

FERROCENE WEIGHT OPTIMIZATION FOR CVD GROWTH OF CARBON NANOTUBES OVER Si/SiO₂/Al₂O₃

Y. KHAN^{a*}, S. SHUKRULLAH^b, M. Y. NAZ^b, A. GHAFAR^b, I. AHMAD^a,
S. ALSUHAIBANI^a

^a*Department of Electrical Engineering, King Saud University, Riyadh, Saudi Arabia*

^b*Department of Physics, University of Agriculture, 38040 Faisalabad, Pakistan*

In this study, the ferrocene weight was increased from 0.1 to 0.2 g to demonstrate the growth of MWCNTs on Si/SiO₂/Al₂O₃ substrate. Ethylene was used as carbon precursor for CNTs nucleation. The as-grown multiwalled carbon nanotubes (MWCNTs) were investigated for the effect of ferrocene weight on yield and crystallinity of nanotubes. TEM, Raman and TGA studies revealed that an increase in ferrocene weight to a certain limit significantly improves the diameter, crystallinity, alignment and %yield of the product. However, above 0.15 g of ferrocene, few nanotubes were having surface defects and some black spots were also evident in TEM images. The lowest inner-shell spacing and I_D/I_G ratio were evident for 0.15 g ferrocene catalyst which was an indication of relatively pure CNTs growth. Raman spectra also confirmed the highly crystalline and relatively pure CNTs structures with I_D/I_G ratio of 0.851 for 0.15 g ferrocene. TGA data also revealed the formation of pure MWCNTs especially for 0.15 g ferrocene with oxidation temperature of 620°C.

(Received April 6, 2017; Accepted October 2, 2017)

Keywords: Ferrocene; chemical vapor deposition; carbon nanotubes; catalyst weight

1. Introduction

During the recent years, several methods have been proposed for synthesis of nanotubes, including arc discharge, chemical vapor deposition (CVD), plasma enhanced CVD, laser ablation, etc [1-4]. Each method has its own merits and demerits. The major drawbacks of laser ablation and arc discharge approaches are the consumption of large amount of energy, uncontrolled process parameters, limited in volume of sample and the final product mostly consists of amorphous carbon. Therefore, comparing with such techniques, CVD is considered relatively simple, low cost with low deposition rates and easily scalable technique. Being continuous growth process, CVD is the best-known technique for large-scale production of defects' free CNTs at low operational cost and relatively moderate process temperatures [5-7]. It is a flexible method and can be employed in different ways, for example, floating catalyst CVD is a form of CVD, which allows nanotubes to grow under reactive gas environment. The precursor gas is cracked over a catalyst at higher process temperatures [8]. Through this technique, one can control the diameter, growth rate, shape, diameter, length and alignment of CNTs. This technique is also capable of producing larger amounts of nanotubes at reduced operational cost even under mild operating conditions.

Using the above discussed technique, Andrews et al. [7] performed the catalytic decomposition of ferrocene:xylene mixture and synthesized well-aligned CNTs. On the other hand, Ren et al. [8] synthesized the nanotubes of almost same quality through plasma assisted CVD. Many researchers have reported that other than the synthesis technique, the type of the catalyst is also important in determining the structural traits of nanotubes [9]. Bonard et al. [10]

* Corresponding author: yasink@ksu.edu.sa

concluded that the type and size of the catalyst particle govern the tube diameter since the tube nucleation initiates from the catalyst. Similar findings were reported by Min Shin et al. [11] where the size of the transition metal particles was found controlling the growth parameters of CNTs. Basaev [12] proved that with decrease of ferrocene concentration the melt's free energy increases which leads to the growth of smaller diameter nanotubes with a lower wall number. He also concluded that an increase in the ferrocene concentration in catalyst mixture can have adverse effect on quality of grown CNTs via degradation process.

Therefore, in this note, MWCNTs were synthesized in a double zone FCCVD reactor at a process temperature of 800°C. The ferrocene was added to the growth process as a catalyst. Ethylene gas was taken as a carbon source at a flowrate of 60 sccm, whereas argon with a flowrate of 40 sccm and hydrogen with a flowrate of 100 sccm were used as carrier and supporting gases, respectively. The objective of the study was to investigate the effect of catalyst weight on the CNTs production quality, type, diameter, length, alignment and crystallinity. For this purpose, the synthesized CNTs were characterized for their structural properties via transmission electron spectroscopy, thermogravimetric analysis and Raman spectroscopy. The effects of the catalyst and other growth parameters on CNTs characteristics were investigated and presented in results and discussion section.

2. Materials and methods

Silicon wafer substrate, having 20 mm thickness, was produced and processed through a RCA method. In RCA, the cleaning was carried out in two steps. In first step, a mixture of de-ionized H₂O, NH₄OH and H₂O₂ (5:1:1; v/v) was used for Standard Clean 1. The silicon wafer was sodden for 20 minutes at 75°C and then washed twice in distilled water. After cleaning with SC-1, the wafer was soaked for 5 minutes in a buffer solution of distilled water and HF (50:1; v/v). In second step, a solution of H₂O, H₂O₂ and HCl (6:1:1; v/v) was used to clean the wafer. The wafer was cleaned for 20 minutes in the solution at 75°C and washed twice with distilled water. Finally, the wafer was dried in an electric oven.

Clean and dry silicon substrate was placed in a furnace for oxidation at 1100°C temperature with the ramping rate of 15°C per minute. After getting the desired temperature, the oxygen was purged into the furnace. A SiO₂ layer of 300 nm thickness was achieved after oxidizing the substrate for 4 hours. The oxidized substrate was exposed to E beam followed by oxidation to form a buffer (Al₂O₃) layer. This time, the oxidation was carried out at 600°C temperature for 2 hours. The formation of Al₂O₃ of 40 nm thickness helps in synthesizing the aligned and high density CNTs.

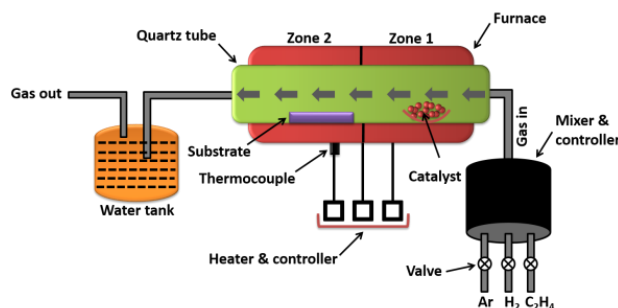


Fig. 1. Schematic of horizontal furnace CVD reactor.

Schematic of the CVD reactor (OTF-1200-80mm) used for growth of MWCNTs is shown in Fig. 1. Initially, a quartz boat, carrying 0.1 g of ferrocene, was placed in lower temperature zone of the furnace. Metal catalyst was vaporized at 230°C in lower temperature zone and carried by the

argon gas to the higher temperature zone, where the substrate was placed for CNTs formation. In CNTs growth process, first of all, argon gas was flushed into the furnace tube at a flowrate of 100 sccm and waited unless the furnace temperature reaches 800°C at a ramping rate of 15°C/min. At this point, the argon flowrate was lowered to 40 sccm and carbon precursor and hydrogen gas were added to the process at flowrates of 60 sccm and 100 sccm, respectively as explained in the Fig. 1.

After one hour of CVD operation, the ethylene and hydrogen supplies to the reactor were stopped and the furnace tube was allowed to cool-down to the ambient temperature by passing argon gas at a flowrate of 100 sccm. The silicon substrate, implanted with MWCNTs, was stored in a moisture free glass container. A similar procedure was repeated to produced MWCNTs with ferrocene weights of 0.125, 0.15, 0.175 and 0.2 g.

The morphology, diameter, thickness and crystallinity of the as-grown MWCNTs were elaborated via transmission electron microscopy, Raman spectroscopy and thermogravimetric analysis. The results have been presented and discussed intensively in the next sections.

3. Results and discussion

In the presented work, the formation of vertically aligned MWCNTs was confirmed by generating the TEM micrographs of the as-grown samples. The TEM technique is important in measuring the inner and outer diameters, inner-layer spacing and number of layers in a CNT. The TEM images, obtained at high resolution, were analyzed further for inter-shell spacing of the MWCNTs. In these investigations, the inner-shell spacing was ranging from 0.350 to 0.355 nm. This range of shell-spacing was somewhat higher when compared with the inter-planar spacing of graphite (0.336 nm) [13]. 0.15 g of ferrocene produced the lowest inner-shell spacing, which was an indication of relatively pure and controlled growth of CNTs. For all other ferrocene weights, the inner-shell spacing was somewhat higher than 0.15 g ferrocene. This increase in inner-shell spacing might be due to graphene sheet curvature modification by the tube diameter and size.

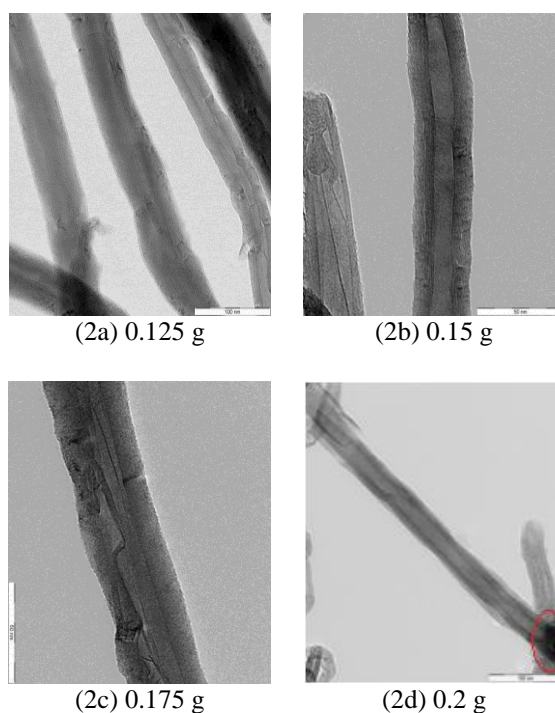


Fig. 2. TEM images of MWCNTs grown with different weights of the catalyst.

As shown in Fig. 2, some of the CNTs grown with 0.2 g of catalyst were found defective and few black spots were also seen in TEM images. These spots were an indication of the presence

of some Fe particles encapsulated by the tube, as shown in Fig. 2d. It reveals that when used catalyst weight crosses 0.15 g, the impurity level also increases. For such high values, all available catalyst particles do not take part in chemical reaction and formation of CNTs, therefore, the unused particles get trapped in tube wall causing defects in CNTs structure. However, very few amorphous carbons were found in CNTs grown with 0.15 g ferrocene which was an evidence of highly crystalline structures of CNTs. It also revealed that average diameter of MWCNTs can be narrowed down and controlled by using optimized weights of the catalyst (0.15 g). Number of walls also correlates with the tube diameter; smaller tube diameter corresponds to small number of walls.

The crystallinity is one of the key parameter for study of CNTs quality in terms of degree of graphitization [13]. A typical Raman spectrum of the MWCNTs grown with 0.125 g ferrocene is shown in Fig. 3. The Raman spectrum shows two band, namely D and G bands. The D-band was due to the disorderliness of the structure and the G-band was due to the graphitic nature of CNTs. In these studies, the D and G bands were found at around 1365-1369 cm^{-1} and 1600-1605 cm^{-1} , respectively. The degree of crystallinity of grown CNTs can be expressed in terms of band intensity ratio (I_D/I_G). The lower values of I_D/I_G ratio correspond to the high degree of crystallinity. The I_D/I_G values for the pure and aligned CNTs should be less than unity. In these studies, the I_D/I_G ratio was found in range 0.851-0.861.

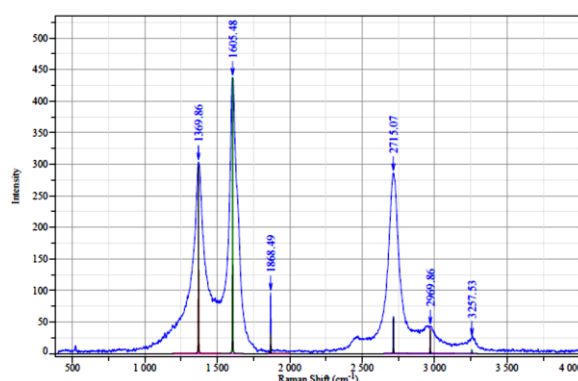


Fig. 3. A typical Raman spectrum of MWCNTs grown with 0.125 g ferrocene.

The lowest I_D/I_G values were noticed with 0.15 g ferrocene as expressed in Table 1. It reveals that increase in catalyst weight results in highly pure CNTs but up to certain limit, because further increase in weight causes the high value of I_D/I_G which indicates the low degree of crystallinity. Some studies also show the evidence that low degree of graphitization obtained due to increase in catalyst weight ratio [10-16]. Basaev [12] also indicated in his studies that the degradation of quality of growing nanotubes increases with an increase in ferrocene concentration. Lim et al. [14] also reported similar results with highest degree of crystallinity (0.48) when 0.1 g ferrocene was used rather than 0.2 g. In their studies, they also varied the reaction temperature but in presented research work, the reaction temperature was kept constant at 850°C.

Table 1. Data extracted from Raman spectra of as-grown MWCNTs.

| Ferrocene (g) | Wave number (cm^{-1}) | | I_D/I_G ratio |
|---------------|----------------------------------|---------|-----------------|
| | D band | G band | |
| 0.1 | 1369.86 | 1605.48 | 0.853 |
| 0.125 | 1368.01 | 1605.63 | 0.852 |
| 0.15 | 1365.18 | 1603.70 | 0.851 |
| 0.175 | 1367.12 | 1600 | 0.854 |
| 0.20 | 1369.09 | 1590.12 | 0.861 |

Apart from TEM and Raman spectroscopy, TGA tests were also carried out for the study of the purity of the CNTs. TGA is a very simple and accurate analytical technique which can deliver the results very quickly. The purity of the CNTs is often considered as a vital factor for structural and chemical characterization. This is because most normal strategies for CNTs growth bring about is formless carbon being available on the CNT surface and remaining metal catalyst nano-particles installed inside the empty inner part. The thermal stability and purity of the nanomaterials may be accessed by generating their TGA profiles. Fig. 4 show a typical TGA thermogram of the as-grown MWCNTs. The significant parameters, investigated from the weight reduction bends of the nanotubes, are the initial and oxidation temperatures, as expressed in Table 2.

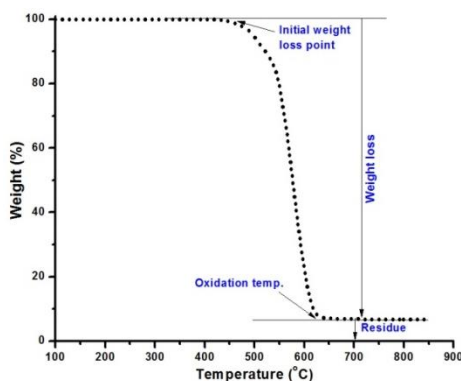


Fig. 4. A typical TGA thermogram of MWCNTs grown with 0.15 g ferrocene

The initial temperature on the thermogram is characterized as the point where the sample starts to deteriorate. The oxidation temperature is characterized by the point on the thermogram where no further weight loss takes place. It is a good indicator of thermal stability of the sample under investigation. Lima et al. [15] reported that the decomposition of the amorphous carbon happens in the temperature range of 200 to 400°C. Similarly, Dunens et al. [16] observed that amorphous carbon contaminates had lower oxidation temperatures (200 to 300°C). Same results were obtained in CNTs samples synthesized with different constant weights of the ferrocene as shown in Table 2. However, in case of 0.15 g ferrocene, a negligible quantity of the amorphous carbon was observed in the product. Nevertheless, the oxidation temperature for MWCNTs varies from material to material, but typically ranges from 400 to 650°C [16].

Table 2. Data extracted from TGA thermograms of as-grown MWCNTs

| Ferrocene (g) | Initial weight loss temperature(°C) | Oxidation temperature(°C) |
|---------------|-------------------------------------|---------------------------|
| 0.1 | 200 | 590 |
| 0.125 | 250 | 600 |
| 0.15 | 500 | 630 |
| 0.175 | 250 | 615 |
| 0.2 | 300 | 610 |

Ravindra et al. [17] noted 550°C oxidation temperature with ferrocene as a catalyst. They also found relatively high purity in the grown sample. TGA of the as grown samples was clearly indicating the presence of negligible amount of the amorphous carbon and iron content. In the present case, similar kinds of the results were obtained in case of 0.15 g ferrocene. For TGA, the CNTs were heated in the oxygen rich atmosphere at temperature ranging from 30 to 800°C with ramping of 10 min/°C. As it was seen that in case of 0.15 g ferrocene, the amorphous carbon disappeared at temperature around 500°C and oxidation temperature was much higher as compared

to other samples. It was an indication of relatively pure MWCNTs production [18, 19]. In addition, the temperature of MWCNTs removal was found in the range of 590 to 620°C.

4. Conclusions

In this study, MWCNTs were synthesized using a FCCVD technique at a fixed process temperature of 800°C. The as-grown MWCNTs were accessed for their structural properties with TEM, TGA and Raman spectroscopy techniques. This study confirmed the growth of relatively pure MWCNTs, having graphitic structures, with a ferrocene weight of 0.15 g. The I_D/I_G ratio was decreased with increasing ferrocene weight. The lowest I_D/I_G ratio was noticed with 0.15 g. For relatively large amounts of the ferrocene, some of the grown CNTs were found defective, where one side of the tube surface was very smooth whilst the waves like structures were evident on the other side of the surface. These studies also revealed that average diameter of MWCNTs can be narrowed down and controlled by using optimized weights of the catalyst (0.15 g). Number of walls also correlates with the tube diameter; smaller tube diameter corresponds to low number of walls. The smallest inner-shell spacing was found around 0.350 nm which was closer to graphite inter-planar spacing (0.336 nm). TGA of the grown CNTs also confirmed the formation of relatively pure and aligned MWCNTs especially for 0.15 g ferrocene with oxidation temperature of 620°C.

Acknowledgments

Authors would like to extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for funding this work through Research Group No. RG1438-012.

References

- [1] S. Shukrullah, N. M. Mohamed, M. S. Shaharun, M. Y. Naz, Trends Appl. Sci. Res. **9**(3), 121 (2014).
- [2] K. S. Triantafyllidis, S. A. Karakoulia, D. Gournis, A. Delimitis, L. Nalbandian, E. E. Maccallini, Micropor. Mesopor. Mater. **110**, 128 (2008).
- [3] K. B. Kouravelou, S. V. Sotirchos, X. E. Verykios, Surf. Coat. Technol. **201**, 9226 (2007).
- [4] M. Schneider, M. Weiser, S. Dörfler, H. Althues, S. Kaskel, A. Michaelis, Surf. Eng. **28**(6), 435 (2012,)
- [5] S. Iijima, Nature **354**, 56 (1991).
- [6] M. Schneider, M. Weiser, S. Dörfler, H. Althues, S. Kaskel, A. Michaelis, Surf. Eng. **29**(6), 427 (2013).
- [7] R. Andrews, D. Jacques, A. M. Rao, F. Derbyshire, D. Qian, X. Fan, E. X. Dickey, J. Chen, Chem. Phys. Lett. **303**, 467 (1999).
- [8] Z. P. Huang, J. W. Xu, Z. F. Ren, J. H. Wang, M. P. Siegal, P. N. Provencio, Appl. Phys. Lett. **73**, 3845 (1998).
- [9] A. Khettaiche, T. Staedler, M. Z. Touhami, H. Weiß, X. Jiang, Surf. Eng. **29**(6), 474 (2013).
- [10] J. M. Bonard, Th. Stöckli, O. Noury, A. Chatelain, Appl. Phys. Lett. **78**, 2775 (2001).
- [11] Y. M. Shin, S. Y. Jeong, H. J. Jeong, S. J. Eum, C.W. Yang, C.Y. Park, Y. H. Lee, J. Cryst. Growth **271**, 81 (2004).
- [12] A. S. Basaev, Semiconductors **46**(13), 1613 (2012).
- [13] A. Aqel, M. M. Kholoud, Abou El-Nour, Reda A. A. Ammar, Abdulrahman Al Warthan: Arab. J. Chem. **5**(1), 1 (2012).
- [14] S.Y. Lim, M. M. Norani, S. Suriati, AIP Conf. Proc. **1502**, 242 (2012).
- [15] A. Lima, A. Musumeci, H. W. Liu, E. Waclawik, G. Silva, J. Therm. Anal. Calorim. **97**(1), 257 (2009).

- [16] O. M. Dunens, K. J. MacKenzie, A. J. Harris, *Environ. Sci. Technol.* **43**(20), 7889 (2009).
- [17] R. Ravindra, B. R. Bhat, *J. Metals, Mater. Minerals* **21**(2), 95 (2011).
- [18] S. Shukrullah, N. M. Mohamed, M. S. Shaharun, M. Y. Naz, *Main Group. Chem.* **13**(3), 251 (2014).
- [19] B. Liu, L. R. Liu, X. J. Liu, *Surf. Eng.* **29**(7), 507 (2013).