

3.1 Flow Chart

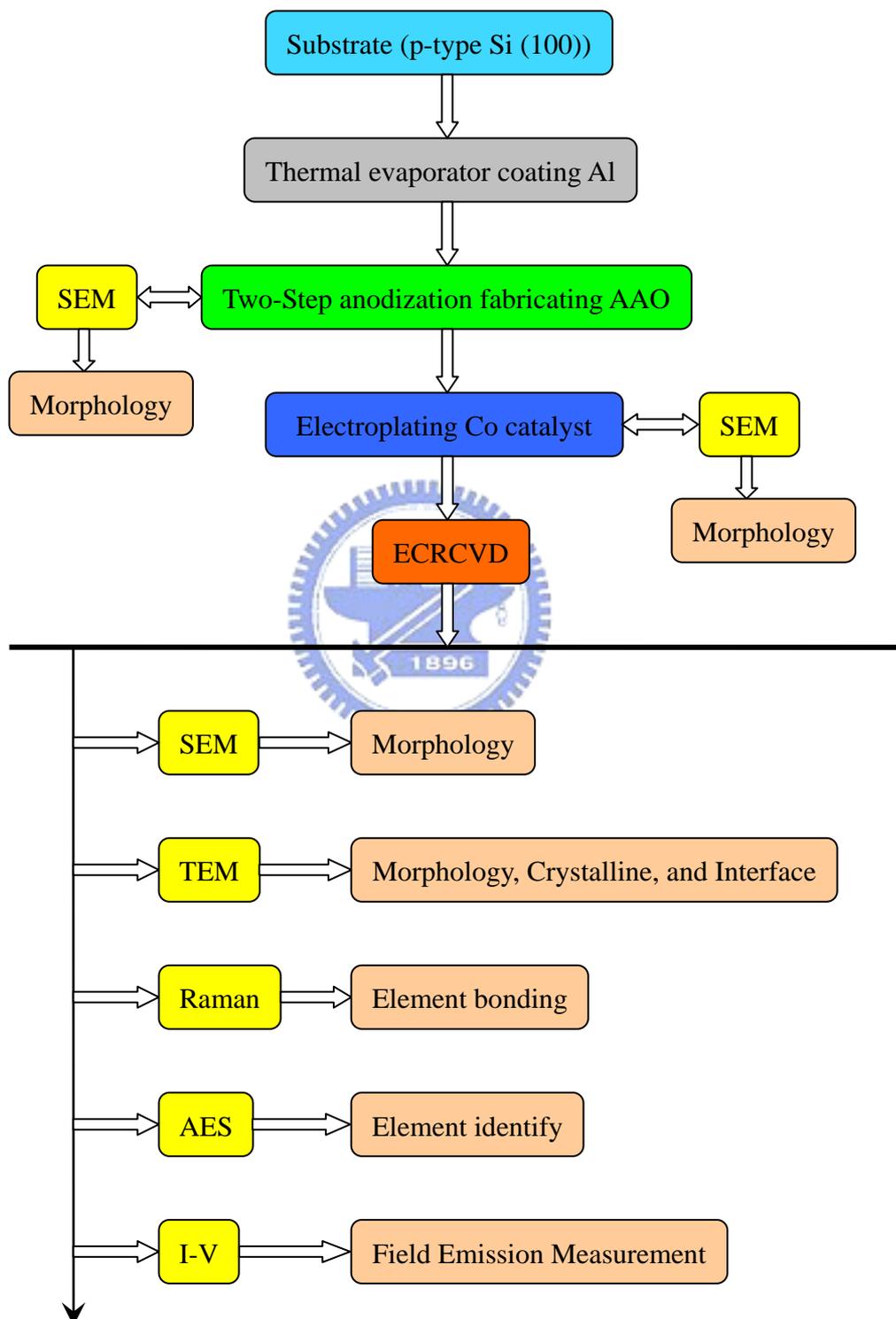


Fig. 3-1. Flow Chart of the experiment.

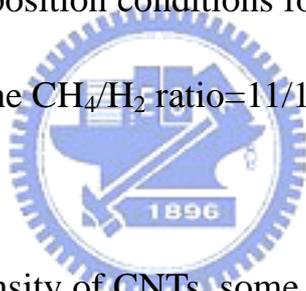
3.2 AAO Nanofabrication

For the preparation of the AAO template, an Al film of about 6 μm in thickness was first deposited on the *p*-Si (100) wafer by thermal evaporation in a high vacuum chamber ($<5 \times 10^{-7}$ Torr). The purity of Al source is 99.999%. The two-step anodization, which has been reported in detail elsewhere^[Masuda-1995-1466, Masuda-1996-L126], was used to prepare ordered pore channel arrays of AAO. Anodization was first carried out in a 0.3 M oxalic acid solution at 21 °C under a constant polarization voltage of 40 V for 30 min. The resulting nanoporous AAO about 4.3 μm in thickness was then removed by wet chemical etching at 60 °C with a mixed solution of H_3PO_4 and CrO_3 , and thereby a relatively ordered indent pattern was produced on the surface of the Al film. The second anodization of the pre-patterned Al film was then performed for 5 min under the same anodization condition as the first one. At the end of the second anodization, the voltage was dropped gradually from 40 to 10 V by 1 V steps. The decrease of polarization voltage accompanied the decrease of the alumina barrier thickness under each pore bottom. After the voltage drop process, the pore diameter of the AAO template was widened in a 5% H_3PO_4 solution for 1 hour.

Before CNT growth, the Co catalyst was electrochemically deposited at the pore bottom in an electrolyte of 5% $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 2% H_3BO_3 by applying 12.3 V_{rms} ac voltage for 1 min.

3.3 Plasma pretreatment and CNTs deposition by ECR-CVD

Finally, the catalyst pretreatment and the CNT growth were all carried out in a microwave plasma ECR-CVD system [Fig. 3-2] under 875-Gauss magnetic field strength. The ECR-CVD system used a 2.45GHz microwave source. Below the sample holder was a heater, and the holder could be applied a bias relative to chamber. The Co catalyst pretreatment condition were: microwave power 700 W, -150 V substrate bias, working pressure 0.25 Pa, sample temperature 600 °C, and H₂ flow=20 sccm. And deposition conditions for the CNT growth were the same with pretreatment except the CH₄/H₂ ratio=11/11 sccm, and deposition time 7-30 mins for length control.



In order to control density of CNTs, some deposition parameters had a little change. The total gas flow rate was kept constant at 22 sccm. The other growth conditions were: microwave power 700 W, -150 V substrate bias, working pressure 0.25 Pa, growth temperature 600 °C, and growth time 30 min. The CH₄ concentration in precursor gas was varied from 9 to 91% in order to investigate the influence of the CH₄/H₂ ratio on CNT growth.

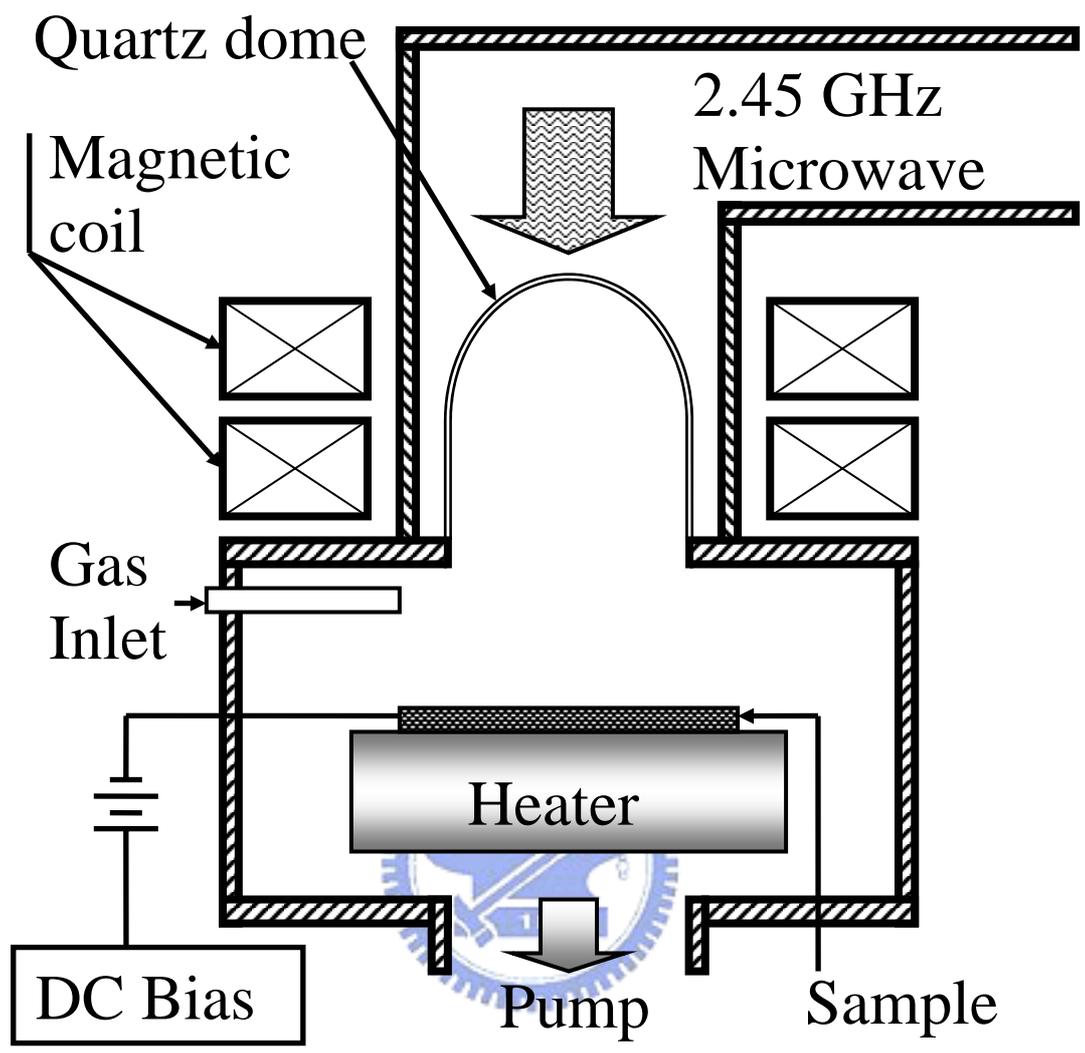


Fig. 3-2. Schematic of ECR-CVD system

3.4 Analyses

3.4.1 SEM & TEM

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are very useful tools for observing surface morphology of specimens. These two instruments utilize the incident electrons reacting with sample to obtain image. SEM has secondary electrons (SE) or backscattered electrons (BSE) detectors passing the signal to computer and forms image. The TEM image is the result of electron transmitting through the sample, and it can get the electron diffraction pattern as well. In the experimental, the morphology and microstructure of the AAO and as-grown CNTs were characterized by field-emission scanning electron microscopy (FE-SEM) (Hitachi S-4000, 25KV) and transmission electron microscopy (TEM) (JEOL JEM-2010F, 200KV and Philips TECNAI 20, 200KV).

3.4.2 Raman Spectroscopy

Raman scattering was discovered by Raman in 1928. If an incident photon occurs inelastic scatter with molecules of the sample and causes the energy change of the photon, that is called raman scattering. By this mechanism, one can measure the difference between incident and scattering light by a spectrometer to obtain the element and bonding types of the specimen. The

beam of incidence usually uses a laser source, and the raman spectroscopy are generally expressed as the raman shift ($\Delta\sigma$, unit: Δcm^{-1}). Following equation indicates the relation of raman shift and energy difference of photons:

$$\Delta\sigma = \sigma(\text{energy of incident photon}) - \sigma(\text{energy of scattering photon}) = \frac{\Delta E}{hc}$$

In order to understand carbon bonding of CNTs, the micro-raman spectrometer (Jobin Yvon LabRam HR) with a He-Ne laser beam (wavelength: 632.8nm) was utilized in the experiment.

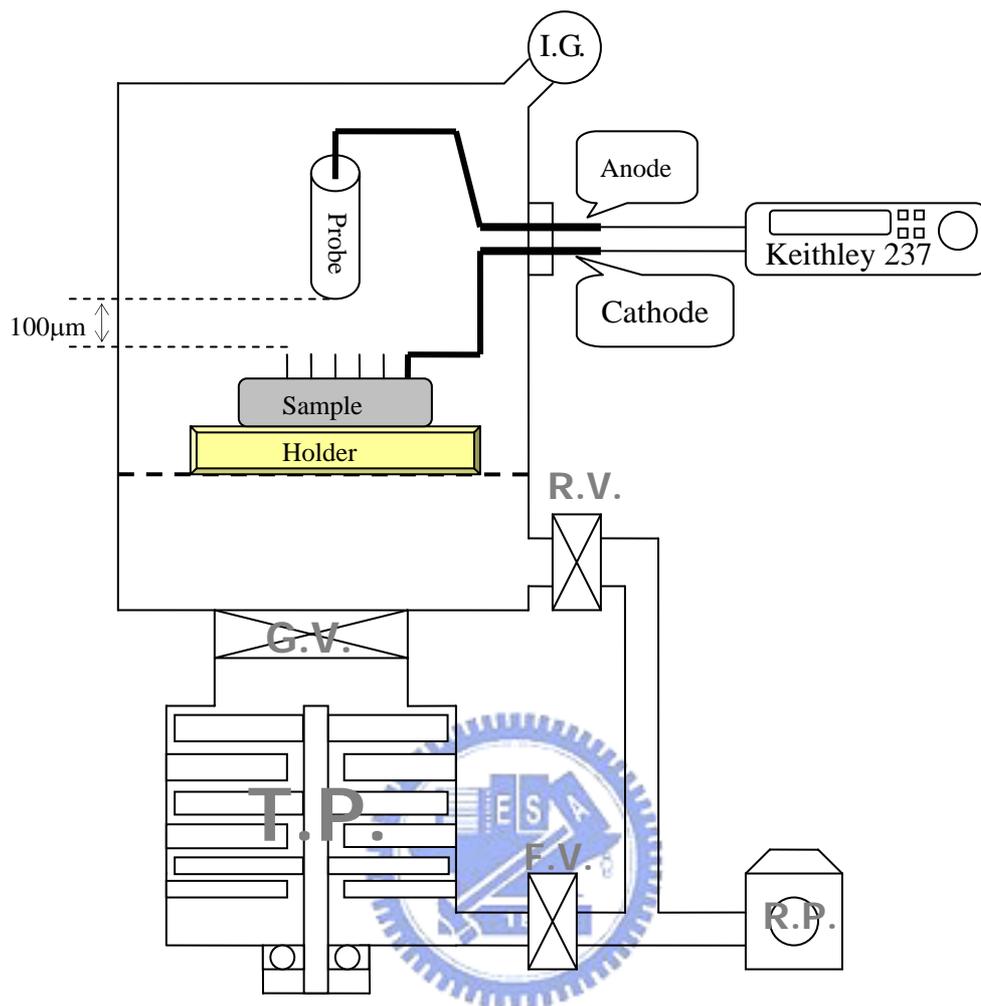
3.4.3 Auger Electron Spectra (AES)

The AES analysis technique employs an electron beam (2-30KeV) incident the surface of sample to excite the auger electrons which possess specific energy. Through assaying the kinetics energy of auger electrons by an analyzer, one can get to know the element compose and chemical state of the sample. Because the incident electron with low-energy (1-3KeV) has a very short inelastic mean free path (5\AA - 20\AA) inside a solid phase material, AES technique is usually used to obtain the information within 50\AA away from the surface. The Auger electron spectroscopy (AES) analyses were conducted using a VG Microlab 310F with Schottky field emission electron source and Concentric hemispherical analyzer (CHA) nanoprobe system to analyze the CNTs and distinguish between graphite and amorphous carbon in the experiment.

3.4.4 Field Emission Measurement

In section 2.4, the field emission properties of CNTs have been described. The measurements were conducted by the simple diode configuration and performed in a high vacuum chamber with a base pressure about 10^{-6} torr. [Fig. 3-3] The distance between the CNTs and anode was about 100 μm and effective field emission area of anode was 0.0012 cm^3 .





T.P. : Turbo Molecular Pump

R.P. : Rotary Vane Pump

F.V. : Fore Valve

R.V. : Rough Valve

G.V. : Gate Valve

I.G. : Bayard-Alpert Ionization Gauge

Fig. 3-3. Diagram of field emission measurement.