FESEM images showing the surface morphology of sample F, (b) the magnified FESEM image for (a), and (c) the high-magnified FESEM image for (b).

decreasing the cycling on/off modulation time ratio for the C_2H_2/SF_6 flows in the reaction. With further increasing the SF_6 incorporation in the reaction via increasing the numbers of cycles, even the diameters of carbon nanofilaments composed the coils decreased and the entangled geometries, instead of coiled geometries, could be developed. Finally, the dominant formation of the controlled geometry of carbon coils could be achieved by manipulating the cycling on/off modulation time ratio for C_2H_2/SF_6 flows in the reaction.

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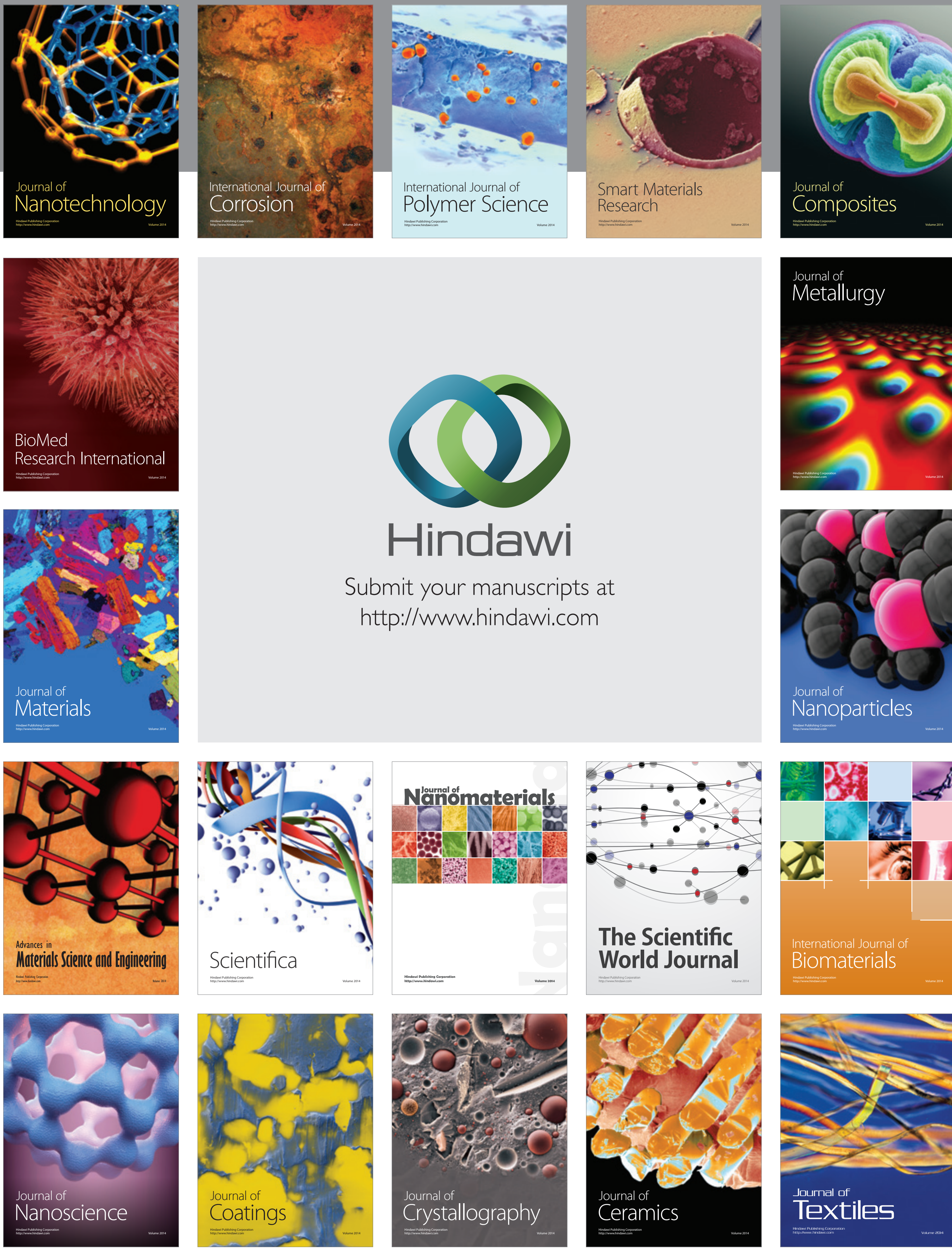
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