Chapter 3. Experimental Details

3.1 Growth of Density-Controlled Carbon Nanotubes

3.1.1 Heat Treatment of the Deposited Thin Film Substrate with Thermal Furnace

Figure 3.1 shows the experimental procedure. We used *n*-type (100) polished silicon as substrate. After RCA cleaning, a 300 nm thick silicon dioxide layer was grown on Si wafer by wet oxidation. We then coated nickel and then gold onto the SiO_2 layer by e-gun deposition system with different thickness as shown in the table below. During heat treatment process, we put the substrate in the middle of cleaned fused silica tube and then evacuate to the pressure about 10^{-3} torr. Argon was introduced into the tube to create an inert passive atmosphere. After the gas pressure increasing back to 1 atm, the furnace was gradually heated to 500℃, 680℃, 780℃, 880℃, and 1000℃, respectively and maintained for 2 hours. The sample was cooled down with various rates. When the sample was cooled to room temperature, we took it out from furnace and used several instruments to analyze the substrate.

Sample	Thickness (Å)	
	Ni	Au
A	200	0
B	150	50
C	130	70
D	100	100
E	70	130
F	0	200

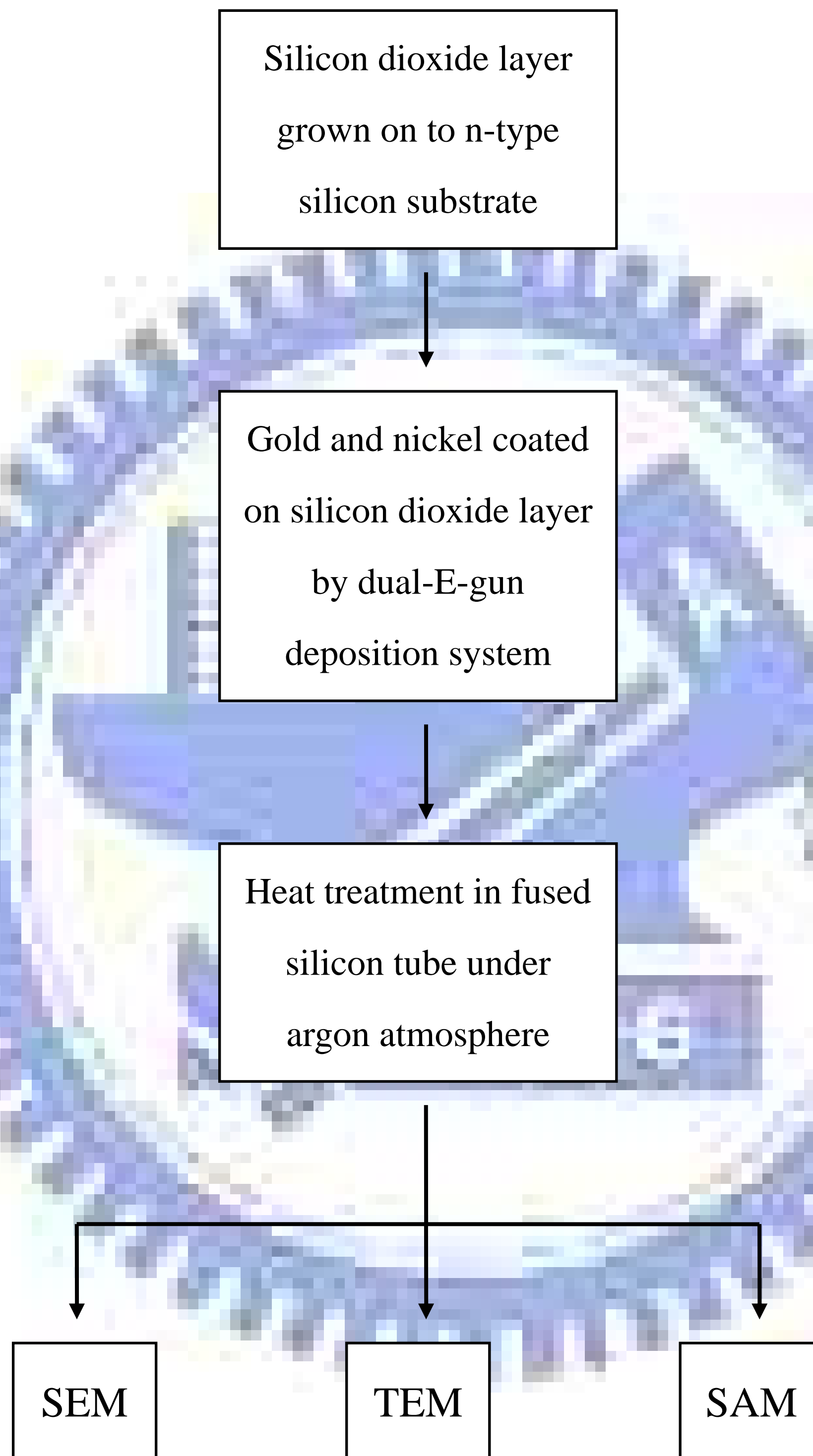

Fig.3.1 Flow chart of heat treatment procedure

3.1.2 Growth of Carbon Nanotubes by Bias Assisted Microwave Plasma Chemical Vapor Deposition

Figure 3.2 shows the experimental procedure of growing carbon nanotubes after heat treatment of the substrates. The substrates were first cleaned with organic solvents and were washed with de-ionized water. Pure nitrogen gas is then introduced to dry the substrate. The substrate is lastly loaded into the bias assisted microwave plasma chemical vapor deposition (BAMPCVD) chamber.

The chamber was then evacuated to a pressure of ~10^{-2} torr with a rotary pump. Initially, the reactant gases hydrogen and methane, were introduced into the chamber at the pressure set of 15 torr. The microwave power of 400W was applied and bright plasma was obtained. The position of plasma was adjusted by the sliding short circuit and, by doing so, the substrate was fully immersed into the plasma. The reflected power was minimized below 10 W with the assistance of a three-stub tuner. In order to verify the properties and characteristics of density-controlled CNTs, several instruments are used for analysis. The reasons why that CNTs can grow with different density are discussed later.

3.1.3 Bias Assisted Microwave Plasma Chemical Vapor Deposition (BAMPCVD) system

Figure 3.3 schematically depicts the layout of the BAMFCVD system. A quartz tube is vertically attached to a rectangular waveguide used as deposition chamber. The microwave from a magnetron source (model IMG 2502-S, IDX Tokyo, Japan) is supplied to the quartz tube through an isolator, three-stub tuner, and a power meter. Then the microwave power is coupled to the quartz tube through an aluminum waveguide with a hole drilled through from top to bottom face.

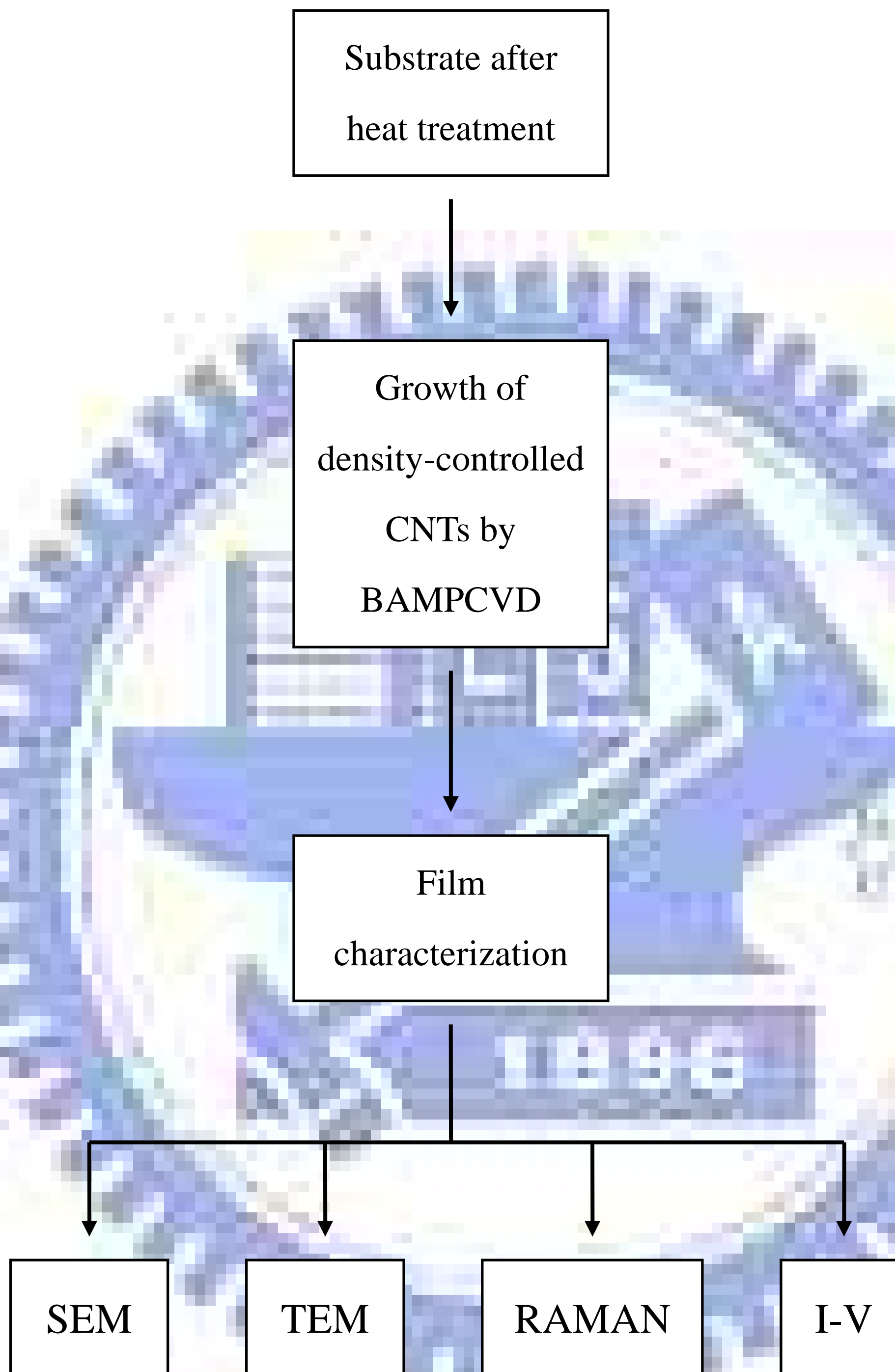

Fig.3.2 Flow chart of CNTs growth procedure

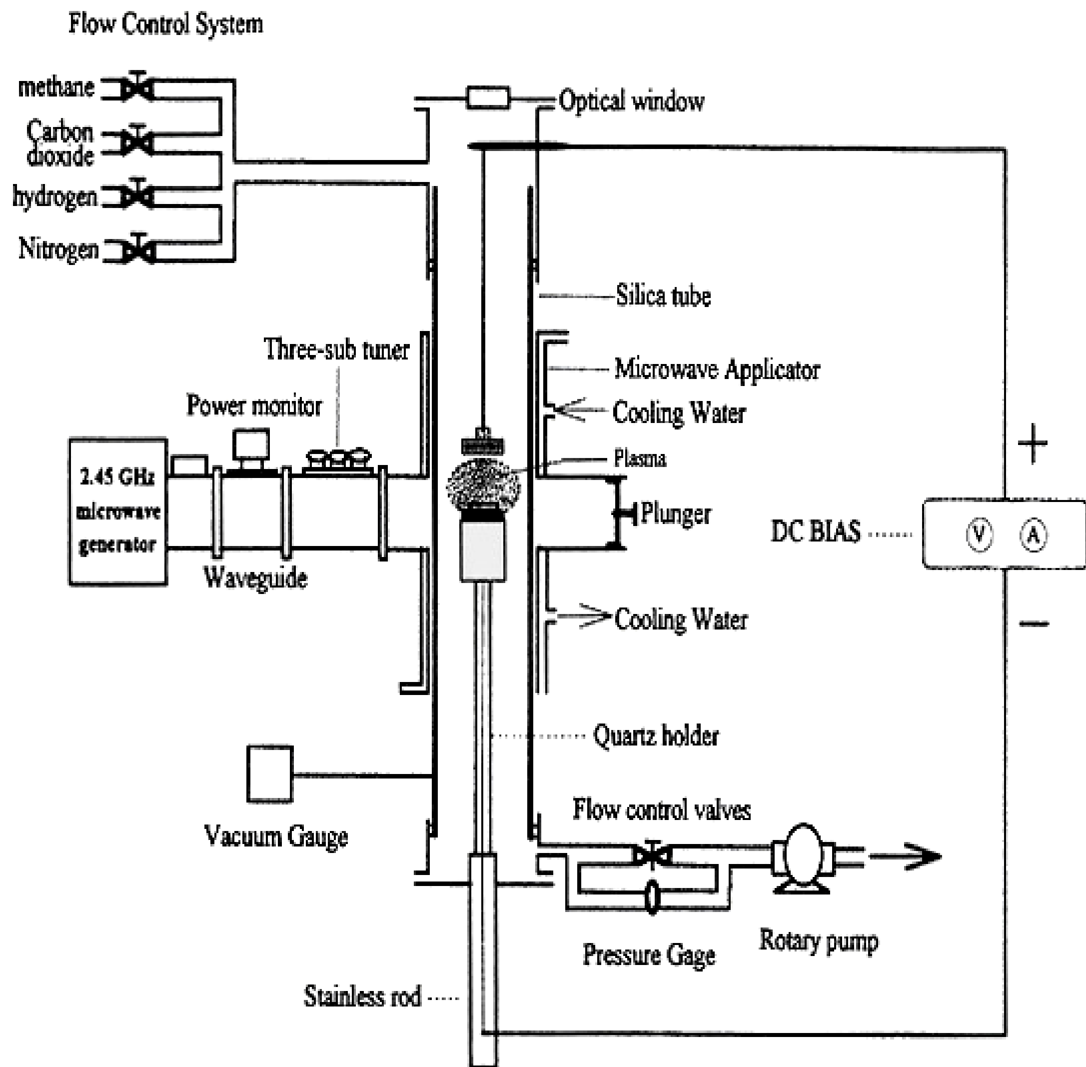

Fig. 3.3 Schematic diagram of the bias assisted microwave plasma chemical vapor deposition system.

Aluminum tubes extend out from both holes; the tube extensions are water-cooled as well. A sliding short circuit is then attached at the end of the waveguide. The lower position of the quartz tube is connected a stainless steel multi-port chamber equipped with a rotary pump.

The substrates are positioned in the middle of the quartz tube waveguide intersection and held vertically by a substrate holder which is 20 mm in diameter, made of molybdenum. Under the holder, attached a tantalum wire which is connected to the bias system; it was used as the lower electrode in the bias treatment stage. A quartz protector under the holder to protect the plasma not attracted to the tantalum wire attached to the molybdenum. The upper electrode, a molybdenum plate of 20 mm in diameter which is placed 35 mm above the substrate, also attached to a tantalum wire. The controlled amount of the source gases was introduced into the chamber by mass flow controllers (model 647B, MKS instrument, Inc., USA) from the upper end of the quartz tube. A small window is cut in the waveguide at the center of the plasma cavity, allowing direct observation of the plasma.

3.2 Analytical Instruments

3.2.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is used to observe the surface morphology of wide range kinds of objects [68]. It has the advantage of rather easy sample preparation, high image resolution, large depth of field, and high magnification.

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

3.2.2 Transmission Electron Microscopy (TEM)

In a typical TEM a static beam of electrons at 100-400 kV accelerating voltage illuminate a region of an electron transparent specimen which is immersed in the objective lens of the microscope. The transmitted and diffracted electrons are 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 are used to project either the image or the diffraction patter onto a fluorescent screen for observation. The screen is usually lifted and the image formed on photographic film for recording purposes.

3.2.3 Raman Spectroscopy

While photons illuminate a molecule or a crystal, they react with the atoms accompany with momentum change or energy exchange. By collecting the scatter photons, we can obtain a sequence of spectrum, including Raman scattering (inelastic scattering) and Reyleigh scattering (elastic scattering). The photon of Raman scattering can 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 is used to characterize the material.

As Raman spectrum provides information of crystallinity and bonding, it has become the most direct and convenient way to identify carbon related materials. The Raman spectrum peaks of C-C and C=C bonds in crystalline graphite are 1380 and 1580 cm^{-1}, respectively, as shown in fig. 3.6.

The instrument we use is Renishaw Raman microscope, Model 2000, equipment settings are shown in fig. 3.7. The source we use is He-Ne laser with wavelength of 632.82 nm and power of 200 mW. The spectral slit width is $0.4cm^{-1}$.

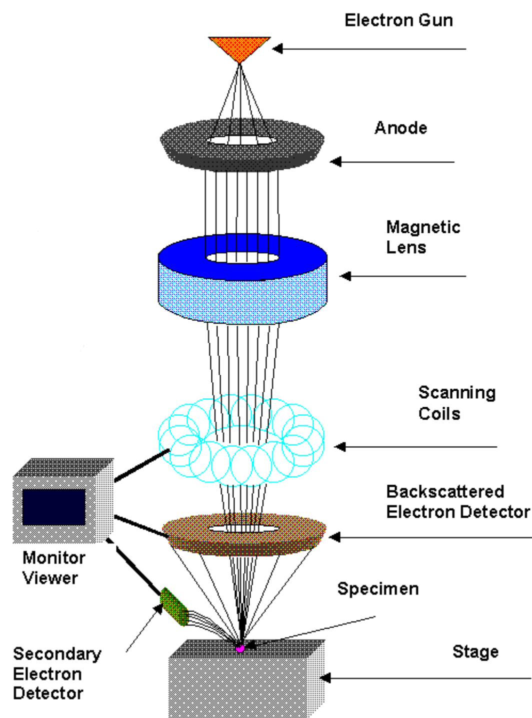

Fig. 3.4 Schematic diagram of scanning electron microscopy

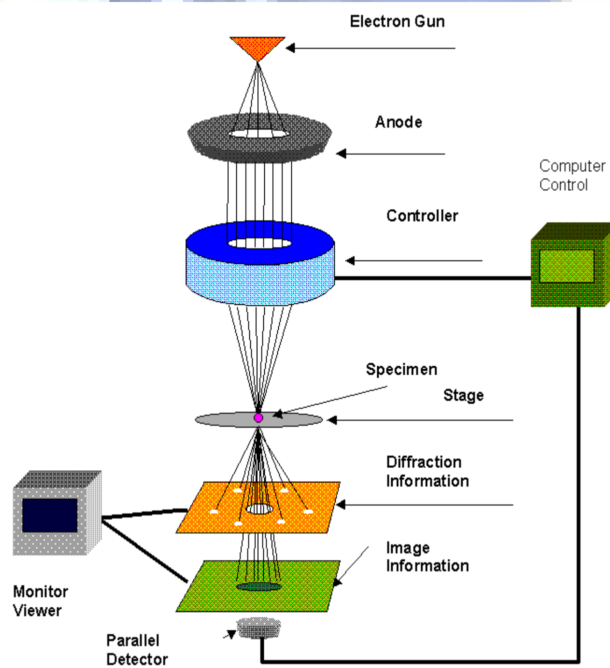

Fig. 3.5 Schematic diagram of transmission electron microscopy

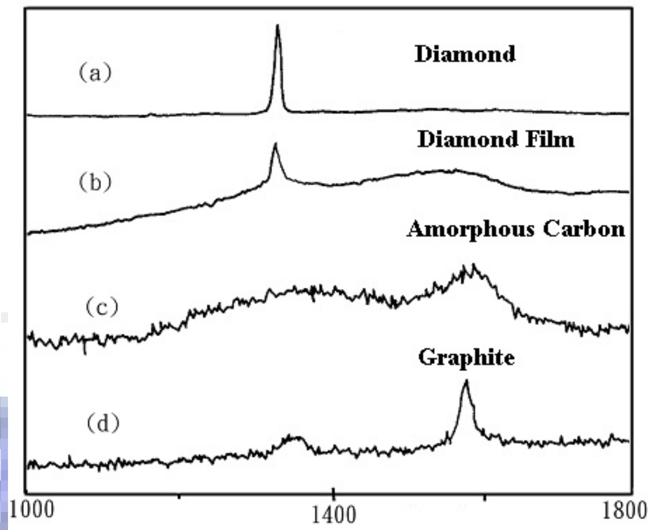

Fig. 3.6 Raman shift of (a) diamond, (b) diamond film, (c) amorphous carbon, (d) graphite

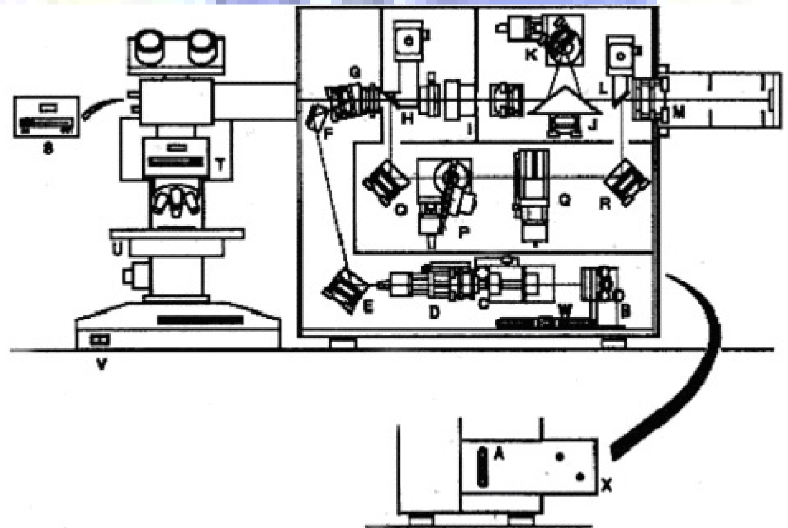

Fig. 3.7 Schematic diagram of micro-Raman equipment

3.3 Field Emission Measurement

A display needs ~0.1 mA/cm^2 current density assuming an anode voltage of ~2 kV. The turn-on and threshold field for 10 μA/cm^2 and 10 mA/cm^2, respectively have been used as the merit parameters to distinguish various emitter materials [69]. Figure 3.5 presents the field emission properties of the triode-type gated structure, which were measured using a triode technique. An anode plate (ITO Glass, MBC 6R1697) was placed at 100 μm above the Pt gate 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.

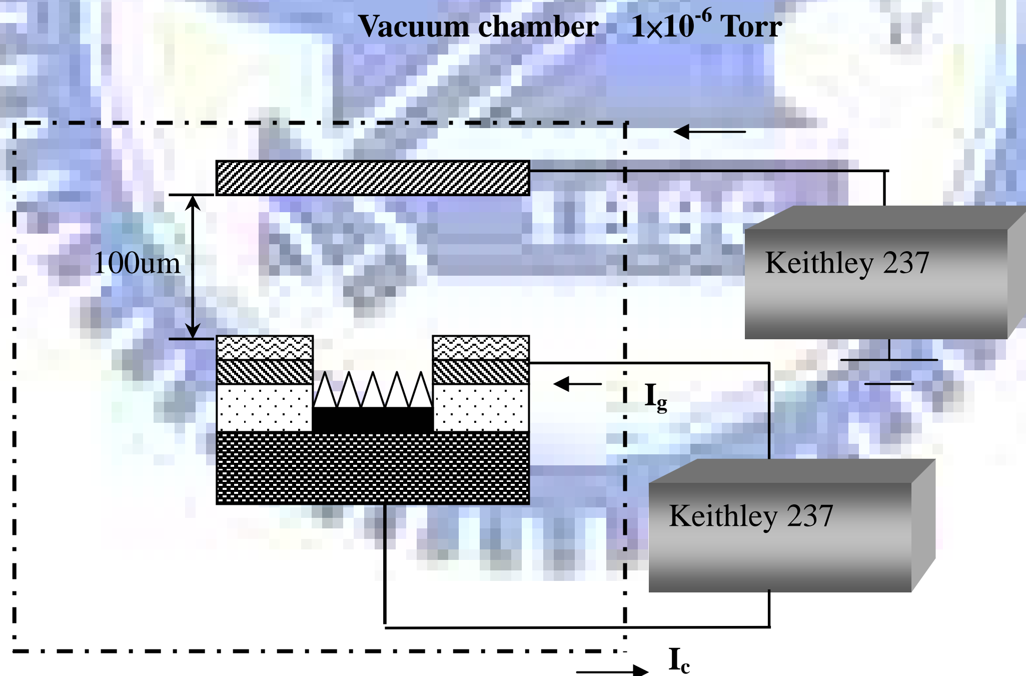

Fig. 3.8 Schematic diagram of the instrument for I-V measurement.

3.4 Scanning Auger Microscope (SAM)

Scanning Auger Microscope (SAM) is one of the surface analysis instruments; it detects auger electrons from the electron beam collision with samples. Because the auger electron signals come from the very shallow depth about several nanometers, the auger electron signals are collected by the energy analyzer, and we can gain the auger electron spectrum. Auger spectroscopy allows determining the chemical composition of a surface. This characterisation can be achieved up to 1 nm depth. The smallest surface that can be characterised is a few nm wide for the best instruments.