3. Experimental Details

3.1. Deposition system- Microwave plasma chemical vapor deposition MPCVD

The sketch of MPCVD system used in this study is shown in Fig.2.5. Components of the system can be classified into several parts:

(1) Microwave generator: frequency 2.45 GHz, power= 2 kW

(2) Wave guide: 86 mm x 43 mm x 65 mm.

(3) Reaction chamber: including reaction tube, sample holder, thermal couple embedded in the holder

(4) Mass flow control (MKS model 247) with different range (1-10 s.c.c.m).

(5) Gas pressure controller: work pressure of chamber can be regulated stably by throttling valve. The degree of the throttling valve was controlled by APC controller (MKS model 263)

(6) Pumping system

(7) Heating system

(8) Cooling system: made up of the refrigerator with closed cooling water and the condition.

In the MPCVD, the standing wave is coupled by the resonant cavity and formed a plasma ball with a diameter of about 5cm at the center of stainless holder. Figure 3.1 shows the simulation of plasma excitation of MPECVD [5]. The location of plasma excitation is almost the same as the place where the electrical field is strongest. The sample is immersed in plasma during catalyst pretreatment and nanotube deposition. The substrate is heated by plasma collision and its temperature is detected by thermal couple embedded in the holder.

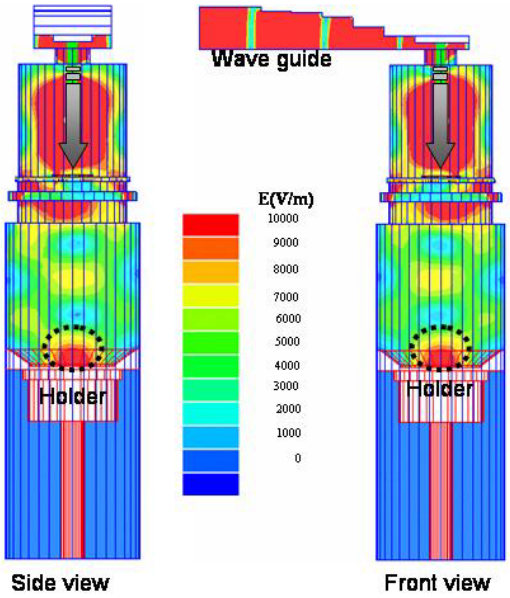

Figure 3.1: Simulation of plasma excitation of MPECVD. Microwave is imported into the resonant cavity through wave guide and cause field distribution to excite the plasma. Dashed black circle is the location of strongest field, that is, the location of plasma excitation. [5]

3.2. Experiment procedure

Figure 3.2 is the flow chart of this study. Our experiments were carried out in following steps:

1. **Substrate preparation**: Ni thin films with a thickness of 20nm were deposited using E-Gun vapor deposition on Silicon substrates on which Titanium films (=40nm) had been deposited to enhanced adhesion of the Ni films.

2. **Plasma pretreatment**: hydrogen plasma was generated and employed to activate the Ni film and change surface morphology of Ni film. The purpose of this treatment is to obtain the small, average size, uniform distribution and appropriate density of catalyst particles.

3. **Growth of carbon nanotube**: mixture of CH_4/H_2 was employed to synthesis the carbon nanotubes. Many important parameters of this part are involved, including gases flow ratio, gases flow rate, microwave power, bias applied, chamber pressure, and growth time. Many differences in the results would arise from these parameters change during growth period. The results that these parameters could strongly affect the morphology, uniformity, quality of the carbon nanotubes was obtained empirically. Details of process parameter used this study are listed in Table 3.1

Table 3.1:*Growth condition of carbon nanotubes by MPECVD*

Substrate	Ni(=20nm)/Ti(=40nm)/SiO2/Si
H2/Ch4(sccm)	150/1~~150/10
Temperature(C)	200~450
Chamberpressure(torr)	5*10^2
Microwave power(W)	600~1200
Pretrement time(mins)	3~10
Growth time(min)	2~10
Bias voltage(voltage)	0~250

4. **Characterizations of as-grown nanotubes:** I-V measurement, SEM, and Raman spectra were carried out to identify the emission characteristics of as-grown nanotubes for the first time.

5. **Post-treatment by laser irradiation**: CNTs was deal with post treatment by laser irradiation. The post-treatment process conditions of plasma refer to Table 3-2 in detail. The expectation of the CNTs after laser irradiation exhibit higher current density, lower turn-on and threshold electric field than as-grown well-aligned CNTs. Such a result can be anticipated on physical grounds in many reports

6. **FE measurement of as-post-treatment nanotubes:** After post-treatment, the same characterizations were carried out again to investigate the change or improvement due to laser irradiation with various conditions.

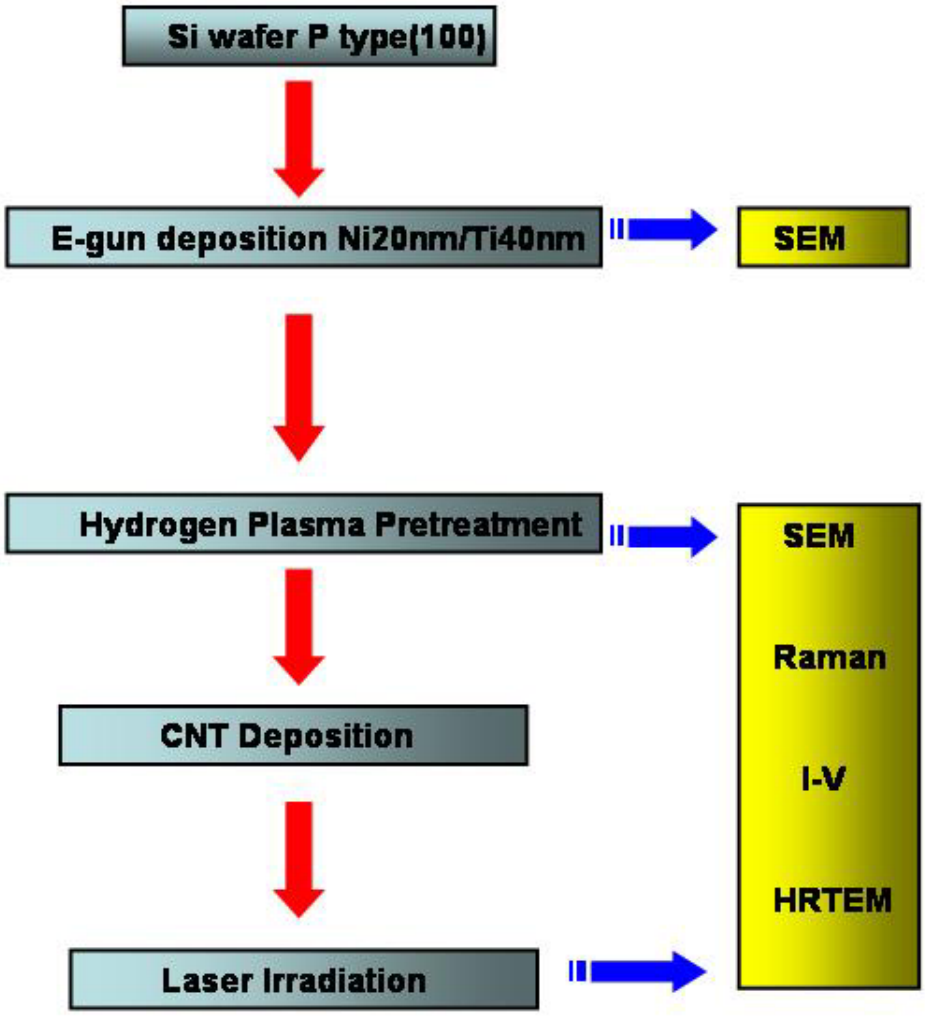

Figure 3.2: The flow chart of experiment.

3.3. Characterization and analysis of carbon nanotubes

3.3.1. FE-SEM

JEOL 7000F FE-SEM was employed to investigate the morphologies of pretreatment substrate and top view, cross-section, and surface morphology of as-grown nanotubes. FESEM is a powerful analysis for scientists to observe nanostructure which is in such tiny size (micrometer~nanometer).

3.3.2. Raman

Raman Spectra is an easy, powerful microscopy method capable of nondestructively analyzing carbon based material for structure composition. The understanding of CNTs Raman spectra is based on vibration and electronically properties of pure sp^2 and sp^3 hybridized carbon allotropes of graphite and diamond. There are several characteristic marks in the Raman spectra:

1. **D-band (disorder-induced)**: It appear at 1350cm^{-1} in MWNT spectra and between 1330~1381 cm^{-1} in SWNT spectra, corresponding to sp_3 bonding as well as defects of CNTs such as pentagons and heptagons, and the size effects of graphite crystallites in the carbon-based materials.

2. **G-band (mode G)**: It appears at 1581 cm^{-1} in MWNT and between 1595cm^{-1} and 1605cm^{-1} in the SWNT, corresponding to tangential strength mode (E_2g) of high oriented paralytic graphite(HOPG) [3.1] and indicates presence of crystalline grapheme sheets. The second-order G' band appears at 2724cm^{-1} in MWNT and at 2679cm^{-1} and 2689cm^{-1} in the SWNT.

3. **The ratio of I_D to I_G (I_D / I_G)**: It indicates the amount of disorder in the nanotubes [2]. A small value of I_D / I_G means the better crystallite quality. In the other hand, an estimate for the in-plane crystallite size L in MWNT materials can be obtained from the ratio via the relationship $L[nm] = 4.4\frac{I_G}{I_D}$, which holds for Raman excitation with 514.5nm laser photons [3.2].

In this study, the investigation was carried out with Raman spectrometer which Nd: YAG LASER (wavelength= 532 nm) is used to excite the sample and the scan

spectrum range is from 480 cm^{-1} ~3500cm^{-1}.

3.3.3. HRTEM

The HRTEM is used to obtain high magnification and high resolution image of nanotube in this experiment. Information obtained from TEM image is electron diffraction pattern which can decide type of structure and the relation of crystalline plane. JEOL 2000FX (200Kev) and high resolution transmission electron microscopy (HRTEM): Philips Tecnai 20 (200KeV) is used to examine the carbon nanostructures.

3.3.4. IV-measurement

Figure 3.3 is a diagram of FE measurement instrument. It is consisted of stainless steel chamber, sample binder, two-gate electrode, Keithley (type 237) high voltage power supply, mechanical pump, and turbo pump. The vacuum level during measurement is about 10-5 torr. The anode and cathode were made of ITO glass, which space between them is set 180 μm . The bias was applied from 0 to 1100 voltage by 10V step range. The most important features in the FEM profile are listed as follows:

1. **The turn-on electrical fields ($E_{turn-on}$)**: defined as the applied field strength at a current density J=0.1㎃/cm^2.
2. **The threshold electrical fields (E_{th}):** defined as the applied field strength at J=10mA/cm^2.
3. **Field enhancement factor β:** It is defined as the ratio of field strength on the tip to local field (average field strength between anode and cathode), and can be estimated from the I-V characteristics and corresponding F-N plots.

The improvement of FE measurement is the main goal of post-treatment in our experiment. All what we done is to getting the field emission property better, such as increase the current density and level down the $E_{turn-on}$ and E_{th} as low as possible.

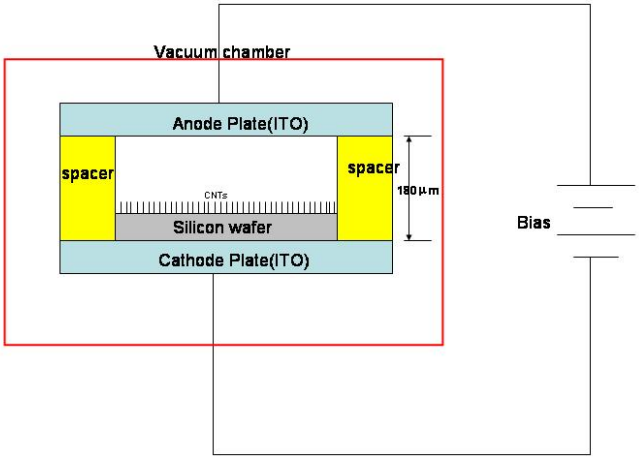

Figure3.3: Sketch diagram of field emission measurement system .Field emission current is measured in a vacuum chamber with two diode type device. Spacer between anode and cathode is 180μm and is large enough compared to the length of CNTs [4].

Reference

[3.1] M. Sveningsson, R,-E. Morjan, O. A Applied Physics A73,409-418(2001).

[3.2] M.S. Dresselhaus, M.APimenta, P.C.Eklund. Raman Scattering in Materials Science(2000)p.314.

[3.3] Journal of the Mechatronic Industry, volume255, 2004, p11.