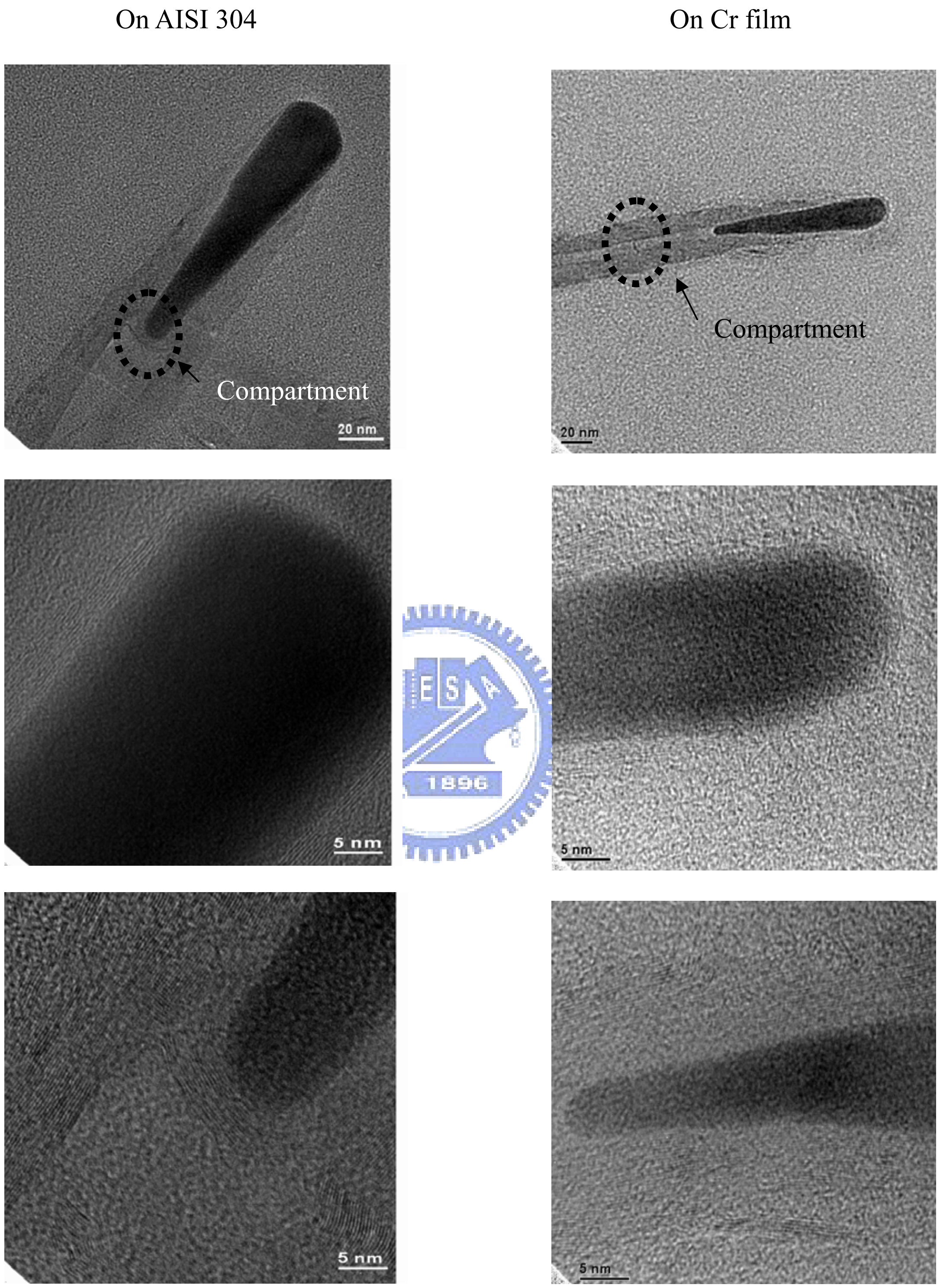
4.6 Growth Model of Carbon Nanotubes by Using MPCVD

According to the results that obtained from that aligned carbon nanotubes grown on stainless steel and bias-enhanced hydrogen plasma-pretreated Cr film. Here the growth model of CNTs by MPCVD was proposed.

In both cases, TEM studies show that the top ends of the nanotubes are closed and encapsulated metal nanoparticles are observed at the top ends of the nanotubes, as shown in Fig. 59 (also see Fig. 43-45, 57). We believe that the growth process reported here is coincided with the 'tip-growth' (detached particle) model for catalytically grown nanotubes proposed by Amelinckx et al. [183]. From this model, it can be clearly found that the hollow cavity of the depicted nanotube is directly connected with the surface of the substrate. The tip-growth mode proposes that a nanotube lengthens while carrying away a metal catalyst particle at its end. The interaction between the metal catalyst particle and the substrate is an important factor that influences the nanotube growth mode [126]. The strong interaction between most of the catalyst particles and the substrate, resulting in the failure of catalyst particles to depart from the substrate, accounts for the formation of nanotubes by the 'base-growth' mode. In contrast, under a certain condition (such as small, sharp catalyst particles), when the metal/substrate interaction is weak, the nanotube grows while carrying away a catalyst particle at the end by the tip-growth mode.



On AISI 304

On Cr film

Fig. 59. TEM images of the CNTs grown on AISI 304 and Cr film by using MPCVD.

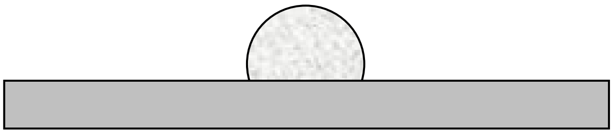
Besides, according to the reaction species during plasma processing and catalyzed growth characterization, many various growth mechanisms were proposed [184,185]. Base on the previous study, a growth model of CNTs growth model, as shown in Fig. 60, is considered as followed.

(a) Initially, metal particles resulted from the rupture of the surface which suffering the plasma etching. This process leads to the formation of catalytic particles.

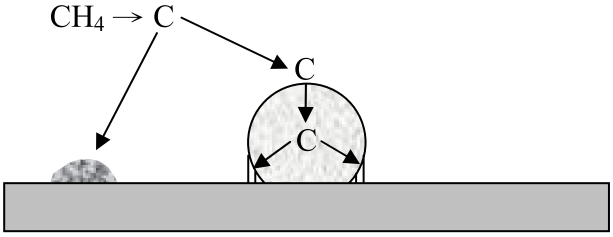
(b) Carbon atoms, dissociated from the CH_4 sources gas, are deposited on the surface of catalyst particles. Then a physical absorption of carbon atoms occurred. After carbon absorption, saturated carbon film will formed from the continuous decomposition of source gas. The catalyst and substrate surfaces were saturated with carbon layers.

(c) Catalyst was pushed upward due to the diffusion and weak metal/substrate interaction (tip-growth mode). Core is formed below catalyst particle because the C atom is too late to diffuse. After the wall of carbon nanotube was formed and rolled up in spherical and cylindrical shapes, hollow carbon nanotubes grown.

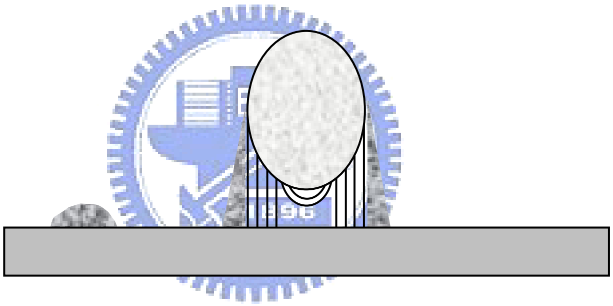
(d) Random CNTs and other defective carbon materials are anisotropic etching by bias-enhanced plasma. In the meantime, vertically aligned CNTs due to the crowing effect, which suffering less etching, were lengthening by continuous carbon species supplied and diffused into the growing carbon nanotubes.



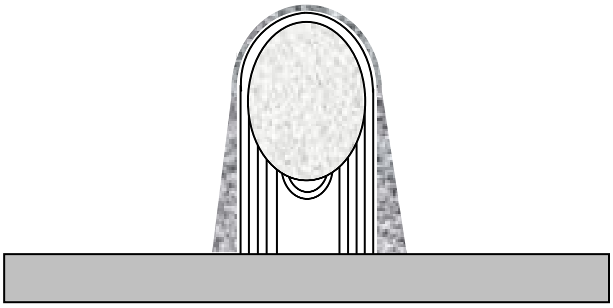
(a) Formation of catalytic particles



(b) Movement of carbon atoms



(c) Hollow carbon nanotubes grown



(d) Lengthening of carbon nanotubes

Fig. 60. Growth model of CNTs by using MPCVD

4.7 Comparisons between HWCVD and MPCVD

The main purpose of this thesis is to provide a modified HWCVD method to synthesis CNTs, and characterize the field emission properties. In this thesis, HWCVD and MPCVD have been used for the growth of CNTs film. By using HWCVD, it was reported that method for preparing MWCNTs on silicon. The effect of different carrier gases and synthesized aligned CNTs by changing flow direction of carrier gas in directed HWCVD method, and developed the growth mechanism of this method. Furthermore, CNTs were grown by MPCVD to compare the differences between these two methods. By using MPCVD, the bias effect, growth period, and catalytic effect of CNTs grown on AISI 304 by MPCVD were studied. CNTs were synthesized by using CH_4/CO_2 or CH_4/H_2 reactant gas. The mechanism of aligned CNTs grown by MPCVD was also proposed. In this section, the differences between deposition systems, characterization and field emission properties of CNTs grown by these two methods will be presented.

4.7.1 Deposition System

Table 8 shows the comparisons between HWCVD and MPCVD deposition system. In both deposition systems, similar catalysts were used. Alcohol and methane are the carbon sources in HWCVD and MPCVD, respectively. The most important feature of direct HWCVD synthesis method is that no obvious cost or technological obstacles arise in scaling up the method for continuous high-quantity production. This simplified design possesses many advantages. The carrier gas is nonflammable, alcohol is nontoxic, and all complex vacuum seals are eliminated. The direct HWCVD system has the potential to inexpensively synthesize large quantities of CNTs continuously. In contrast, MPCVD needs expensive microwave generator and vacuum system. Therefore, HWCVD should be simpler and less expensive than MPCVD.

Table 8 Comparisons between HWCVD and MPCVD deposition system

	HWCVD			MPCVD		
	A	B	C	E	F	G
Main Catalysts	Fe, Cr	Fe, Cr	Fe, Cr	Fe, Ni, Cr	Cr	Cr
Main effect	Carrier gas: CO_2	Carrier gas: Ar	CO_2 Flow direction	Time	Reactant	H_2 plasma Pretreatment
Reactant	Alcohol	Alcohol	Alcohol	CH_4 / CO_2	CH_4 / CO_2	CH_4 / H_2
Pressure	~ 1 atm	~ 1 atm	~ 1 atm	1333 Pa	2666 Pa	2666 Pa
Temperature	~ 700 ℃	~ 700 ℃	~ 700 ℃	~ 600 ℃	~ 700 ℃	~ 700 ℃
Cost	Low			High		
Scale up	Easy			Hard		

The data listed in HWCVD is acquired at flow rate of 15 sccm.

4.7.2 CNTs Characterization and Field Emission Properties

Table 9 shows the comparisons between characteristics and field emission properties of CNTs grown by using HWCVD and MPCVD. In general, MPCVD yield higher density and uniformity than HWCVD does. This thesis demonstrated that the uniformity of the CNTs grown on the sample must be further improved. By HRTEM images, it was found that location of catalysts at CNTs is different by these two methods. It is believed that the interaction between the metal catalyst particle and the substrate is an important factor that influences the nanotube growth mode [126]. Base-growth model can describe the CNTs grown by HWCVD. The strong interaction between most of the catalyst particles and the substrate may result in the failure of catalyst particles to depart from the substrate. In contrast, tip-growth model can describe the CNTs grown by MPCVD under the certain condition (such as small, sharp catalyst particles). The weak interaction between catalyst particles and the substrate may result in a catalyst particle carrying away at the end.

Table 9 Comparisons between characteristics and field emission properties of CNTs grown by using HWCVD and MPCVD

	HWCVD			MPCVD		
	A	B	C	E	F	G
Morphology	Random	Random	Vertical	Vertical	Short rod-like	Vertical
Density	High	Low	Medium	High	Medium	High
Uniformity	Fair	Fair	Fair	Good	Fair	Fair
Inner diameter (nm)	20	—	2	10-20	—	10
Outer diameter (nm)	60-80	—	10	30-40	180	30
Turn-on field (V/μm)	1.34	1.84	1.1	1.4	1.44	1.34
Current density (mA/cm^2), at 2 V/μm	0.234	0.258	0.540	0.140	0.237	0.305

The data listed in HWCVD is acquired at flow rate of 15 sccm.

Most reports on the field emission present a typical I-V curve. The turn-on fields are as low as 1 V/μm and threshold field around 5 V/μm are typical. CNT films are capable of emitting current densities up to a few A/cm^2 at fields below 10 V/μm. In this thesis, it was found that vertical CNTs grown by HWCVD have lower turn-on field and higher emission current density than random CNTs grown by HWCVD and vertical CNTs grown by MPCVD. It was reported [2] that random alignment MWCNT will perform better than short vertical MWCNT. Beside, it was reported [139] that the films of medium densities with CNTs protruding over the film surface show emission at the lowest fields. The reason origins from the combination of two effects: the intertube distance and the number of emitters. When the intertube distance is large, the field amplification factor is determined only by the diameter and the height of the CNT. When the intertube is decreased, screening effects become significant. There is an ideal compromise between these two extremes, where the length of the tubes and the distance between neighboring emitters are both sufficient to reach a high field amplification along with an emitter density that is high enough to ensure homogeneous emission at low voltages. Furthermore, according to their surface treatment, ta-c coated MWCNT will perform better than MWCNT as produced. In these studies, it is desirable that CNTs grown by both methods possess with ta-c coated. Moreover, an enhancement factor β reflects the ability of the emitter to amplify the field. β is also determined by the geometrical shape of the emitter. The literature includes arguments based on values of β that have been determined from the shape of the emitter, and especially from its radius of curvature at the tip, R_{tip}. Therefore, it is believed that smaller R_{tip} may result in a higher enhancement factor β. Summary, it is believed that vertical CNTs grown by HWCVD possess good field emission properties due to: (i) alignment MWCNT, (ii) the medium density, (iii) ta-c coated, and (iv) the smallest diameter, for enhancing their field emission properties. In these studies, label E is hard to explain why it is with the lowest current density. It should be noted that the sample size and substrate material is different between this group and others.