Chapter 3

Experimental Procedures

3.1 Catalyst Preparation

In this study, we used two methods to prepare the thick films with catalysts on the soda lime glass substrates. The two ways were solution deposition method and sol-gel methods, respectively. These two methods were commonly used to prepare films in the optoelectronic techniques for low cost. The details of fabrication were introduced later.

3.1.1 Solution Deposition Method

For preparing the catalysts, the silver (Ag) powders were dispersed in the water and then added with the ammonia (NH_3) solution under heating for 30 min.. Afterward $Ni(NO_3)_2 \cdot 6H_2O$ was added in the solution, and NH_3 solution also added in for maintaining pH value to be 10.5 by heating at 100 ℃ for 3 hr. The HCHO solution was added to make the nickel (Ni) particles deposit on Ag powders by heating at 100 ℃ for 3 min. Then the solution was washed with distilled water and dried at 110 ℃.

After Ni/Ag powders dried, fritz powders were added and put into the mill pot. Then the equivalent weight of binders was mixed with the powders and dispersed the powders by three roller grinding mill to mix the paste for printing.

The pastes of Ni/Ag were deposited on the soda-lime glass with thickness of about 1.1 mm by screen printing. Finally, the thick films with Ni/Ag were placed into a quartz furnace to de-binder and sintered.

3.1.2 Sol-Gel Method

The catalyst was prepared by a sol-gel technique. The A and B solutions were prepared individually. For the A solution, anhydrous alcohol (Ethyl alcohol) were added with $Ni(NO_3)_2 \cdot 6H_2O$ until the solution was 100 ml under vigorous stirring for 30 min. For the B solution, tetraethoxysilane (TEOS) were mixed with anhydrous alcohol under vigorous stirring for 30 min. Next, A solution and B solution were mixed under vigorous stirring for one day.

Then, the pastes of Ag were deposited on the soda-lime glass with thickness of about 1.1 mm by screen printing. Subsequently the mixture of A and B solutions was spun coating on glass structure with an Ag cathode layer, and stayed on 1 min. Finally, the thick SOG (spin-on glass) films were transferred into a quartz furnace, baked at 100 ℃ in air for 30 min and then sintered at 500 ℃ in air for 30 min.

3.2 Growth of Carbon Nanotubes

The as-deposited samples with nickel (Ni) nanoparticles were synthesized by microwave plasma chemical vapor deposition (MPCVD) (model IMG 2502-S, IDX Tokyo, Japan). The schematic diagram of the microwave plasma chemical vapor deposition system was shown in fig. 3.1 showed. The catalyst-coated substrate was placed in a CVD chamber. First, the chamber was evacuated at 10^{-2} Torr with a rotary pump. Then, the hydrogen (H_2) gas was introduced into the chamber at the flow rate of 200 sccm and the pressure at 6 Torr. The samples were posited in the middle of the plasma sphere.

After pretreatment by hydrogen (H_2) plasma for 5min, the reactive gases, methane (CH_4) and H_2, were introduced into the chamber with the total pressure of 6 Torr. The CH_4 gas was used as a carbon source and H_2 was used as a catalytic gas. In order to verified the samples, several parameters were used, including pretreatment time of

hydrogen plasma, CH$_4$ and H$_2$ concentration, growth time of CNTs, flow rate of reactive gas and the power of MPCVD.
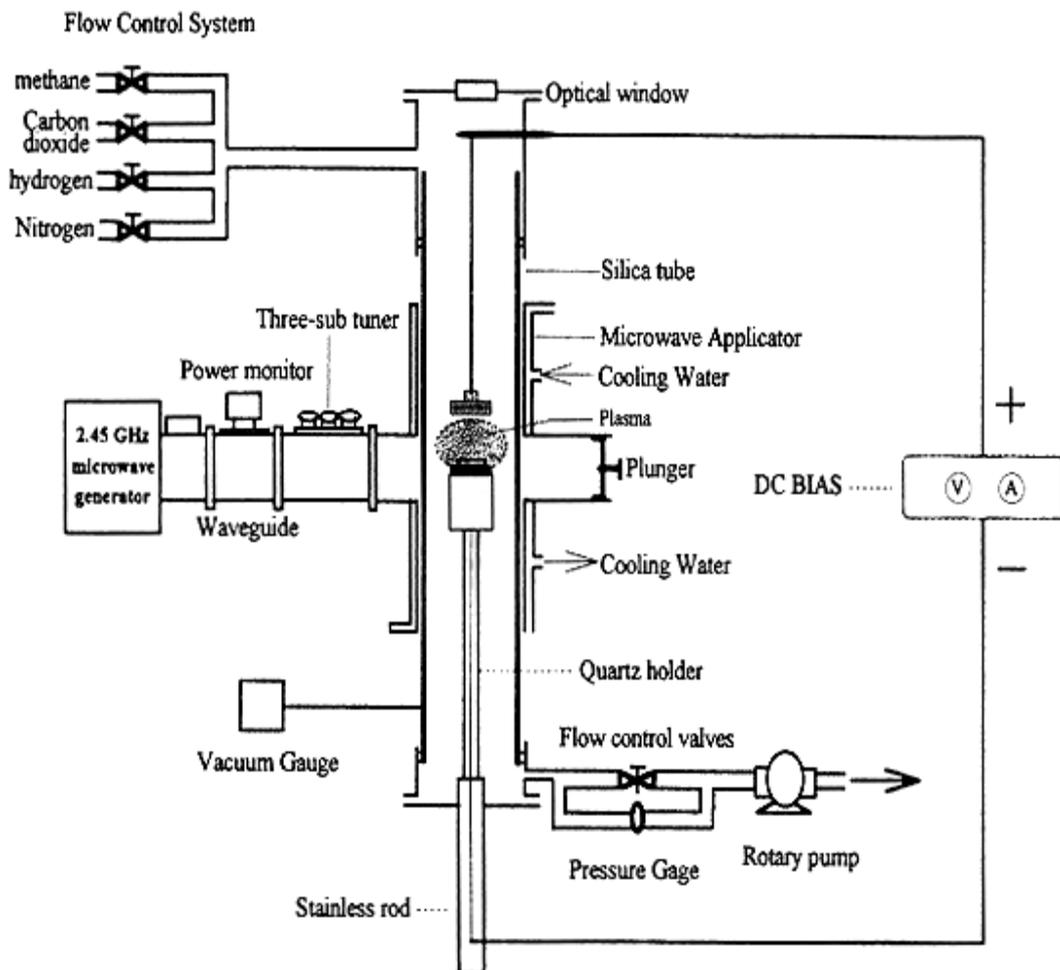

Fig. 3.1 Schematic diagram of microwave plasma chemical vapor deposition (MPCVD) system.

Then the as-grown samples were characterized by scanning electron microscope

(SEM, Hitachi S-4000), transmission electron microscope (TEM), Raman spectroscope and field emission measurement. Fig 3.2 showed the flow chart of experimental procedures.

3.3 Characterization of materials

3.3.1 Scanning Electron Microscopy, SEM

We used the scanning electron microscopy to observe the surface morphology and crystallinity of wide range kinds of objects [52]. It had the advantage of rather easy sample preparation, high image resolution, large depth of field, and high magnification.

A common SEM contained an electron gun to generate electron beams, which could be accelerated under 0.4-40 kV voltage. By deflecting the incident beams with the focusing coils, a two dimensional image could be obtained by detect the reflected secondary electrons and the backscatter electrons.

The model we used was Hitachi S-4000, with field emission electron source and 25 kV accelerate voltage.

3.3.2 Transmission Electron Microscopy, TEM

In a typical TEM a static beam of electrons at 100-400 kV accelerating voltage illuminated a region of an electron transparent specimen which was immersed in the objective lens of the microscope. The transmitted and diffracted electrons were recombined by the objective lens to form a diffraction patter in the back focal plane of that lens and a magnified image of the sample in its image plane. A number of intermediate lenses were used to project either the image or the diffraction patter onto a fluorescent screen for observation. The screen was usually lifted and the image formed on photographic film for recording purposes.
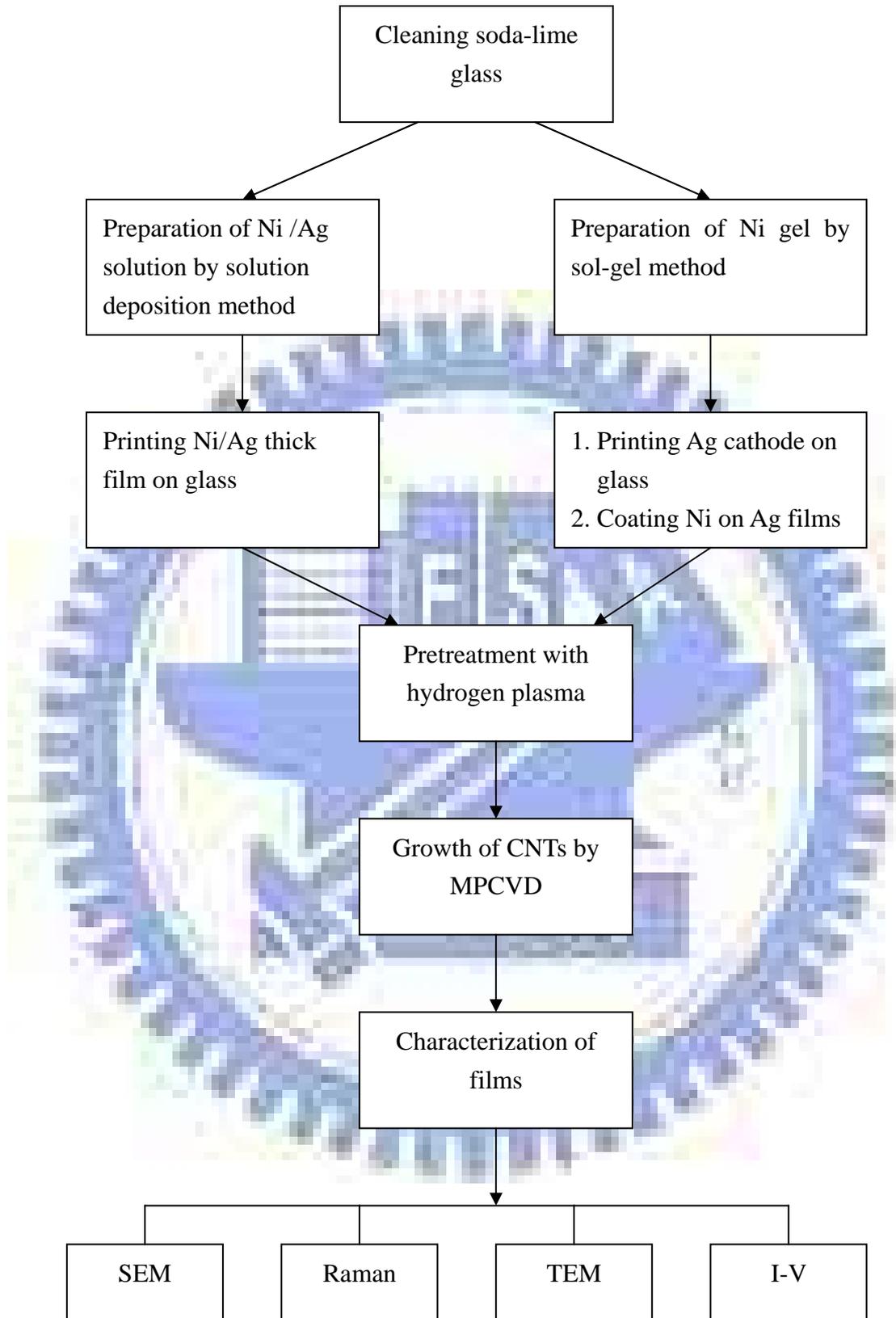
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                    ┌──────────────────┐
                    │ Cleaning soda-lime│
                    │      glass        │
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Cleaning soda-lime glass

Preparation of Ni /Ag solution by solution deposition method

Preparation of Ni gel by sol-gel method

Printing Ni/Ag thick film on glass

1. Printing Ag cathode on glass
2. Coating Ni on Ag films

Pretreatment with hydrogen plasma

Growth of CNTs by MPCVD

Characterization of films

SEM

Raman

TEM

I-V

Fig. 3.2 The flow chart of experimental procedures.

3.3.3 Raman Spectroscopy

While photons illuminated a molecule or a crystal, they reacted with the atoms accompany with momentum change or energy exchange. By collecting the scatter photons, we could obtain a sequence of spectrum, including Raman scattering (inelastic scattering) and Reyleigh scattering (elastic scattering). The photon of Raman scattering could be classified into two kinds, Stoke side which photons loss energy or the molecules gains energy, and anti-Stoke side, which photons gains energy or molecules loss energy. Generally, Stoke side was used to characterize the material.

As Raman spectrum provided information of crystallinity and bonding, it had become the most direct and convenient way to identify carbon related materials. The Raman spectrum peak of C-C and C=C bond in crystalline graphite were 1380 cm^{-1}, and 1580 cm^{-1}, respectively.

The instrument we used was Renishaw Raman microscope, Model 2000, equipment settings were shown in fig. 3.3. The source we used was He-Ne laser with wavelength of 632.8 nm and power of 200 mW. The spectral slit width was 0.4 cm^{-1}.

3.3.4 Field Emission Measurement

Because of many useful applications of the carbon nanotubes as the field emitters, the field emission property in particular has been extensively investigated. The turn-on and threshold field defined as the electric field at an emission current density of 10 μA/cm^2 and 10 mA/cm^2, respectively have been used to distinguish various emitter materials [53]. Fig. 3.4 showed the field emission properties of the diode-type gated structure, which were measured by using a diode technique. An anode plate (ITO Glass, MBC 6R1697) was placed at 100 μm above the CNT films and was biased to +800 V. The anode current (I_A) was then measured as a function of

gate-to-cathode bias voltage in a vacuum of 1×10^{-6} Torr using a Keithley SMU 237. The gate-to-cathode voltage (V_{gc}) was biased from 0 to 120 V using a Keithley SMU 237 system. During testing, the device was in a common emitter configuration and both the anode and gate being positive potentials to turn the device on.
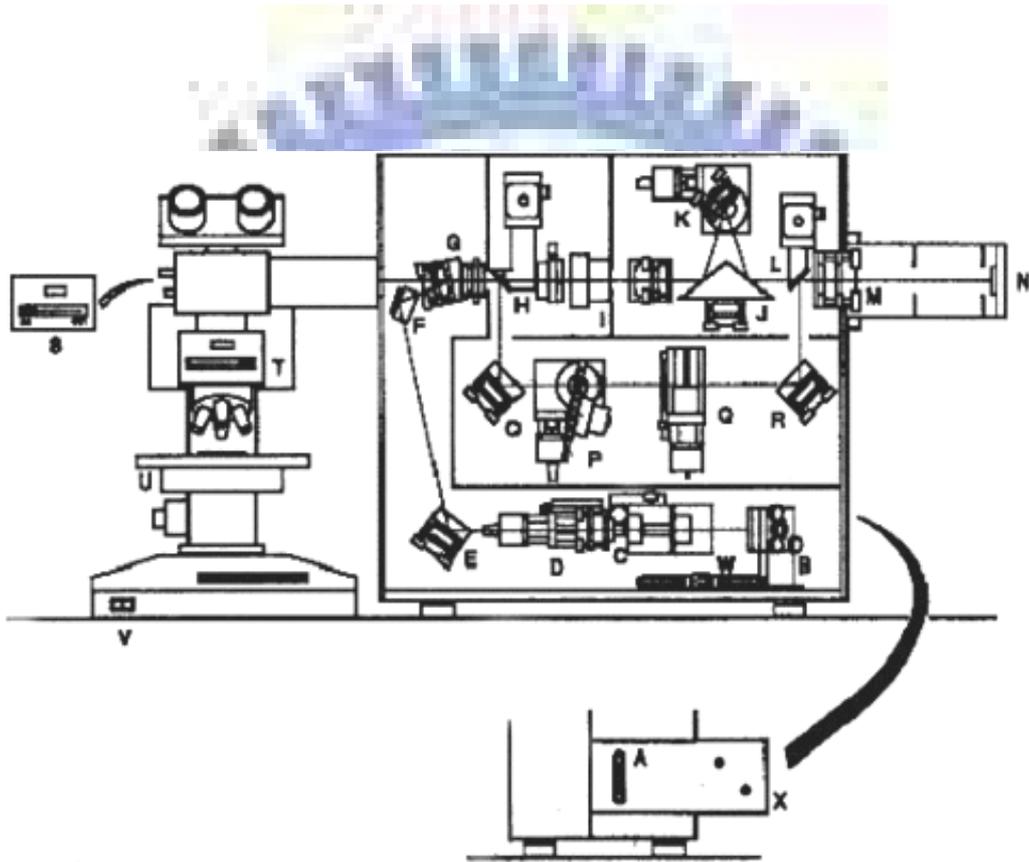

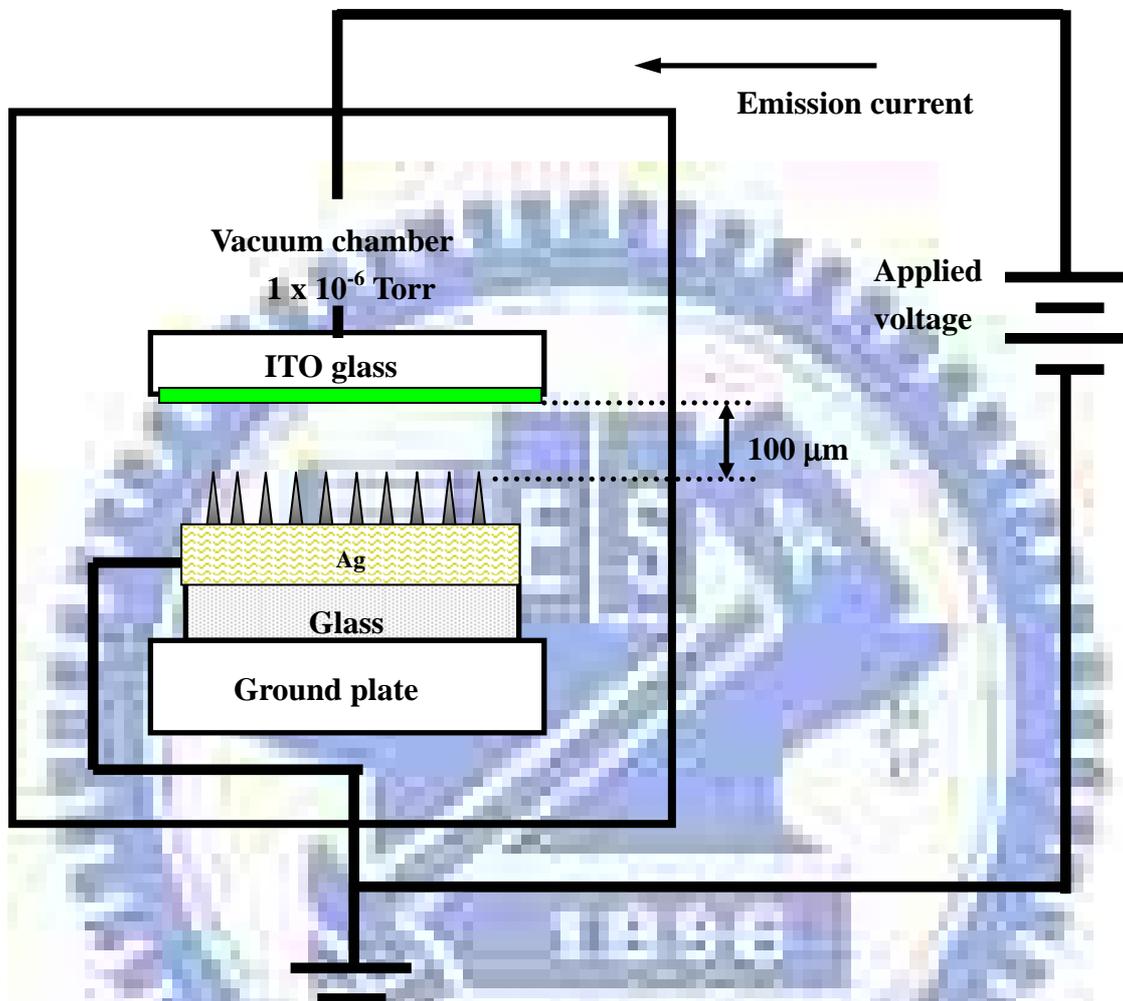Fig. 3.3   Schematic diagram of Raman equipment.

Fig. 3.4 Schematic diagram of the instrument for field emission measurement.