Optimization of water assisted chemical vapor deposition parameters for super growth of carbon nanotubes

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ABSTRACT

The optimization of water assisted chemical vapor deposition (WA-CVD) was carried out to synthesize ultra long, vertically aligned, densely packed carbon nanotube (CNT) forests. The effect of various WA-CVD parameters (viz. the flow rate of the reactant gas mixture and its injection temperature, growth kinetics, ramp rate and growth temperature) on the height of the CNTs was studied. A hypothesis for catalytic activity is proposed on the basis of the X-ray photoelectron spectroscopic analysis of the CNT grown substrates and further verified at the optimum condition. The effect of temperature on the growth of the CNTs is studied. The gas flow rate and injection temperature influence the onset of oxidation of the substrates, which in turn affects the CNT growth rate. A growth kinetics study is performed in order to monitor the growth temperature. The role of the onset of oxidation of the iron catalyst in the growth of the CNTs is studied by varying the ramp rate. The precise CNT growth temperature for WA-CVD is determined by growth temperature studies. The optimum condition allows ~2.2 ± 0.002 mm long CNTs to be obtained.

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1. Introduction

Carbon nanotubes (CNTs) have been extensively explored in an attempt to take advantage of their unique properties for specific applications [1–5]. The synthesis of super-grown CNTs is of technological importance because of their integration into fibers and sheets for lightweight and high-strength material applications [6]. The height of CNTs synthesized by water assisted chemical vapor deposition (WA-CVD) [7] is ~2.5 mm, whereas that of CNTs synthesized by standard CVD [8] varies in the range of 10–200 μm. In the case of WA-CVD, introducing a small and controlled amount of water enhances and retains the activity as well as the lifetime of the catalyst particles [9,10]. As a result, the overall efficiency of the synthesis can be increased, resulting in the formation of densely packed, defect-free, vertically aligned CNT forests [11,12]. By controlling the level of water in the reaction ambient [13], brush-like CNT forests with a height of ~7 mm were grown in a period of 12 h. Half-centimeter-high mats of vertically aligned single-walled carbon nanotubes were grown at 600 °C by point-arc microwave plasma chemical vapor deposition [14]. A considerable amount of work has been carried out related to the CVD synthesis of CNTs [15–17]. However, in general, not much attention has been paid to the optimization of the various WA-CVD parameters in order to achieve the super growth of CNTs.

In this communication, the optimization of various WA-CVD parameters, such as the flow rate of the reactant gas mixture, its injection temperature and growth temperature, is discussed in an attempt to synthesize super-grown CNTs. We report that CNT forests with a height of up to 2.2 ± 0.002 mm could be achieved in a synthesis time of about 16 min using
Initially, 15 nm thick aluminum (Al-barrier) and 0.5–1 nm thick iron (Fe catalyst) layers were deposited on a silicon wafer by electron beam (e-beam) evaporation. The e-beam evaporation chamber was evacuated to a pressure of $3 \times 10^{-6}$ Torr and Al deposition was carried out at a rate of $0.1 \text{ Å/s}$ to obtain a $\sim 15$ nm thick Al layer. Following this, the Al target was replaced by the Fe target without breaking the vacuum. In a similar fashion, an Fe layer with a thickness of $0.5–1$ nm was deposited at a deposition rate of $0.1 \text{ Å/s}$.

Surface oxidation and contamination were avoided by keeping the substrate under dry conditions in a high-vacuum chamber. In a similar fashion, an Fe layer with a thickness of $0.5–1$ nm was deposited at a deposition rate of $0.1 \text{ Å/s}$. Surface oxidation and contamination were avoided by keeping the substrate under dry conditions in a high-vacuum chamber maintained at $\sim 10^{-6}$ Torr.

The existing WA-CVD set-up consists of a water bath coupled to a standard CVD furnace. The water bath is maintained at $\sim 60$ °C and coupled to the argon gas nozzle. The set-up consists of a horizontally mounted quartz tube (diameter $\sim 5$ cm and length $\sim 70$ cm) coupled to a rapid thermal heating system, equipped with various gas lines and standard mass flow controllers. In order to achieve different heating ramp rates, tungsten lamp furnace with programmable heater controller (Hanyoung Electronic Co. Ltd., Model NP200) is used. The mass flow of the gases, i.e. the feed stock (acetylene – $\text{C}_2\text{H}_2$), diluant (argon – Ar) and water carrier gas (argon) is controlled electronically.

One of the Fe/Al/Si wafers (hereafter referred to as the substrate) was cut into $5 \times 5$ mm samples and used to synthesize the CNTs. Three samples at a time were mounted on the quartz plate and shuttled into the reactor. The reactor was evacuated to a pressure of less than $0.1$ Torr. The reactant gas mixture was injected into the CVD reactor at room temperature (RT) unless otherwise stated.

In the first experiment, the effect of the flow rate of reactant gas mixture on the growth of the CNTs was studied. The temperature of the reactor was ramped up to 800 °C at a rate of 200 °C/min. After 12 min of growth, the gases supply was completely turned off and the system cooled to RT. A fast-heating process was utilized to accommodate a large number of samples. The gas flow meters were calibrated for the feed stock, diluant, and water carrier gas. The synthesis experiments were conducted by (a) keeping the flow rate of argon constant at 500 sccm (sccm – cm$^3$ STP per min) in the feed-stoke/diluant composition while varying the acetylene flow rate from 5 to 500 sccm and (b) keeping the total mass flow rate of argon and acetylene in the feed-stoke/diluant composition constant at 700 sccm while varying the flow rate of acetylene from 5 to 500 sccm. During all of the experiments, the mass flow rate of the water carrier gas (argon) was kept constant at 185 sccm.

To study the growth kinetics and the effects of temperature on the growth rate, four experiments were carried out. In the first experiment, the reactant gas mixture was injected into the CVD reactor at different temperatures. In the second experiment, the substrate was removed from the reactor chamber after 1 min interval and analyzed by scanning electron microscopy (SEM). In the third experiment, the time interval (i.e. ramp time, $R_t$ = 1–6 min) required to attain the growth temperature (i.e. 800 °C) was varied. In the fourth experiment, growth was carried out at various temperatures (i.e. 700–1000 °C).

After removing them from the reactor, the samples were analyzed by scanning electron microscopy (SEM; JSM6700F, JEOL) in order to precisely determine their height and morphology. The height was measured at various places and the average height was estimated. After removing the CNT forests from the surface, the surface states of a few of the samples were characterized by X-ray photoelectron spectroscopy (XPS; ESCA 2000 spectrometer), using an Al K$_\alpha$ (1486.6 eV) X-ray source. Subsequently, the CNTs removed from the substrates were dispersed in methanol and drop coated on a copper grid for observation by high resolution transmission electron microscopy (HRTEM; JEOL 300 kV) to explore their structural properties.

### 3. Results and discussion

#### 3.1. Effect of the flow rate of the reactant gas mixture on CNT growth

Fig. 1 shows the variation in the height of the CNT films with the acetylene flow rate. In plot (a) the argon flow rates were kept constant at 500 sccm and in plot (b) total flow rate of argon and acetylene were kept constant at 700 sccm. In both cases, the flow rate of acetylene was varied from 5 to 500 sccm. Plot (a) shows that at an acetylene/argon ratio of 5/500 sccm, the height of the CNT film is 200 ± 15 nm. As the flow rate of acetylene is increased, the height of the CNT film is observed to increase. The resonance condition, at which the height of the CNT forest is a maximum of...
1.4 ± 0.002 mm, is observed at an acetylene/argon ratio of 200/500 sccm. Thereafter, its height decreases with increasing acetylene flow rate. At a composition ratio of 500/500 sccm, the height of the CNT film is observed to be 270 ± 20 μm. The resonance condition provides the information required for the future experiments in which the total flow rate of acetylene and argon is kept constant at 700 sccm [19]. In plot (b), one can see that the overall height of the CNT film is increased at each composition ratio as compared to that in plot (a). At the lowest composition (i.e. 5/695 sccm), the CNT film attains a height of 800 ± 15 nm, whereas at the highest composition (i.e. 500/0 sccm) its height is 700 ± 20 μm. This shows that the feed-stoke/dilutant composition ratio plays an important role in the super growth of the CNTs.

However, at a lower acetylene flow rate, the nanotubes in the CNT film were observed to be neither densely packed nor vertically aligned. The resonance condition was perfectly reproducible and remained unaltered when obtaining both of the plots. The decrease in the height of the CNT film from that observed at the resonance condition towards both ends of the graph (i.e. lower and higher acetylene flow rates) indicates that the activity and lifetime of the Fe catalyst layer varies, which in turn influences the growth rate of the CNT film. It seems that at a lower acetylene flow rate, the onset of the oxidation of Fe is predominant, whereas in the higher acetylene flow rate regime the excess carbonization hinders the growth of the CNTs. At this optimum condition, a balance between oxidation and carbonation is achieved, which ultimately maximizes the height of the CNTs.

To verify the above hypothesis, the surface of the substrate, after removing the CNT forest, was studied using XPS. The CNT forest grown on the surface of the substrate can be easily removed using a razor blade or tweezers. The nanotubes are grown in the base growth mode, so the surface states of the catalyst as well as the iron–aluminum phases present on the substrate. One virgin sample (as prepared substrate) and three other samples used for the plot in Fig. 1b, were chosen to carry out the surface analysis. The as-prepared virgin sample is designated as S_A. The substrates synthesized at acetylene/argon ratios of 5/695, 200/500, and 500/200 sccm are designated as S_B, S_C, and S_D, respectively.

The XPS spectra were analyzed using Peak Fit 6.0 software. All of the spectra were calibrated using the adventitious C-1s peak with a fixed value of 284.8 eV. Fig. 2 shows the Fe-2p XPS spectra recorded for the substrates (a) S_A, (b) S_B, (c) S_C, and (d) S_D. The analysis of the high resolution Fe-2p spectra was carried out by fitting two Shirley backgrounds, one each for the 2p_3/2 and 2p_1/2 envelopes. For sample S_A, 2p_3/2 is observed at ~710.2 eV and 2p_1/2 at ~723.7 eV which could be attributed to the formation of a native oxide layer (FeO) for the virgin sample [20]. For samples S_A to S_C, a shift of the Fe-2p_3/2 peak is observed from ~710.2 to ~712.3 eV. The peak positions for S_B and S_C are observed at ~711.4 and 712.3 eV, respectively, which indicate the formation of FeO–OH surface phase for these samples. The presence of hydroxyl species on the surface of the sample indicates the participation of water molecules during the growth of the nanotubes. This also shows that at low acetylene content, surface oxidation via hydroxyl cations is predominant. For sample S_D, Fe-2p_3/2 is downshifted to ~711.3 eV, which shows the formation of an iron–carbon complex and indicates that at a higher acetylene content the process of carbonization dominates the growth of the CNTs.

The Fourier deconvolution of these spectra was carried out and the peak area was estimated using the following equation [21]:

![Fig. 2 – Fe-2p XPS spectra recorded for samples (a) S_A, (b) S_B, (c) S_C, and (d) S_D.](image-url)
where \( C_s \) is the concentration of species in atomic %, and \( H_i \) and \( S_i \) are the height and atomic sensitivity factor of the \( i \)th peak for the sample under consideration, respectively. The analysis showed that the concentration of Fe\(^{3+}\) states (at \( \sim 717.8 \text{ eV} \)) decreased from 11.68% to 1.34%, whereas the gross area of the Fe\(^{2+}\) (at \( \sim 716.27 \text{ eV} \)) bump increased from 3.83% to 19.2% from samples \( S_A \) to \( S_D \). Thus, the analysis of the Fe-2p XPS spectra indicates that the Fe precipitates are mainly in the Fe oxide phase for the virgin sample, \( S_A \). On the other hand, for samples \( S_A \) to \( S_D \), the formation of Fe\(^{2+}\) shake-up and its multiplet splitting suppresses oxidation and favors carbonization which, in turn, influences the growth rate and height of the CNTs.

This assignment is further supported by the deconvolution of the O-1s, Al-2p, and C-1s peaks, whose characteristics indicate the existence of the oxide phase, namely the presence of a chemical shift, peak broadening, satellite features, and its composition in atomic %. The O-1s feature (which is not shown in the figures) is distinctly different for \( S_A \) as compared to \( S_B-D \). A gradual peak shift was observed from \( \sim 531.3 \) to \( \sim 532.3 \text{ eV} \) for samples \( S_A \) to \( S_D \). The O-1s peak for sample \( S_A \) includes contributions mainly from iron-oxide phases (\( \sim 24.58\% \)), Al\(_2\)O\(_3\) (\( \sim 22.81\% \)) and amorphous hydrogenated carbon species (C/Al\(_2\)O\(_3\), \( \sim 11.40\% \)). However, for samples \( S_B-D \), the major contribution was from the iron-oxide species. The overall peak deconvolution analysis revealed that the concentration of oxygen atoms in the surface region increased gradually from 20.33% to 26.15% for samples \( S_A \) to \( S_C \) and thereafter an abrupt decrease was observed for \( S_D \) (22.91%).

Simultaneously, the deconvolution of the C-1s XPS peaks showed (which is not shown in the figures) that the concentration of carbon atoms increased from 1.19% to 2.25% for samples \( S_A-C \), however, for sample \( S_D \), the surface concentration of carbon atoms is observed to be highest at \( \sim 2.99\% \). This indicates that the process of carbonization dominated at a higher acetylene content in the mixture of acetylene and argon gases.

It is interesting to note that similar experiments were conducted at the standard CVD conditions (i.e. without water); however, no specific trend was observed with regard to the variation of the height of the CNT film with the gas composition ratio. In this case, the height of the CNT film was \( \sim 800 \text{ nm} \) at the optimum condition. The absence of water molecules in the growth ambient reduces the activity as well as the lifetime of the catalyst particles \([9,10]\).

### 3.2. Effect of temperature on CNT growth

If the oxidation and carbonation of the catalyst are the main parameters which influence the height of the CNTs, then the temperature is a key parameter which can be used to monitor catalyst oxidation and control CNTs height. This hypothesis was further examined by studying the effect of temperature on the growth of the CNTs. In order to get the super growth of CNT the optimum condition for temperature is set for WA-CVD.

The effect of the onset of oxidation on the growth of the CNT films was studied by injecting the reactant gas mixture (hereafter referred to as the gases) at different reactor temperatures. The synthesis was carried out at the optimum condition of the gases described in Section 3.1 (acetylene/argon gas composition ratio of 200/500 sccm and heating ramp rate of 200 °C/min). For the sake of clarity, we consider growth rate instead of the total height of the CNT film. It was calculated by dividing the total height of the CNT film (in μm) by the total synthesis time (in min). Fig. 3 shows the variation in the growth rate as a function of the gases injection temperature. The time scale is also drawn at the top of the x-axis. The inset shows the temperature evolution in the reactor during the CNT synthesis. The maximum growth rate is estimated to be 93.12 ± 2.0 μm/min when the gases are injected at RT. As the injection temperature increases from 100 to 800 °C, the growth rate decreases from 91.5 ± 2 to 53.31 ± 2 μm/min. The incubation of the substrate without the gases favors the oxidation of the Fe catalyst. The onset oxidation of the catalyst is minimized when the gases are injected at RT, which results in a higher growth rate. However, as the injection temperature increases, the oxidation of the catalyst gradually increases and this hinders the growth rate. The results of this experiment confirm the hypothesis described above.

Knowledge of the growth kinetics is critically important to understand the mechanism of super growth and further improve the synthesis. It was of interest to study the growth kinetics, i.e. the variation in the height of CNT film with time. Three samples at a time were shunted into the reactor and growth time was kept 1 min, cumulatively, for next sample growth time was increased by 1 min. The synthesis was carried out at the optimum condition obtained in Section 3.1 (acetylene/argon gas composition ratio of 200/500 sccm and heating ramp rate of 200 °C/min). The evolution of the CNT forest with time is shown in Fig. 4a. Up to ~3 min, the varia-

![Fig. 3 – Variations in the growth rate (μm/min) with the CVD reactor temperature used for the injection of the reactant gas mixture. The top x-axis is the time scale at a given temperature. The inset shows the evolution of the temperature in the reactor.](image)
tion in the height of the CNT film is almost negligible. However, from 4 to 19 min, the height monotonically increased from $80 \pm 20 \mu m$ to $1.39 \pm 0.002 mm$ and thereafter a saturation region was observed in which the variation in the height of the CNT film is insignificant. The growth rate was computed to be $/C_{24}93.07 l/min$ over the linear region of the plot (i.e. the slope of the linear fit).

An in-depth analysis was carried out by computing the first differential, $D/\Delta t$, with time. In plot (b), the three regions are separated by dotted lines. Region (I): $D/\Delta t$ increases from 0.4 to 90.4 $\mu m/min$, (II): $D/\Delta t$ stabilizes at $93.12 \pm 2.0 \mu m/min$, and (III): $D/\Delta t$ decreases to 0.5 $\mu m/min$.

![Fig. 4](image)

**Fig. 4** – (a) Height of CNT film and (b) variations in first differential, $D/\Delta t$, with time. In plot (b), the three regions are separated by dotted lines. Region (I): $D/\Delta t$ increases from 0.4 to 90.4 $\mu m/min$, (II): $D/\Delta t$ stabilizes at $93.12 \pm 2.0 \mu m/min$, and (III): $D/\Delta t$ decreases to 0.5 $\mu m/min$.

In general, water acts as a weak oxidizer which selectively removes the amorphous carbon deposited at the graphene–catalyst interface and enhances the activity and lifetime of the catalyst [10]. However, the small statistical fluctuations observed in the growth rate, in region II, could be attributed to the variation in the amount of water molecules in the growth ambient. Recently we also have shown a versatile growth interruption technique to study growth kinetics [22].

From the results described above, it is clear that the onset of oxidation of the catalyst can be minimized by injecting the gases at RT. Also, it was mentioned that the maximum growth rate is observed at a growth temperature of $800 ^\circ C$. It is interesting to note that by avoiding the onset of oxidation of the catalyst caused by exposing it to the air, we can achieve CNTs with a height of $\sim 1.7 mm$ at the above optimized condition. Then, the next idea is to increase the ramp rate in order to avoid the redundant oxidation of the catalyst while heating it to the growth temperature. For the sake of simplicity, the growth temperature of $800 ^\circ C$ is achieved in an integer time span (i.e. ramp time, $t_R = 1–6 min$). The graph of the growth rate as a function of the ramp time is shown in Fig. 5a. The maximum growth rate is seen at a ramp time of 1 min. The growth rate falls gradually as the ramp time increases from 1 to 4 min, but thereafter it shows a rapid fall up to a ramp time of 6 min. The growth rate decreases from 116.56 to 73.06 $\mu m/min$ within the 5 min ramp time. The onset of oxidation occurs during incubation before the system reaches the growth temperature and this reduces the growth rate. This shows that the use of a smaller ramp time can enhance the growth rate of the CNTs. In order to achieve zero ramp time, the sample could be placed in the reactor at the growth temperature using different techniques such as a conveyor belt. Due to technical limitations, we were not able to perform this experiment.

In all of the above experiments, the growth of the CNT forest was carried out at $800 ^\circ C$. Hata et al. [7] carried out the growth of CNTs at $750 ^\circ C$ using WA-CVD. The activity of the water molecules in the reactor chamber determines the super growth of the CNTs, which in turn depends upon the growth temperature. To determine the precise value of the growth rate as a function of synthesis temperature.

![Fig. 5](image)

**Fig. 5** – (a) Growth rate as a function of ramp time $t_R$, and (b) growth rate as a function of synthesis temperature.
temperature, the growth of CNTs was carried out at different growth temperatures. The synthesis was carried out at the optimum condition as discussed in Section 3.1 (acetylene/argon gas composition ratio of 200/500 sccm and ramp rate of 200 °C/min). Fig. 5b shows the growth rate as a function of the growth temperature. It is interesting to note that the graph forms a triangular shape. From the graph, it is seen that at 700 °C the growth rate is 21.13 μm/min, increases to 124.37 μm/min at 810 °C and then falls again to 17.87 μm/min at 1000 °C. The rise and fall of the growth rate near 810 °C is so sharp that it forms an apex. This clearly indicates that the activity of the water molecules is maximized at 810 °C and that this is the growth temperature for the super growth of the CNTs. It is interesting to note that when the growth temperature is 810 °C and the ramp rate is 810 °C/min, the growth rate is 137.5 μm/min. This is the highest growth rate among all of the above experiments, which corresponds to the height of the CNT forest of ~2.2 mm.

The typical SEM micrographs recorded for the CNT films grown at the optimum condition (acetylene/argon composition ratio of 200/500 sccm, the growth temperature of 810 °C and the ramp rate of 810 °C/min) are shown in Fig. 6a. It can be seen that the CNT films attain a height of 2.2 ± 0.002 mm. The ledge of the CNT cake reveals that the nanotubes are uniform in height, densely packed and vertically aligned from the substrate. Moreover, this condition is well maintained for the CNT film synthesized at a higher acetylene partial pressure, but the overall height of the film is reduced. The close view of ridge is shown in Fig. 6b. The synthesis of a uniform CNT cake indicates that the catalyst sites participating in the growth process have identical activity. HRTEM observation shows the presence of CNTs with 2–5 walls and an inner diameter of 5–6 nm. Fig. 6c shows a typical HRTEM image of the CNTs with 2 walls. Fig. 6d shows the SEM image of the patterned CNTs deposited using a mask pattern. A 1 nm Fe layer was deposited inside the TEM mesh serving as the shadow mask. Image shows the morphology of the CNT pillars that were grown. It can be seen that the height of the CNT pillars is uniform. To acquire the SEM images, the CNT grown sample was cut into small pieces using a diamond cutter and, while doing so, the pillars near the edge of the sample became misaligned, moreover several pillars became folded.

4. Conclusions

The effect of the flow rate of the reactant gas mixture and temperature on the growth rate of the CNTs was studied in detail. The optimum condition for the WA-CVD system was observed at an acetylene/argon gas ratio of 200/500 sccm, a heating ramp rate of 810 °C/min and a growth temperature of 810 °C. At this optimum condition, the CNT forest attained a height of 2.2 ± 0.002 mm. The XPS analysis showed that at a lower acetylene content, oxidation hinders the activity and lifetime of the catalyst, whereas, at a higher acetylene content, excess carbonization influenced the growth rate and overall height of the CNT forest. Due to the onset of oxidation...
of the catalyst layers, the growth rate is affected by the injection of gases at higher temperature. The growth rate decreased from 91.5 ± 2.0 μm/min to 53.31 ± 2.0 μm/min as the gases injection temperature was increased from 100 to 800 °C. The analysis of the growth kinetics showed a maximum ΔH/Δt at 800 °C. ΔH/Δt increases from 0.4 to 90.4 μm/min in the first 5 min, remains constant at 93.12 ± 2.0 μm/min up to ~16 min and then decreases to 0.5 μm/min. The analysis of the ramp rate shows that the growth temperature should be achieved in a short period of time to avoid the onset of oxidation. The growth temperature studies showed that 810 °C is the optimum growth temperature for the synthesis of the CNTs in this WA-CVD system.

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