CARBON 49 (2011) 1395–1400

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Very fast growth of millimeter-tall aligned carbon nanotubes between two stacked substrates coated with a metal catalyst

Jia-Qi Huang, Qiang Zhang, Meng-Qiang Zhao, Kai Zhou, Fei Wei *

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 23 August 2010
Accepted 1 December 2010
Available online 5 December 2010

ABSTRACT

A simple method is reported for the fast growth of millimeter-tall aligned carbon nanotubes (CNTs). Two silicon substrates were stacked with catalyst layers face to face and CNT growth occurred between them. Based on *in situ* monitoring, the growth rate of aligned CNTs in stacked area was found to be much (over one magnitude) higher than that in the area with a single substrate. The phenomenon was also valid for different catalyst layers and cap substrate materials. This provided an easy way to improve the efficiency of CNT synthesis without changing catalyst compositions and growth parameters.

1. Introduction

Aligned carbon nanotubes (CNTs) attracted great interest due to the intrinsic properties of CNT structure and the alignment as well. Millimeter-tall CNT arrays with certain wall number were extraordinary platforms to demonstrate excellent mechanical, electrical, electrochemical, optical, and thermal properties of CNTs. Recently, several groups have succeeded in growing vertically-aligned single/double/multi-walled CNTs (S/D/MWCNTs) [1,2]. Up to now, developing strategy for the fast growth of aligned CNTs is still a key step to realize the efficient production and to meet their large scale applications in microelectronic, composites, energy conversion and storage. Various methods, including the deposition of barrier layer [3], the assistance of oxidants [4,5], the development of multi-component catalysts [6], and growth parameter optimizations [7], have been explored. Accompanying the high interest in the fast growth of CNT arrays, some method for monitoring the growth rate was also developed, such as *in situ* telecentric height monitoring system [8] and *ex situ* growth mark method [9]. However, fast growth of millimeter-tall CNT arrays through an efficient way and a simple but effective way to monitor the growth of aligned CNT are still highly needed.

In this contribution, we explored an idea that the growth rate of aligned CNT arrays can be greatly increased when CNTs grow between two stacked substrates, and a digital camera recording system was employed to *in situ* monitor this process. Normally, researchers tried to avoid the cover of the substrates during the synthesis of aligned CNTs, and the high pressure was considered to be harmful for the growth of aligned CNTs [10]. Surprisingly, we found that the stack of substrate significantly promoted the growth of aligned CNTs, which grew faster and longer between two stacked substrates. As schematically shown in Fig. 1, the substrates were stacked with the catalyst layers face to face for the growth of CNT arrays. After the chemical vapor deposition (CVD), aligned CNTs in stacked area grew much faster than those in the non-stacked area. This provides an easy route for the fast synthesis of millimeter-tall CNT arrays, which can promote the production efficiency of aligned CNTs at an industrial scale.

2. Experimental

A Si/SiO_2 (600-nm-thick thermally grown SiO_2 layer) wafer was selected as the substrate. Several kinds of catalyst layers were deposited by electron beam evaporation, including Al_2O_3

* *Corresponding author:* Fax: +86 10 6277 2051.
E-mail address: wf-dce@tsinghua.edu.cn (F. Wei).
0008-6223/$ - see front matter
doi:10.1016/j.carbon.2010.12.006

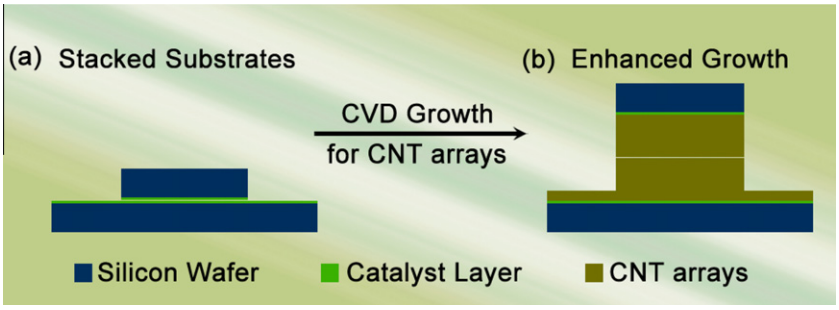

Fig. 1 – Schematic illustration of silicon wafer stacked growth of aligned CNTs.

(10.0 nm), Fe (1.0 nm) and MgO (1.0 nm), named *Substrate 1*; and Al_2O_3 (10.0 nm), Fe (0.5 nm) and MgO (1.0 nm), named *Substrate 2*; and catalyst layer of 3.0-nm-thick Fe. CVD growth of CNT arrays were then carried out on these substrates stacked with different cap substrates, including silicon wafer with/without catalyst layer and 1-mm-thick quartz plate. Generally, they were set into a horizontal tubular furnace. The temperature ramped to 750 °C in 15 min under the gas flow of Ar and H_2, which was identified as "annealing" process. C_2H_4 was then introduced as carbon source for CNT array growth at the temperature of 750 °C, which is called "growth" process. The typical flow rates for Ar, H_2 and C_2H_4 were 250, 200, and 100 sccm, respectively. After 1-h growth of aligned CNTs, the supply of H_2 and C_2H_4 was cut off and the furnace was cooled down to room temperature under Ar atmosphere.

To explore the fast growth of aligned CNTs between two stacked substrates, several control experiments were carried out. To verify the effect of the different cap substrates, the control experiments were carried out as follows: three different plates, including Si/SiO_2 wafer (without catalyst), Si/SiO_2 wafer with Fe catalyst film, and 1-mm-thick quartz plate, were used as the cap substrates. Typical growth procedures were applied in this control experiment. To further identify whether the enhancement was brought by the applied pressure of cap substrate or by the influence on the catalyst, the cap substrate was used only in the annealing process in another control experiment. Substrate 1 was covered by a small piece of substrate with the same catalyst and was heated to the setpoint of 750 °C under typical flow rate of Ar and H_2, after which the furnace was cooled down and the cap substrate was removed from Substrate 1. Substrate 1 was then used for another cycle of aligned CNT growth without cap substrate. The influence of different H_2 concentrations was also investigated, and the typical growth recipe was applied except that the H_2 flow rate was changed to 100 sccm (50% flow rate) and 400 sccm (200% flow rate).

The growth process was *in situ* monitored by a digital camera Nikon D700 through a glass observation window at one side of the tubular quartz reactor. The pictures were taken with an interval of 30 s and the height of the CNTs was determined with the thickness of silicon wafer (500 μm) as reference. The as-obtained products were characterized using scanning electron microscopy (SEM, JEOL JSM 7401F), transmission electron microscopy (TEM, JEOL JEM 2010), and Raman spectrophotometer (Renishaw RM2000 with laser excitation line at 633.0 nm). Tapping mode atomic force microscopy (AFM) imaging was performed on a Shimadzu SPM-9500J3 at room temperature. The AFM cantilever used was microfabricated from silicon with the spring constant and resonant frequency of 11.5 N m^{-1} and 255 kHz, respec-

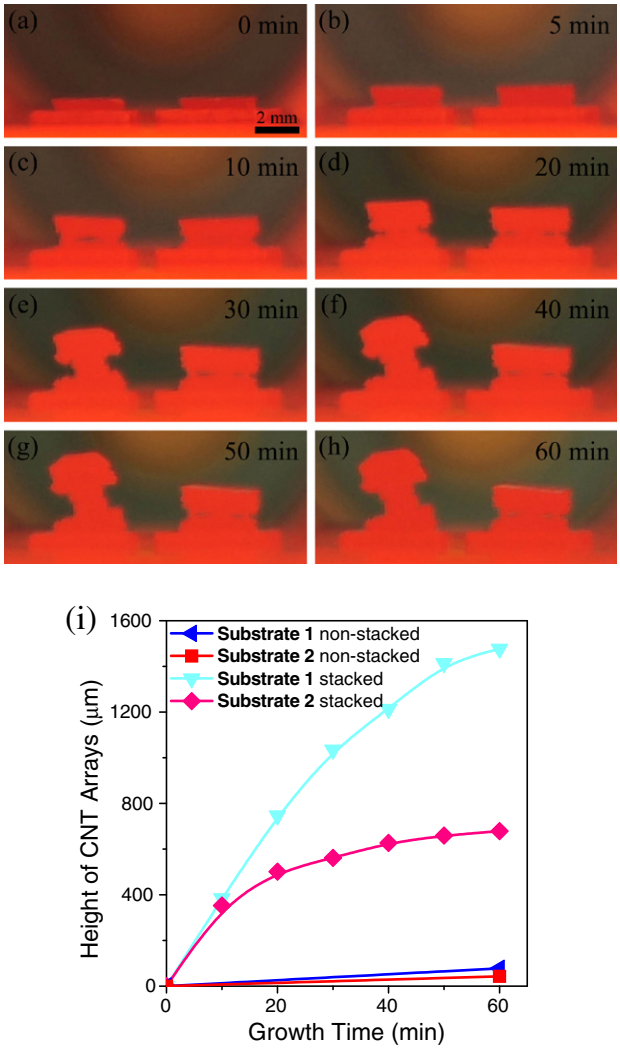

Fig. 2 – (a)–(h) The *in situ* recorded images for the growth of aligned CNTs on Substrate 1 (left part) and Substrate 2 (right part). (i) Growth curves of CNT arrays with and without the stacked of the cap substrates.

tively. Image analysis was performed using the corresponding commercial software.

3. Results and discussion

The growth behaviors of Substrate 1 (left part) and Substrate 2 (right part) can be real-time monitored (Fig. 2a–g). When the CVD growth started, the growth rate of CNTs on Substrate 1 at the stacked area was notably faster compared with the non-stacked area and the CNT arrays pushed the upper substrate away throughout the whole growth period. The height of aligned CNTs in stacked area became uneven and split into blocks with continuous growth. Similar growth enhancement of aligned CNTs was also observed on Substrate 2. The growth curves of CNT arrays in the stacked and non-stacked area were obtained by the analysis of the photos (Fig. 2i). The normal growth mode gave rise to the CNT film with a height of *ca.* 50 μm and a growth rate of *ca.* 0.8 μm/min. However, the stacked mode supported an initial growth rate of *ca.* 38 and 35 μm/min for Substrates 1 and 2, respectively.

To explore the unique substrate-stacked growth behavior, Substrate 1 was selected as model substrate for further investigation. Aligned CNTs grown on the whole substrate after CVD (Fig. 3a). However, a higher aligned CNT block, which was over 1 mm tall and outclassed the CNT arrays on the non-stacked area by over an order of magnitude, could be found in the side view of the capped area (Fig. 3b). This unambiguously indicated that the growth of aligned CNTs was promoted when they grew between two stacked substrates. Some of aligned CNTs around the high column split toward outside and formed the flowerlike morphology. The as-grown CNTs on Substrate 1 showed good alignment (Fig. 3c). What's more, CNT arrays with similar height and shape were also obtained on the small cap substrate (Fig. 3d). The fine structure of CNTs obtained under stacked and non-stacked area was characterized by transmission electron microscopy (TEM) (Fig. 4a and b). It was observed that the CNTs on both the stacked and non-stacked areas were mainly composed of S/DWCNTs, which mainly depended on the initial catalyst film composition on the substrate (Fig. S1). Based on the statistic of about one hundred CNTs, the average diameter of CNTs in the covered area was estimated to be 5.9 nm, with a standard deviation of 0.7 nm. Meanwhile, the average diameter of CNTs in the non-stacked area was found to be 5.8 nm with a standard deviation of 0.6 nm. The I_G/I_D ratio (obtained by Raman spectra) of aligned CNTs grown on non-stacked area for Substrates 1 and 2 were 0.90 and 0.79, which slightly decreased to 0.74 and 0.73 in cases of stacked growth (Fig. 4c and d). This indicated the graphitization of CNTs was slightly lower when the growth area was stacked by another substrate. But generally, no significant structure change was observed between CNTs obtained in stacked and non-stacked areas.

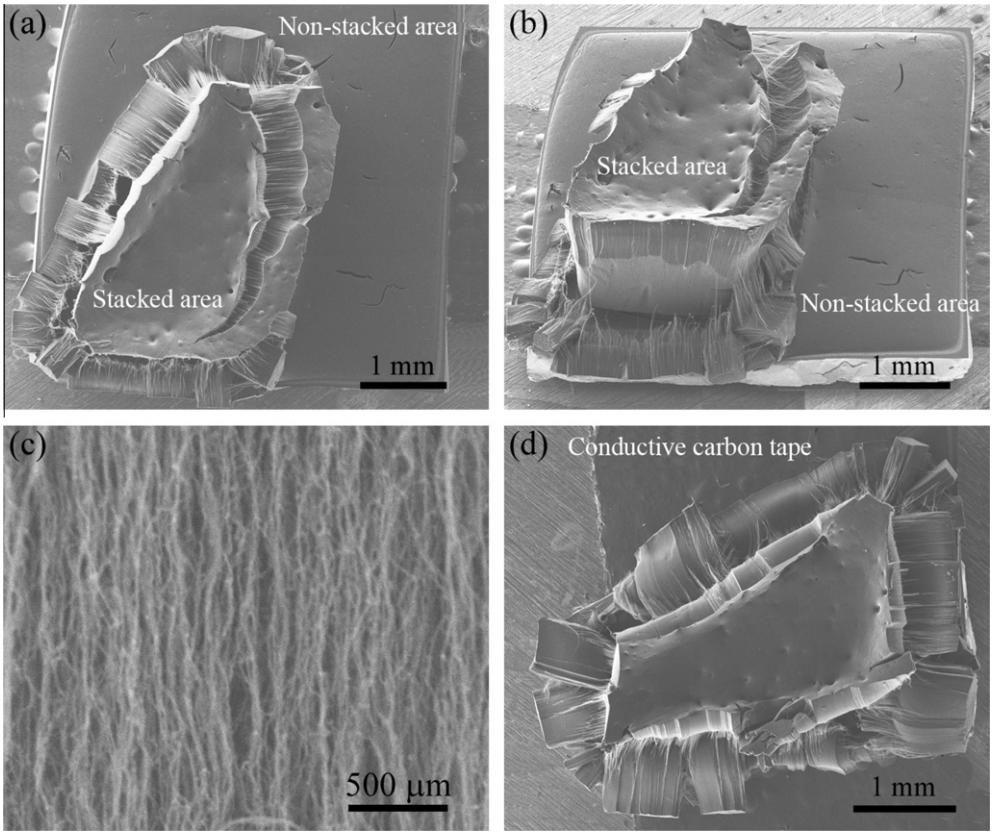

Fig. 3 – The SEM images of CNT arrays obtained on Substrate 1: (a) top view and (b) tilt view of the bottom substrate, the higher part corresponded to the stacked area; (c) alignment of CNTs in the millimeter-tall CNT arrays; (d) the top view of the CNTs grown on the cap substrate.

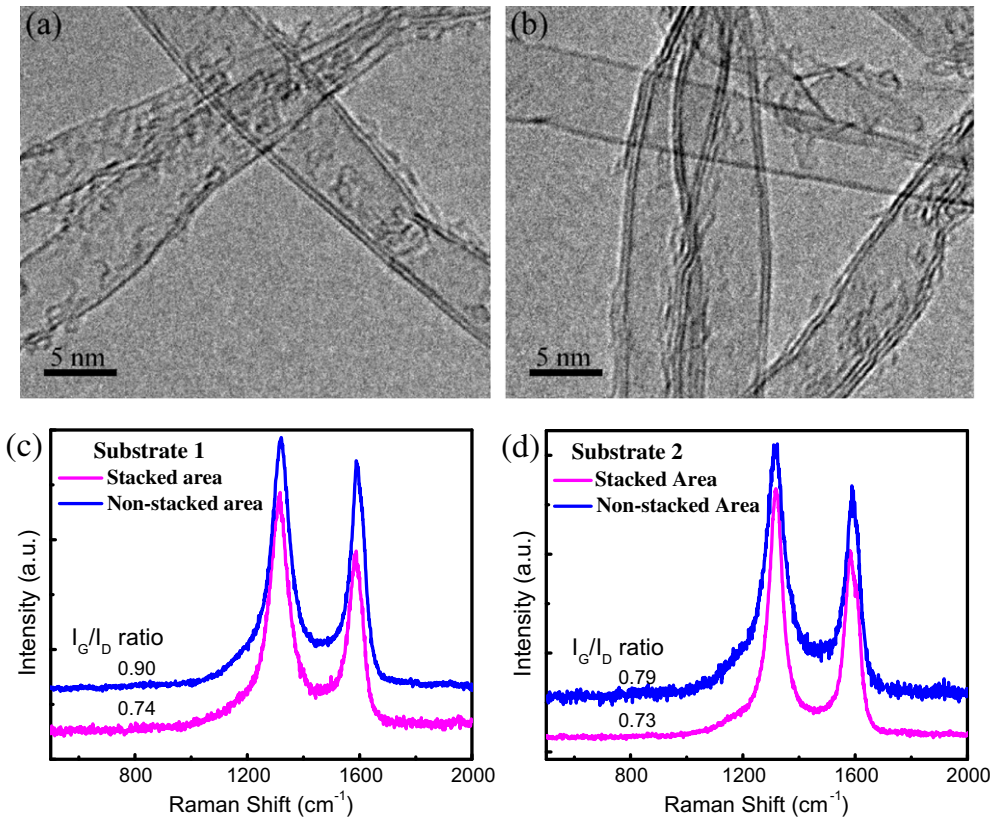

Fig. 4 – TEM images of CNTs obtained on Substrate 1 in (a) stacked area and (b) non-stacked area; Raman spectra of CNTs obtained on (c) Substrate 1 and (d) Substrate 2.

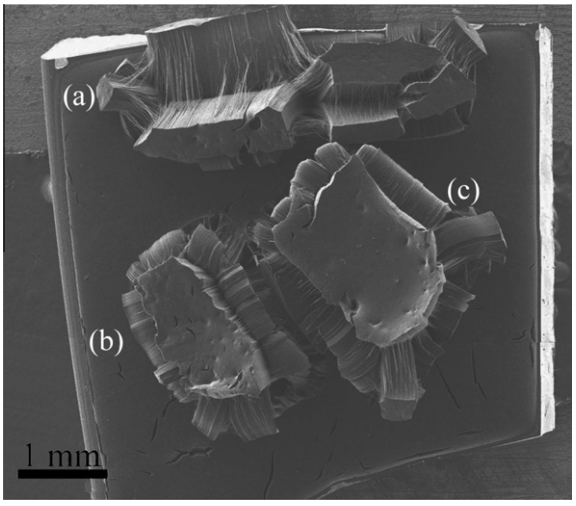

Fig. 5 – The morphology of as-grown CNT arrays on the substrate (silicon wafer with 3-nm-thick Fe catalyst film) by substrate stacking: (a) Si/SiO_2 wafer; (b) Si/SiO_2 wafer with Fe catalyst film; (c) 1-mm-thick quartz plate. In all cases, the CNT arrays grew faster in the stacked area of the substrates.

To further verify the growth enhancement effect, different bottom substrates and cap materials were tested. As shown in Fig. 5, when using a large silicon wafer (3-nm-thick Fe as catalyst film) as bottom substrate and different cap substrates (Si/SiO_2 wafer, Si/SiO_2 wafer with Fe catalyst, and 1-mm-thick quartz plate), the aligned CNTs in all the three stacked areas grew faster and longer. The heights of CNT arrays under the cover of substrates with and without catalyst layers were 1.10 and 0.94 mm after a 60-min CVD growth, respectively (Fig. S2), indicating the Fe catalyst on the cap substrate was not a main factor for rapid growth of aligned CNTs between two stacked substrates.

To determine whether the enhancement was induced by the applied pressure on the aligned CNTs when growing [10] or by the effect on the catalyst nanoparticles, we carried out a two-stage CVD growth procedure as follows: the substrate was stacked by a small piece of substrate during the first annealing process with H_2, following by the cooling and the removal of the cap substrate; then the bare substrate was heated and annealed again for the growth of CNTs. The results turned out that the stacked area in the first stage still gave rise to higher aligned CNTs compared with the non-stacked area (Fig. S3), though these two areas were under the same condition during the growth period (second stage). This indicated that the enhancement was induced by the changing of the catalyst conditions rather than the pressure applied to the CNTs. In fact, the applied pressure in this work was only about 10 Pa, which is much smaller than the pressure that can suppress the growth of CNT arrays (over 10^3 Pa) reported by Hart et al. [10].

To investigate the difference of catalyst in the stacked/non-stacked areas, the substrate was annealed to 750 °C and

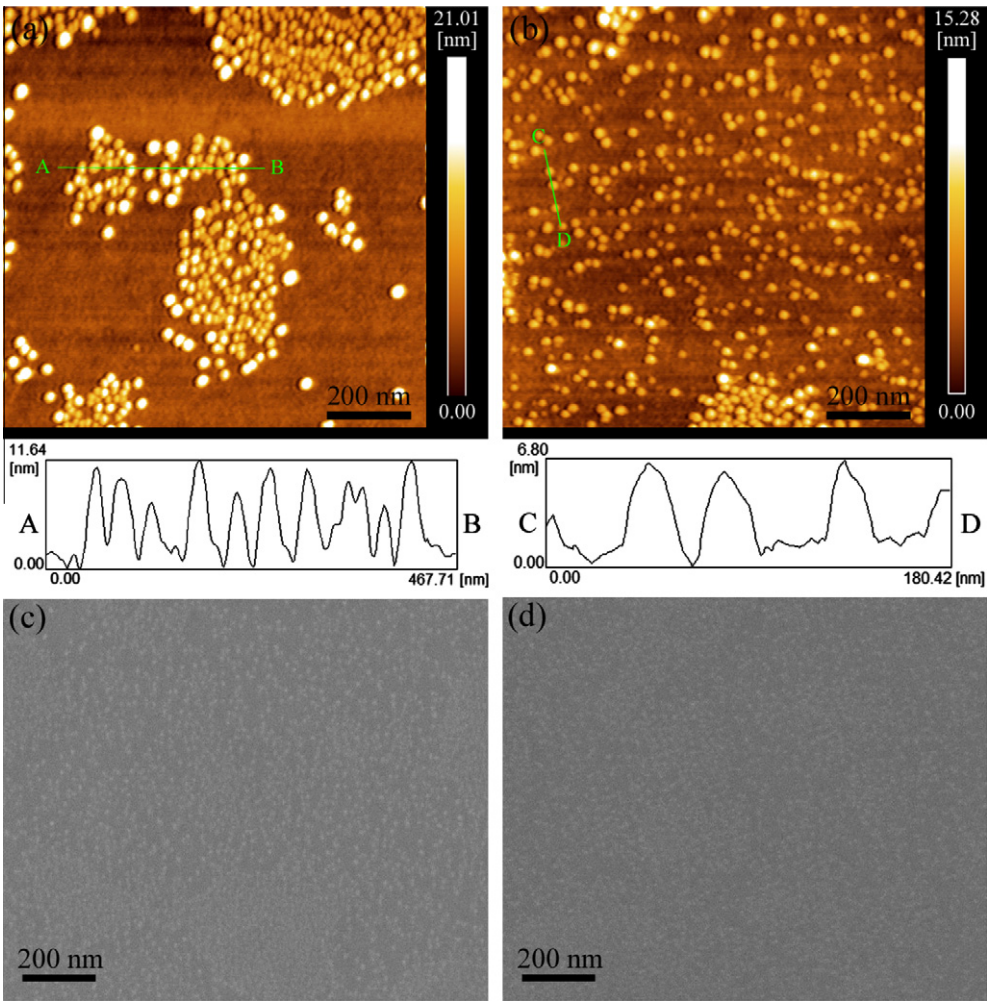

Fig. 6 – AFM topograph and height profiles of the catalyst surface after the annealing (a) in the non-stacked area of substrate and (b) in the stacked area; SEM images of catalysts after annealing in the (c) non-stacked area and (d) stacked area.

cooled down without the introduction of C_2H_4. When the catalyst film was annealed without the covering of another piece of substrate, the catalyst particles (height at about 8.6 nm from Fig. 6a) were larger than those annealed with the covering (height at about 6.0 nm from Fig. 6b). Meanwhile, the SEM images (Fig. 6c and d) also demonstrated the formation of uniform catalyst nanoparticles on the silicon wafer. The difference of catalyst particle status may be responsible for the different growth behaviors in the two areas. During the annealing process, the introduction of H_2 was an important factor that influenced catalyst particle formation by altering the kinetics of reducing process and the CNT growth rate was reported to reach 154 μm/min by Nessim et al. [11]. For our experiments, in both the situations of higher or lower H_2 flow rate (200% and 50% H_2 flow rates to the typical conditions) in the annealing process, the CNTs under the stacked area always grew faster (Fig. S4), which indicated that the stack of substrate extended the growth window of long CNT arrays. It was speculated that during the annealing process, the stacked area was with limited H_2 supply for the reduction of catalyst layer because of the diffusion resistance through the thin slot in the edge. Therefore, the catalyst layers in the stacked area were reduced in a more mild condition, which was prone to form small catalysts. In the growth process, smaller catalyst particles showed higher catalytic activities for fast growth of aligned CNTs. Though the stacking growth may cause diffusion resistance for the carbon source during the beginning period, it will soon be relieved because that the growing CNT array pushed the cap substrate apart. Hart et al. reported that the growth of CNT arrays can be flow-mediated by the cap substrate due to the consumption of carbon sources [12]. Similarly, with the cap substrate, the supplied of reduction agent (H_2) was limited, which was helpful to form uniform small catalysts (Fig. 6). Therefore the fast growth of aligned CNTs on small Fe catalysts in the stacked area was realized.

4. Conclusions

In summary, by the *in situ* monitoring of CVD growth, the fast growth of millimeter-tall aligned CNTs were observed between two stacked substrates coated with catalyst films. This method was valid for different top substrate materials, which can be utilized to improve the efficiency for mass production

of long aligned CNTs. This provides an easy route for the fast synthesis of millimeter-tall CNT arrays, which can promote the production efficiency of aligned CNTs in industrial scale.

Acknowledgements

This study was supported by the foundation for the Foundation for the China National Program (No. 2006CB932702) and Natural Scientific Foundation of China (Nos. 2007AA03Z346 and 20736007).

Appendix A. Supplementary data

A GIF video of the growth and TEM, SEM images, are provided and are available online. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2010.12.006.

REFERENCES

[1] Hata K, Futaba DN, Mizuno K, Namai T, Yumura M, Iijima S. Water-assisted highly efficient synthesis of impurity-free single-waited carbon nanotubes. Science 2004;306(5700):1362–4.
[2] Li XS, Zhang XF, Ci LJ, Shah R, Wolfe C, Kar S, et al. Air-assisted growth of ultra-long carbon nanotube bundles. Nanotechnology 2008;19(45):455609.
[3] de Los Arcos T, Garnier MG, Oelhafen P, Mathys D, Seo JW, Domingo C, et al. Strong influence of buffer layer type on carbon nanotube characteristics. Carbon 2004;42(1):187–90.
[4] Huang JQ, Zhang Q, Zhao MQ, Wei F. Process intensification by CO_2 for high quality carbon nanotube forest growth: double-walled carbon nanotube convexity or single-walled carbon nanotube bowls? Nano Res 2009;2(11):872–81.
[5] Pint CL, Pheasant ST, Parra-Vasquez A, Horton C, Xu YQ, Hauge RH. Investigation of optimal parameters for oxide-assisted growth of vertically aligned single-walled carbon nanotubes. J Phys Chem C 2009;113(10):4125–33.
[6] Christen HM, Puretzky AA, Cui H, Belay K, Fleming PH, Geohegan DB, et al. Rapid growth of long, vertically aligned carbon nanotubes through efficient catalyst optimization using metal film gradients. Nano Lett 2004;4(10):1939–42.
[7] Liu K, Sun YH, Chen L, Feng C, Feng XF, Jiang KL, et al. Controlled growth of super-aligned carbon nanotube arrays for spinning continuous unidirectional sheets with tunable physical properties. Nano Lett 2008;8(2):700–5.
[8] Zhao B, Futaba DN, Yasuda S, Akoshima M, Yamada T, Hata K. Exploring advantages of diverse carbon nanotube forests with tailored structures synthesized by supergrowth from engineered catalysts. ACS Nano 2009;3(1):108–14.
[9] Liu K, Jiang KL, Feng C, Chen Z, Fan SS. A growth mark method for studying growth mechanism of carbon nanotube arrays. Carbon 2005;43(14):2850–6.
[10] Hart AJ, Slocum AH. Force output, control of film structure, and microscale shape transfer by carbon nanotube growth under mechanical pressure. Nano Lett 2006;6(6):1254–60.
[11] Nessim GD, Hart AJ, Kim JS, Acquaviva D, Oh JH, Morgan CD, et al. Tuning of vertically-aligned carbon nanotube diameter and areal density through catalyst pre-treatment. Nano Lett 2008;8(11):3587–93.
[12] Hart AJ, Slocum AH. Rapid growth and flow-mediated nucleation of millimeter-scale aligned carbon nanotube structures from a thin-film catalyst. J Phys Chem B 2006;110(16):8250–7.