# Effect of $NH_3$ on the Synthesis of Carbon Nanotubes Using Thermal Chemical Vapor Deposition

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**Abstract**
*This study investigates the effect of $NH_3$ gas upon the growth of carbon nanotubes (CNTs) using thermal chemical vapor deposition. It is considered that the CNT synthesis occurs mainly through two steps, clustering of catalyst particles and subsequent growth of CNTs. We thus introduced $NH_3$ during either an annealing or growth step. When $NH_3$ was fed only during annealing, CNTs grew longer and more highly crystalline with diameters unchanged. An addition of $NH_3$ during growth, however, resulted in shorter CNTs with lower crystallinity while increased their diameters. Vertically aligned, highly populated CNT samples showed poor field emission characteristics, leading us to apply post-treatments onto the CNT surface. The CNTs were treated by adhesive tapes or etched back by dc plasma of $N_2$ to reduce the population density and the radius of curvatures of CNTs. We discuss the morphological changes of CNTs and their field emission properties upon surface treatments.*

**Keywords :** carbon nanotubes, $NH_3$, thermal CVD, annealing, growth, field emission, dc plasma etching, tape activation

## 1. Introduction

Since carbon nanotubes (CNTs) were first discovered by Iijima in 1991[1], they have attracted much attention due to their excellent electrical, mechanical and chemical properties. CNTs are promising candidates, in particular, for field emitters because of their unique electrical properties, high aspect ratios and small radii of curvature at their tips. CNTs have been produced by various methods such as arc discharge[2], laser vaporization[3], pyrolysis[4], plasma-enhanced or thermal chemical vapor deposition (CVD)[5,6]. Among them, the thermal CVD has been used long in most cases to deposit vertically aligned CNTs over a large area at low temperatures[7]. In the growth of CNTs, a gas composition plays an important role in determining their morphologies and properties. It has been known that reaction gases, in particular, $NH_3$, can have a great effect on the population densities, diameters, and lengths of CNTs[8], but their effect has been controversial and not yet clear. This study investigates the effect of $NH_3$ on the synthesis of CNTs in either an annealing or a growth step. The CVD synthesis under an optimal condition produced highly populated, vertically aligned CNTs, which revealed poor field emission. We report here an enhancement of field emission characteristics of those CNTs by $N_2$ plasma.

## 2. Experimental

CNTs were synthesized by thermal CVD. Silicon (100) wafer was used as a substrate. The 50 nm-thick Ti layer served as a diffusion barrier, followed by deposition of the 15 nm-thick Al underlayer and finally the 2-nm-thick Invar (Fe-Ni-Co alloy) catalyst for the CNT synthesis. All metallic thin films were deposited by thermal evaporation. The standard pretreatment and growth conditions are shown in Figure 1. The chamber temperature and pressure were fixed at 650 °C and 1.5 Torr, respectively. Annealing and growth were carried out for 8 and 10 min, respectively. $C_2H_2$ was used as a feedstock, while Ar and $NH_3$ were used for dilution and catalyst etching, respectively. A total gas flow rate of

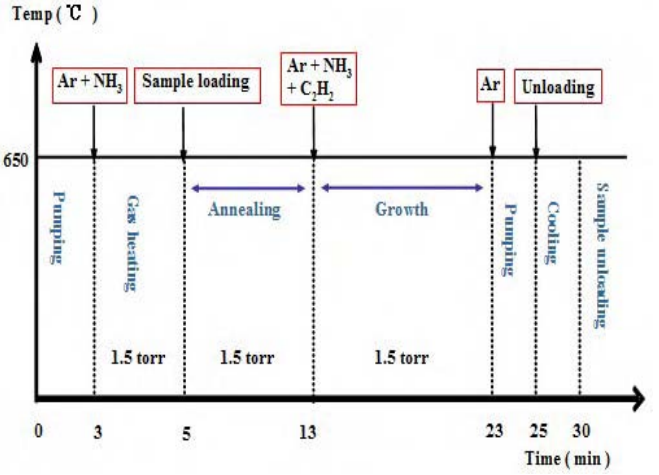


**Figure 1. Schematic of annealing and growth steps employed in this study.**

$NH_3$ and Ar was fixed at 150 sccm. $NH_3$ flow was changed from 0 to 150 sccm and. Since the CNTs are usually synthesized on separate catalyst particles which are previously clustered from a thin film during annealing, $NH_3$ may affect their synthesis in different ways during annealing and growth. We thus studied the effect of $NH_3$ on their synthesis by separately feeding $NH_3$ during annealing or growth following the growth, the MWCNT films were subsequently exposed to DC plasma of $N_2$ (415 V). After treatment, we measured the field emission characteristics. The anode to cathode distance is fixed at 550 μm by using alumina spacers, where an ITO glass was used for anode. The applied electric fields, with a duty ratio of 1/100 and a frequent of 100 Hz, were swept to a maximum of 8 V/μm with an increment of 10 V and an interval of 2 s between steps. The field emission measurements were performed at ~$10^{-7}$ Torr. The CNTs were characterized by SEM (S-4700, HITACHI, Japan), TEM (Tecnai f20, PHILLIPS) and Raman spectroscopy (Renishaw system 3000, Renishaw PLC, UK).

## 3. Results

Figure 2 shows SEM images of the substrates annealed at 650 °C for 8 min in at different gas

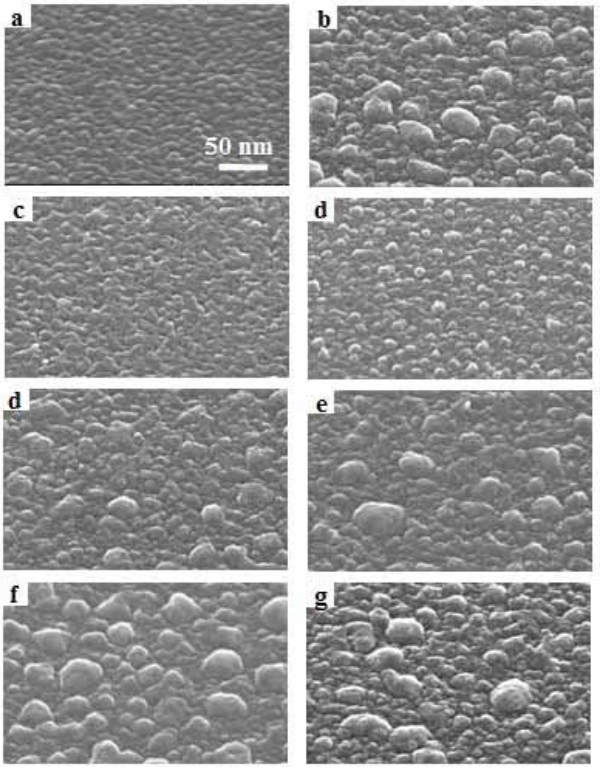


**Figure 2. SEM images of catalyst layers (a) just as-grown and annealed at 650 °C for 8 min with different $NH_3$ flow rates of (b) 0, (c) 13, (d) 25, (e) 50, (f) 75, (g) 100, and (h) 150 sccm. The total flow rates of Ar and $NH_3$ was kept 150 sccm.**

compositions of Ar and $NH_3$. All the images are in the same scale. It is noticed that $NH_3$ considerably affects the clustering of catalyst layers during annealing[9-14]. The cluster sizes proportionally increases with the $NH_3$ flow rates. In Figure 2c, the clusters are not agglomerated probably due to an insufficient amount (13 sccm) of $NH_3$, but in Figure 2d (25 sccm) small clusters are uniformly distributed. Figure 3 shows SEM images of CNTs grown by introducing different amounts of $NH_3$ during annealing, which correspond to Figures 2b-h. With increasing $NH_3$ up to 25 sccm, as summarized in Figure 5b, the lengths of CNTs increase, but slowly decrease above 25 sccm. Their lengths with the flow rates of $NH_3$ can vary with a correlation to the catalyst cluster sizes. The catalyst layer is spherically granulated to the minimum size of ~45 nm at 25 sccm, where the longest CNTs occur. The smaller

catalyst clusters result in the longer CNTs. The crystallinity of CNTs, measured in $I_G/I_D$ using Raman spectroscopy, shows the exactly same behavior of their lengths. In a TEM image of CNTs grown 25 sccm $NH_3$, given in Figure 3h, the CNTs are multi-walled with an outer diameter of ~15-25 nm, consisting of hollow compartments with a bamboo structure which has frequently occurred in CNTs grown by CVD. Figure 4 presents SEM images of CNTs grown by varying the flow rates of $NH_3$ during the growth step. The annealing and the growth were performed for 5 and 10 min, respectively. The longest CNTs occurred for the 5-min annealing with a flow of only Ar, but for the 8-min annealing with any addition of $NH_3$. As given in Figure 5, an addition of larger amounts of $NH_3$ during growth decreases the CNT lengths while increasing their diameters. It seems that he CNTs are shortened probably due to the etching of $NH_3$ against defective CNTs during growth. The CNTs shows lower crystallinity with increasing amounts of $NH_3$ fed during growth. Here their crystallinity also shows the same variation of the lengths as a function of flow rates. The crystallinity of CNTs could be improved by $NH_3$ etching, but could also be simultaneously deteriorated due to an incorporation of N atoms into CNT lattices. In this study, the latter effect of $NH_3$ fed during growth appears to be stronger, giving rise to the lower crystallinity of CNTs with larger flow rates of $NH_3$. Figure 4h shows a TEM image of CNTs given in Figure 4g, revealing more defective bamboo structure than

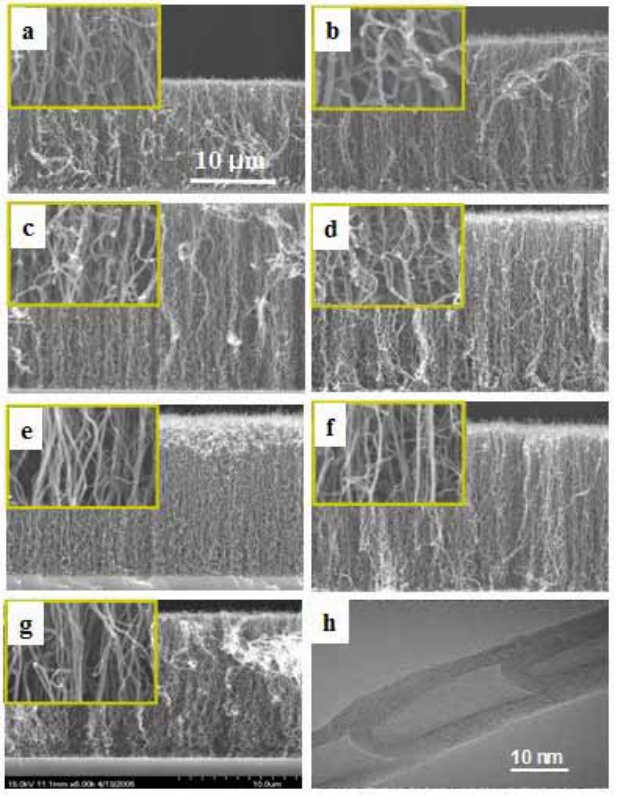


**Figure 3. SEM images of CNTs grown with various $NH_3$ flow rates during annealing, where CNTs (a-g) grew on catalyst layers given in Figures. 2 (b-h), respectively and (h) a TEM image of CNTs grown using 25 sccm $NH_3$.**

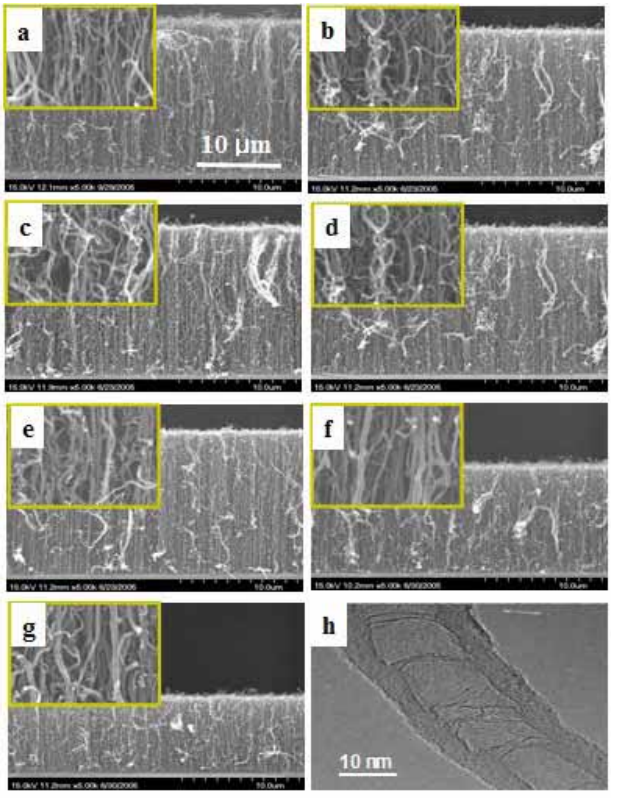


**Figure 4. SEM images of CNTs grown using $NH_3$ flow rates of (a) 0, (b) 13, (c) 25, (d) 50, (e) 75, (f) 100, (g) 150 sccm., fed during growth, and (h) a TEM image of CNTs grown using 150 sccm $NH_3$.**

Figure 3h. TEM observations agree with crystallinity measurements ($I_G/I_D$) of Raman spectra, depending upon whether $NH_3$ was fed during annealing or during growth. The crystallinity of CNTs was deteriorated by an addition of $NH_3$ during annealing, but improved by its addition during annealing. Figure 6 shows SEM images of MWCNTs etched for 0, 5, 10, 15, and 20 min by $N_2$ plasma treatments [15]. It was observed that the dc plasma treatment could damage the MWCNTs. The CNTs became shorter, rougher on surface, and formed bundles with a lower density, as increasing an etching time, as recently reported by Liu et al. [16]. Most of CNTs were etched out after 20 min or longer, as shown in Figure 6e. A TEM observation given in Figure 6f, g presents that a CNT tip was sharpened by etching and its wall became thicker, probably due to the formation of an amorphous carbon layer surrounding an original CNT body by re-deposition of etched carbon. Figure 7a are $I_G/I_D$ ratios, calculated from Raman spectra, of the CNTs samples etched for different time.

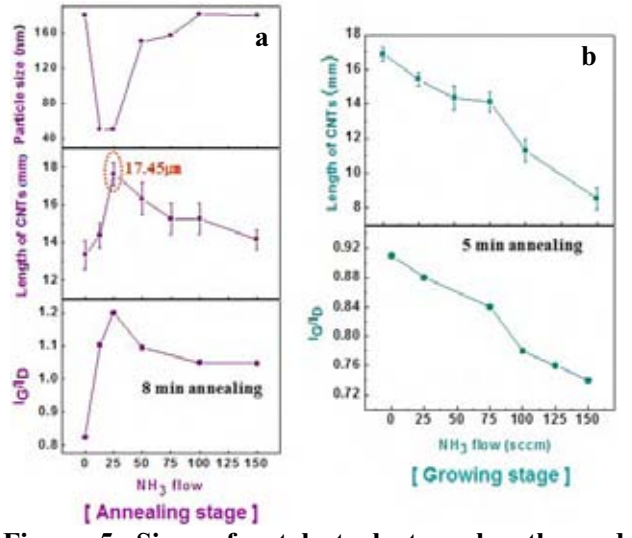


**Figure 5. Sizes of catalyst clusters, lengths and crystallinity ($I_D/I_G$) of CNTs with various flows of $NH_3$ introduced during (a) annealing and (b) growth.**

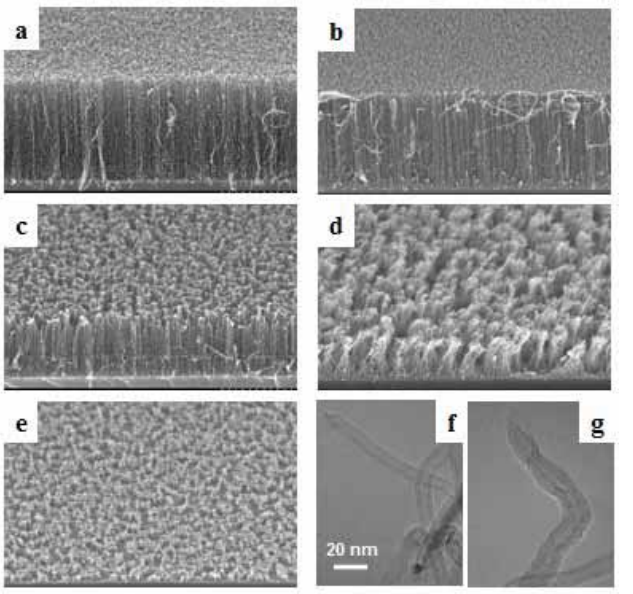


**Figure 6. SEM images of MWCNTs etched by $N_2$ plasma for (a) 0, (b) 5, (c) 10, (d) 15, (e) 20 min and TEM images of (f) as-grown and (g) plasma-etched (10 min) CNTs.**

As increasing the etching time, the crystallinity drastically decreased. It seems that the CNTs were strongly damaged by ion bombardment during the plasma treatment [17]. Figure 7b gives field emission I-V curves of MWCNTs etched for 0, 5, 10, 15 and 20 min. With longer etching up to 10 min, the emission properties were improved, but deteriorated thereafter, finally worse than the as-grown ones at 20 min. Consequently, the 10-min-treated CNTs show the lowest turn-on field of 2.1 V/μm and the highest emission current density of 350 μA/cm$^2$ at ~ 4.5 V/μm. A measurement area was 0.49 cm$^2$. The plasma-etched CNTs revealed better field emission characteristics than the CNTs treated by tape activation, which has been frequently engaged to reduce the CNT density. The enhancement of field emission properties by the plasma etching seems to be attributed to tip sharpening as well as a reduced density of CNTs.

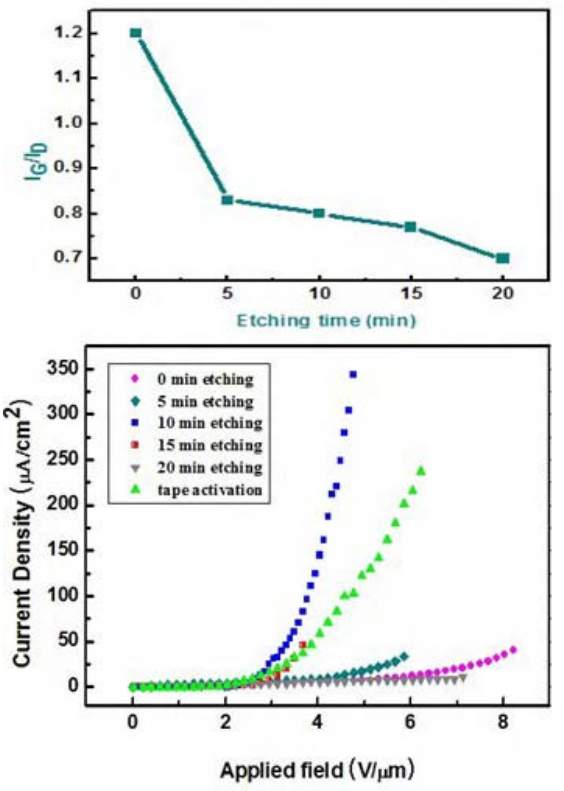


**Figure 7. (a) Field emission I-V curves and (b) Raman spectra of MWCNTs subject to the plasma etching for 0, 5, 10, 15, and 20.**

## 4. Conclusion

Addition of $NH_3$ has different effects upon the CNT synthesis when introduced either during annealing or growth. When $NH_3$ was introduced during annealing, CNTs became longer and more highly crystalline with unchanged diameters. Feeding $NH_3$ during growth resulted in shorter CNTs with lower crystallinity, but increased their diameters. Addition of $NH_3$ seems to be beneficial to the synthesis of CNTs in the annealing stage likely due to the etching effect of catalyst, but not in the growth stage probably due to etching defective CNTs and more likely due to simultaneous incorporation of N atoms into the CNT lattices. The highly populated, vertically aligned CNTs, which ordinarily occurred at our CVD, were etched by $N_2$ plasma, to reduce the density and tip radii of CNTs. With a longer etching time, the CNTs became shorter, rougher on surface, formed bundles, and became less crystalline. The emission properties were enhanced with an etching time up to 10 min, but became worse for etching longer than 10 min.

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