

# Chapter 3 Experiment

## **3.1** **Process description and flow chart**

The Co-assisted well-aligned carbon nanotubes were synthesized by electron cyclotron resonance chemical vapor deposition (ECR-CVD) with a mixture of methane and hydrogen as the source gases. The main experimental purpose is trying to carry out nonresolution storage media via loading of phase-change alloy on CNTs tips. Because the solubility of carbon in germanium, stibium, and tellurium are very small, it is difficult to take  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  alloy as catalyst for CNTs deposition to be encapsulated to tubes, therefore, the key point is how to make the open-ended CNTs and then load the opened-tips with phase-change alloy. The methods of fabricating open-ended CNTs and loading CNTs tips with material will be noted later.

The analysis instruments include SEM, TEM, Raman, AES, and field emission apparatus and the flow chart of this experiment is presented in Fig 3-1.

## **3.2** **Raw materials**

Hydrogen gas (purity 99.9 %) and methane gas (purity 99.9 %) are obtained from San Fu Chemical Co., and Jian Ren Chemical Co., respectively. The substrate material is P-type (100) silicon wafer.

## **3.3** **ECR-CVD system**

The experimental apparatus of electron cyclotron resonance chemical vapor deposition (ECR-CVD) system is shown in Fig.3-2. ECR-CVD system consists of microwave generator (2.45 GHz) which can reach the maximum power of 1200 W, three-spot circulator, tuner, wave guides, microwave applicator, reaction chamber, mass flow controller, electric coils, cooling copper coils, substrate heating stage, vacuum pump, and D.C. bias.

The main advantages of ECR-CVD system include high dissociation efficiency, low deposition temperature of CNTs, wider deposition area. The ECR-CVD system can be characterized by the electronic field  $E$  and the magnetic field  $B$ . In this system, the electrons are accelerated by  $E$  to the direction perpendicular to  $B$  and orbited in a plane perpendicular to  $B$ . The cyclotron radius is  $r_c$ .

The working principle is as noted later. When the microwave angular frequency ( $\omega$ ) is identical to the angular frequency of the electron ( $v / r_c$ ), the electrons will be in phase with the field at either positive or negative  $E$ . This phenomenon is so called electron cyclotron resonance (ECR). It will occur when  $B = 875$  Gauss for frequency of activated media = 2.45 GHz. The cyclotron radius,  $r_c$ , for electrons orbiting in a magnetic field can be expressed by  $r_c = m_e v / eB$ . These symbols such as  $v$ ,  $e$ ,  $m_e$  and  $\omega$  mean the electron velocity ( $v$ ) component perpendicular to  $B$ , the electron charge (coulombs), mass of electron, and the electron angular frequency respectively.

### **3.4 Catalyst deposition and H-plasma pretreatment**

In this experiment, catalyst-assisted method for CNTs deposition was adopted. There are some methods to cover Si wafer with a layer of catalyst. For example, spin coating, electroless plating, and sputtering process, were used by many researchers. We

chose the sputtering process for catalyst deposition owing to the advantages of large area deposition and good surface uniformity. The transition metal, Co, was used as catalyst. The Si wafers were deposited 10 or 15 nm catalyst layer via sputtering process.

After catalyst deposition, the specimens were subsequently pretreated in ECR-CVD system. Specimens were put on steel holder in the chamber. The specimens are heated and maintained at about 630 °C by a D.C. power supply. In the period of pretreatment, the substrate was at 630 °C and enforced -150 V bias, the other parameters of H-plasma pretreatment are shown as follows : Microwave power, 800 W; magnetic field, 875 G; pressure,  $\sim 10^{-3}$  Torr and H<sub>2</sub> flow rate, 15 sccm for 15 min.

## **3.5**

## **CNTs growth in ECR-CVD**

After pretreatment, the mixed composition plasma composed of methane and hydrogen (H<sub>2</sub>/CH<sub>4</sub> : 20/10, 10/10, 10/20 sccm/sccm) was immediately applied to be the source gas for CNTs deposition. The substrate temperature increased about 20 ~ 30 °C as a result of plasma bombardment energy. The main parameters of CNTs growth are as follows : Growth temperature,  $\sim 655$  °C; bias, -150 V; microwave power, 800 W; magnetic field, 875 G; pressure,  $\sim 10^{-3}$  Torr for 15 min. The conditions of CNTs growth is illustrated in Table 3-1.

## **3.6**

## **Post-treatment**

### **3.6.1 H-plasma and chemical etching**

In order to fabricate open-ended CNTs, H-plasma post-treatment was adopted to remove carbon layers on as-grown CNTs tips. Specimens were slightly etched by H-

plasma from room temperature to higher temperatures in virtue of the energy of H-plasma bombardment. When the substrate was treated for 1, 4, 7, 10 min, the substrate temperature reached about 130 °C, 145 °C, 160 °C and 170 °C, respectively. The other parameters of H-plasma post-treatment are listed as follows : Bias, -200 V magnetic field, 875 G; pressure  $\sim 10^{-3}$  Torr; microwave power, 575 W and H<sub>2</sub> flow rate, 10 sccm.

After H-plasma post-treatment, the CNTs specimens were then followed by chemical etching post-treatment, i.e., the specimens were immersed in nitric acid solution (HNO<sub>3</sub> : 0.25 M) for 2 or 3 min. Then the samples were subsequently rinsed by deionized water for about 1 min, after that, they were dried out on hot plate at 150 °C for 5 min. The main conditions of H-plasma and chemical etching post-treatment were divided into Con. 1 ~ 7, as displayed in Table 3-2.

### **3.6.2 Alloy sputtering and high temperature tip trimming**

The main purpose of this section is to load tips of open-ended CNTs with phase-change alloy. The open-ended CNTs were coated with a Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> layer of 200 nm in thickness via sputtering process. After that, the samples were heated to 400 °C, 420 °C, and 440 °C for 30 min.

## **3.7**

## **Analysis methods**

### **3.7.1 SEM and TEM examinations**

Morphologies and microstructures of CNTs in each process as previously

mentioned were examined by scanning electron microscopy (SEM, Hitachi S-4100) and transmission electron microscopy (TEM, Hitachi-600, JEM-2010).

Secondary electrons were gathered to generate SEM image and utilized to observe the surface morphology of specimen. The preparation of SEM specimen is very simple and causing no damage to CNTs. TEM is a powerful tool to analyze the microstructure of specimen. The preparation for TEM specimens was carried out by followed processes :

- (1) CNTs powder was scraped from the specimens by using a diamond tip.
- (2) The CNTs powder was gathered and immersed in acetone, and then evenly distributed by sonicating for about 5 min.
- (3) Then, a drop of well-dispersed CNTs solution was dripped on a Cu-grid coated with carbon film.
- (4) The Cu-grid specimens were then dried on hot plate at 120°C for several minutes, and then the TEM specimens were obtained.

### **3.7.2 Raman and AES analyses**

In this experiment, Raman spectroscopy was adopted to detect the bonding structure of CNTs. Raman scattering produced by a He/Ne laser beam with a wave length ( $\lambda$ ) of 532.8 nm. The apparatus of micro-raman spectrometer (Jobin Yvon LabRam HR) can be employed to investigate the graphitization degree of CNTs by detecting the  $I_D / I_G$  ratio. The main advantages of this analyzing apparatus are easy to prepare specimens and causing no structure damage to specimens.

In this experiment, scanning auger microscopy (SAM, VG Microlab 310F) was used to analyze the elemental composition of phase-change alloy loaded with CNTs tips.

Because the inelastic mean free path is very short (5 ~20 Å), the detected depth of specimen is within or no more than 50Å. Thus, Auger analysis can be used to detect the elemental composition in ultrathin depth on bulk surface.

### **3.7.3 Field emission measurements**

Field emission phenomenon is related to the extraction of electrons from an emitter by tunneling effect through the surface potential barrier. For I-V measurement, CNTs were adopted as emitters applied negative bias in a field emission apparatus. The field emission properties of CNTs were analyzed by I-V detector (Keithley 237), and the distance between anode and cathode (CNTs) was set at about 100 µm.

Table 3-1 Specimen designation and processing conditions of CNTs.

Specimen designation	Catalyst (thickness : nm)	CNTs growth conditions <sup>#</sup>		Remark
		Temperature (°C)	H <sub>2</sub> / CH <sub>4</sub> (sccm / sccm)	
A1	Co (100)	660	10 / 20	Figs. 4-1 (a) and 4-2 (a)
A2	Co (100)	653	10 / 10	Figs. 4-1 (b) and 4-2 (b)
A3	Co (100)	646	20 / 10	Figs. 4-1 (c) and 4-2 (c)
B1	Co (150)	660	10 / 20	Figs. 4-1 (d) and 4-2 (d)
B2	Co (150)	653	10 / 10	Figs. 4-1 (e) and 4-2 (e)
B3	Co (150)	646	20 / 10	Figs. 4-1 (f) and 4-2 (f)
C1	Co (150)	657	20 / 10	Figs. 4-5 (a) and (b)

Notes :

- <sup>#</sup> (1) H-plasma pretreatment conditions : substrate temperature ~ 630°C; bias, -150 V; magnetic field, 875 G; microwave power, 800 W; pressure ~ 10<sup>-3</sup> Torr; H<sub>2</sub> flow rate, 15 sccm, and 15 min pretreatment time.
- (2) The other deposition conditions of CNTs : substrate bias, -150 V; magnetic field, 875 G; pressure ~ 10<sup>-3</sup> Torr; microwave power, 800 W, and 15min deposition time.

Table 3-2 H-plasma and chemical etching post-treatment conditions.

Post-treatment designation	H-plasma etching time* (min)	Chemical etching <sup>+</sup> (etching time, min)
Con. 1	1	No
Con. 2	1	Yes (2)
Con. 3	1	Yes (3)
Con. 4	4	No
Con. 5	7	No
Con. 6	7	Yes (3)
Con. 7	10	No

\*The other parameters of H-plasma post-treatment : temperature ~ 150°C; bias, -200 V; pressure ~ 10<sup>-3</sup> Torr; magnetic field, 875 G; microwave power, 575 W and H<sub>2</sub> flow rate, 10 sccm.

<sup>+</sup>CNTs specimen was immersed in 0.25 M HNO<sub>3</sub> for 3 min.

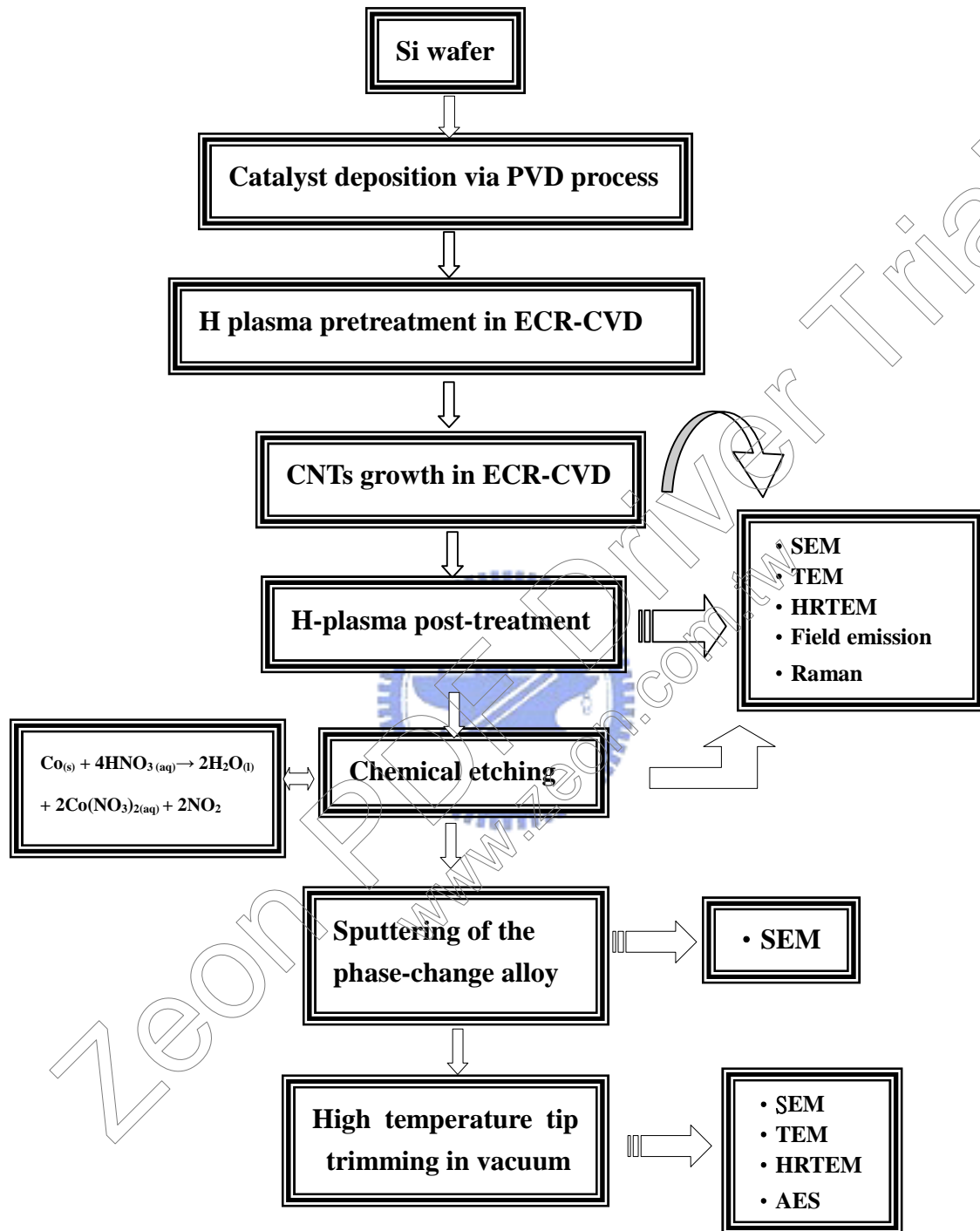


Fig. 3-1 Flow chart of this experiment.



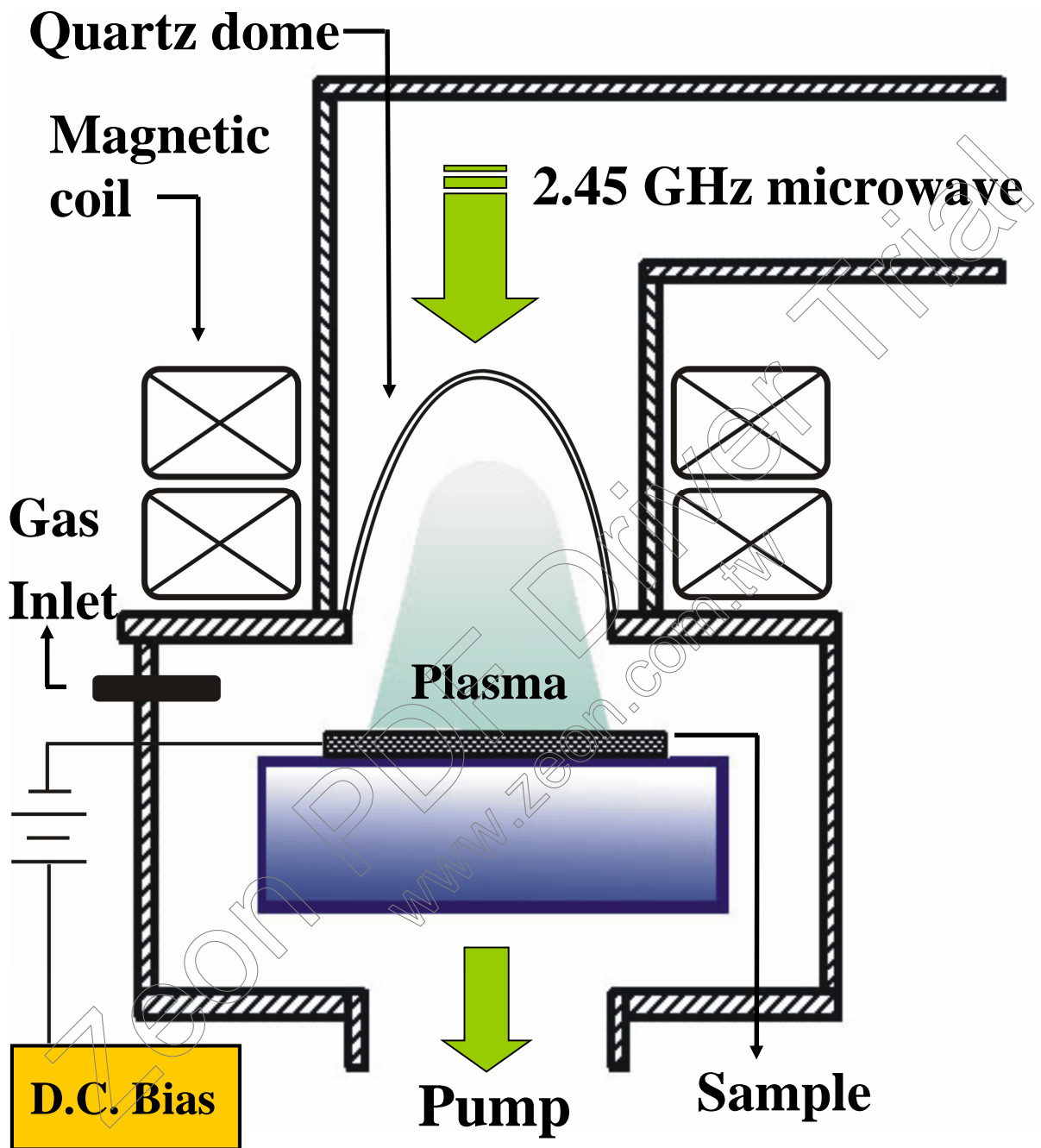


Fig. 3-2 Schematic diagram of ECR-CVD system