Synthesis of aligned carbon nanotubes on double-sided metallic substrate by chemical vapor deposition

*Huan Wang, Jiyun Feng, Xijun Hu and Ka Ming Ng**

Department of Chemical Engineering
Hong Kong University of Science and Technology
Clear Water Bay, Hong Kong

Abstract

Aligned multi-walled carbon nanotubes (MWCNTs) were grown on both sides of a metallic or metal-coated substrate by water vapor-assisted chemical vapor deposition (CVD). Aligned CNT films of thickness ranging from 1 μm to over 100 μm were obtained. By manipulating various operating factors – position of substrate in the reactor, amount of water vapor, amount of catalyst, reactor temperature, and growth time, the morphology and thickness of these carbon nanotube films could be adjusted.

Keywords: Carbon nanotubes; Chemical vapor deposition; Thermal interface material

1. Introduction

With the continually diminishing size of electronic devices, the heat generated by such devices can cause structural damage due to over-heating.[1] It is highly desirable to design and fabricate thermal interface materials (TIMs) with exceptionally high thermal conductivity for transporting heat efficiently from electronic components to a heat sink.[2, 3]

One of such materials is carbon nanotube (CNT) which has shown unique and attractive mechanical,[4] electrical,[5] and thermal properties[6] since its discovery by Iijima.[7] Several studies have revealed that CNTs have unusually high thermal conductivity in their axial direction. For example, molecular dynamic simulations of a single-walled nanotube (SWCNT) by Berber et al. indicated that the thermal conductivity of the SWCNT can be as high as 6600 $Wm^{-1}K^{-1}$ at room temperature.[1] Kim et al.[8] measured the thermal conductivity of a single multi-walled carbon nanotube (MWCNT) using a micro-fabricated suspended device, and their measurement showed that the thermal conductivity was larger than 3000 $Wm^{-1}K^{-1}$ at room temperature. Realizing that CNTs are good TIM candidates, efforts have been made on the use of dispersed CNTs as thermal conducting fillers in polymer composites. For example, Liu et al.[9] reported a thermal conductivity ranging from 1.1 to 1.9 $Wm^{-1}K^{-1}$ as the CNT loading in a polymer composite increased from nil to 3.8 wt%. The below expectation enhancement could be attributed to the random orientation of CNTs in the polymer matrix and the existence of interface thermal resistances between the actual heat source/ sink and CNTs. To avoid these problems, Huang et al.[10] grew aligned CNTs on a silicon substrate and then fabricated a polymer composite film with such protruded, aligned CNTs running from one side of the TIM device to the other. An enhancement in thermal conductivity from 0.56 $Wm^{-1}K^{-1}$ for the pure elastomer matrix to 1.21 $Wm^{-1}K^{-1}$ for the same polymer embedded with a 0.4 vol % aligned CNT array was obtained. Despite the fact that aligned CNTs should have formed ideal thermal conducting paths through the composite structure, this enhancement was still far below expectation.

In this study, the use of aligned CNTs as TIM was further explored in order to take advantage of the exceptional thermal conductivity of CNTs. Instead of growing the CNTs on silicon, they were grown on a metal surface by water vapor-assisted chemical vapor deposition (CVD). Figure 1 shows the proposed multilayer composite structure, with two films of aligned CNTs grown on the opposite faces of a suspended substrate. Provided that the substrate is sufficiently thin and highly conductive, this double-sided design for a TIM device has the distinct advantage that it can fit between the heat source and heat sink to minimize the resistance to heat flow due to the presence of an air gap.

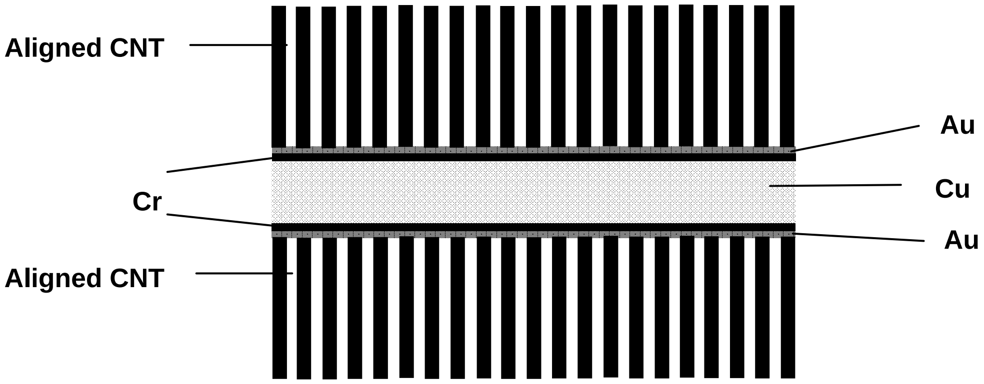


Figure 1. The proposed structure of thermal interface material.

In addition, operating factors that can significantly influence the growth of CNTs on such a double-sided metal substrate were investigated in detail. It was very difficult to characterize samples with ductile substrate such as thin metal plate or foil by scanning electron microscopy (SEM). Therefore, optimization of the operating factors was accomplished by using silicon wafer as substrate. The effect of water vapor was included because it was known to significantly influence the growth of aligned CNTs. For example, Hata et al.[11] synthesized aligned single-walled carbon nanotubes on silicon wafer with a height of up to 2.5 mm in the presence of water vapor.

2. Experimental

Materials

The carbon source was industrial grade ethylene and the gaseous phase was made up of industrial grade argon and hydrogen for the synthesis of CNTs. The catalyst used was ferrocene purchased from Aldrich. Double-sided polished P-type silicon wafer with a thickness of 400 μm, copper plate with a thickness of 0.3 mm, and copper foil with a thickness of 125 μm and 7 μm were used as substrates for aligned CNT growth.

CVD reactor operations

CVD synthesis of aligned CNTs was performed in a horizontal quartz tube (2.5 cm in diameter and 70 cm in length) housed in a single-zone furnace (Carbolite, UK) as shown in Figure 2. A quartz boat (2.2 cm wide and 10 cm long) was placed in the middle of the quartz tube, where the temperature was the highest along the whole tube. The substrates used in this study were placed in the middle of the boat except otherwise specified. It has been known that ferrocene decomposition forms iron particles as the catalysts for aligned CNTs growth. With a sublimation temperature of about 175 ºC, it was stationed at the inlet of the quartz tube where the temperature was above the sublimation temperature of ferrocene (about 200 ºC).

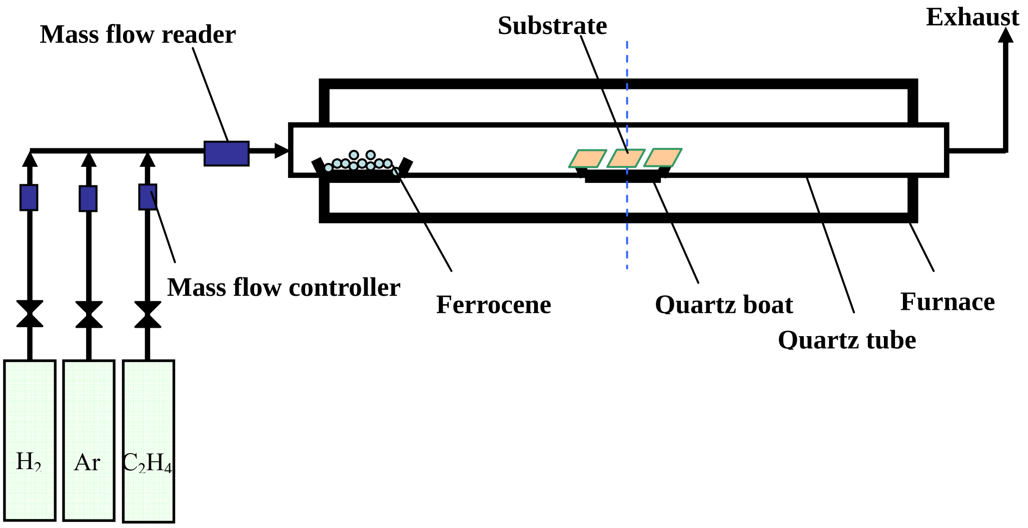


Figure 2. Experimental setup for aligned CNT synthesis by chemical vapor deposition.

Each reaction run started with the CVD reactor at room temperature. A specified amount of double deionized (DDI) water was injected using a micro-syringe under the quartz boat holding the ferrocene. Then, flow of argon was initiated while heating up the CVD reactor. Typically 20 min was required to reach the desirable reactor temperature and at that point ethylene and hydrogen were introduced. CVD growth of aligned CNTs was carried out at about 725~ 800 ºC with the flow rates of ethylene, hydrogen and argon set at 40, 16 and 200 sccm, respectively. The flow of ethylene/hydrogen/argon mixture was maintained for the entire growth period ranging from 10 to 60 min. After the reaction, the furnace was allowed to cool down to room temperature while maintaining the flow of argon.

Preparation of substrates

Different metals including silver, copper, and gold were used as substrates for aligned CNTs growth. Gold was found to be the best substrate. However, copper is much cheaper and has a higher thermal conductivity (388 $Wm^{-1}K^{-1}$) than that of gold (315 $Wm^{-1}K^{-1}$). For these reasons, a thin film of gold was sputtered on the surface of the copper substrate. It is known that the adhesion of gold on copper is not sufficiently strong. By trial and error, it was found that good adhesion could be achieved with chromium between gold and copper. Thus, chromium films of thickness 12 nm and gold films of thickness 20 nm were deposited on both sides of the basis substrates using an ARC-12M sputtering machine.

Characterization of aligned CNT on metal-coated substrate

The aligned CNTs synthesized by CVD were characterized by SEM (JEOL-JSM 6700F operating at an accelerating voltage of 5 kV). For the ductility of copper, attempts to prepare SEM samples with copper substrates by cutting were not successful. Silicon wafer, which can easily be cut by a quartz knife, was used to replace the copper substrate to observe cross section of the aligned CNT samples by SEM. In addition, the detailed structure of the CNTs was determined by high-resolution transmission electron microscopy (HRTEM) using JEOL-2010 operating at an accelerating voltage of 200 kV. TEM samples were prepared by dispersing the CNTs in ethanol with mild sonication for 30 min, and then air-drying a drop of the solution on a copper grid coated with a holey carbon film. X-ray diffraction patterns of samples were recorded with a new powder x-ray diffraction system (Model X'pert, Panalytical). This provides a simple way to characterize the alignment of as-grown CNTs without damaging their original orientation. The XRD pattern was shown in Figure 3. The well resolved XRD peaks of aligned CNTs sample which can be assigned to (002), (100), and (110) diffractions, indicating that such a material has well alignment. Raman spectra were recorded with a RM3000 (Renishaw) in backscattering mode using an Ar+ laser excitation (514.5 nm, 5mW; resolution 1 cm^{-1}) in Figure 4. The Raman spectra, obtained in the range 800- 2000 cm^{-1}, shows a strong characteristic peak is located at 1590 cm^{-1}, corresponding to the C-C optical mode vibration along the graphite sheet. The peak in at 1343 cm^{-1} is a Raman scattering peak due to defects in the mixture of amorphous carbon and CNTs. In this work, Raman spectroscopy was mainly used to verify the multi-walled nature of the CNTs and the overall homogeneity of the sample.

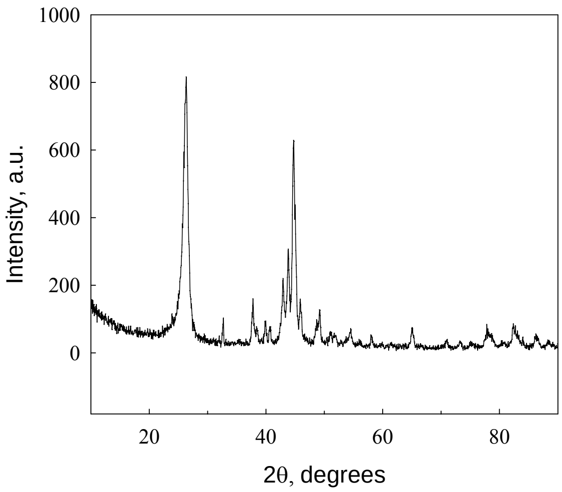


Figure 3. XRD pattern of aligned CNTs.

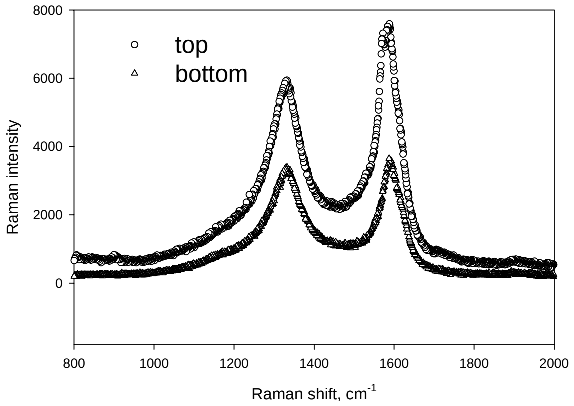


Figure 4. Raman spectra of aligned CNTs.

Measurement of thermal resistance

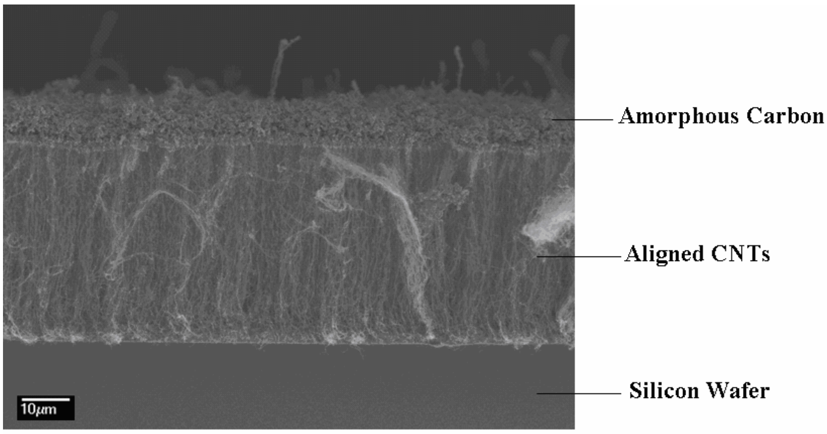
The thermal resistance of the TIM sample with metal substrate was evaluated using a steady state measurement system which was designed in accordance with ASTM D5470. The sample pressed between two copper blocks was subject to a constant heat flow rate of Q generated by resistive cartridges heaters embedded in one copper block while the counter block was cooled with circulating water. A load cell was used to control the sample contact pressure to 0.3 MPa. Class A platinum resistance temperature detectors (RTD) with an accuracy of 0.3 ^{o}C were used to measure the temperature at various points along the two copper blocks. Details of the design, operations, and calculations can be found in Zhang et al.[12]

Results and discussion

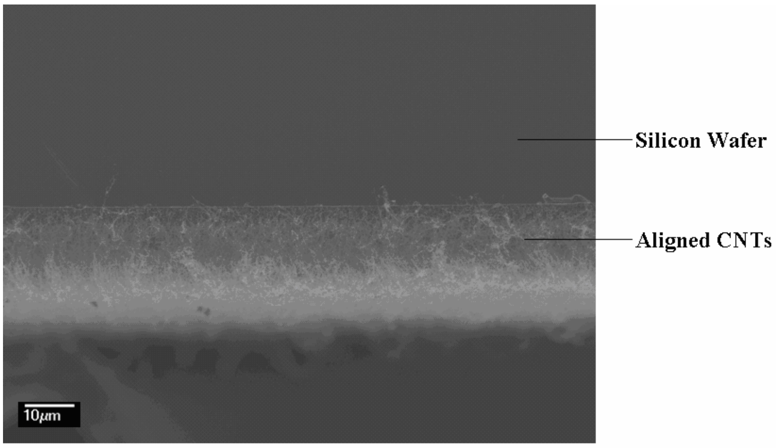
Effect of position of the substrate in the quartz boat

The first issue addressed was the effect of the position of a substrate in the quartz boat. Note that the substrate was simply laid flat on the boat in all cases. Figures 5(a)-(b), (c)-(d) and (e)-(f) show the photomicrographs of the top and bottom of the substrates placed in three different positions – front, middle and rear of the quartz boat, respectively. When the substrate was placed in the front of the quartz boat, amorphous carbon was found on top of the aligned CNTs layer (Figure 5(a)). Normally, the water vapor in the CVD system which could have removed amorphous carbon produced by pyrolysis was not effective when the substrate was in the front of the quartz boat. With the substrate in the middle, the morphology of aligned CNTs was good (Figures 5(c)-(d)). The CNT layer thickness was measured at three positions as indicated by A, B, and C in Figure 5(c) and an average thickness was obtained from these three values. Under these conditions, the thicknesses of the CNT films were almost the same on both sides of the substrate at about 50 µm. When the substrate was placed on the rear of the quartz boat, aligned CNTs could grow on both sides of the substrate. However because the substrate was far away from the catalyst, the aligned CNT layer on the bottom face of substrate (about 10 µm) was thinner than that on the top (about 25 µm) (Figures 5(e)-(f)). Based on these results, all substrates were placed in the middle of the quartz boat in the subsequent experiments.

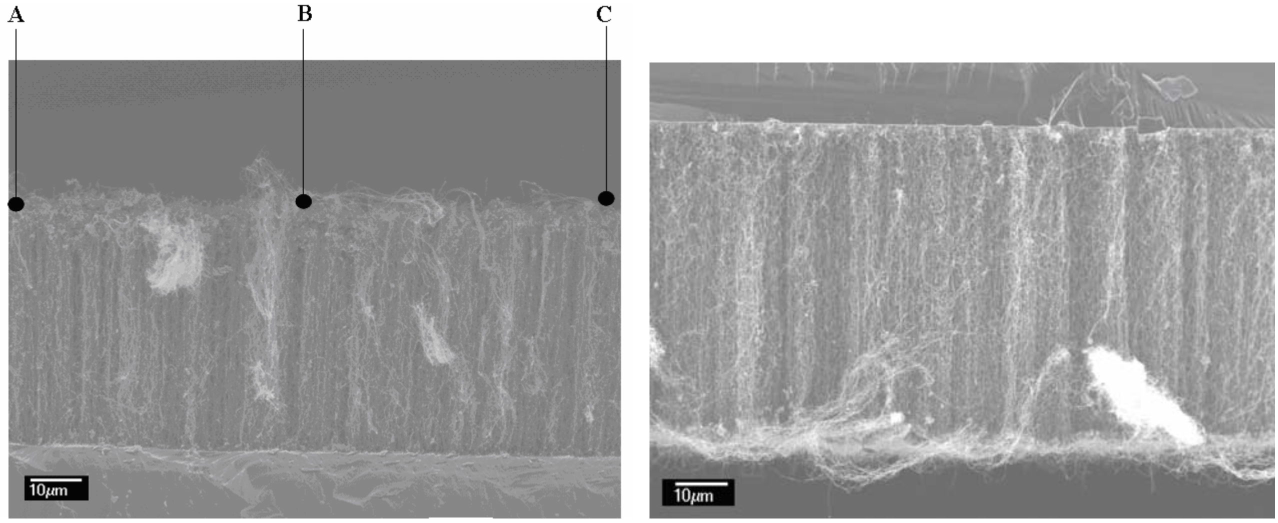
a) Position: front (top)



b) Position: front (bottom)



c) Position: middle (top) d) Position: middle (bottom)



e) Position: rear (top) f) Position: rear (bottom)

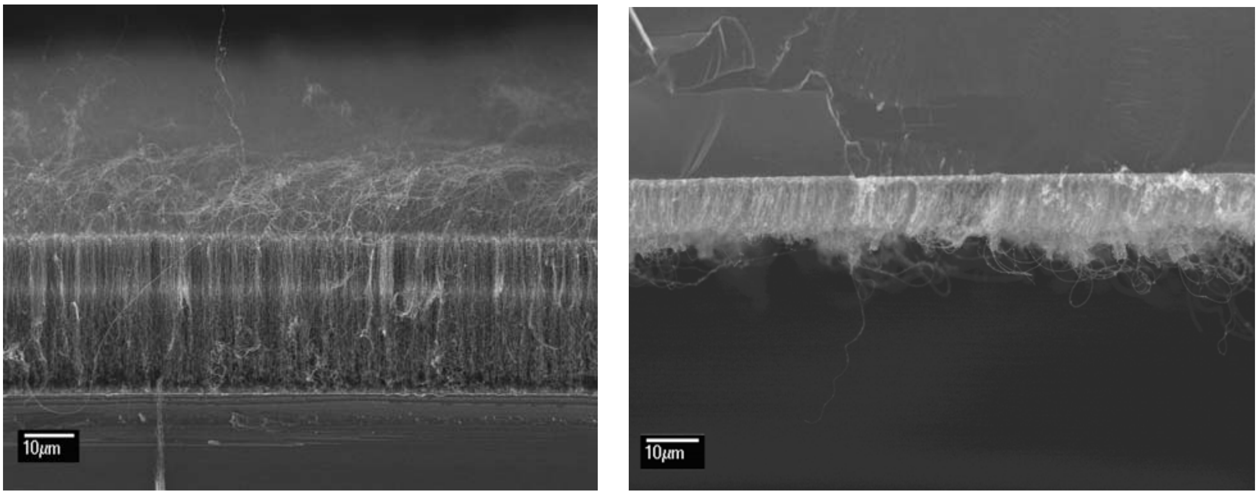
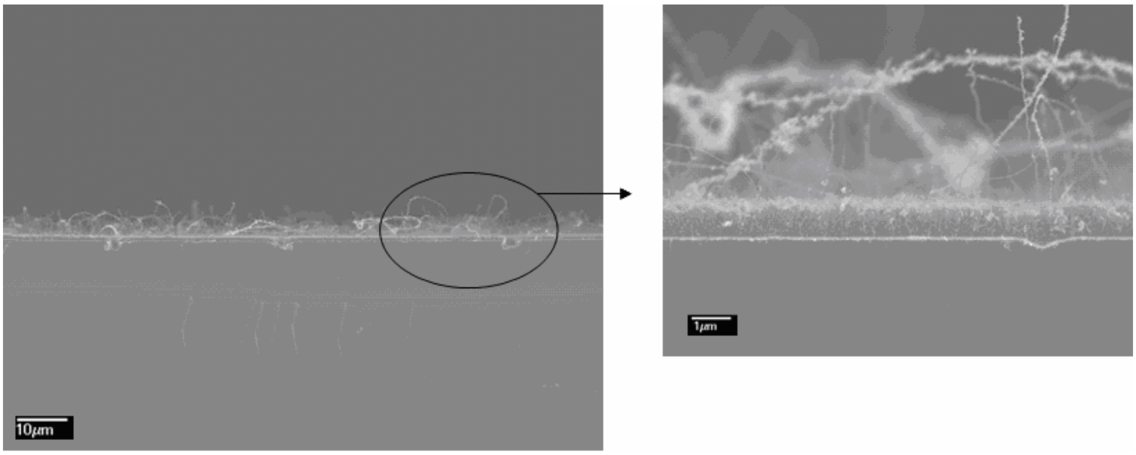


Figure 5. SEM images of aligned CNT layer with the substrate placed at various positions of the quartz boat: (a)-(b) front; (c)-(d) middle; (e)-(f) rear of the quartz boat. (Volume of water injected: 0.3 mL, catalyst: 100 mg ferrocene, growth temperature: 750 °C, growth time: 20 min)

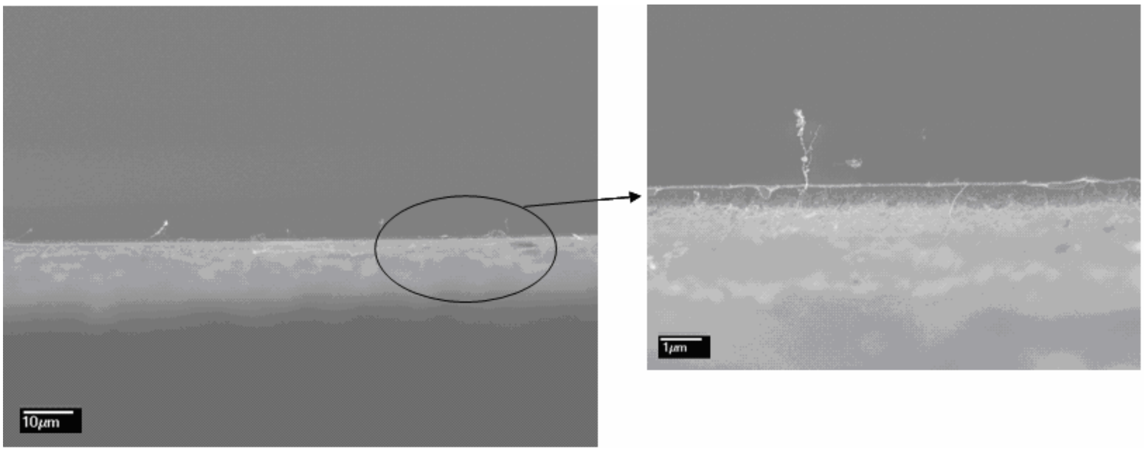
Effect of water vapor

It is well known that water vapor can significantly influence the growth of aligned CNTs on substrates[13]. Figures 6(a)-(l) show CNT layers on the top and bottom surfaces of the substrate when different volumes of water were injected into the quartz tube. Figures 6(a) and (b) show that relatively thin CNT layers (top: 1 μm, bottom: 1 μm) were synthesized when no water was injected into the quartz tube. Much longer and denser aligned CNTs were obtained with the injection of water. The relationship between the thickness of CNTs film and the increasing volume of water is shown in Figure 7. Figures 6(c)-(l) are the corresponding photomicrographs.

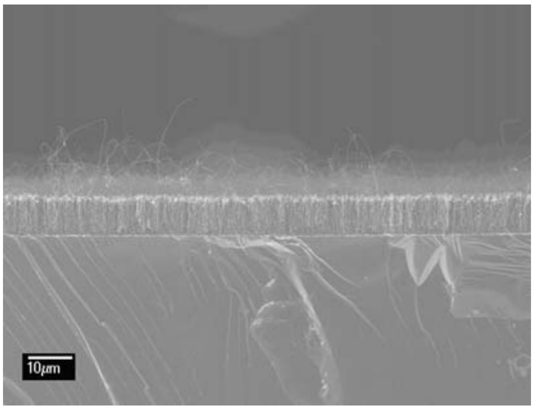
a) Volume of water: 0.1 ml (top)



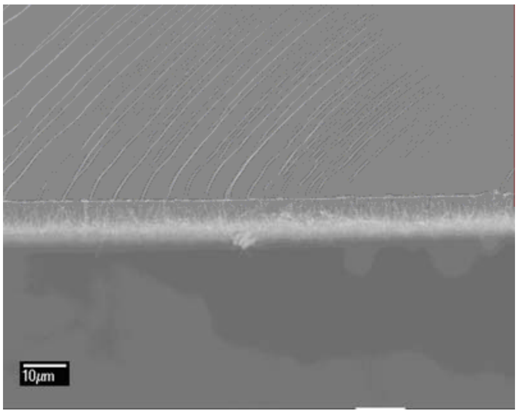
b) Volume of water: 0.1 ml (bottom)



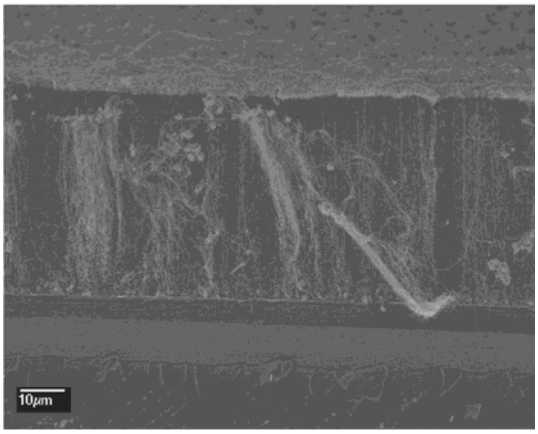
c) Volume of water: 0.2 ml (top)



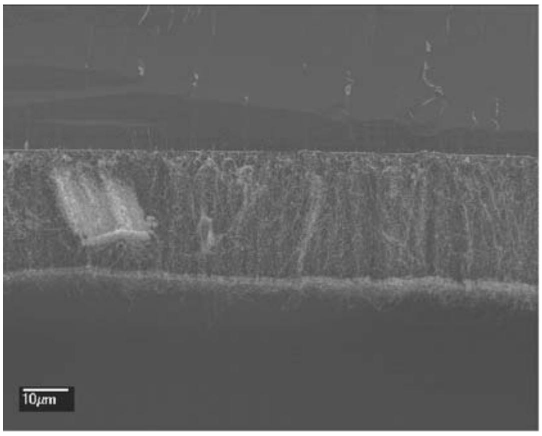
d) Volume of water: 0.2 ml (bottom)



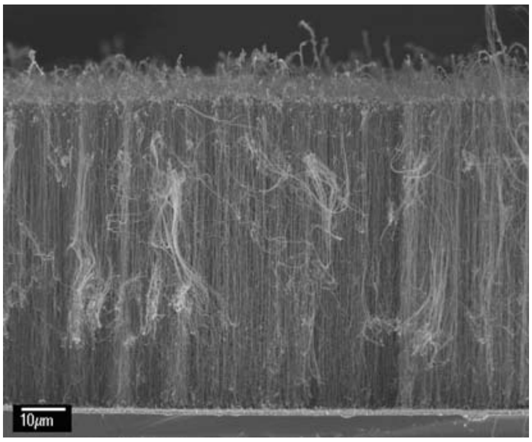
e) Volume of water: 0.3 ml (top)



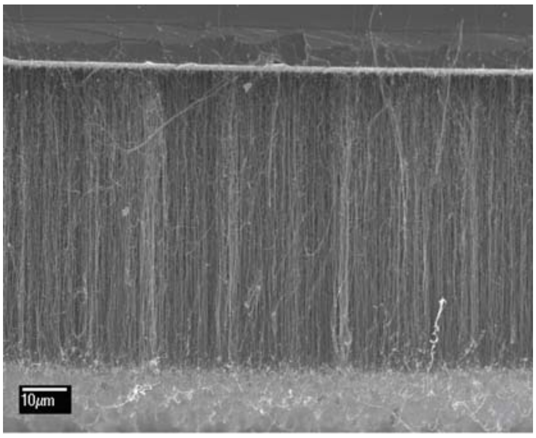
f) Volume of water: 0.3 ml (bottom)

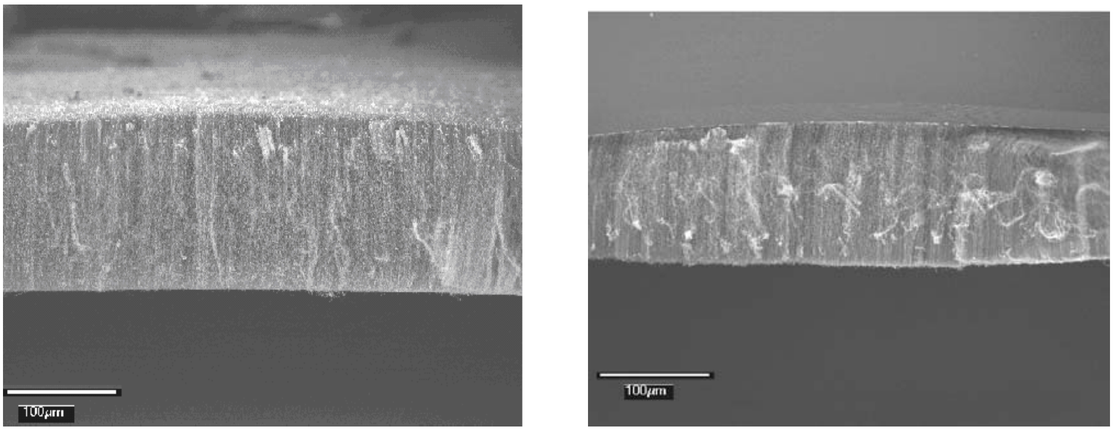


g) Volume of water: 0.4 ml (top)



h) Volume of water: 0.4 ml (bottom)




i) Volume of water: 0.6 ml (top) **j) Volume of water: 0.6 ml (bottom)**

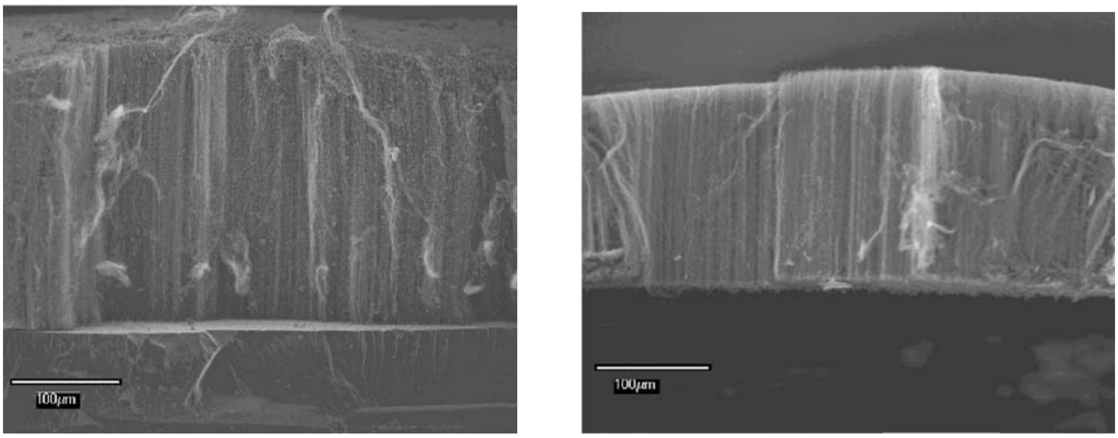

k) Volume of water: 0.8 ml (top) **l) Volume of water: 0.8 ml (bottom)**

Figure 6. SEM images of aligned CNT layer with various amounts of water injected: (a)-(b) nil; (c)-(d) 0.1 mL; (e)-(f) 0.2 mL; (g)-(h) 0.3 mL; (i)-(j) 0.4 mL; (k)-(l) 0.6 mL. (Catalyst: 100 mg ferrocene, growth temperature: 750 °C, growth time: 20 min)

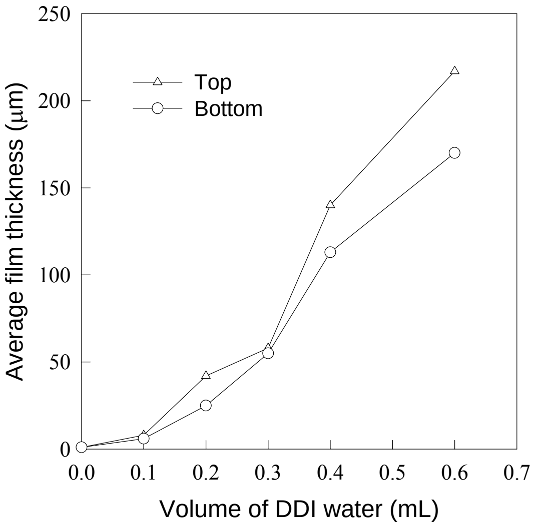
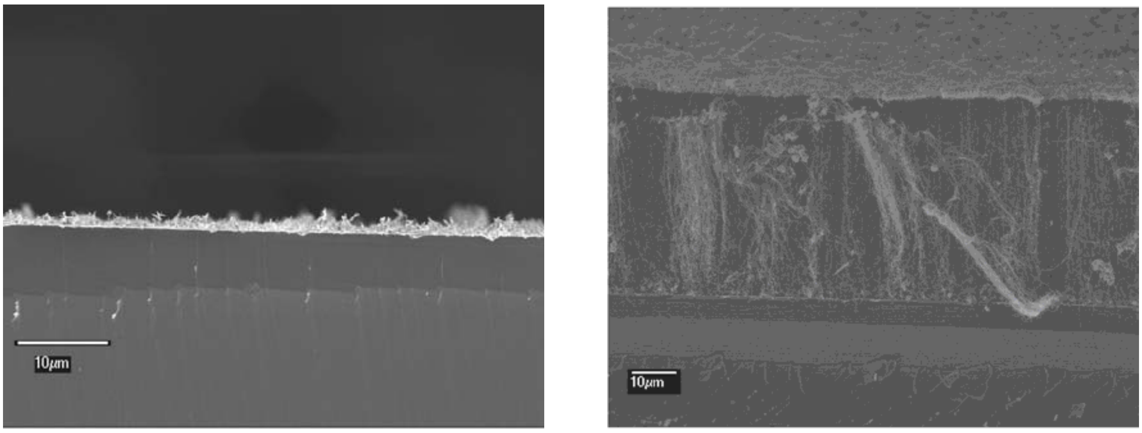


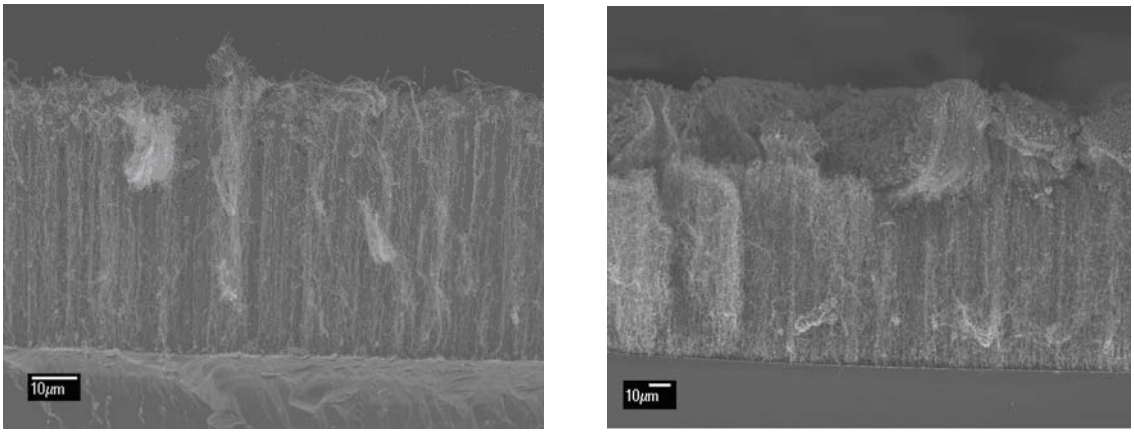
Figure 7. Effect of volume of water injected on the CNT film thickness.

Effect of the weight of ferrocene catalyst

Apart from the position of substrate in quartz boat and the amount of water injected into the quartz tube, the amount of ferrocene catalyst can also render a significant impact on the morphology and thickness of the CNT layer. Figures 8(a)-(d) depict SEM images of CNTs on the top face of substrate produced with different amounts of catalyst ranging from 30 to 200 mg. Figure 8(a) shows that few aligned CNTs could be found on the substrate when only 30 mg of ferrocene was used. Figure 9 shows the dependence of CNT layer thickness on the weight of ferrocene. Thicker CNT films could be synthesized by using a larger amount of ferrocene.


a) m= 30 mg

b) m= 100 mg



c) m= 150 mg

d) m= 200mg

Figure 8. SEM images of aligned CNT layer on top of the substrate for various amounts of ferrocene: (a) 30 mg; (b) 100 mg; (c) 150 mg; (d) 200 mg. (Volume of water injected: 0.2 mL, growth temperature: 750 ^oC, growth time: 20 min)

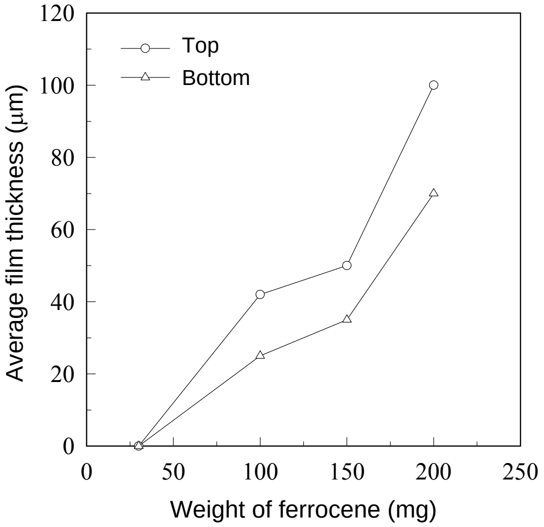
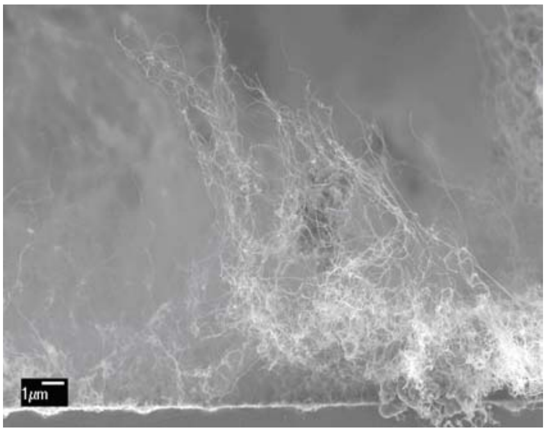


Figure 9. Effect of ferrocene amount on the CNT film thickness.

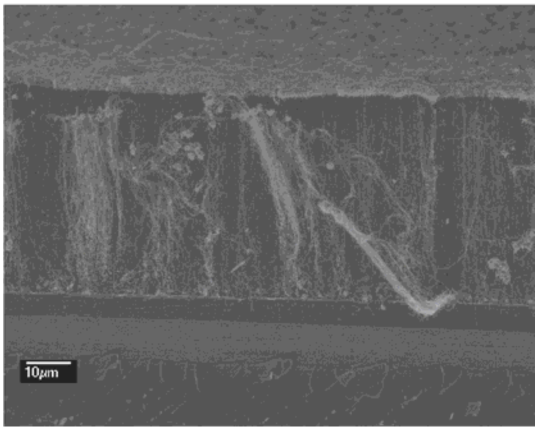
Effect of growth temperature

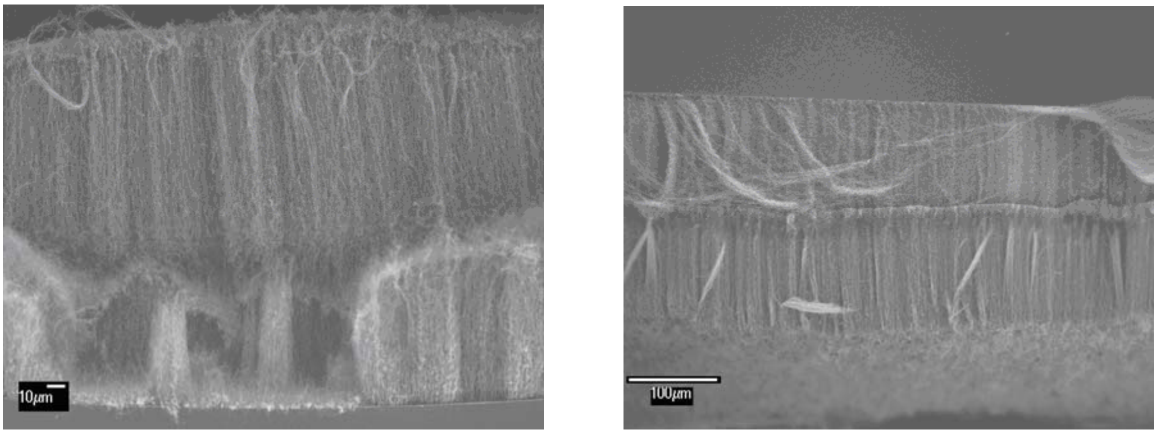
The SEM images of CNTs grown on the top face of the substrate at increasing growth temperatures are shown in Figure 10. The relationship between the thickness of CNT layer and these growth temperatures is shown in Figure 11. At 725 °C, the temperature was not sufficiently high for having catalyst deposited on the substrate and no aligned CNTs were found (Figure 10(a)). The decomposition of ferrocene to Fe catalyst particles was possible at a higher temperature and an aligned CNT layer could be synthesized at 750 °C. This experimental result is in agreement with those of Hata et al.[11] who reported water-assisted synthesis of single-walled carbon nanotubes on silicon wafer at 750 °C by CVD. At a temperature of 800 °C, the aligned CNT film was 220 μm and 125 μm on the top and bottom surfaces of the substrate, respectively. However, the CNT film was actually made up of two layers with one on top of the other at the higher growth temperatures (Figures 10(c), (d)). Zhang et al.[14] and Zhu et al.[15] reported similar observations. The mechanism for the formation of these multiple layer stacks was discussed by Zhu et al.[15] They suggested that the interfaces between the aligned CNT and catalyst particles on the substrate were etched away by water vapor. In the presence of ethylene, new CNTs grew from the original catalyst particles to form a new layer of CNTs. It is unclear whether the boundary between two layers might present additional thermal resistance because one layer could be readily peeled away from the other.[15]

a) T= 725 °C



b) T= 750 °C





c) T= 775 ^{o}C **d) T= 800 ^{o}C**

Figure 10. SEM images of aligned CNT layer on top of the substrate grown at different temperatures: (a) 725 °C; (b) 750 °C; (c) 775 °C; (d) 800 °C. (Volume of water injected: 0.2 ml, catalyst: 100 mg, growth time: 20 min)

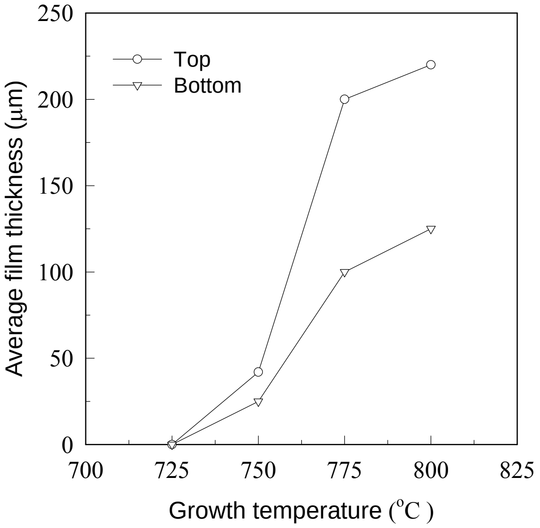
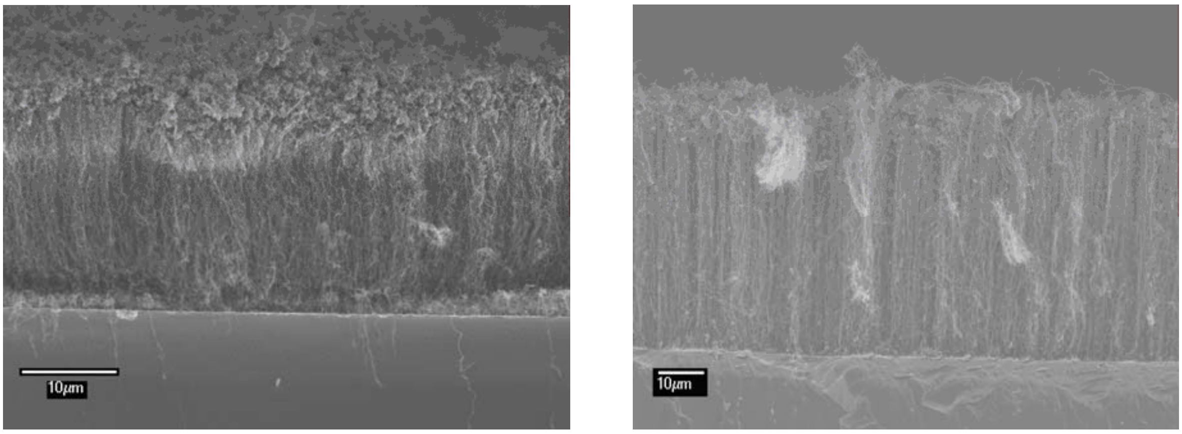


Figure 11. Effect of growth temperature on the thickness of aligned CNT film.

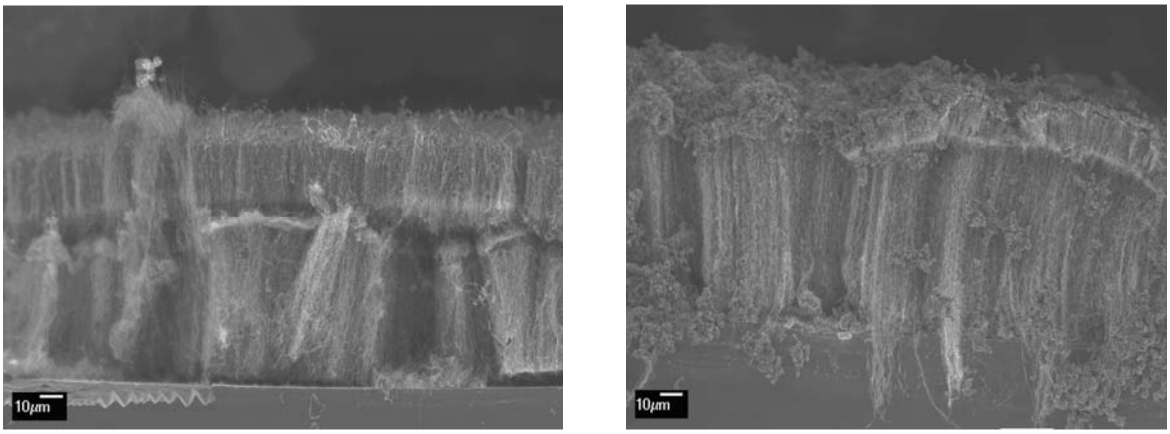
Effect of growth time

Figure 12 shows the SEM images of CNTs grown on the top face of substrate at different growth times. The relationship between the thickness of aligned CNT film and growth time at 750 °C is shown in Figure 13. The thickness of the CNT films on both sides of the substrate stayed relatively constant from 30 min to 60 min. This decreased growth rate could be attributed to the fixed amount of ferrocene and water in the reaction system.



a) t= 10 min

b) t= 20 min



c) t= 30 min

d) t= 60 min

Figure 12. SEM images of aligned CNT layer on top of the substrate for various growth time: (a) 10 min; (b) 20 min; (c) 30 min; (d) 60 min. (Volume of water injected: 0.2 mL, catalyst: 100 mg ferrocene, growth temperature: 750 °C)

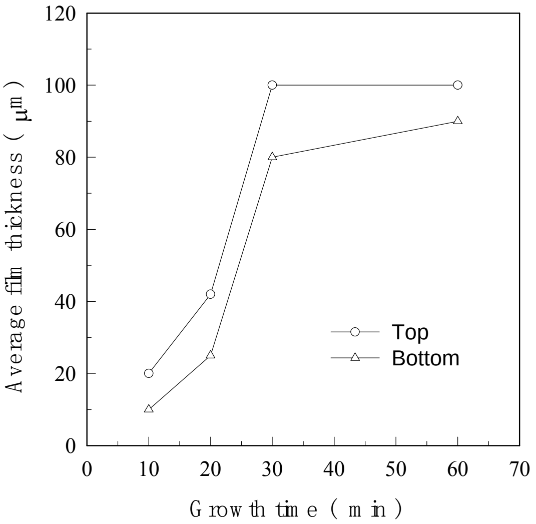
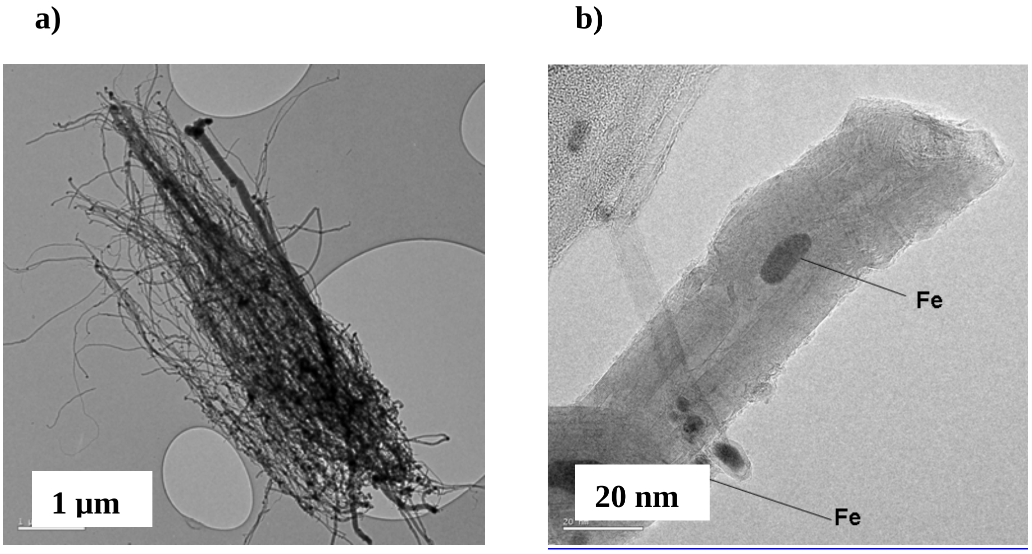


Figure 13. Effect of growth time on thickness of aligned CNTs film.

Detailed structure of aligned CNTs by TEM

The detailed structure of the CNTs was studied by HRTEM (Figure 14). We found that the CNTs were of different sizes but had a similar structure. Figure 14(a) shows a bundle of synthesized aligned CNTs, comprising mainly small carbon nanotubes. Figure 14(b) shows a CNT with trapped Fe catalyst particles. Most of the CNTs had an end closed with a metal particle at the tip (Figures 14(c)). Similar results were reported by Zhang et al.[16] Figure 14(d) shows a particular nanotube with an inner and outer diameter of approximately 8 and 20 nm, respectively, and contained about 25 graphitic layers in each sidewall.



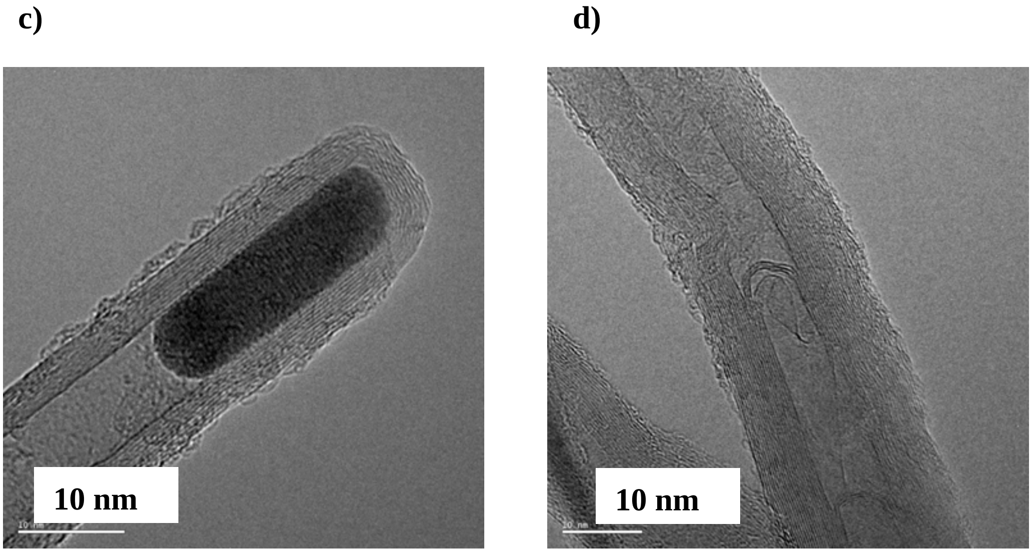


Figure 14. Detailed structure of aligned CNTs by TEM. (a) a bundle of CNTs; (b) a CNT with trapped Fe catalyst particles (indicated by arrows) (c) a CNT with a metal particle at its tip and (d) a typical CNT with bamboo structure. (Volume of water injected: 0.3 mL. catalyst: 100 mg ferrocene, growth temperature: 750 °C, growth time: 20 min)

Aligned CNTs grown on copper plate and copper foil as TIM

Based on experiments on silicon substrate, the following conditions were used to synthesize 50 μm thick CNT films on both sides of a copper substrate sputtered with Cr and Au: volume of water injected: 0.3 mL, catalyst: 100 mg ferrocene, growth temperature: 750 °C, growth time: 20 min. Figure 15 shows the photographs of copper plate (12.7 mm diameter; 0.3 mm thickness) and copper foil (12.7 mm diameter, 0.007 mm thick; 25.4 mm by 25.4 mm, 0.0125 mm thick) with aligned CNTs grown on both sides. Recall that the average film thickness was about 50 μm under these conditions (Figure 7).

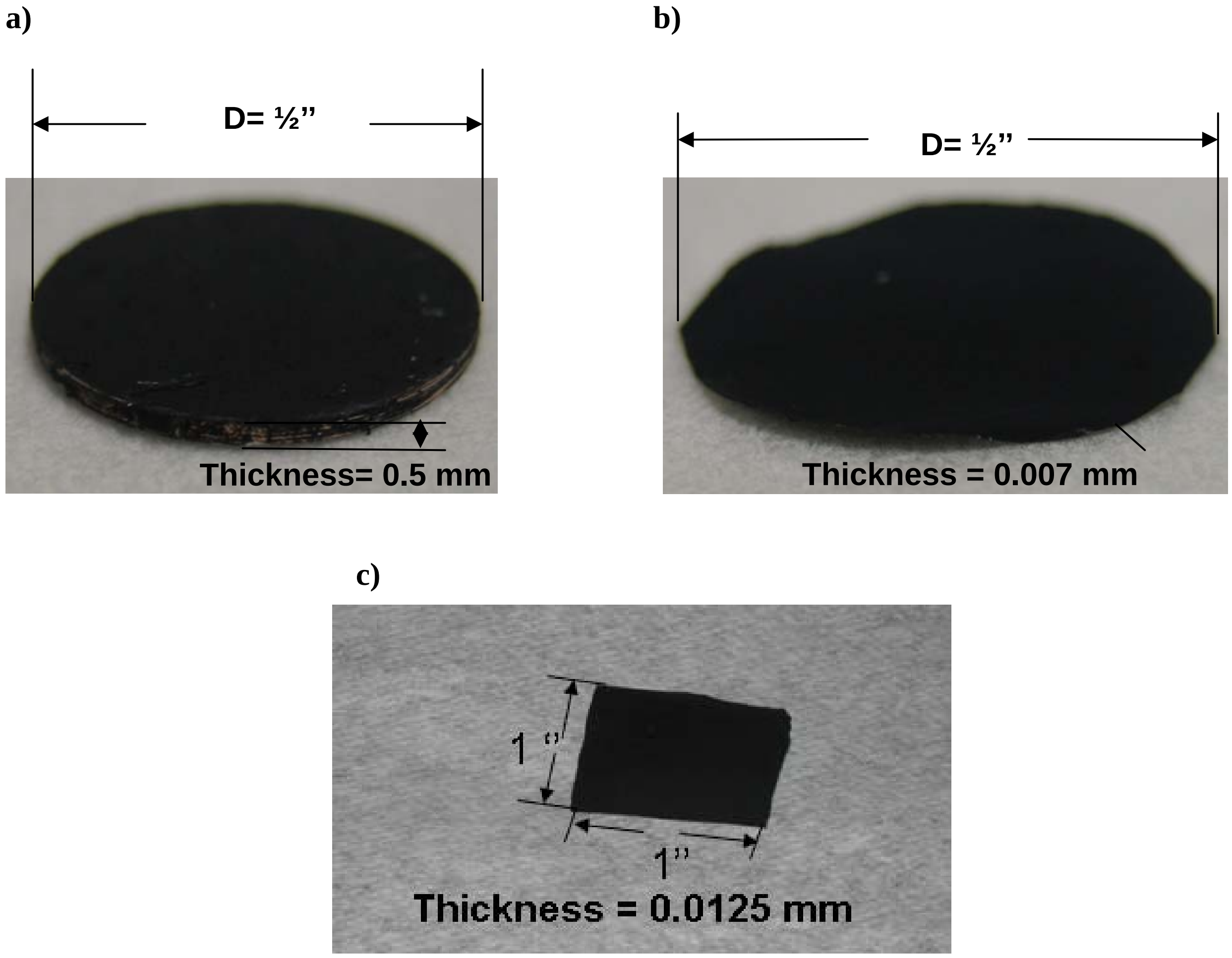


Figure 15. Photos of the aligned CNT TIM: (a) 0.5 mm thick copper plate as substrate, (b) 0.007 mm thick copper foil as substrate, (c) 0.0125 mm thick copper foil as substrate. (Volume of water injected: 0.3 mL, catalyst: 100 mg, growth temperature: 750 °C, growth time: 20 min)

Measurement of thermal resistance

Using the system and calculation procedure developed by Zhang et al.,[12] the thermal resistance of the 12.5 μm copper foil (or a total TIM sample thickness of 112.5 μm) was determined to be 12 mm^2 K/W under an applied contact pressure of 0.3 MPa. This is lower than those reported in the literature[10, 12, 17, 18] (Table 1). For example, the thermal resistance of the aligned CNT composite film synthesized by Huang et al.[10] ranged from 100 to 450 mm^2 K/W as the sample thickness increased from 100 to 500 μm. The thermal resistance of the CNT film synthesized by Xu and Fisher[17] using plasma enhanced CVD was 100 mm^2 K/W under a contact pressure of 0.16 MPa and

23 mm^2 K/W under 0.445 MPa. Our results are comparable to those of Zhang et al.,[12] who reported a thermal resistance of 15 mm^2 K/W with a film thickness Ranged from 30 to 70 μm.

TABLE 1: Thermal performance of different TIMs in the literature

TIM device	Authors	Pressure (MPa)	Thermal resistance (mm^2 K/W)
Aligned carbon nanotube composite film	Huang et al.	3	100~450
CNT by PECVD	Xu et al.	0.16	100
		0.445	23
Aligned CNTs by CVD	Zhang et al.	0.1	15
Aligned CNTs on double-sided copper foil	This study	0.3	12

4. Conclusions

A TIM consisting of aligned CNTs on double-sided metal substrate was designed and synthesized by water vapor assisted CVD. The morphology and thickness of CNT films were strongly influenced by the position of substrate in the quartz boat, amount of water injected, amount of catalyst, growth temperature, and growth time. Thicker CNT films could be synthesized by higher growth temperature, a larger amount of ferrocene, or longer growth time.

This study can be extended in different ways. The thermal conductivity of the aligned CNT TIM sample can be determined by varying the film thickness. At present, the film thickness could not be directly measured but we can get around this problem by using the injection molding method of Huang et al.[10] Instead of fixing the amount of water, the humidity level in the reactor can be controlled. Clearly, thermal resistance smaller than 12 mm^2 K/W can be realized by using thinner copper foils and shorter aligned CNTs. The performance of this double-sided TIM device for minimizing the well-known air gap thermal resistance should be directly investigated. Efforts in these directions are now underway.

Acknowledgments.

We thank K. Zhang and M. Yuen for their assistance in measuring the thermal resistance.

References

(1) Berber, S.; Kwon, Y. K.; Tomanek, D. *Phys. Rev. Lett.* **2000**, *84*, 4613.

(2) Gwinn, J. P.; Webb, R. L. *Microelectronics J.* **2003,** *34*, 215.

(3) Mahajan, R.; Chiu, C. P.; Prasher, R. *Electronics Cooling* **2004**, 10.

(4) Treacy, M. M.; Ebbesen, T. W.; Gibson, J. M. *Nature* **1996**, *381*, 678.

(5) Dai, H. J.; Wong, E. W.; Lieber, C. M. *Science* **1996**, *272*, 523.

(6) Hone, J.; Whitney, M.; Piskoti, C.; Zettl, A. *Phys. Rev. B* **1999**, *59*, R2514.

(7) Lijima, S. *Nature* **1991**, *354*, 56.

(8) Kim, P.; Shi, L.; Majumdar, A.; McEuen, P. L. *Phys. Rev. Lett.* **2001**, *87*, 215502-1.

(9) Liu, C. H.; Huang, H.; Wu. Y.; Fan, S. S. *Appl. Phys. Lett.* **2004**, *84*, 4248.

(10) Huang, H.; Liu, C. H.; Wu, Y.; Fan, S. S. *Adv. Mater.* **2005**, *17*, 1652.

(11) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Lijima, S. *Science* **2004**, *306*, 1362.

(12) Zhang, K.; Yuan, M. F.; Wang, N.; Miao, J. Y.; Xiao, G. W.; Fan, H. B. *2006 Electronic components and Technology Conference*, 177.

(13) Zhao, Z. B.; Qu, J. Y.; Qiu. J. S.; Wang, X. Z.; Wang, Z. Y. *Chem. Commun.* **2006**, 594.

(14) Zhang, H. R.; Liang, E. J.; Ding, P.; Chao, M. J. *Phys. B* **2003**, *337*, 10.

(15) Zhu, L. B.; Xiu, Y. H.; Hess, D. W.; Wong, C. P. *Nano. Lett.* **2005**, *5*, 2641.

(16) Zhang, X. F.; Cao, A. Y.; Wei, B. Q.; Li, Y. H.; Wei, J. Q.; Xu, C. L.; We, D. H. *Chem. Phys. Letts.* **2002**, *362*, 285.

(17) Xu, J.; Fisher, T. S. *Proc 9th intersociety conference on thermal and thermomechanical phenomena in electronic systems* **2004**, *34*, 549.

(18) Liu, C. H.; Huang, H.; Wu, Y.; Fan, S. S. *Appl. Phys. Lett.* **2004**, *84*, 4248.