Control of growth mode of multiwalled carbon nanotubes

Nguyen Hong Quang\(^1\) and Do-Hyung Kim\(^2\)

\(^1\) Department of Physics, Vinh University, 182 Le Duan Street, Vinh City, Vietnam
\(^2\) Department of Physics, Kyungpook National University, 1370 Sangyeok-dong, Bukgu, Daegu 702-701, Korea

E-mail: quangnh2007@yahoo.com

Abstract. We have conducted an experimental study to investigate the synthesis of multiwalled carbon nanotubes (CNTs) by a dc plasma-enhanced chemical vapour deposition (PECVD) technique. The synthesis of base and tip-type of CNTs was selectively controlled by changing the catalyst size, catalyst film thickness correlated with altering the NH\(_3\) pretreatment plasma current. These types of CNT showed distinctive properties in nanotube structure, growth rate and vertical alignment, which were confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and in situ optical interference measurement. The vertically aligned behaviour of CNT was systematically studied by using a fine-patterned catalyst layer with diverse critical dimensions. Freestanding single CNT was successfully realized by optimum tip-type CNT growth, conventional photolithography and wet-etch process.

Keywords: Carbon nanotube (CNT), multiwalled, growth, synthesis.

1. Introduction
Since their discovery in 1991, carbon nanotubes (CNTs) have attracted much attention due to their unique electronic and outstanding mechanical properties [1]. A wide range of potential applications including electron field emitters [2-6], gas sensors [7-11], nanoelectronic devices [12-14], supercapacitors [15], have been well demonstrated. Among various applications, the use of CNTs as electron field emitters is one of the most fascinating areas. Up to now, CNT can be mainly synthesized by arc discharge, laser ablation and chemical vapor deposition (CVD) [16]. Among these methods, the arc-discharge method can produce CNT on a large scale but the production usually contains several impurities [17]. Laser ablation process enables to synthesize CNT with higher purity but it is not amenable for scale up [18]. In recent years, CVD techniques have been widely used to produce CNTs with large scale and high quality [19, 20]. In this approach, a feedstock such as CO or hydrocarbon is heated to 800-1000°C with a transition metal catalyst to promote nanotube growth [21].

In comparison with conventional CVD, plasma-enhanced chemical vapour deposition (PECVD) is advantageous for direct growth of CNTs on substrates at a relatively low temperature due to the presence of uniform plasma [22-24]. In addition, PECVD has been considered as a good controllable method for growing vertically aligned and highly selective-positioned CNTs for field emitter applications [25-28], which are currently being considered for use in flat panel displays [29, 30]. Vertically aligned CNTs have also been proposed as nano-electrodes for sensitive biosensors [31, 32].
Here we report on a simple method of control the growth mode between base and tip type CNTs as well as properties of grown CNTs. The dynamics of the CNT growing in each mode are also discussed in this work.

2. Experimental procedures

CNTs were grown by a dc glow discharge PECVD technique. The substrates used were n-type Si wafers and Ni films were sputtered as catalyst with various thicknesses. Acetylene (C$_2$H$_2$) and ammonia (NH$_3$) was used as a carbon source and etchant, respectively.

Firstly, the NH$_3$ pretreatment with a flow rate of 180 sccm was maintained for 5 minutes in order to etch the continuous catalyst Ni thin film. The initial smooth Ni catalyst film was transformed into nanometer-scale islands after the NH$_3$ pretreatment and reserved as seeds for the CNT nucleation. The NH$_3$ flow rate of 180 sccm and treating time of 5 minutes were kept for all catalyst film samples. A -450 V bias was applied to the substrate in order to create a dc-plasma. The plasma current with different thicknesses was adjusted from 20 mA to 60 mA in order to alter the morphology of the films. In the next step, C$_2$H$_2$ gas with the flow rate of 60 sccm was additionally introduced for CNT growth. To eliminate sample-to-sample variations and maintain a growth environment, the substrates experienced to various NH$_3$ pretreatments were processed under identical CNT growth condition.

The CNTs growth was performed at 600°C and monitored using an in situ optical interference system [33, 34]. It consists of a focused 650 nm laser diode with 1 mm beam diameter and a photodetector. The growth experiments and measurements were automatically controlled by a personal computer with an in-house prepared software [34]. The SEM and TEM images of the grown CNT samples were performed using a FE-SEM 4300 and Hitachi 9000 system, respectively.

3. Results and discussions

In the PECVD techniques for CNT growth, it is believed that the catalyst particles play a crucial role. The thickness of catalyst film and its pre-treatment were also essential to control the size and shape of the subsequent products. This belief was verified by the experimental results as illustrated in figure 1.

Figure 1. SEM images of Ni islands from the catalytic film thickness of 10 nm, 30 nm and 20 nm, respectively (top panel) and CNT arrays grew on the corresponding substrates (bottom panel).
Figure 1 (top panel) shows the typical SEM images of catalytic Ni islands which were formed during the NH$_3$ pretreatment and served as the CNT nucleation sites. The uniformity and size of the Ni islands were affected and controlled by altering the thickness of Ni film and NH$_3$-pretreatment. The initial thin 10 nm-Ni film was changed to uniform Ni islands with an average 20 nm diameter after 60 mA-NH$_3$-pretreatment as shown in figure 1 (a, top panel). The etched Ni islands using thick 30 nm-Ni film showed a much larger average diameter of about 100 nm as illustrated in figure 1 (b, top panel). After 40 mA-NH$_3$-pretreatment using 20 nm-Ni film, the Ni islands have broad distribution in diameter (ranged from 20~70 nm) as depicted in figure 1 (c, top panel). The thinner Ni film or/and stronger plasma current of pretreatment were used, the smaller average size of catalyst islands were created and the thinner diameter of grown CNT could be produced. The initial thickness of the catalyst film did not only affect the diameter of grown CNTs, but also influenced their growth mode. As depicted in the bottom panels of figure 1 (a, b, c) which is corresponding to the thin film (10 nm), thick film (30 nm), and medium film (20 nm), respectively. It is observed that the CNTs which grew on the thin Ni film are predominantly vertical with an average diameter of 20 nm and height of 10 μm. Some tubes are curved due to its weight and aspect (the height-to-diameter ratio). The growth rates of these CNTs have values ranged from 100 nm/sec to 120 nm/sec in the initial stage with no catalyst particles were observed at the tubes top. The dependence of CNT length on growth time in base and tip mode is depicted in figure 2.

![Figure 2](image-url)

**Figure 2.** The dependence between CNT length and growth time in the base and tip mode growth.

As one can see from the figure that the tip-type CNT grew very slowly compared to the base type CNTs. Meanwhile the base type CNT rapidly grew and could achieve to 6 μm in length within one minute, the tip CNTs took more than one hour (80 minutes) to get 3-μm length. The length of tip CNTs almost no longer developed after the synthesis time lasted for more than two hours.

The magnified TEM images of the CNTs clearly showed that the catalyst particles located at the base of the tubes in case a thin film of Ni catalyst was used (figure 3a) or at the tip tube when a thicker size of Ni catalyst was employed (figure 3b). If medium size of Ni catalyst particles were used, a mixture of base and tip CNTs were formed (figure 3c). The similar result could be taken place when plasma current of NH$_3$ pretreatment was raised to 40 mA. No catalyst particles were observed at the
tip of the longest CNT tube, inferring that the catalyst particles, if they have, must locate on the base of the substrate. In this case, the CNT has a small diameter (about 5 nm, see the inset in figure 3c). The fraction of base mode CNTs increased when the plasma current increased from 40 mA to 60 mA.

![Figure 3. TEM images of CNT in base, tip and mixed growth mode, respectively.](image)

From the experimental results, we assure that the stronger plasma current had formed smaller catalytic islands on the substrates. In case of thin Ni catalyst film (10 nm), the pretreatment with relatively weak plasma current had transformed the initial smooth film into Ni particles with uniform shape and size. The annealing temperature during CNT growth might melt the catalyst particles, changing them into wetting islands. The adhesion force between the wetting islands and the substrate which must be larger than that between solid state particles and the substrate is probably responsible to stick the catalyst particles on the substrate. That is the reason why the base growth of CNTs was promoted when a thin Ni film was used as catalyst. Moreover, when plasma current of the pretreatment was stronger than 60 mA, most of etched catalyst Ni islands had gone with no CNTs observed on the substrate. For thicker catalyst Ni films, other effects might take place during the plasma etching pretreatment. Due to thermal influence, some etched Ni particles could be agglomerated into coarsened islands. In this case, the splitting is inhomogeneous, giving a broad size distribution of catalyst islands, including very larger clusters [35] as seen from figure 1b, c (top panels). The small catalyst islands usually support the base mode of CNT growth, meanwhile the larger ones promote for the tip growth mode. However, it is possible for large CNTs to grow in base mode if they were supported by large-wetting catalyst islands because of large adhesion force between substrate and catalyst islands in the wetting phase. Subsequently, the CNTs grown on the thick films have a wide distribution of diameter with a mixture of base and tip growth modes.

4. Conclusions
In summary, we have discussed the experimental results on the CNT synthesis via a dc PECVD technique with Ni used as catalyst in different film thicknesses. The C₂H₂ and NH₃ were used as feedstock and etching gas, respectively. The diameter and growth mode of CNT were controlled by changing the film thickness and the plasma current of the NH₃ pretreatment. For thin catalyst film, the CNT grew in base mode for all of the available plasma currents. For thicker catalyst film, a tip mode of CNT was observed only when a 20 mA plasma current of pretreatment had been applied. In the other films, a mixture of base and tip mode CNT coexisted on the substrate. The mechanism of growth mode change has been discussed in this work.

References
[1] Saito R and Dresselhaus M S 1998 Physical Properties of Carbon Nanotubes (Imperial College Press) p 35
[2] Gulyaev Y V, Chernoziatonskii L A, Kosakovskaja Z J, Sinitsyn N I, Torgashov G V and Zakharchenko Y F 1995 J. Vacu. Sci. Technol. B 13 435
[1] deHeer W A, Bonard J M, Stockli T, Chatelain A, Forro L and Ugarte D 1997 Zeitschrift Fur Physik D-Atoms Molecules and Clusters 40 418
[2] Manohara H M, Bronikowski M J, Hoenk M, Hunt B D and Siegel P H 2005 J. Vacuum Sci. Technol. B 23 157
[3] Sakai Y, Haga A, Sugita S, Kita S, Tanaka S I, Okuyama F and Kobayashi N 2007 Rev. Sci. Instrum. 78 013305
[4] Rakhi R B, Reddy A L M, Shaijumon M M, Sethupathi K and Ramaprabhu S 2008 J. Nanopart. Res. 10 179
[5] Ahn K S, Kim J H, Lee K N, Kim C O and Hong J P 2004 J. Korean Phys. Soc. 45 158
[6] Liang Y X, Chen Y J and Wang T H 2004 Appl. Phys. Lett. 85 666
[7] Quang N H, Van Trinh M and Huh J S 2005 Eco-Materials Processing & Design Vi 486-487 485
[8] Maklin J, Mustonen T, Kordas K, Saukko S, Toth G and Vahakangas J 2007 Phys. Stat. Sol.B 244 4298
[9] Terrones M 2004 Int. Mater. Rev. 49 325
[10] Johnston D E, Islam M F, Yodh A G and Johnson A T 2005 Nat. Mater. 4 589
[11] Wu F and Xu B 2006 New Carbon Materials 21 176
[12] Dresselhaus M S, Dresselhaus G and Avouris P 2001 Carbon nanotubes: synthesis, structure, properties, and applications, in Topics in applied physics (Berlin - Heiselberg: Springer-Verlag) p 1
[13] Ando Y and Zhao X L 2006 New Diamond Front. Carbon Technol. 16 123
[14] Zhang M F, Yudasaka M and Iijima S 2001 Chem. Phys. Lett. 336 196
[15] Kasumov Y A, Shailos A, Khodos I I, Volkov V T, Levashov V I, Matveev V N, Gueron S, Kobylyk M, Kocia M, Bouchiat H, Agache V, Rollier A S, Buchaillot L, Bonnot A M and Kasumov A Y 2007 Appl. Phys. A-Mate. Sci. & Proc. 88 687
[16] Lee W Y, Lin H, Gu L, Leou K C and Tsai C H 2008 Diam. Relat. Mater. 17 66
[17] Meyyappan M, Delzeit L, Cassell A and Hash D 2003 Plas. Sour. Sci. Technol 12 205
[18] Park D, Kim Y H and Lee J K 2003 Carbon 41 1025
[19] Hesamadeh H, Ganjipour B, Mohajerzadeh S, Khodadadi A, Mortazavi Y and Kiani S 2004 Carbon 42 1043
[20] Yeh C M, Chen M Y, Hwang J, Gan Y J and Kou C S 2006 Nanotechnology 17 5930
[21] Kim D, Lim S H, Guilley A J, Cojocaru C S, Bourée J E, Vila L, Ryu J H, Park K C and Jang J 2008 Thin Solid Films 516 706
[22] Wei S, Kang W P, Davidson J L, Choi B K and Huang J H 2006 J. Vacu. Sci. Technol. B 24 1190
[23] Ma Y P, Shang X F, Gu Z Q, Li Z H and Xu Y B 2007 Acta Phys. Sinica 56 6701
[24] Nguyen C V, Delzeit L, Cassell A M, Li J, Han J and Meyyappan M 2002 Nano Lett. 2 1079
[25] Yu X, Kim S N, Papadimitrakopoulou F, and Rusling J F 2005 Mol. BioSyst. 1 70
[26] Kim D H, Jang H S, Kim C D, Cho D S, Yang H S, Kang H D, Min B K and Lee H R 2003 Nano Lett. 3 863
[27] Hofmann S, Cantoro M, Kleinsorge B, Casiraghi C, Parvez A, Robertson J and Ducati C 2005 J. Appl. Phys. 98 034308