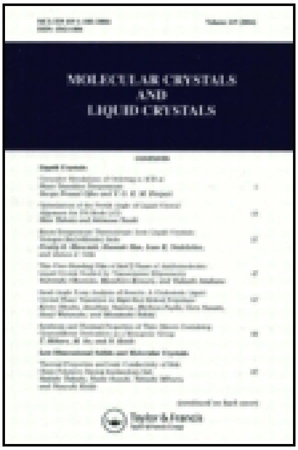

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Enhancement of Carbon Nanofilaments Formation Density and the Surface Electrical Conductivity by the Gas Phase Composition Cycling

Kwang-Duk Kim [a], Sung-Hoon Kim [a], Soung Soo Yi [b] & Kiwan Jang [c]

[a] Department of Engineering in Energy & Applied Chemistry, Silla University, Busan, Korea

[b] Department of Electronic Materials Engineering, Silla University, Busan, Korea

[c] Department of Physics, Changwon National University, Changwon, Korea

Version of record first published: 10 Nov 2009

Mol. Cryst. Liq. Cryst., Vol. 513, pp. 179–186, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903196260

Taylor & Francis
Taylor & Francis Group

Enhancement of Carbon Nanofilaments Formation Density and the Surface Electrical Conductivity by the Gas Phase Composition Cycling

Kwang-Duk Kim[1], Sung-Hoon Kim[1], Soung Soo Yi[2], and Kiwan Jang[3]
[1]Department of Engineering in Energy & Applied Chemistry, Silla University, Busan, Korea
[2]Department of Electronic Materials Engineering, Silla University, Busan, Korea
[3]Department of Physics, Changwon National University, Changwon, Korea

For the enhancement of carbon nanofilaments (CNFs) formation density and the surface electrical properties, the source gas flow was intentionally manipulated as the cyclic on/off modulation of C_2H_2/H_2 flow in a thermal chemical vapor deposition system. CNFs formation density on the substrate and surface electrical conductivity of as-deposited substrate were investigated as a function of the cyclic modulation interval time for one cycle, namely the time for $H_2 + C_2H_2$ flow (C_2H_2 flow on) plus the time for H_2 flow (C_2H_2 flow off). The optimal interval time for the enhancement of both CNFs formation density and the surface electrical conductivity was around 3.5 minutes. The cause for the variation in the characteristics of CNFs according to the interval time of the cyclic modulation process was discussed in association with the variation of the remaining time of pure hydrogen gas concentration.

Keywords: carbon nanofilaments; composition cycling; formation density

1. INTRODUCTION

The most difficult problems to overcome in producing suitable CNFs for active nanoelectronic devices would be the mass production of CNFs having the controlled-characteristics. Up to date, various techniques have been introduced for the mass production of CNFs [1–7]. Recently,

Address correspondence to Sung-Hoon Kim, Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, Korea. E-mail: shokim@knu.ac.kr

we have introduced an in-situ cyclic on/off modulation process of C_2H_2/H_2 flow to enhance the formation yield of CNFs [8]. It can be simply achieved by turning a source gas flow rate in a reaction system on or off during the initial deposition stage. The density of CNFs was enhanced by the application of the cyclic modulation process during the initial deposition stage. The optimal ratio of the cyclic modulation period for the enhancement of CNFs formation density was known to be around 23% to total reaction time [9]. Then the next step would be the determination of the optimal cyclic modulation interval time, namely the time for one cycle in the cyclic modulation process.

In the present work, the influence of the cyclic modulation interval time of C_2H_2/H_2 flow on CNFs morphology and the formation density was studied. According to the different reaction processes, different cyclic modulation interval times of C_2H_2/H_2 flow were applied in the reaction process. The variation of the CNFs characteristics, namely the formation density and the surface electrical conductivity was examined.

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 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 using the vacuum sublimation method [10].

For CNFs 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 progressed by the modulation of the source gas flow during the initial deposition stage. According to the reaction processes, the sequence of source gas flow was the iterative order of procedures, $H_2 + C_2H_2$ flow (C_2H_2 flow on) and then H_2 flow (C_2H_2 flow off). The cycle was defined as the source gases were fluctuated as C_2H_2 and H_2 flows plus just H_2 flow. The interval time for one cycle was defined as the time for $H_2 + C_2H_2$ flow (C_2H_2 flow on) plus the time for H_2 flow (C_2H_2 flow off).

To examine the effect of the cyclic modulation interval time on the CNFs formation density, we fixed H_2 flow rate, C_2H_2 flow rate and the total reaction time as 40 sccm, 10 sccm, and 90 min, respectively. The C_2H_2 flow on/off time ratio was set as 90/15 s, 180/30 s, 360/60 s. So, the interval time for one cyclic were varied as 1.75 minutes, 3.5 minutes and 7 minutes and the numbers of cycles were also varies

TABLE 1 Experimental Conditions for the Deposition of CNFs on the Substrates for Samples A, B, C, and D

Conditions / Samples	C_2H_2 flow rate (sccm)	H_2 flow rate (sccm)	Substrate temp. (°C)	Total pressure (Torr)	Total deposition time (min)	Application of cyclic process	Cyclic on/off modulation of C_2H_2/H_2 flow (sec)	The interval time for one cycle (min)	Number of cycles (No.)	Overall cyclic modulation period (min)
Sample A	10	40	750	100	90	No	–	–	0	0
Sample B	10	40	750	100	90	Yes	90/15	1.75	12	21
Sample C	10	40	750	100	90	Yes	180/30	3.5	6	21
Sample D	10	40	750	100	90	Yes	360/60	7	3	21

as 12, 6, 3 times. The 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). Surface electrical properties were measured on $2 \times 2\,cm^2$ as-deposited substrate using four- point probe.

3. RESULTS AND DISCUSSION

To elucidate the effect of the cyclic modulation interval time, we made four samples which have the different reaction processes. Sample A is the steady process, the process without incorporating the cyclic modulation process, at the substrate temperature = 750°C. For sample B, the on/off modulation of C_2H_2/H_2 flow was applied for twelve cycles at the initial deposition stage. Namely, it was started from $C_2H_2 + H_2$ flow (1.5 min) and ended in H_2 flow (0.25 min), thus: $C_2H_2 + H_2$ flow → H_2 flow → ··· $C_2H_2 + H_2$ flow → H_2 flow. Therefore, the interval time for one cycle ($C_2H_2 + H_2$ flow → H_2 flow) was 1.75 minutes. The overall cyclic modulation period was 21 minutes. After the cyclic modulation process, the steady deposition process ($C_2H_2 + H_2$ flow) was progressed for 69 minutes. This means that the solely hydrogen gas feeding (H_2 flow) times would be 3 min and the carbon source gas ($C_2H_2 + H_2$ flow) feeding times were 87 min. For samples C and D, the numbers of cycles were 6 and 3. The interval times for one cycle ($C_2H_2 + H_2$ flow → H_2 flow) were 3.5 and 7 minutes, respectively. Therefore the overall cyclic modulation periods were consistently maintained as 21 minutes. It also indicates that the solely hydrogen gas feeding (H_2 flow) times and the carbon source gas ($C_2H_2 + H_2$ flow) feeding times for samples B, C, and D were same. The different points of cyclic process according to the different samples are the interval times for one cycle and the numbers of cycles.

The detailed reaction processes according to the different samples were shown in Figure 1.

Figure 2 shows FESEM images showing the surface morphologies for these samples. These images indicate the enhancement of the CNFs formation density by the cyclic process (compare Figs. 2a with b, c, and d). In addition, the CNFs formation density seems to increase with increasing the interval time for one cycle from 1.75 minutes to 3.5 minutes (see Figs. 2b and c) although they have the same overall cyclic modulation period.

Above 3.5 minutes of the interval time for one cycle, however, the CNFs formation density of the samples seems to decrease with increasing the interval time (compare Figs. 2c with d). These results

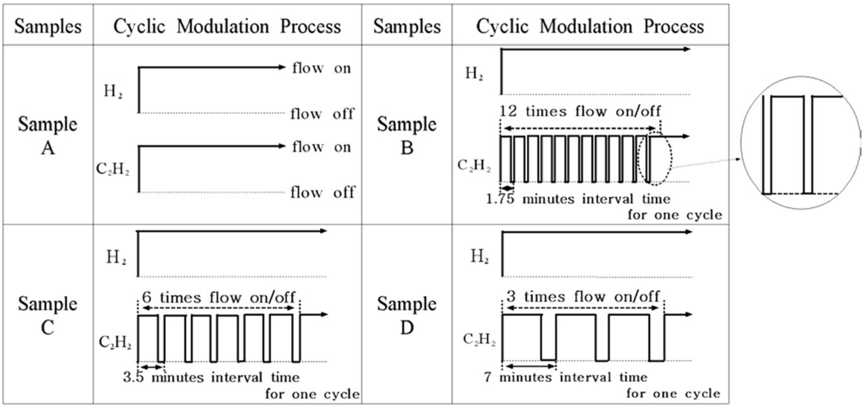

FIGURE 1 Different reaction processes: the steady process (sample A), the cyclic process having the interval time for one cycle were 1.75 minutes (sample B), 3.5 minutes (sample C), and 7 minutes (sample D).

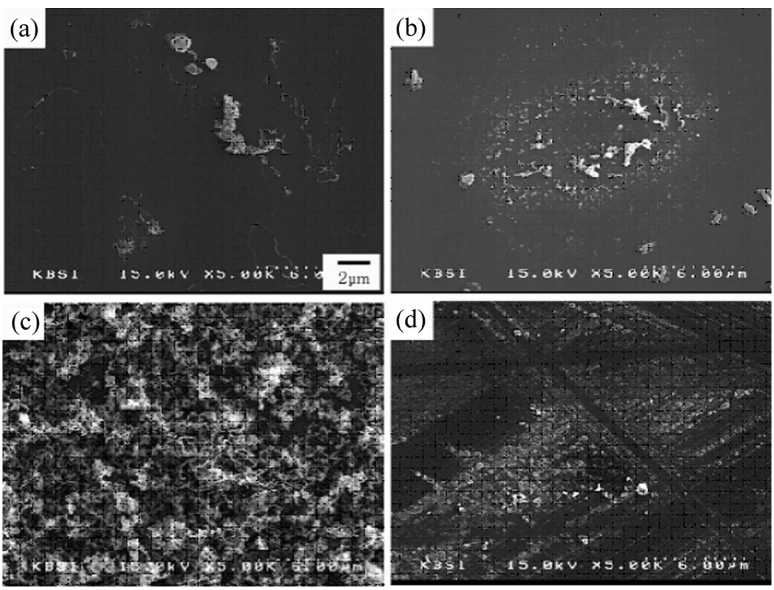

FIGURE 2 FESEM images of as-deposited substrate for (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

reveal that the optimal interval time for the enhancement of CNFs formation density would be around 3.5 minutes. It is equivalent to around 17% of the overall cyclic modulation process period (21 minutes).

The high-magnified images of Figure 2 also confirm the enhancement of the CNFs formation density by 3.5 minutes interval time for one cycle (see Fig. 3).

Figure 3 also indicates that the diameters sizes of CNFs were not much varied by the application of the cyclic modulation process. These results confirm that the cyclic modulation process having 3.5 minutes application time would be the favorite interval time for the enhancement of CNFs formation density without varying the diameter sizes.

The study for the surface electrical properties of as-deposited substrate according to the different samples was also carried out.

As shown in Figure 4, it indicates the increase in the surface electrical conductivities for the samples having the cyclic process, as compared with that for the steady process (compare Figs. 2a with b, c, and d). In addition, the surface electrical conductivity seems to increase with increasing the interval time for one cycle from 1.75 minutes to

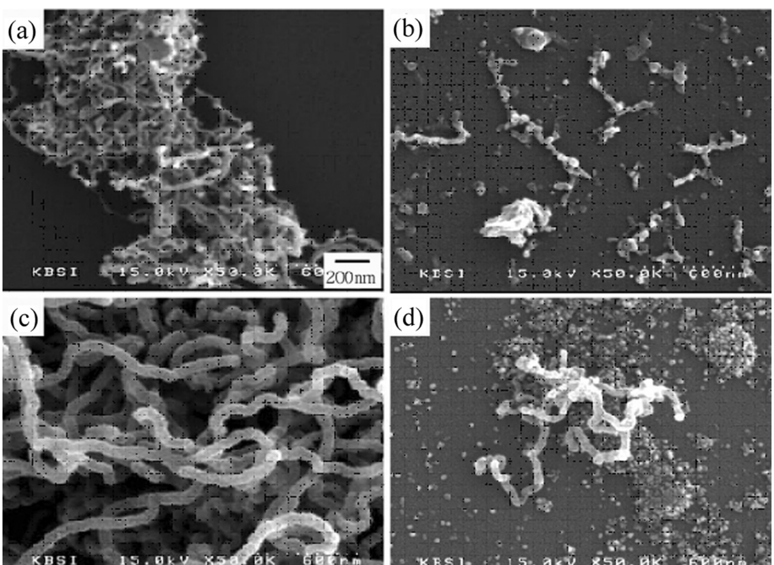

FIGURE 3 High-magnified FESEM images of the CNFs surface morphologies for (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

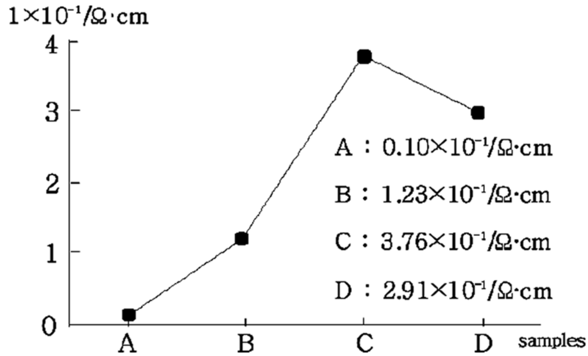

FIGURE 4 Surface electrical conductivities of as-deposited substrate for (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

3.5 minutes (see Figs. 4b and c) although they have the same overall cyclic modulation period. Above 3.5 minutes of the interval time for one cycle, on the contrary, it seems to decrease with increasing the interval time (see Figs. 4c and d). These results also indicate that, from the enhancement of the surface electrical conductivity points of view, the optimal interval time for one cycle would be around 3.5 minutes. The results from Figures 2 to 4 informed that the surface electrical conductivities of samples are considered to be strongly related with the CNFs density.

Based on the results shown in Figures 1–4, we propose that the application of the cyclic modulation process during the initial deposition stage having 3.5 minutes interval time (sample C) may play an important role for the enhancement of CNFs formation density and the increase in the surface electrical conductivity. The cause for these results was considered to be due to the slight increase in the remaining time of pure hydrogen gas concentration by the cyclic modulation process. It may facilitate the suitable CNFs nucleation sites, although hydrogen itself was known to have the etching ability to remove subcritical size carbon nuclei as well as nucleation sites on the substrate [11]. However, the interval time less than 3.5 minutes (sample B) may reduce the etching ability due to the remaining time limitation of pure hydrogen gas concentration. So, it would not much enhance the formation densities of CNFs. On the contrary, the interval time more than 3.5 minutes (sample D) may extend the pure hydrogen gas remaining time. Consequently it may exceedingly elevate the etching ability. Thus not only subcritical size carbon nuclei but also nucleation sites on the substrate would be etched away.

4. CONCLUSIONS

The application of the cyclic modulation process having around 17% interval time ratio to the overall cyclic modulation process time would enhance both CNFs formation density and the surface electrical conductivity. The optimal pure hydrogen gas remaining time (3.5 minutes in this work) is considered to facilitate the suitable CNFs nucleation sites. However, the interval time less than the optimal condition may not much enhance the formation densities due to the immature of the etching activity caused by the limitation of the pure hydrogen gas remaining time. On the contrary, the excess of the pure hydrogen gas remaining time may exceedingly elevate the etching ability. In this case even the formed nuclei on the substrate may be etched away. Consequently the CNFs formation density will be decreased.

REFERENCES

[1] Iijima, S. (1991). *Nature*, *354*, 56.
[2] Bethune, D. S., Kiang, C. H., Devries, M. S., Gorman, G., Savoy, R., Vazquez, J., & Beyers, R. (1993). *Nature*, *363*, 605.
[3] Terrones, M., Grobert, N., Olivares, J., Zhang, J. P., Terrones, H., Kordatos, K., Hsu, W. K., Hare, J. P., Townsend, P. D., Prassides, K., Cheetham, A. K., Kroto, H. W., & Walton, D. R. M. (1997). *Nature*, *388*, 52.
[4] Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y. H., Kim, S. G., Rinzler, A. G., Colbert, D. T., Scuseria, G. E., Tomanek, D., Fisher, J. E., & Smalley, R. E. (1996). *Science*, *273*, 483.
[5] Li, W. Z., Xie, S. S., Qain, L. X., Chang, B. H., Zou, B. S., Zhou, W. Y., Zhao, R. A., & Wang, G. (1996). *Science*, *274*, 1701.
[6] Lee, C. J., Park, J. H., & Park, J. (2000). *Chem. Phys. Lett.*, *323*, 560.
[7] Han, J. H., Choi, S. H., Lee, T. Y., Yoo, J. B., Jung, T., Yu, S. G., Yi, W., Han, I. T., & Kim, J. M. (2003). *Diamond Relat. Mater.*, *12*, 878.
[8] Kim, K.-D., Kim, S.-H., Kim, N. S., & Kim, D.-U. (2007). *J. Nanosci. Nanotechnol.*, *7*, 3969.
[9] Gao, Y. X., Kim, S.-H., Lee, S.-H. (2008). *J. Kor. Soc. Imaging Sci. Technol.*, *14*, 173.
[10] Kim, N. S., Kim, K.-D., & Kim, S.-H. (2007). *J. Kor. Cryst. Growth & Cryst. Tech.*, *17*, 18.
[11] Park, S. S. & Lee, J. Y. (1993). *J. Mater. Sci.*, *28*, 1799.