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Enhancement of the characteristics of carbon nanofibers by the on/off cyclic modulation of C_2H_2/H_2 flow

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Abstract Carbon nanofibers were deposited on silicon oxide substrate by thermal chemical vapor deposition method. For the enhancement of the characteristics of carbon nanofibers, the source gases (C_2H_2, H_2) flows were intentionally manipulated as the cyclic on/off modulation of C_2H_2 flow. By the cyclic modulation process during the initial deposition stage, the formation density of carbon nanofibers on the substrate could be much more enhanced. The diameter of as-grown carbon nanofibers was also reduced by the cyclic modulation process. The cause for the variation in the characteristics of carbon nanofibers by the cyclic modulation process was discussed in association with the hydrogen gas etching ability.

Key words Carbon nanofibers, Cyclic modulation of C_2H_2/H_2 flow, Nucleation density, Surface morphology, Thermal CVD

1. Introduction

Due to their fascinating geometries and unique electrical properties, carbon nanofilaments, called carbon nanotubes if hollow and carbon nanofibers if filled [1-3], have been regarded as the promising materials to fabricate the nanoelectronic devices [4-6]. For the formation of the carbon nanofilaments, up to the present, various methods have been introduced, such as arc discharge [7], pyrolysis [8], laser ablation [9], plasma or thermal chemical vapor deposition methods [4, 10], and so forth. Among these methods, chemical vapor deposition methods have been noted for having the advantages of the high purity and the high yield of carbon nanofilaments formation [11]. Despite these advantages, however, the practical applications of carbon nanofilaments to fulfill the industry's expectations still requires the massive production and/or the higher purity of carbon nanofilaments. Therefore, the development of their formation process to enhance their purity and formation yield would be inevitable to achieve the practical applications.

In this work, an in-situ cyclic on/off modulation process of C_2H_2/H_2 flow was proposed to enhance the formation yield of carbon nanofibers [12, 13]. Because an in-situ process can be applied with an ex-situ process, it has the advantages to enhance the characteristics of carbon nanofibers. The density of carbon nanofibers formation on the substrate and the surface morphology of the as-grown carbon nanofibers were investigated. The cause for the enhancement of the characteristics of carbon nanofibers by the cyclic modulation process of C_2H_2/H_2 flows was discussed in association with the gas phase composition cycling during the reaction.

2. Experimental

The SiO_2 substrates in this work were prepared by the thermal oxidation of the $2.0 \times 2.0\ cm^2$ p-type Si (100) substrates. The thickness of silicon oxide (SiO_2) layer on Si substrate was estimated to be about 300 nm. A 7.18 M iron pentacarbonyl, $Fe(CO)_5$, solution was prepared as the precursor for Fe metal catalyst nanograins. We deposited Fe metal catalyst nanograins on the substrate.

For carbon nanofibers deposition, thermal chemical vapor deposition (TCVD) system was employed. C_2H_2 and H_2 were used as source gases. Total flow rate was fixed at 50 standard cm^3 per minute (sccm). The in-situ cyclic modulation process was carried out through on/off control of C_2H_2 flow. The sequence of source gas flow was the iterative order of procedures, C_2H_2 flow on and then off.

Detailed morphologies of carbon nanofibers-deposited substrates were investigated by using field emission scanning electron microscopy (FESEM). Nanostructures of the carbon nanofibers were examined by a transmission electron microscopy (TEM). The samples for TEM were prepared by dispersing carbon nanofibers using acetone in an ultrasonic bath. A drop of suspension was

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dropped onto a carbon film which was supported by a Cu grid. Then the Cu grid was placed into TEM chamber and the detailed morphologies of carbon nanofibers could be investigated.

3. Results and Discussion

To elucidate the effect of the cyclic modulation process, we made four samples which have the different reaction processes and conditions. For sample A, the cyclic modulation process was applied during the overall deposition process. Indeed, this process was started from $C_2H_2 + H_2$ flow for 1 min and ended in H_2 flow for 1 min during the overall deposition process (90 min). This means that the carbon source gas ($C_2H_2 + H_2$ flow) feeding times are just a 45 min. Therefore the total amount of the carbon source gas seems to be nearly half of that for the steady process.

For sample B, however, the cyclic modulation process was applied during only the initial deposition stage (7 min). Namely, this process was progressed via two-cycle. It was started from $C_2H_2 + H_2$ flow (3 min) and ended in H_2 flow (0.5 min), thus: $C_2H_2 + H_2$ flow $\rightarrow$ H_2 flow $\rightarrow$ $C_2H_2 + H_2$ flow $\rightarrow$ H_2 flow. After the cyclic modulation process during the initial deposition stage, the steady deposition process ($C_2H_2 + H_2$ flow) was progressed for 83 minutes. This means that the solely hydrogen gas feeding (H_2 flow) time would be just merely 1 min and the carbon source gas ($C_2H_2 + H_2$ flow) feeding times were 89 min.

We also made the samples without the cyclic modulation process. Sample C is the steady process having the ratio of C_2H_2 flow to the total gas flow as 0.4. This ratio is the standard in this work. Sample D is also the steady process. In this case, however, the ratio was cut in half as 0.2 to compare with sample A. The detailed reaction conditions and processes were shown in Table 1 and Fig. 1, respectively.

Figure 2 shows FESEM images showing the surface morphologies of these samples. As shown in Fig. 2, the density of carbon nanofilaments at sample B is higher than those of any other samples. Indeed, the carbon nanofilaments densities of the other samples are not much var-

Table 1
Experimental conditions for the deposition of carbon nanofilaments

Condition / Samples	H_2 flow rate (sccm)	C_2H_2 flow rate (sccm)	Substrate temp. (°C)	Total pressure (torr)	Total deposition time (min)	Application of cyclic process	Cyclic on/off modulation time of C_2H_2 flow (min)	Number of cycles (No.)	Total cyclic process application time (min)
Sample A	30	20	750	100	90	Yes	1/1	45	90
Sample B	30	20	750	100	90	Yes	3/0.5	2	7
Sample C	30	20	750	100	90	No	0	0	0
Sample D	40	10	750	100	90	No	0	0	0

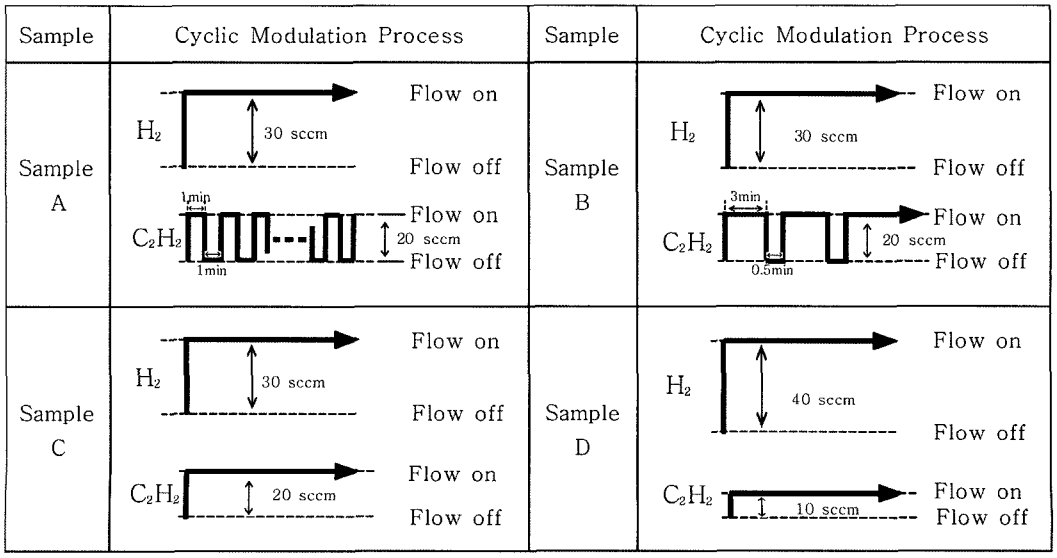

Fig. 1. Cyclic modulation processes of source gases flows for sample A, sample B, sample C and sample D.

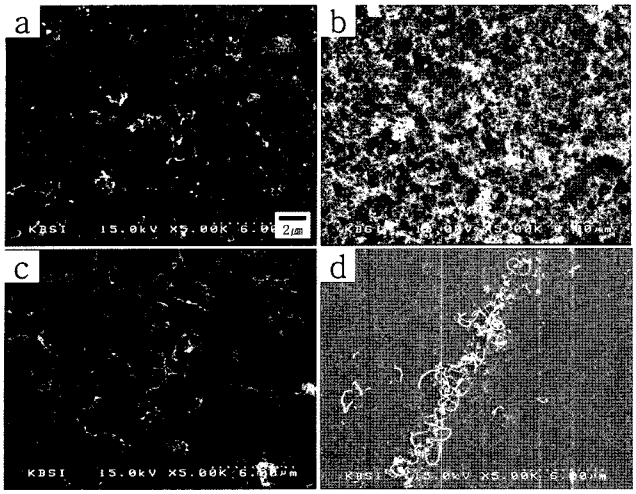

Fig. 2. FESEM images of the surface morphologies for (a) sample A, (b) sample B, (c) sample C and (d) sample D.

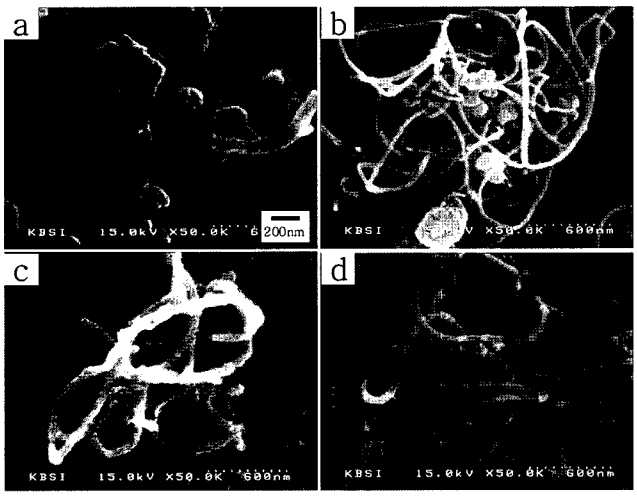

Fig. 3. High magnified FESEM images of the surface morphologies for (a) sample A, (b) sample B, (c) sample C and (d) sample D.

ied. This result reveals that the application of the cyclic modulation process during only the initial deposition stage, instead of the overall process, may be favorable for the enhancement of the carbon nanofilaments density.

Figures 3a~3d show the high-magnified FESEM images of Figs. 2a~2d, respectively. As shown in Fig. 3b (sample B), the diameters size of carbon nanolaments was obviously reduced by the application of the cyclic modulation process during an initial deposition stage. Furthermore, the surface morphology of carbon nanofilaments in sample B was clearly observed than those of any other samples.

To identify whether these carbon nanofilaments applied by the cyclic modulation process are carbon nanotubes or carbon nanofibers, we carried out TEM study. Figure

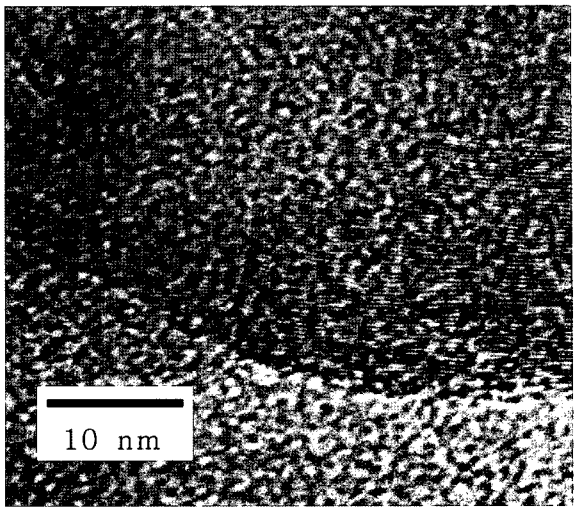

Fig. 4. TEM image for one of the carbon nanofibers from sample B.

4 shows the detailed structure for one of the carbon nanofilaments from sample B. From the stacking lattices and the filled image at the inside of the filaments, we confirmed that these carbon nanofilaments from sample B were carbon nanofibers [14].

The various aspects for the density and the diameter size of carbon nanofibers by the application of the cyclic modulation process during the initial deposition stage could be reconfirmed under a different deposition temperature condition. Figsure 5 and 6 show FESEM images of as-deposited substrates at 850°C and the various aspects in the diameter size of carbon nanofibers as a function of the temperature, respectively. For the density of carbon nanofibers at 850°C it seems to be slightly increased by the application of the cyclic modulation process (compare Figs. 5a with 5b). For the diameter size of carbon nanofibers, however, it is much more reduced at 850°C compared with those at 750°C (see Fig. 6). Anyway, we could confirm the enhancement of the density and the reduction of the diameter size by the cyclic modulation process even at 850°C.

Based on the results shown in Figs. 1~6, we propose that the solely hydrogen gas feeding (H_2 flow) in a relative short time (1 min) during only the initial deposition stage can play an active role in the density enhancement and the diameter size reduction of carbon nanofibers. For the density enhancement, we believe that the slight increase in the hydrogen gas concentration at the initial deposition stage may facilitate the suitable carbon nanofilaments nucleation sites, although atomic hydrogen itself was known to remove subcritical size carbon nuclei as well as nucleation sites on the substrate [15]. For the diameter size reduction, it seems to be due to

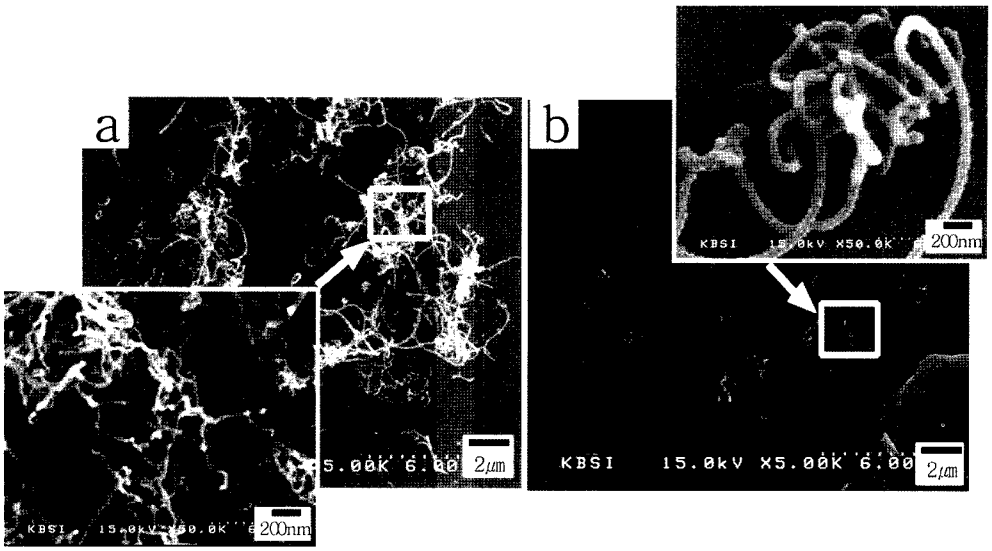

Fig. 5. FESEM images of as-deposited substrates at 850°C for (a) the sample with the cyclic modulation process, (b) the sample without the cyclic modulation process (Insets show the magnified images at the arrow position areas.).

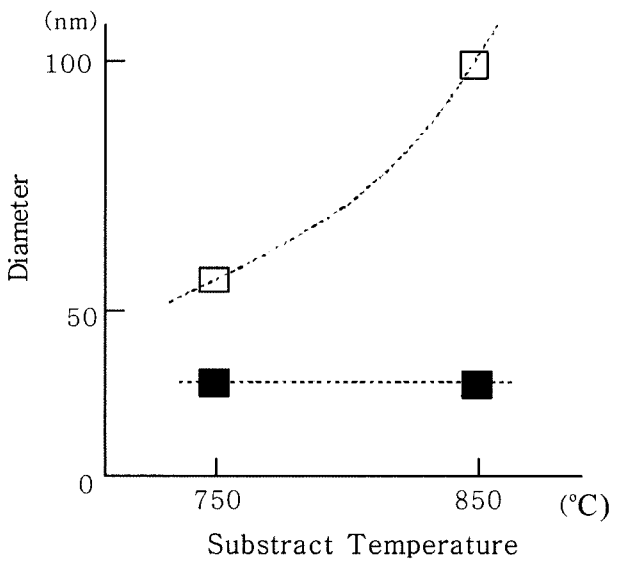

Fig. 6. The variation aspects in the diameter size of carbon nanofibers as a function of the substrate temperature (Hollow and filled squares indicate those of the steady and the cyclic process, respectively.).

the hydrogen gas ability for etching and then reducing Fe metal catalyst nanograins or the precursor of carbon nanofilaments. However, the solely hydrogen gas cyclic feeding during the overall process (sample A) seems to merely provide just a similar situation to that of the steady processes (samples C or D).

4. Conclusions

The cyclic on/off modulation of C_2H_2 flow during the initial deposition stage can give rise to not only the density enhancement of the carbon nanofibers formation but also the size reduction of the carbon nanofibers diameter. The slight increase in the hydrogen gas concentration during the initial deposition stage seems to provide the diameter size reduction of carbon nanofibers via the hydrogen gas etching as well as the facilitation of the suitable nucleation sites.

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