

Controlling the Diameter Size of Carbon Nanofilaments by the Cyclic on/off Modulation of $C_2H_2/H_2/SF_6$ Flow in a Thermal Chemical Vapor Deposition System

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To control the diameter size of the carbon nanofilaments (CNFs), SF_6 was incorporated in the source gases (C_2H_2/H_2) during the initial deposition stage. The source gases and SF_6 were manipulated as the cyclic on/off modulation of $C_2H_2/H_2/SF_6$ flow in a thermal chemical vapor deposition system. The characteristics of the CNFs formation on the substrate were investigated according to the different cyclic modulation processes and the substrate temperatures. By $SF_6 + H_2$ flow injection during the cycling etching interval time, the diameter size of CNFs was extremely decreased. The cause for the decrease in the diameter size of the individual CNFs by the cyclic on/off modulation process of $C_2H_2/H_2/SF_6$ flow was discussed in association with the slightly enhanced etching ability by the incorporation of SF_6 .

Keywords : Carbon nanofilaments, Diameter size, Cyclic modulation process, Thermal chemical vapor deposition

I. INTRODUCTION

The electrical properties of CNFs were known to be varied asmetallic, insulating, or semiconductor characteristics according to their diameter size [1,2]. Therefore the controlled diameters of CNFs would be essential to achieve the controlled electrical properties of CNFs. As one of the methods to achieve the controlled electrical properties of CNFs, the low temperature (lower than $600^\circ C$) growth technique has been noticed [3,4]. At the low temperature condition, the surface migration of the metal catalysts wouldn't be much activated therefore the possibility for the agglomeration of the metal catalysts would be

suppressed [5]. This suppression might prevent the wide range variation in the diameter size of the catalyst particles by the thermal migration. Because the diameter sizes of CNFs were known to be associated with the catalyst particle sizes [6,7], the size distribution of the diameters of CNFs at the low temperature would have a narrow range. In addition, the low temperature process might enlarge the application area of CNFs. For the manufacturing, it would be the cost effective method for the CNFs production.

Despite these advantages of the low temperature deposition for the CNFs, the mass production of the CNFs at the low temperature would be difficult to

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achieve. Therefore, for the CNFs production, the high temperature (higher than 600°C) deposition technique would be more noticed as a practical method. Up to date, various methods might be introduced, such as arc-discharge [8], pyrolysis [9], laser ablation [10], plasma or thermal chemical vapor deposition methods [11,12,13], and so forth. Recently, we have introduced an in-situ cyclic on/off modulation process of C₂H₂/H₂ flow to enhance the formation yield of CNFs [14]. It can be simply achieved by turning a source gas flow rate in a reaction system on or off during the initial deposition stage.

In this work, in order to control the diameter size of CNFs at the high temperature deposition, we employed an in-situ cyclic on/off modulation method and incorporated SF₆, as an additive component, in the source gases during the initial deposition stage. During this incorporation, we also applied the gas composition cycling technique for C₂H₂, H₂ and SF₆. According to the different reaction processes, different cyclic modulation processes of C₂H₂/H₂ and/or SF₆ flow were carried out. The variation of the as-grown CNFs characteristics, namely the formation density and the diameter size, was examined.

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 7.18M iron pentacarbonyl, Fe(CO)₅, solution was prepared as the precursor for Fe metal catalyst nanograins. We deposited Fe metal catalyst nanograins using the vacuum sublimation method [15].

For CNFs deposition, thermal chemical vapor deposition system was employed. C₂H₂ and H₂ were used as source gases. SF₆ was injected as an additive in a gas composition cycling manner. Total flow rate was fixed at 50 standard cm³ per minute (sccm). The in-situ cyclic modulation process was progressed with the modulation of these gases flows during the initial deposition stage. According to the different reaction processes, the flows of source gases were the continual H₂+C₂H₂ flow and the two kinds of iterative orders of the procedures.

Namely,

Process I: H₂ + C₂H₂ flow,

Process II: H₂ + C₂H₂ flow → H₂ flow → H₂ + C₂H₂ flow and

Process III: H₂ + C₂H₂ flow → H₂ + SF₆ flow → H₂ + C₂H₂ flow.

Fig. 1 shows the detailed manipulation of these gases flows according to the processes.

Carbon species to form CNFs are generated from the H₂ + C₂H₂ flow (C₂H₂ flow on). This is termed as the growing time. On the contrary, the solely H₂ flow

Table 1. Experimental conditions for the deposition of CNFs on the substrates for samples A~I.

Processes	Conditions 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)	Cyclic on/off modulation of Source Gases flow (sec)			Number of cycles (No.)	Total cyclic process Application time (min)	Substrate Temp. (°C)
							C ₂ H ₂	H ₂	SF ₆			
I	A, D, G	15	35	0	100	90	—	—	—	0	0	750°C for samples A,B,C
II	B, E, H	15	35	0	100	90	180/30	—	—	2	7	850°C for samples D,E,F
III	C, F, I	15	35	35	100	90	180/30	—	30/180	2	7	950°C for samples G,H,I

Process Samples	Cyclic Modulation Process	Process Samples	Cyclic Modulation Process	Process Samples	Cyclic Modulation Process
Process I Sample A Sample D Sample G		Process II Sample B Sample E Sample H		Process III Sample C Sample F Sample I	

Figure 1. Different reaction processes: the steady process (process I: samples A, D and G), the cyclic process having H₂ as the etching component (process II: samples B, E and H), the cyclic process having SF₆ + H₂ as the etching components (process III: samples C, F and I).

or H₂ + SF₆ flow (C₂H₂ flow off) may etch carbon components. Therefore these times are termed as the etching time. The cycle was defined as the source gases were fluctuated as C₂H₂ flow on plus C₂H₂ flow off. The interval time for one cycle was defined as the time for C₂H₂ flow on plus the time for C₂H₂ flow off.

We fixed H₂ flow rate, C₂H₂ flow rate, SF₆ flow rate and the total reaction time as 35 sccm, 15 sccm, 35 sccm and 90 min, respectively. The C₂H₂ flow on/off time ratio was set as 180/30 s. So, the interval time for one cyclic was 3.5 minutes and the numbers of cycles were 2 times. The total cyclic modulation time was 7 minutes. The detailed reaction conditions according to the different samples were shown in Table 1.

Detailed morphologies of CNFs–deposited substrates were investigated by using field emission scanning electron microscopy (FESEM).

III. RESULTS AND DISCUSSION

To elucidate the effect of SF₆ incorporation and the cyclic modulation process on the diameter size for the CNFs, we made 9 samples which have the different reaction processes and the different substrate temperatures. Process I (samples A, D and G) is the steady process, the process without incorporating the cyclic modulation process, at the substrate temperature

=750, 850 and 950 °C For process II (samples B, E and H), the on/off modulation of C₂H₂/H₂ flow was applied for two cycles. Namely, it was started from C₂H₂ + H₂ flow (3.0 min) and ended in H₂ flow (0.5 min), thus: C₂H₂ + H₂ flow → H₂ flow → C₂H₂ + H₂ flow → H₂ flow. For process III (samples C, F and I), the on/off modulation of C₂H₂ flow and the off/on modulation of SF₆ flow were applied for two cycles. Namely, it was started from C₂H₂ + H₂ flow (3.0 min) and ended in SF₆ + H₂ flow (0.5 min), thus: C₂H₂ + H₂ flow → SF₆ + H₂ flow → C₂H₂ + H₂ flow → SF₆ + H₂ flow.

For processes II and III, the interval time for one cycle (C₂H₂ flow on → C₂H₂ flow off) was 3.5 minutes and the number of cycles was 2. Therefore the overall cyclic modulation time was 7.0 minutes. After the cyclic modulation process, the steady deposition process (C₂H₂ + H₂ flow) was progressed for 83 minutes. It indicates that the etching gas (solely H₂ or SF₆ + H₂ gas) feeding time (1 min) and the carbon source gas (C₂H₂ + H₂ flow) feeding time (89 min) for the different samples were same throughout the

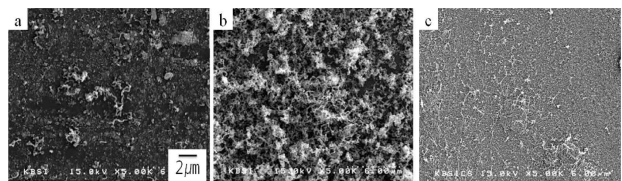


Figure 2. FESEM images of the CNFs–deposited substrate for (a) sample A, (b) sample B and (c) sample C.

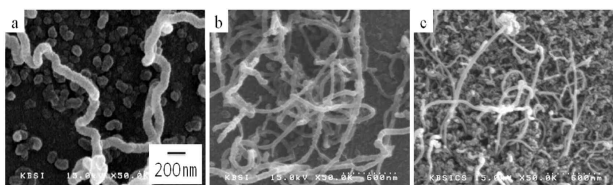


Figure 3. High-magnified FESEM images of the CNFs-deposited substrate for (a) sample A, (b) sample B and (c) sample C.

samples at processes II and III. The different points are the etching gases components namely, solely H_2 (process II) or $SF_6 + H_2$ (process IV).

Fig. 2 shows FESEM images showing the surface morphologies for the samples at $750^\circ C$. The CNFs-related materials formations could be observed irrespective of the different processes. By the cyclic modulation process, the enhancement of the CNFs formation density could be observed (compare Figs. 2a with b and c). The high-magnified images (Fig. 3) confirm the enhancement of the CNFs formation density by the cyclic modulation process (compare Figs. 3b and c with a). In addition, the incorporation of SF_6 in the source gases (process III) seems to reduce the diameter size of the individual CNFs, as compared with that of processes I and II (compare Figs. 3c with a and c). Consequently, the number density of the individual CNFs is much higher at process III.

Figs. 4 and 5 show the as-grown CNFs on the substrate at the substrate temperature of $850^\circ C$. For the formation density of CNFs, at $850^\circ C$ a similar tendency to that of $750^\circ C$ as observed by the cyclic modulation process as shown in Fig. 4. Fig. 5a

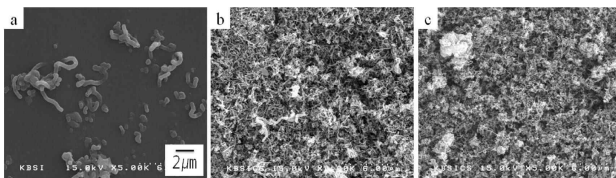


Figure 4. FESEM images of the CNFs-deposited substrate for (a) sample D, (b) sample E and (c) sample F.

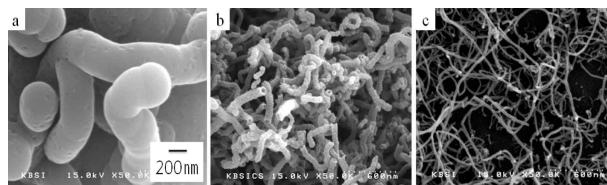


Figure 5. High-magnified FESEM images of the CNFs-deposited substrate for (a) sample D, (b) sample E and (c) sample F.

(process I) shows the embryo for CNFs formation. On the contrary Figs. 5b and c (processes II and III) show the well-developed CNFs formation instead of the embryo. In this temperature the diameter size of the individual CNFs at process III (Fig. 5c) was extremely lower than those of the other processes (Figs. 5a and b).

Fig. 6 shows FESEM images showing the surface morphologies for the samples at $950^\circ C$. In this temperature the CNFs-related materials formations could not be observed irrespective of the different processes. Instead, the embryo for the CNFs formation could be observed. Indeed, process III seemed to give rise to more well-developed embryos than those of the other process (compare Figs. 6c with a and b). Even in the embryo case, a tendency for the reduction of the diameter size of the individual CNFs by the cyclic modulation process were observed.

Based on the results shown in Figs. 2~6, we propose that the cyclic modulation process results in a reduction of the diameter size of the individual CNFs. And this tendency is pronounced by the incorporation of SF_6 during the cyclic modulation

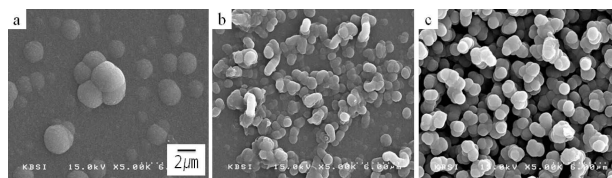


Figure 6. FESEM images of the CNFs-deposited substrate for (a) sample G, (b) sample H and (c) sample I.

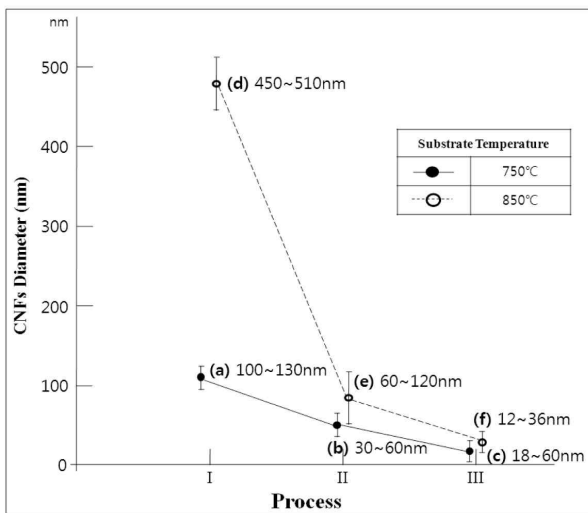


Figure 7. The diameter size of the individual CNFs for (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F, (g) sample G, (h) sample H and (i) sample I.

process. In addition, the number density of the individual CNFs is found to be much higher at process III because the diameter size of the individual CNFs was reduced. Fig. 7 shows the variation of the diameter size of the individual CNFs as functions of the substrate temperature and the different process to summarize our results.

The cause for these results at process III may be attributed to the slightly increased etching ability by SF₆ addition to H₂ gas concentration during the etching time in the cyclic modulation process. It may facilitate the suitable CNFs nucleation sites. Furthermore, it may etch away the superfluous materials of the as-grown CNFs. Consequently the diameter size of the as-grown CNF at process III would be reduced.

IV. CONCLUSIONS

The diameter size for the individual CNFs could be reduced by the cyclic on/off modulation process of C₂H₂/H₂ flow. In addition, the SF₆ incorporation in the cyclic process could promote the formation

density of the well-developed CNFs. The cause for these results may be attributed to be due to the slightly increased etching ability by SF₆ addition to H₂ gas concentration during the etching time in the cyclic modulation process.

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C₂H₂/H₂/SF₆ 기체들의 사이클릭 유량 변조를 통한 탄소 나노 필라멘트 직경크기 조절

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탄소나노필라멘트의 직경크기를 조절하기 위하여 증착 반응초기에 SF₆를 증착원료기체(C₂H₂, H₂)에 주입하였다. 증착 원료 기체와 SF₆를 열화학기상증착시스템에서 시간에 따라 사이클릭 유량 변조시켰다. 사이클릭 유량 변조 프로세스와 기관의 온도에 따라 기관위에 증착된 탄소나노필라멘트들의 특성을 조사하였다. 사이클릭 에칭기간에 SF₆를 투입하자 탄소나노필라멘트의 직경크기는 급격히 감소하였다. 이러한 탄소나노필라멘트 직경의 크기 감소 원인은 SF₆ 기체의 주입에 따른 에칭능력 향상에 기인하는 것으로 이해되었다.

주제어 : 탄소나노필라멘트, 직경크기, 사이클릭 변조프로세스, 열화학기상증착

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