Chapter 5 Conclusions and Suggestions

In this thesis, vertically aligned CNTs were synthesized successfully by using HWCVD and MPCVD methods. A direct HWCVD method, which is the main feature of this thesis, is proposed for *in situ* synthesis of MWCNTs. Meanwhile, MPCVD by using CH_4/CO_2 gas mixture was used to grow CNTs directly on substrates, which were self-catalyzed.

5.1 Concluding Remarks

Direct HWCVD

1. A simplified CVD method is reported for *in situ* synthesis of multiwalled carbon nanotubes.
2. This simplified design possesses many advantages. The carrier gas is nonflammable, alcohol is nontoxic, and all complex vacuum seals are eliminated.
3. CO_2 or Ar gas can be used as the carrier gas in growing the CNTs, and lower flow rate yields more CNTs.
4. Curved CNTs were deposited when the carrier gas flowed vertically to the substrate.
5. Aligned CNTs (<10 nm) were deposited when the carrier gas flowed horizontally to the substrate.
6. The direction of the gas mixture flow, namely, vertically toward the substrate, will benefit the CNT yield because the evaporated metal atoms can more easily contact the substrate surface.
7. The direct HWCVD system has the potential to inexpensively synthesize large quantities of CNTs continuously.

8. Curved CNTs show field emission characteristics that include a turn-on voltage of 1.34 V/ μm and an emission current of 0.234 mA/cm^2 at 2 V/μm. Aligned CNTs show field emission characteristics that include a turn-on voltage of 1.1 V/ μm and an emission current of 0.54 mA/cm^2 at 2 V/μm.
9. From HRTEM images, curved CNTs comprise the following structural features: (i) There is no encapsulated metal particle at the closed tip and (ii) A bamboo-like structure with a compartment curvature directed to the tip.
10. From HRTEM, aligned CNTs comprise the following structural features: no encapsulated metal particle at the closed tip.
11. We propose the base-growth model to explain the structure of the CNTs.

Microwave Plasma CVD

1. CNTs were grown on AISI 304 by microwave plasma chemical vapor deposition using CH_4/CO_2 source gases at a negative bias of -300 V.
2. EDX analyses indicate that the alloy particles at the top ends of the CNTs have various contents of Fe and Ni. However, Cr was not found at the top of the CNTs, perhaps because the higher eutectic point of C-Cr causes Cr to remain on the substrate, and chromium carbide to precipitate on the grain boundary.
3. The field emission properties of the resultant carbon nanotubes obtained at a negative bias -300V were as follows; the emission current was 194 μA at 2.2 V/μm, and the turn-on field, which is the field needed to extract a current density of 10 $\mu A/cm^2$, was 1.4 V/μm.
4. Using CH_4/CO_2 source gases, no obvious CNTs were grown on a Cr film by MPCVD. Rod-like structure was formed when bias voltage was over -150 V. The emission current was 0.237 mA/cm^2 at 2 V/μm. Turn-on field was around 1.44 V/μm.

5. Using CH_4/H_2 source gases, vertically aligned CNTs were grown by MPCVD on a Cr film, which had been pretreated in bias-enhanced H_2 plasma for 5 min. Following this pretreatment, the Cr film provided the catalysts for growing CNTs.
6. The surface roughness, average grain size and particle size of the pretreated Cr film were 26.871 nm, 928.74 nm^2 and 80.409 nm, respectively.
7. The resultant CNTs were vertically aligned; had a notable high-aspect-ratio structure and a diameter of 30 nm. The TEM image indicates that the intrinsic structure is truly that of a CNT, and includes teardrop-shaped Cr at the end.
8. The field emission properties of the resultant carbon nanotubes included an emission current of 0.305 mA at 2 V/μm; and a turn-on field of 1.7 V/μm.
9. Tip-growth model can describe the CNTs grown by MPCVD.

Comparison between HWCVD and MPCVD

1. In deposition system, HWCVD is simpler than MPCVD.
2. HWCVD has higher possibility for scale up.
3. According to CNTs grown, MPCVD yield higher density than HWCVD does.
4. According to CNTs grown, MPCVD yield higher uniformity than HWCVD does.
5. By HRTEM images, location of catalysts at CNTs is different by these two methods.
6. Base-growth model can describe the CNTs grown by HWCVD.
7. Tip-growth model can describe the CNTs grown by MPCVD.
8. In field emission properties, HWCVD has lower turn-on voltage than MPCVD does in these studies.
9. In field emission properties, HWCVD has higher emission current density than MPCVD does in these studies.

5.2 Suggestions for Further Study

1. This thesis demonstrates that the uniformity of the CNTs grown on the sample must be further improved, especially with respect to wire configuration.

2. An auxiliary heating may be considered to keep a constant temperature over a large zone.

3. To scale up the HWCVD system. Some technical problems may arise: (i) large current need to heat the wire, (ii) wire configuration and deformation.

4. The roles of hydrogen and oxygen in carbon nanotubes synthesis should be investigated

5. Carbon nanotubes growth on the various substrates of larger area, such as glass, at low temperature by cooling should to be investigated.