Chapter 3 Experimental methods

3-1 Flow chart and process descriptions

The flow chart of this experiment is depicted in Fig.3-1. The experimental steps can be divided into four parts, all steps are utilized the MPCVD system beside substrate preparing as follows:

(1) Substrate preparing: 10 nm-Co-coated Si wafer [P-type (100)], where the Co film is coated by physical vapor deposition (PVD) to act as catalyst.

(2) Plasma pretreatment: hydrogen plasma was utilized to activate the cobalt film and change surface morphology of Cobalt film. The process conditions of plasma pretreatment refer to Table 3-1 in detail. The purpose of this part is finding out the optimum conditions of H pretreatment to obtain the small average size distribution and appropriate density of catalyst particles.

(3) Growth of carbon nanostructure: different species of source gases was employ to synthesis of the carbon nanostructure, such as Ar, H_2, NH_3, CH_4 and C_2H_2. The important parameters of this part are gases ratio, gases flow rate, microwave power, negative substrate bias applied, gas pressure, process time on carbon nanostructures growth. These parameters may affect the morphology, uniformity, quality of the carbon nanostructures. Two purposes in this part as follows:

(a) Synthesis of the aligned CNTs: due to high aspect ratio CNTs can enhance field emission properties, thus different species of source gases and applied negative substrate bias was utilized to approach this target. The process conditions of grow CNTs refer to Table 3-2 in detail.

(b) Synthesis of the aligned CNCs: many researches have reported the cone-shape carbon-based nanostructures also show the excellent field emission property. Here H_2 +CH_4 source gases and applied negative substrate bias attempted to approach synthesized high oriented with sharp tip CNCs arrays. The process conditions of grow

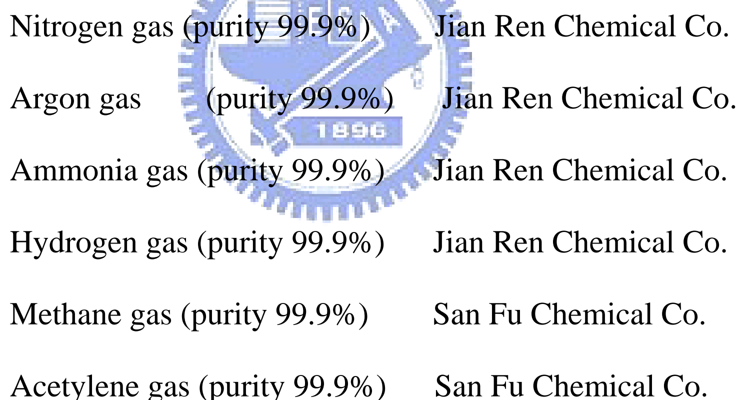
CNCs refer to Table 3-4 in detail.

(4) Plasma post-treatment: in this part the well-aligned CNTs was picked to plasma post-treatment. Different species of plasma were employed to trim the CNTs. It was presumed open-end and more dangling bonds of CNTs will appear after plasma trimming. The plasma process conditions of plasma post-treatment refer to Table 3-3 in detail. The expectation of the CNTs after plasma post-treatment will exhibit higher current density, lower turn-on and threshold electric field than as-grown well-aligned CNTs.

3-2 Raw materials

Substrates: silicon wafer [P-type (100)] was coated 10 nm cobalt film by PVD sputter

Source gases:



Nitrogen gas (purity 99.9%) Jian Ren Chemical Co.

Argon gas (purity 99.9%) Jian Ren Chemical Co.

Ammonia gas (purity 99.9%) Jian Ren Chemical Co.

Hydrogen gas (purity 99.9%) Jian Ren Chemical Co.

Methane gas (purity 99.9%) San Fu Chemical Co.

Acetylene gas (purity 99.9%) San Fu Chemical Co.

3-3 Microwave plasma chemical vapor deposition system

The schematic diagram of MPCVD system is shown in Fig.3-2. The main components of the system can be divided into six parts: the microwave generator and wave guides, reaction chamber, gas flow controller, gas pressure controller and pumping system. The microwave generator of microwave source system (Frequency 2.45 GHz, Power 1.3 kW) was produced by Tokyo electronic Corp. Ltd. The reaction chamber contains quartz tube (inner: 47 mm, outer: 50 mm, China Quartz Corp. Ltd), stainless chamber, stainless holder and rotary pump (Hitachi Corp. Ltd). As Fig. 3-3 shown, sample holder is manufactured by stainless steel, it can bear high working temperature and reduce vacuum pollutions while plasma working. The upper electrode that was made by stainless steel is connected to the DC power supply output. The upper electrode (ground) and substrate holder (negative) were employed to applying the substrate negative bias. The substrate temperature is measured by thermal couple which equipped in the holder. Mass flow control (MKS model 247) system is used to regulate the flow rate of reacting gas while depositing. Besides, the flow rate controller with different range (1-10 sccm, 10-100 sccm) of flow rate of mass flow control system can be properly adjusted for different gas (Ar, NH_3, H_2, CH_4, C_2H_2). The low pressure (0.1~100 Torr) of chamber can be detected by thermal couple of vacuum gauge and absolute pressure gauge (MKS Baratron). The 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). There is no external heater system equipped on MPCVD. The plasma is used to heat the substrate as the heat source. Cooling cycle system is made up of the refrigerator with closed cooling water and the conduit

3-4 Procedures of carbon nanostructures deposition

The carbon nanostructure was synthesized following the sequence steps on MPCVD as described following:

(1) Load sample on the holder, close the chamber door and vent valve.

(2) Turn on the mechanical pump, open the throttling valve and exhaust the camber until the chamber pressure down to $1*10^{-3}$ Torr.

(3) Turn on the microwave power supply and set the gas flow rate of mass flow controller.

(4) Open the mass flow controller valve, introduce hydrogen gas into the chamber and set the working pressure on the APC controller.

(5) Set the microwave power and adjust the turner of waveguide let the reflection power reduce to zero until plasma trend toward stable.

(6) Setting others parameters of hydrogen plasma pretreatment and record the substrate temperature.

(7) After hydrogen plasma pretreatment, introduce the source gases to synthesize carbon nanostructure and setting others parameters such as the microwave power, working pressure and substrate bias in proceeding process and record the substrate temperature.

(8) When processing is complete, first turn off the input of the microwave power gradually. Then close the valve of the mass flow controller and open the throttling valve, exhaust the chamber until the substrate temperature down to 70℃.

(9) Close the throttling valve and open the vent valve. Unload the sample from the holder, then open the throttling valve again exhaust chamber until pressure down to $1*10^{-3}$ Torr.

(10) Finally close the throttling valve and turn off the mechanical pump.

3-5 Analysis methods

3-5-1 Scanning Electron Microscopy (SEM)

JEOL 6300 SEM was used to observe the cross-section profile and morphologies of hydrogen plasma pretreated surface and carbon nanostructures.

3-5-2 Transmission Electron Microscopy (TEM)

The TEM is used to observe high magnification and high resolution image of object. Another analysis can obtain from TEM 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) are used to examine the carbon nanostructures.

The preparation of TEM specimens as shown in following steps:

1. Using the diamond tip to scrape the surface carbon nanostructures on the silicon substrate off and gather the carbon nanostructures powders.
2. Carbon nanostructures powders are collected into the acetone solution and dispersed by sonicating.
3. After sonicating, one droplet of the solution with well-dispersed CNTs was dripped on a copper grids coated with carbon film.
4. Put the grid into the vacuum chamber until dry enough.

3-5-3 Raman Spectroscopy

The Raman spectra are in good agreement with lattice dynamics calculations, based on C-C force constants used to fit the two-dimensional experimental phonon dispersion of a single graphite sheet. Raman Spectroscopy can easily detect carbon based material; the two obvious peaks of the carbon based material are on 1350 cm^{-1}(D band) and 1580 cm^{-1} (G band) that mean carbon sp^3 and sp^2 bonding. The micro-Raman spectrometer (Jobin Yvon LabRam

HR) with He-Ne LASER (wavelength: 623.5 nm) is used to excite the sample and the detected spectrum range is from 500 cm^{-1} ~3500cm^{-1}.

3-5-4 Auger Electron Spectroscopy (AES)

Auger electron spectroscopy (AES) identifies elemental compositions of surfaces by measuring the energies of Auger electrons. Auger electron emission is stimulated by bombarding the sample with an electron beam. The Auger electron energies are characteristic of the elements from which the electrons come. Here AES was utilized to determine the elemental compositions of carbon nanostructures surface and depth profiling. The model of system is VG Microlab 310F with Schottky field emission source resolution：15nm at 25keV. The Concentric hemispherical analyzer（CHA）resolution：0.02％～2％.

3-5-5 Field emission measurement

FE measurement system is utilized to measure the emission current (I) varied with bias (V) which consisted of stainless steel chamber, sample holder, moveable anode, Keithley (type 237) power supply, mechanical pump and turbo pump. The vacuum level of measurement can reach ~ 10^{-6} torr. The anode is made of platinum with spherical shape. The anode X, Y, and Z axis position are controlled by moveable knob in 2 μm accuracy. The space between the sample and the anode was set 100 μm; the bias was applied from 0 to 1000 voltage. This I-V measurement system can measure I-V (current vs. applied voltage) and I-T (current vs. test time) curve. The I-T measurement is the life time test of field emitters, where 900 V bias was applied during the 3600 second of operation.

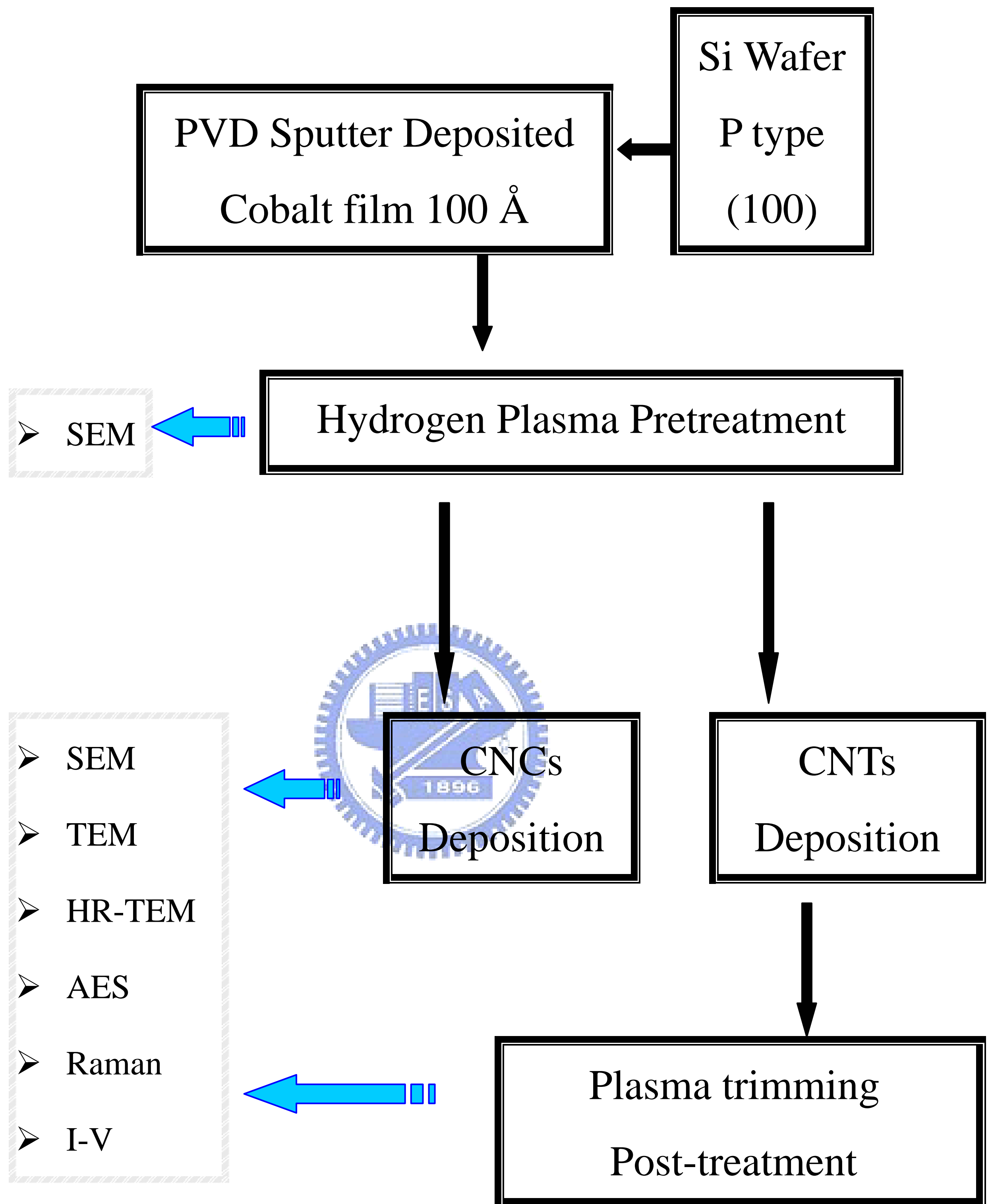


Fig.3-1 Flow chart of the experiment

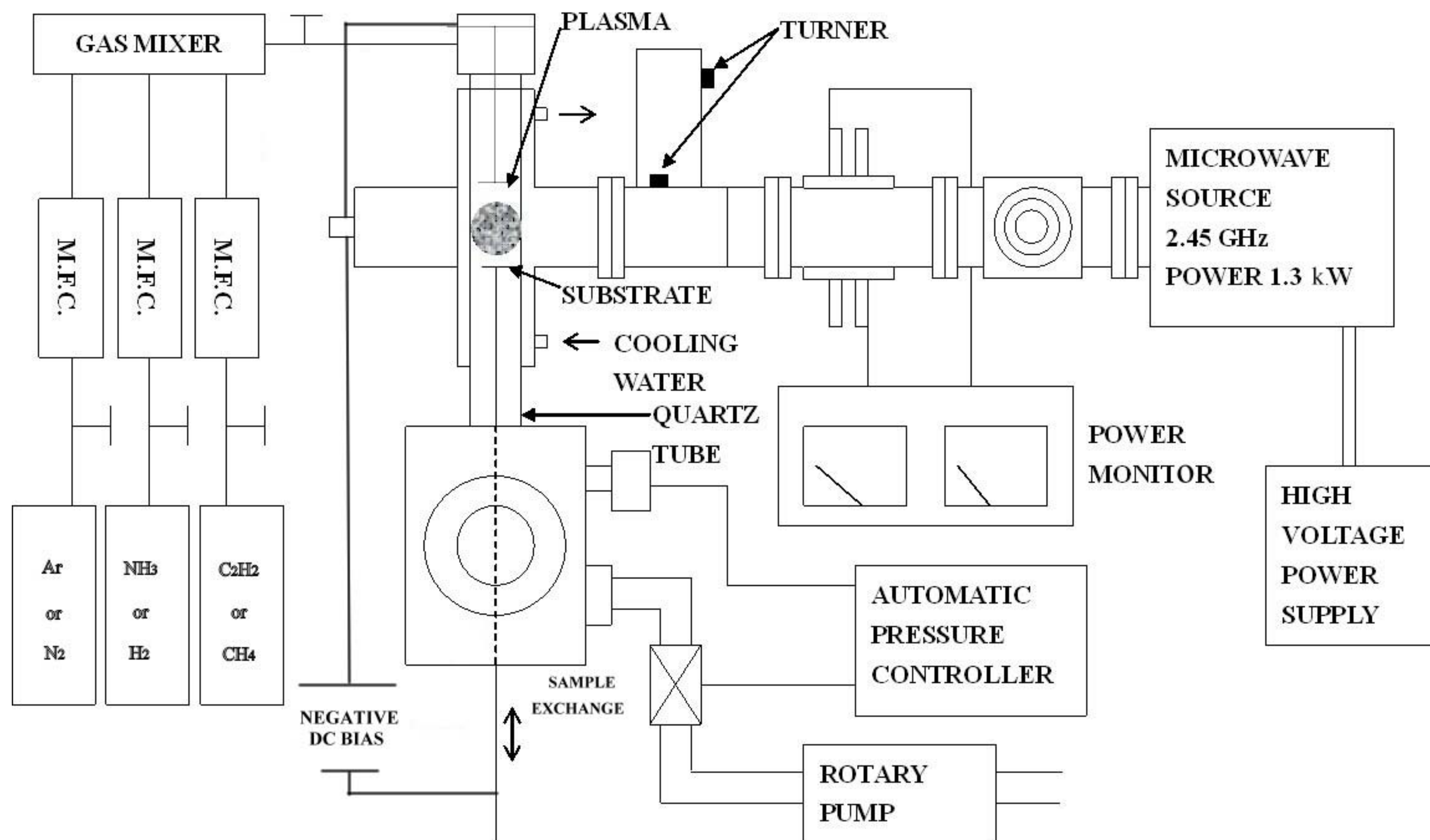


Fig.3-2 Schematic drawing of MPCVD system

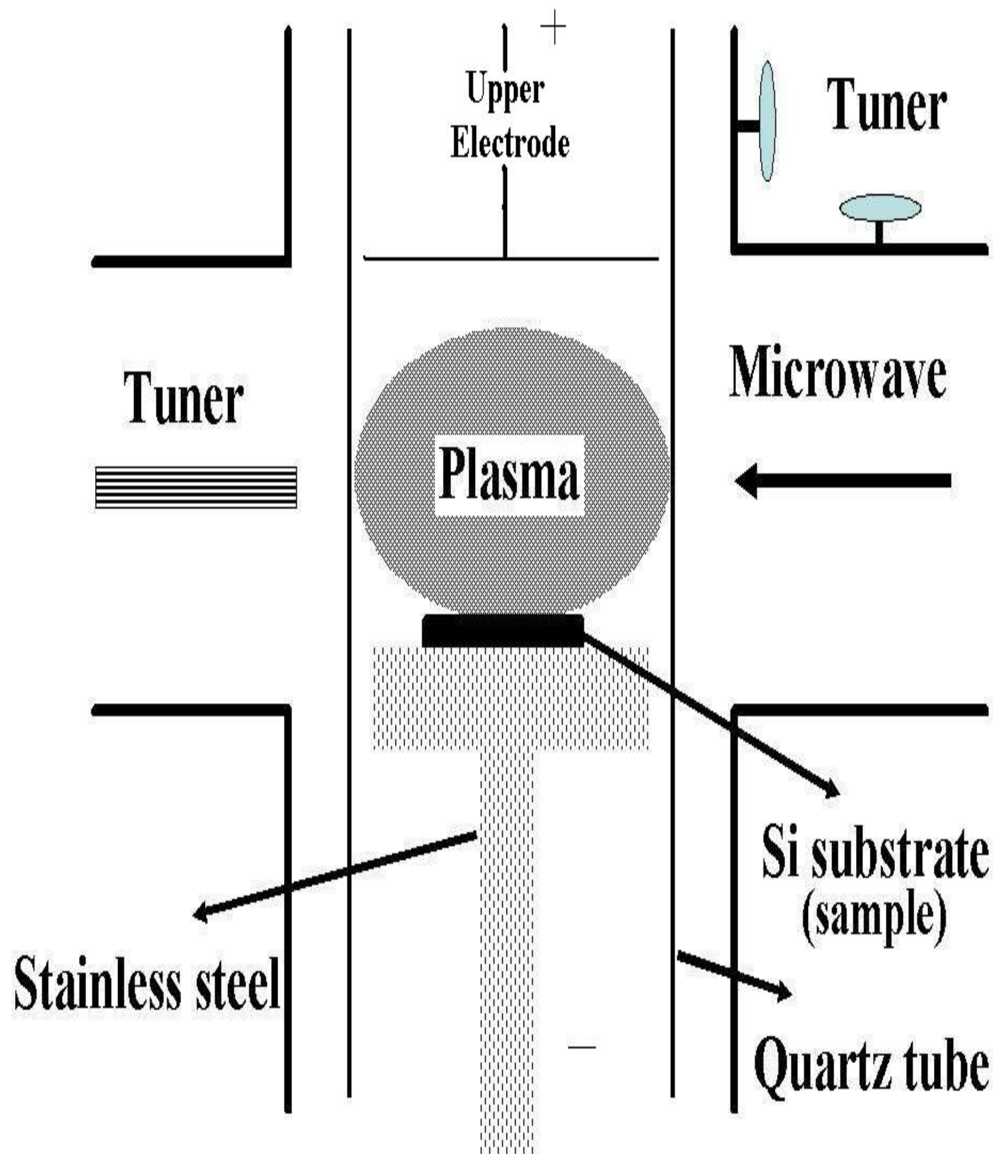


Fig.3-3 Schematic drawing of MPCVD reactor