

Chapter 4 Results and discussion

4-1 Effects of H plasma pretreatment on catalyst particle formation

The morphologies of Co catalyst surface after H-plasma pretreatment are depicted in Figs. 4-1 to 4-4 for seven different pretreatment conditions, respectively. The sizes and size ranges of catalyst particles and the corresponding pretreatment conditions are listed in Table 3-1. Effect of hydrogen plasma is essentially to remove the possible oxide layer on the catalyst film and to activate the surface to become the nano-sized catalyst particles. By comparing Figs. 4-1 and 4-2, it is found that a greater hydrogen pressure can give rise to a greater particle size and a less catalyst number density, where left side images are the corresponding right side images at higher magnifications. It is interesting to note that a greater H pressure results in an increase in substrate temperature.

Referring to Figs.4-3 and 4-4, it shows that a greater microwave power also can give rise to a greater particle size of catalyst. In other words, under higher microwave power conditions, there is a tendency to form more coarse particles or particle clusters, as indicated under conditions PT6 and PT7, where the substrate temperature may reach 600°C. It is obvious that a higher pressure or microwave power is essentially to increase the substrate temperature, which may induce the catalyst particles to agglomerate to become a larger particle or aggregate to become particle clusters.

In summary, under the present pretreatment conditions, the average particle size and particle number density can be manipulated by changing the H-plasma pressure and microwave power, though the particle distribution is not quite sensitive to these parameters. In this experiment, the condition PT1 results in the particle sizes of 20 ~ 70 nm and particle number density of $\sim 8.84 \times 10^8 / \text{in}^2$ which was adopted in proceeding process to grow CNTs.

4-2 Effects of bias, forest supporting and deposition time on CNTs growth

In MPCVD system, the substrate bias can be due to the applied bias and self-bias. Under no applied substrate bias condition, the morphologies of as-grown CNTs under different source gases [H_2+CH_4 (80/3 sccm), $\text{Ar}+\text{C}_2\text{H}_2$ (80/5 sccm) and $\text{NH}_3+\text{C}_2\text{H}_2$ (160/40 sccm)] are shown in Figs.4-5 (a) ~ 4-5(c) for Specimens A1, A2 and A3, respectively, as indicated in Table 3-2. It reveals that the aligned CNTs can be synthesized for Specimens A2 and A3 under $\text{Ar}+\text{C}_2\text{H}_2$ and $\text{NH}_3+\text{C}_2\text{H}_2$ as the source gases, but not for Specimen A1 under H_2+CH_4 . Effects of self-bias due to different sources on CNTs growth was examined by Bower's group [Bower-00-830]. They proposed that the self-bias potential from the source gases can be expressed by:

$$V' = \left(\frac{kT_e}{2e} \right) \ln \left(\frac{m_i}{2.3m_e} \right) \quad (4-1)$$

Where k is Boltzmann's constant; T_e , the electron temperature; e , the charge of the electron; m_i and m_e are the mass of ions and electrons, respectively. In other words, the self-bias potential is proportional to the mass of the ions. In terms of ion mass, therefore, ammonia and argon plasma will establish a stronger local bias at the substrate surface, as compared with other types of source gases, such as hydrogen plasma.

It was proposed that both the applied substrate bias and the system self-bias are the favor conditions to grow the aligned CNTs [Tsai-99-3462]. This is in agreement with the present results that a greater self-bias due to greater ion mass for Specimens A2 and A3 gives rise to a higher tendency to form the aligned CNTs, as comparing with Specimen A1. Another possible mechanism to form the aligned CNTs may come from the effect of source gases to form different tube number density of CNTs, where a higher tube number density of CNTs may act like "forest" to support and align each other by Van der Waal force [Fan-99-512]. The corresponding SEM CNTs morphologies of Figs. 4-5(b) and 4-5(c) at higher magnification are shown in Figs. 4-6(a) and 4-6(b), respectively. Although under the same processing conditions, except the source gases, it reveals that the tube number density of CNTs grown under $\text{NH}_3+\text{C}_2\text{H}_2$ as the source gases is greater than under $\text{Ar}+\text{C}_2\text{H}_2$. This may be related to

the fact that more H plasma in the $\text{NH}_3+\text{C}_2\text{H}_2$ atmosphere can be acted as the etching agent at the beginning processing stage to cut more catalyst particles to become smaller sizes; therefore, a greater tube number density may result.

On effect of the applied bias, morphologies of the as-grown CNTs under different applied negative substrate bias assisted conditions are shown in Figs. 4-7(a) ~ (d) for Specimens A5, A7, A8 and A9, respectively, where other processing conditions are the same. As discussed in the previous paragraph on effect of self-bias, a greater negative applied bias applied is a more favor condition to grow CNTs with better alignment, though the tube number density, length, and diameter of CNTs are no significant differences among these specimens. Nevertheless, their Raman spectra of the CNTs under different applied bias conditions do make a difference, as will be discussed in the next section.

On effect of CNTs deposition time, morphologies of as-grown CNTs under different growth times of 5 min, 10 min and 15 min for Specimens A4, A5 and A6 are shown in Figs. 4-8 (a) to 4-8 (c), respectively. Figures 4-8(c) and 4-8(d) are images that show the CNTs near the substrate side and top side of the tubes for Specimen A6, and there are some damages on the tubes due to specimen handling by tweezers. This signifies a weak bonding between tubes and the substrate. It exhibits that the straightness of the aligned CNTs is depending on the deposition time. At longer deposition time, the tubes may become longer and wave-like in shape near the tips of the tubes, such as Fig. 4-8(c). The reason of the wave-like CNTs formation may relate to a lack of “forest” supporting from neighbor tubes after longer deposition time due to different growth rates of each individual CNT. This may be related to the following reasons. After longer deposition times, the catalysts of the tubes may be poisoned at different deposition periods, thus it gives rise to uneven tube length and obtains less neighbor supporting to become wave-like CNTs.

4-3 Raman spectra of CNTs

Under different applied substrate bias, Raman spectra of the as-grown CNTs for Specimens A5, A7, A8 and A9 are shown in Figs.4-9(a), 4-9(b), 4-9(c) and 4-9(d), respectively. The figures exhibit D band (sp^3 bonding) peaks around $1354 \sim 1359 \text{ cm}^{-1}$ and G band (sp^2 bonding) peaks around $1585 \sim 1589 \text{ cm}^{-1}$. These peaks are believed to be the typical spectra of MWCNT [Choi-02-4007]. It is interesting to note that the I_G/I_D ratios for these specimens are from 0.98 to 1.02 by increasing the applied substrate bias from -50 to -250 V, as shown in Table 4-1. Practically, the I_G/I_D ratio is an index of CNTs quality. A greater value signifies a better graphitized structure.

The reasons for a better CNTs quality at higher negative applied bias may relate to greater ions bombardment energy at higher applied potential which be able to clean the carbonaceous defects on substrate surface efficiency and to maintain carbon diffusion path of catalyst particle to form CNTs. Furthermore, negative substrate bias can enhance the negative potential of the plasma sheath, which is a zone among the plasma bulk and the substrate surface that has negative potential. In the sheath, electrons may be rejected, but the positive ions can concentrate in the plasma sheath and obtain energy to accelerate ions to bombard the substrate. When negative bias applies during CNTs growth, the positive ions will deposit more effectively along the electric field to the substrate, and consequently, the aligned CNT will easily be formed. By contrast, the wave-like CNTs can be considered have more defect than aligned CNTs due to existence of more pentagonal and heptagonal rings [Hiura-94-148].

4-4 Field emission properties of the aligned CNTs

Under different negative applied biases, the J-E curves of the aligned CNTs (Specimens A5, A7, A8 and A9) are shown in Fig.4-10. The corresponding turn on electric field, threshold electric field and current density at 10 V/ μm are listed in Table 4-2. The turn on electric field (E_{to}) and threshold electric field (E_{th}) are defined as the applied electric field to reach the current density of 10 $\mu\text{A}/\text{cm}^2$ and 10 mA/cm^2 , respectively. It indicates that the CNTs of Specimen A5 with the best FE properties which has no applied bias-assisted growth, where E_{to} and E_{th} are ~ 4.4 V/ μm and ~ 8.26 V/ μm , respectively, and the current density at 10V/ μm is ~ 88.7 mA/cm^2 . These FE properties are much better than the CNTs synthesized by ECR-CVD.

Furthermore, by referring to $I_{\text{G}}/I_{\text{D}}$ ratios in Figs. 4-9 (a) ~ (d), it shows that the CNTs with the best FE properties are belong to the CNTs with less $I_{\text{G}}/I_{\text{D}}$ ratios or wave-like in morphology, as reported in the literature [Obraztsov-00-1190; Hiura-94-148; Robertson-96-797]. This may be due to the facts that the wave-like CNTs possesses a greater effective emission surface area or defect centers to emit current and so a higher enhancement factor. The field enhancement factor β is related to so-called “ β' ” and “ r ”, which are a geometric correction factor and the radius of the emitter tip, respectively, as shown in Eq.2-12. The field enhancement factors for these Specimens are ranging from 2481 to 4096, where the highest β value is 4096 for Specimen A5 without the applied bias during CNTs growth as shown in Fig 4-11 (a) ~ (d) and Table 4-3.

Under different growth times, the J-E curves and FE properties of the aligned CNTs (Specimens A4, A5 and A6) are shown in Fig.4-12 and Table 4-4. It indicates that the E_{to} and E_{th} values make no significant differences for different CNTs deposition times. However, under 10 V/ μm condition, there is a maximum current density at an intermediate deposition time (10 min. in this case). It is understood that the current density of CNTs is closely related to the screening effect [Nilsson-00-2071]. At short (5 min) deposition time, uniform tube length and higher tube number density result in a greater screening effect. On the contrary, at longer (15

min) deposition time, the wave-like CNTs may cause more tangling tubes to enhance screening effect. Therefore, at the intermediate deposition time (10 min), the tube length is not quite uniform on the top surface to minimize the screening effect and so to enhance the emission efficiency.

About the stability of the as-grown CNTs, the J-E measurements at the same spots on CNTs were conducted several times to determine its stability. The results show that the most of the CNTs were damaged or stripped off from the substrate by an electric field of $10 \text{ V}/\mu\text{m}$ after repeated measurements for less than ten times. The typical stripped CNTs are shown in Fig. 4-13 (a) and (b). The reason may be due to weak bonding between the substrate and the CNTs which lead CNTs stripping and damage during the repeated applications of electric field. Therefore, the deposited CNTs for applications in FED require developing the packaging technique or improving the adhesion strength to solve the stability problem.



4-5 Effects of post plasma trimming on structure and properties of CNTs

As discussed in the previous paragraph, since the proper defect density on the CNTs may enhance the FE properties, Specimen A5 was conducted several different post trimming processes to vary its defect structures to examine the property change. The gases to generate plasma for post trimming processes include hydrogen, nitrogen, argon and ammonia. Under no applied substrate bias, the corresponding CNTs morphologies after post plasma trimming are shown in Figs. 4-14 to 4-17, respectively, where (a) and (b) of each figure are corresponding to the top and side view images at different magnifications, respectively.

The results indicate that the alignment and defect structure of CNTs make no significant differences among different post treatment processes, except ammonia-plasma trimming process, where the CNTs are almost etched off completely. In other words, ammonia-plasma gives a greater bombardment effect. It is interesting and unexpected to note that the open-ended CNTs can not be obtained under the present post trimming processes.

About effects of post treatments on bonding structure, Raman spectra of CNTs before and after post plasma trimming processes are compared in Figs. 4-18 and 4-19. The results show that the I_G/I_D ratio of CNTs changes from 0.98 for as-grown CNTs to 0.82, 0.86, and 0.76 for CNTs after three different post plasma treatments, as shown in Table 4-5 and 4-6. A decrease in value of I_G/I_D ratio due to post treatments is mainly an increase in D-band intensity. In other words, effect of plasma treatment is essentially making more disorder stretching mode.

The J-E curves and FE properties of CNTs after post treatments are shown in Figs. 4-20 (a) ~ (d) and Table 4-7. The results indicate that the post plasma trimming is detrimental to the FE properties of CNTs. It is interesting to note that a greater decrease in I_G/I_D ratio of CNTs due to different post treatments is accompanied by a greater degrade in FE properties, which is not in agreement with the phenomena discussed in the previous section. This can be explained from the following reasons. First, it must be under the conditions of no significant damage to the stems of CNTs, and then defect density is more favor to enhance FE properties.

However, this is the case of the present post-treated CNTs, where several stems of CNTs have been destructed after post trimming processes, though it accompanies a decrease in I_G/I_D ratios. Therefore, it is concluded that a proper post plasma trimming process must be developed to control the defect density and to maintain the structure integrity of CNTs in order to enhance the FE performance of CNTs.



4-6 TEM and HRTEM of CNTs

TEM and HRTEM micrographs of the as-grown CNTs without applied bias (Specimen A5) are shown in Figs. 4-21 to 4-22. The figures show bamboo-like CNTs, which may be due to the presence of nitrogen in the source gases (NH_3), as proposed by many investigators [Chang-02-793; Lee-200-3397; Yu-00-529]. The figures also indicate no catalysts encapsulated in the tips of the tube, implying the base-growth CNTs. This may be due to a greater tendency of Co catalysts to react with Si to form cobalt silicide (CoSi_x) bonding [Hsu-02-NCTU]. The CoSi_x can form a structure with an inverted triangle shape, which is embedded in the silicon substrate like an “anchor” [Bower-00-2767].

The HRTEM images of tip, middle and bottom of the CNT are shown in Fig.4-22 (a) ~ (c), respectively. It reveals that the outer and inner diameters of CNTs are about ~ 22 nm and ~ 7 nm, respectively, which are corresponding to 23 graphene layers with interlayer distance of ~ 0.33 nm, close to graphene spacing of 0.34 nm for the pure CNTs reported in literature [Ebbesen-97-7]. Due to a great bonding between catalysts with substrate, there are no catalysts at the bottom of the detached CNTs for HRTEM examination. It is speculated that the base-growth CNTs have a better FE properties due to lack of blocking effect of catalysts at the tips of CNTs.

4-7 Effects of applied bias and H₂ / CH₄ ratio on CNCs growth

Under the same H₂/CH₄ ratio (80/5 sccm/sccm), effect of the substrate bias on carbon nanostructures was conducted by varying bias from 0 V to -300 V. The corresponding morphologies are shown in Figs.4-23(a) ~ (e). The results show that the deposited nanostructures gradually change from polyhedral carbon clusters (0 V bias) to needle-like CNCs with sharper tips. The CH₄ concentrations in these cases are greater than for diamond film deposition, but smaller than for CNTs deposition [Chang-02-NCTU; Hsu-02-NCTU].

From Table 3-4 and Fig. 4-23, the nanostructures become the aligned CNCs in shape, when the applied bias is greater than -150 V, and the tips of CNCs will be shaper at higher negative bias. Therefore, it implies that an enough negative bias is an essential condition to form the aligned CNCs. The results also indicate that the average height of the CNCs increases with an increase in the applied bias from 20 ~ 80 nm (at -150V bias) to ~ 500 nm (at -300 V bias). It implies a greater applied bias can enhance the growth rate of CNCs perpendicular to the substrate. However, there is a maximum average bottom diameter of CNCs growth under the intermediate applied bias (-250 V), where the diameter is much larger than the catalyst size. In other words, under too high applied bias (e.g. -300 V), effect of ions bombardment may lead to stronger etching to delaminate the diameter of CNCs, and also lead to a greater deposition rate. This phenomenon is agreement with the observation of the smaller apex angle, more split stems and greater length of the CNCs at higher applied bias, where the apex angles of CNCs are 15° ~ 20° and 9° ~ 12° under -250 V and -300 V applied bias, respectively.

The more split stems of CNCs may be the reason for a greater number density at higher applied bias, as shown in Fig. 4-23 (e) with the split peaks from one CNC. Under -300 V applied bias, the uniform large area of aligned and dense CNCs can be obtained, as shown in Figs. 4-24 (a) and (b).

Under different H₂ and CH₄ flow rate ratios, morphologies of as-grown CNCs for Specimens B6, B7, B8 and B9 with H₂/CH₄ ratios of 80/1, 80/5, 80/10, and 80/15 sccm/sccm are shown in Figs. 4-25 (a) ~ (d), respectively. It shows the CNCs with greater average apex angle and the bottom diameters are deposited under higher CH₄/H₂ ratio in gas sources. In other words, the higher CH₄ concentration may lead to an increase in the lateral growth rate of CNCs to become blunt apex angles. The shapes of CNCs are determined essentially by the results of competition among etching rate of plasma species, the lateral growth rate and the upward deposition rate of carbon along the surface or through the interior of the catalysts. A higher H₂ concentration is essentially to increase the etching rate of carbon on the catalysts to prolong the life of catalysts from poisoning. Under the present deposition conditions, the CNCs with the sharpest tips are synthesized with H₂/CH₄ ratios above 80/5.



4-8 Raman and AES analyses of CNCs

Figure 4-26 is the Raman spectra of CNCs (Specimen B5). It shows the D band and G band are around $\sim 1334 \text{ cm}^{-1}$ and $\sim 1598 \text{ cm}^{-1}$, respectively, where the I_G/I_D ratio is 0.806. It was proposed^[Huang-03-6796] that the $E_{2g}G$ mode shifted from its normal value of 1580 to 1600 cm^{-1} is an indication of the existence of nanocrystalline graphite or sp^2 clusters. The peak at 1334 cm^{-1} is assigned as A_{1g} mode rather than diamond peak at 1332 cm^{-1} , thus peak around 1334 cm^{-1} may attribute to the presence of aromatic rings in disordered graphite. Therefore, the CNCs can be consider as sp^2 clusters in an amorphous carbon (a:C) matrix.

AES spectra and the corresponding SEM image for the as-grown CNCs (Specimen B5) at the tip (P1) and bottom (P2) sites are shown in Fig. 4-27. The magnified spectra of Fig. 4-27 and the reported reference spectra^[Lin-01-126; Ferguson-98-63] are depicted in Figs. 4-28 (a) ~ (d). The results show the carbon, nitrogen, oxygen, cobalt and silicon signals are detected both on the tip and bottom surfaces. It speculates that the signal of oxygen and nitrogen may attribute from atmosphere absorbed by specimen. By comparing Fig. 4-28(a) with Fig. 4-28(b), the peaks at 252 eV and 275 eV for CNCs may be corresponding to the reference peaks at 248 eV and 271 eV for graphite with a shift of 4 eV in value due to AES system shift. According to Figs. 4-28(c) and (d), it shows Co peak intensity at the CNC tip position is weaker than at the CNC bottom position. It implies a greater concentration of Co catalyst particle in CNC at the bottom. This is in agreement with the TEM and HRTEM examination, as will be discussed in next section. Moreover, it is interesting to note that the significant Si signal is present on the CNCs surface. Two reasons for the presence of Si were proposed. First, it may be due to the bias induced Si sputtering from the Si substrate and re-deposit on the surface^[Bai-03-185]. Secondly, it may be due to the diffusion of Si atoms along the CNC from Si substrate^[Yeh-01-3609]. Further study is needed.

4-9 TEM and HRTEM of CNCs

The TEM and HRTEM micrographs of the as-grown CNC (Specimen B5) are shown in Figs.4-29 to 4-30, respectively. The corresponding ED pattern of CNC in Fig. 4-29(a) at bottom, stem and tip sites are shown in Figs.4-29 (b), (c) and (d), respectively. The results indicate the CNC at the bottom is a single crystal Co material embedded in polycrystalline graphite matrix. The Co materials are identified to be FCC in structure with a lattice constant of 0.354 nm, where the camera length and accelerating voltage are 80 cm and 200 KeV, respectively. Furthermore, the diffraction rings of stem and tip of CNC also indicate to be the polycrystalline graphite structure. This is in agreement with AES examination discussed in the previous section and also conforms to HRTEM images in Figs. 4-30(a) and (b) with a short rang ordered graphene layer spacing of 0.34 nm, though there are some amorphous carbons in the matrix. It is interesting to note that Fig. 4-30 shows the existence of Co catalysts in the tips of CNCs. This conforms to a few ED spots on ED patterns of the stem and tips in Figs. 4-29(c) and (d). The existence of cobalt nanoparticle in the tip of CNCs may be due to a two-step growth mechanism of CNCs. At initial step, the tip growth CNTs are formed to push the catalysts upward; subsequently, anisotropic etching, lateral growth and precipitation processes to form CNCs may split the catalysts into two or more parts during growth, where the top part of the catalyst may continue to be pushed in the tips. This is similar to the split catalyst mechanism proposed by Lin, et al ^[Lin-02-922]. Hence the structure of CNCs can be considered as mixture of single crystal Co, polycrystalline graphite, amorphous Si and amorphous carbon.

4-10 Field emission properties of CNCs

Under different negative applied biases, the J-E curves of the CNCs (Specimens B2, B3, B4 and B5) are shown in Fig.4-31 (a) ~ (d). The corresponding turn on electric field, threshold electric field and current density at 10 V/ μm are listed in Table 4-8. The result indicates that the CNCs with the best FE properties are Specimen B5 with -300 V applied bias-assisted growth, where the E_{to} and E_{th} are ~ 5.0 V/ μm and ~ 6.99 V/ μm , respectively, and the current density at 10 V/ μm ~ 173.42 mA/cm².

The field enhancement factor β about 4993 is listed in Table 4-9, that is calculated from F-N plot as shown in Fig. 4-32. The high β value of CNCs may be induced by appropriate field emitter number density and sharp apex angle. Therefore, the FE properties of CNCs are much better than the CNTs in this experiment.

The I-T curve of CNCs (Specimen B5) is depicted in Fig.4-32, where under the 900 V applied bias and the spacing among the specimen and anode is 100 μm during 3600 Sec. (1 hour) measure. The result shows the CNCs with emission ~ 10 μA for 3600 seconds operation is stable. The first 300 seconds reveal emission current is rising with time, it may be due to the defects which attach on the CNCs are removed by intense electric field. Further, the result also indicates the CNCs can bear intense electric field of long time operation. The life time of CNCs is longer than CNTs emitter as described above in section 4-4 so far. In summary, the CNCs have many merits for applied of field emitter as listed in following:

- (1) Smaller radius of tip and aspect ratio
- (2) Uniform grown with appropriate number density on the substrate
- (3) Good adhesion between CNCs and substrate
- (4) Lower temperature process compatible with IC fabrication.