

Low temperature deposition of carbon nanofilaments using vacuum-sublimated $\text{Fe}(\text{CO})_5$ catalyst with thermal chemical vapor deposition

Nam Seok Kim, Kwang-Duk Kim and Sung-Hoon Kim[†]

Department of Electronic Materials Engineering, Silla University, Busan 617-736, Korea

(Received December 18, 2006)

(Accepted January 22, 2007)

Abstract Carbon nanofilaments were deposited on silicon oxide substrate by thermal chemical vapor deposition method. We used $\text{Fe}(\text{CO})_5$ as the catalyst for the carbon nanofilaments formation. Around 800°C substrate temperature, the formation density of carbon nanofilaments could be enhanced by the vacuum sublimation technique of $\text{Fe}(\text{CO})_5$, compared with the conventional spin coating technique. Finally, we could achieve the low temperature, as low as 350°C, formation of carbon nanofilaments using the sublimated Fe-complex nanograins with thermal chemical vapor deposition. Detailed morphologies and characteristics of the carbon nanofilaments were investigated. Based on these results, the role of the vacuum sublimation technique for the low temperature deposition of carbon nanofilaments was discussed.

Key words Carbon nanofilaments, $\text{Fe}(\text{CO})_5$, Low temperature, Vacuum-sublimation, Thermal CVD

1. Introduction

Due to their fascinating shape of the micrometer scale length and the nanometer scale diameter, carbon nanofilaments (CNFs), called carbon nanotubes if hollow and carbon nanofibers if filled, have been regarded as a promising material candidate for the elements of nano-electronic devices, especially for the nanowiring used in the interconnection lines [1-5].

For the nanowiring applications in nanoelectronic devices, the CNFs should show the reproducibility of the electrical properties. Unfortunately, the electrical properties of carbon nanofilaments were uncontrollable, because they were known to be varied as metallic, insulating, or semiconductor characteristics according to their diameters, wrapping angle, or post-growth treatment [6, 7]. One of the methods to achieve the reproducible single electrical properties of carbon nanofilaments might be the low temperature (less than 600°C) growth of the carbon nanofilaments. The carbon nanofilaments diameters were known to be related with the catalyst particle size [8, 9]. At the low temperature condition, the surface migration of the metal catalysts would not be much activated. Consequently, the possibility for the agglomeration of the metal catalysts would be suppressed [10]. This suppression might prevent the wide

variations in the diameter size of the catalyst particle by the thermal migration. Consequently, the size distributions of the carbon nanofilaments diameters would be narrow.

In addition, the low temperature process would enlarge the application area of the carbon nanofilaments. As the field emitters, for example, the low temperature process would be favorable to prevent the softening of the conventional glass sodalime substrate. For use in the hydrogen storage materials and/or in the batteries materials, the low temperature process would be the cost effective method for the manufacturing.

Up to the present, Hofmann *et al.* [11] reported the low temperature process at 120°C by plasma enhanced chemical vapor deposition (PECVD) method. For the thermal chemical vapor deposition (TCVD), more cost effective process than PECVD, Yu *et al.* [12] reported the low temperature process at 330°C using rare earth oxides assistant. Despite these efforts, the low temperature deposition of CNFs still requires the development of the effective process.

In this work, we used the convenient metal catalyst (FeCO_5) and achieved the low temperature deposition of CNFs without the complicated assistant materials such as rare earth oxides or the restricted process such as PECVD. We developed the sublimation process in a vacuum for the metal catalyst deposition before CNFs deposition reaction. Finally, we could achieve the low temperature (350°C) deposition of CNFs under the conventional TCVD system.

[†]Corresponding author
Tel: +82-51-999-5619
Fax: +82-51-999-5806
E-mail: shkim@silla.ac.kr

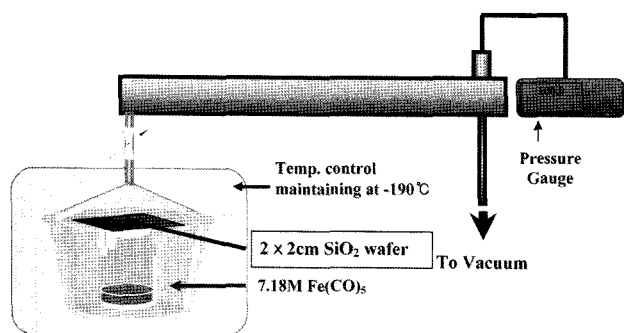


Fig. 1. Schematic diagram of vacuum-sublimation process for $\text{Fe}(\text{CO})_5$ deposition on SiO_2 substrate.

2. Experimental

SiO_2 substrates in this work were prepared by the thermal oxidation of the $2.0 \times 2.0 \text{ cm}^2$ 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, $\text{Fe}(\text{CO})_5$, solution was prepared as the metal catalyst source solution. In a vacuum sublimation process (see Fig. 1), a 7.18 M $\text{Fe}(\text{CO})_5$ solution was frozen using liquid air and Fe-complex nanograins were deposited via sublimation on the SiO_2 substrate in a vacuum line for 2 hours. During the whole sublimation process, $\text{Fe}(\text{CO})_5$ solution was continuously frozen using liquid air, while the total pressure in a vacuum line was maintained at 10 Torr. Detailed experimental condition for the metal catalyst deposition was shown in Table 1.

For CNFs deposition, C_2H_2 and H_2 were introduced to the deposition system after pre-cleaning the substrate. Thermal chemical vapor deposition (TCVD) system was employed for the formation of CNFs as shown in Fig. 2. Table 2 shows the detailed experimental condition for CNFs deposition.

Detailed morphologies of CNFs-deposited substrates were investigated by using field emission scanning elec-

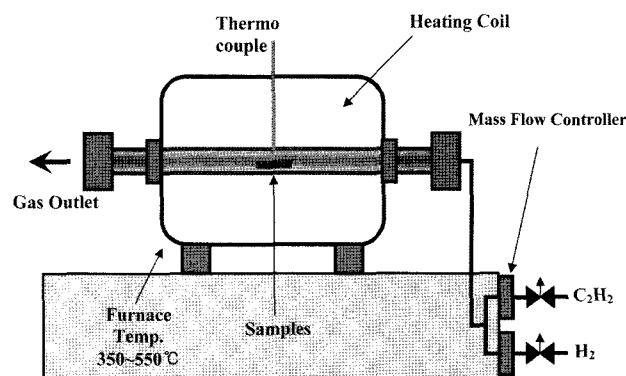


Fig. 2. Schematic diagram of thermal chemical vapor deposition system for the carbon nanofilaments deposition.

tron microscopy (FESEM) and transmission electron microscopy (TEM). The samples for TEM were prepared by dispersing CNFs using acetone in an ultrasonic bath. A drop of suspension was placed 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 CNFs could be investigated.

3. Results and Discussion

After vacuum sublimation reaction of $\text{Fe}(\text{CO})_5$ on the substrate, we investigated the surface morphology of the substrate. As shown in Fig. 3, small grains having about 50 nm diameters could be observed on the substrate surface. They were regarded as Fe nanograins playing as a catalyst role for the CNFs deposition.

Figure 4 shows the surface morphologies of CNFs-deposited substrates using sublimated Fe-complex nanograins (Figs. 4a and 4c) or conventionally spin-coated Fe-complex nanograins (Figs. 4b and 4d) at 750°C (Figs. 4a and b) and 850°C (Figs. 4c and 4d), respectively. As shown in Fig. 4, the densities of the deposited CNFs on

Table 1
Experimental condition for the sublimation of the metal catalyst

Metal catalyst source	Concentration of metal catalyst source	Total pressure during the sublimation process	Freezing method for $\text{Fe}(\text{CO})_5$	Total sublimation time
$\text{Fe}(\text{CO})_5$	7.18 M	10 Torr	By liquid air (about -190°C)	2 h

Table 2
Experimental condition for the deposition of carbon nanofilaments

Kind of source gases	Flow rates of each gas	Total flow rates	Total pressure	Deposition temp.	Reaction times
$\text{C}_2\text{H}_2, \text{H}_2$	C_2H_2 : 15 sccm H_2 : 35 sccm	50 sccm	100 Torr	350, 450, 550, 750 and 850	90 min

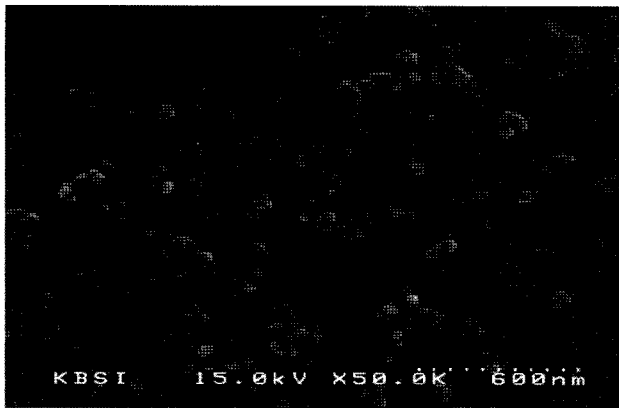


Fig. 3. FESEM image of Fe-complex nanograins deposited substrate surface by the vacuum-sublimation technique.

the substrates could be enhanced by the sublimated Fe nanograins catalyst, irrespective of the substrate temperature. These results inform that the vacuum-sublimation technique of the metal catalyst would be the promising method to enhance the density of CNFs formation on the substrate. The cause for these results seems to be attributed to the difference of the interaction between metal-complex nanograins and the substrate according to the different metal catalyst deposition process. Due to

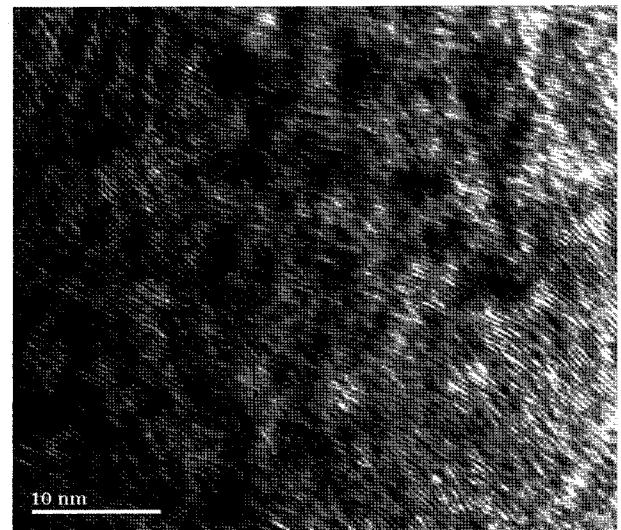


Fig. 5. TEM image for one of the carbon nanofibers.

the vacuum and the freezing requirements, basically, the vacuum sublimation technique may promote more or less a strong adherence of the deposited metal-complex nanograins to the activated surface of the substrate. On the other hand, the conventional spin coating technique may allow just merely the landing of the metal catalyst

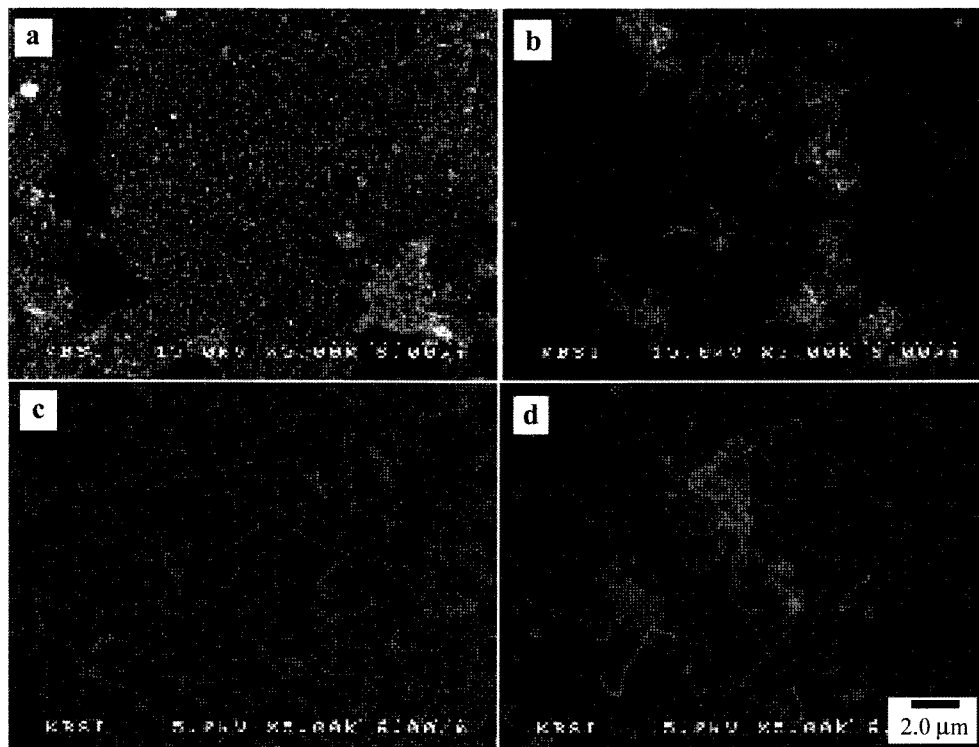


Fig. 4. Surface morphologies of the CNFs-deposited substrate using (a) the sublimated Fe-complex nanograins as a catalyst and CNFs deposition at 750°C, (b) the spin-coated Fe-complex nanograins as a catalyst and CNFs deposition at 750°C, (c) the sublimated Fe-complex nanograins as a catalyst and CNFs deposition at 850°C and (d) the spin-coated Fe-complex nanograins as a catalyst and CNFs deposition at 850°C.

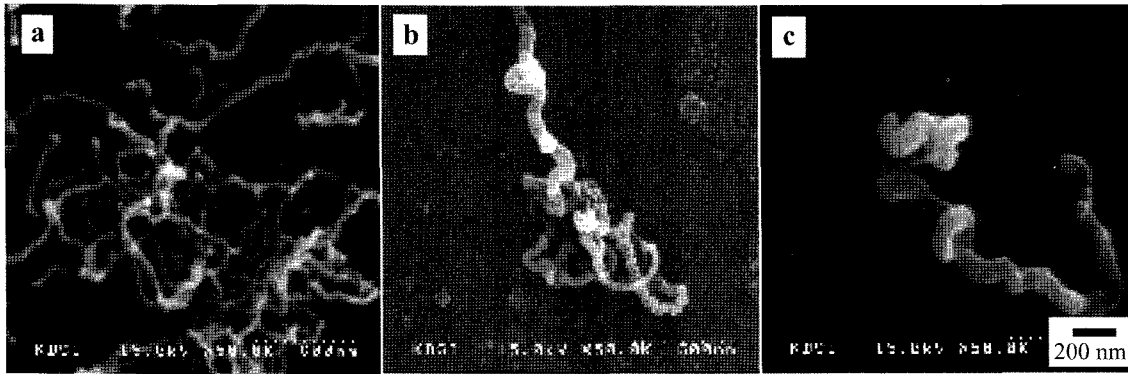


Fig. 6. Surface morphologies of the substrate after the low temperature deposition of CNFs at (a) 350°C, (b) 450°C and (c) 550°C.

on the substrate. Consequently, the vacuum sublimation technique can improve the possibility for the survival of the metal-complex nanograins on the substrate even under the high temperatures (at 750, 850°C) CNFs deposition condition.

To identify whether these CNFs are carbon nanotubes or carbon nanofibers, we carried out TEM study. Figure 5 shows the detailed structure of CNFs. From the stacking lattices and the filled image at the inside of the filaments, we confirmed that these CNFs were carbon nanofibers [13]. The diameters of the carbon nanofibers in this work were measured in the range of between 50 and 150 nm.

Using the vacuum-sublimation method, we deposited Fe-complex nanograins on the substrate and carried out CNFs deposition reaction at the lower substrate temperature (350, 450 and 550°C) in this work. Although the density of CNFs formation is very low, indeed, we could achieve the lowest temperature deposition of CNFs using the sublimated $\text{Fe}(\text{CO})_5$ catalyst under TCVD system as shown in Fig. 6. This result strongly confirms the possibility to form CNFs even around 350°C without the complicated assistant materials such as rare earth oxides [12, 14] or the specific system such as PECVD [11].

The cause for the possibility of CNFs formation at such a low temperature seems to be explained by the previously proposed mechanism [14], namely the super-saturation step after the surface fluidization step of nanoparticles and the carbon diffusion step. Basically, the vacuum sublimation process was carried out under the vacuum and freezing condition. These requirements will lead to the strong adherence of the metal-complex into the substrate surface. Due to the strong adherence of the nanograins, the exposed surface of the metal complex may be reduced, compared with the conventional spin coating technique or the reported decomposition tech-

nique [12, 14]. Consequently, the vacuum sublimation technique can provide more favorable environment for the super-saturation on the reduced exposed surface of the nanoparticles.

4. Conclusions

By the vacuum-sublimation technique, we could enhance the deposition density of CNFs formation on the substrate. In addition, we could achieve the low temperature (350°C) deposition of CNFs using this technique. The vacuum and freezing requirements for this technique seems to provide a favorable environment for not only the enhancement of CNFs deposition density at high temperatures (750, 850°C) but also the achievement of the low temperature (350°C) deposition of CNFs.

References

- [1] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs and C. Dekker, "Individual single-wall carbon nanotubes as quantum wires", *Nature* 386 (1997) 474.
- [2] S.D. Robertson, "Graphite formation from low temperature pyrolysis of methane over some transition metal surfaces", *Nature* 221 (1969) 1044.
- [3] S. Iijima, "Helical microtubules of graphitic carbon", *Nature* 354 (1991) 56.
- [4] M.J. Ledoux, R. Vieira, C. Pham-Huu and N. Keller, "New catalytic phenomena on nanostructured (fibers and tubes) catalysts", *J. of Catalysis* 216 (2003) 333.
- [5] L. Marty, V. Bouchiat, A.M. Bonnot, M. Chaumont, T. Foutnier and S. Decossas, "Batch processing of nanometer-scale electrical circuitry based on in-situ grown single-walled carbon nanotubes", *S. Roche, Microelectronic Engineering* 61-62 (2002) 485.
- [6] M. Knupfer, "Electronic properties of carbon nanostruc-

- tures", *Surface Science Reports* 42 (2001) 1.
- [7] R. Ma, C.L. Xu, B.Q. Wei, J. Liang, D.H. Wu and D. Li, "Electrical conductivity and field emission characteristics of hot-pressed sintered carbon nanotubes", *Mater. Res. Bull.* 34 (1999) 741.
- [8] X.X. Zhang, Z.Q. Li, G.H. Wen, K.K. Fung, J.L. Chen and Y.D. Li, "Microstructure and growth of bamboo-shaped carbon nanotubes", *Chem. Phys. Lett.* 333 (2001) 509.
- [9] E.F. Kukovitsky, S.G. Lvov, N.A. Sainov, V.A. Shustov and L.A. Chernozatonski, "Correlation between metal catalyst particle size and carbon nanotube growth", *Chem. Phys. Lett.* 355 (2002) 497.
- [10] C.J. Lee, J. Park, Y. Huh and J.Y. Lee, "Temperature effect on the growth of carbon nanotubes using thermal chemical vapor deposition", *Chem. Phys. Lett.* 343 (2001) 33.
- [11] S. Hofmann, B. Kleinsorge, C. Ducati, A.C. Ferrari and J. Robertson, "Low-temperature plasma enhanced chemical vapour deposition of carbon nanotubes", *Diamond Relat. Mater.* 13 (2004) 1171.
- [12] G. Yu, J. Gong, D. Zhu, S. He and Z. Zhu, "Synthesis of carbon nanotubes over rare earth zeolites at low temperature", *Carbon* 43 (2005) 3015.
- [13] K. Kamada, T. Ikuno, S. Takahashi, T. Oyama, T. Yamamoto, M. Kamizono, O. Ohkura, S. Honda, M. Katayama, T. Hirao and K. Oura, "Surface morphology and field emission characteristics of carbon nanofiber films grown by chemical vapor deposition on alloy catalyst", *Applied Surface Science* 212 (2003) 383.
- [14] G.J. Yu, J.L. Gong, D.Z. Zhu, S.X. He, J.Q. Cao and Z.Y. Zhu, "Efficient synthesis of carbon nanotubes over rare earth zeolites by thermal chemical vapor deposition at low temperature", *Diamond Relat. Mater.* 15 (2006) 1261.