

Chapter 3

Experiment method

3.1. Experimental Details

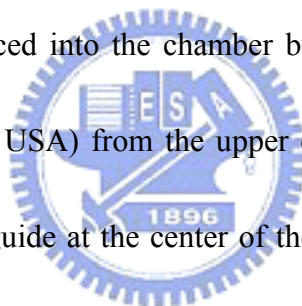
Starting substrates were mirror-polish n-type, (100) oriented wafer with a resistivity of 4.5~5.5 Ω /cm. After the different pre-treatment of substrates, substrates were put in the bias assisted microwave plasma chemical vapor deposition (BAMPCVD) system to deposit various carbon-based nanomaterials with various deposition parameters. Finally, several apparatuses were used to analyze the characterization of these nanomaterials.



3.2. Bias Assisted Microwave Plasma Chemical Vapor Deposition System

Figure 3.1 schematically depicts the layout of the BAMFCVD system. A quartz tube vertically attached to the rectangular wave-guide was used as the deposition chamber. The microwave from a magnetron source (model IMG 2502-S, IDX Tokyo, Japan) was supplied to the quartz tube through an isolator, three-stub tuner, and a power meter. Next, the microwave power was coupled to the quartz tube through an aluminum wave-guide with a hole drilled through a top and bottom face. Aluminum tubes extend out from both holes; the tube extensions are water-cooled as well. A sliding short circuit was then attached at the end of the wave-guide. The lower position of the quartz tube was connected a stainless steel multiport chamber that was

equipped with a rotary pump. The substrates were positioned in the middle of the quartz tube waveguide intersection and held vertically by a substrate holder. The substrate holder of 20mm diameter is made of molybdenum. Under the holder, it was attached to tantalum wire which was connected to the bias system; it was used as the lower electrode in the bias treatment stage [1]. A quartz protector under the holder to protect the plasma was not attracted to the tantalum wire attached to the molybdenum. The upper electrode, a molybdenum plate of 20mm diameter, was placed 35 mm above the substrate; it was 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 was cut in the waveguide at the center of the plasma cavity, allowing direct observation of the plasma



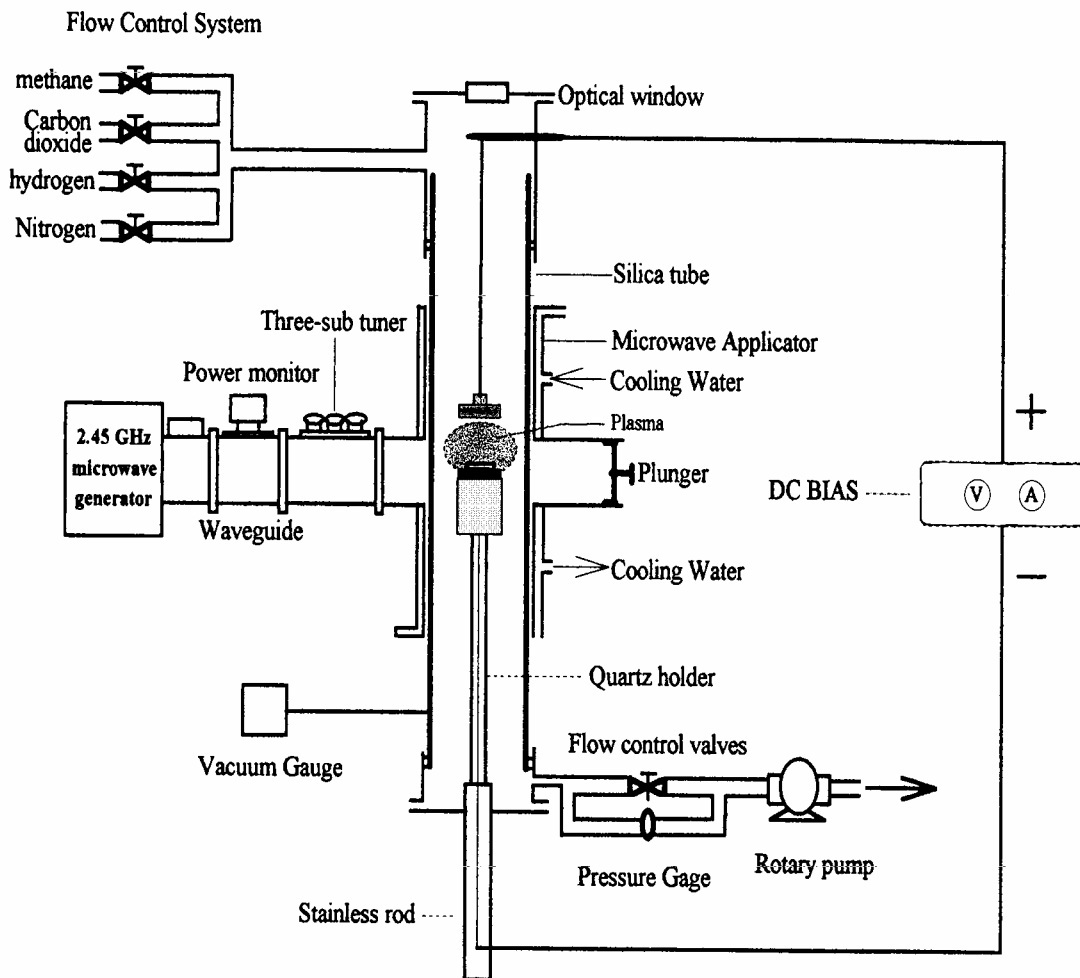


Fig. 3.1 Schematic diagram of the bias assisted microwave plasma CVD system.

3.3. Deposition conditions of various carbon-based nanomaterials

As various carbon-based nanomaterials synthesized by different deposition parameters, the detail of experiment procedure is described in the following chapter.

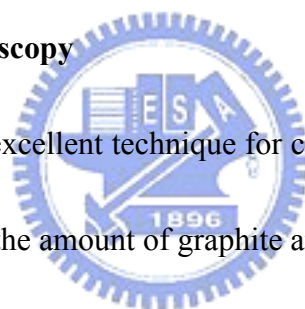
3.4. Characterization of carbon-based nanomaterials

3.4.1. Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) was used the secondary electron mode to observe the morphology of various carbon-based nanomaterials. The model of the SEM used here is HITACHI S-4000.

3.4.2. Micro-Raman Spectroscopy

Raman spectroscopy is an excellent technique for characterization of the crystalline quality of diamond films and the amount of graphite and amorphous carbon impurities in them. Figure 3.2 shows a typical Raman spectrum of a CVD diamond film and its optical micrograph, showing the film morphology [2]. The Raman spectra possess three main features: (1) a sharp peak at 1332.5 cm^{-1} , i.e. the characteristic line of a well-crystallized diamond, (2) narrow at about 1580 cm^{-1} , i.e. characteristic of a well-crystallized graphite, and (3) the diamond quality identified by the full width at half-maximum (FWHM) value of diamond peak at about 1332.5 cm^{-1} . The Raman scattering efficiency for the sp^2 bonded graphite is more than 50 times greater than for the sp^3 bonded diamond. Therefore, small amounts of sp^2 bonded carbon in the



diamond deposits can be readily detected.

The accepted figure of merit for the evaluation of the quality of diamond film is the ratio of the integrated intensity of the sp^3 related peak at 1332.5cm^{-1} to that of the sp^2 related background and the bandwidth (FWHM) of the feature at ca. 1332.5cm^{-1} . The spectrum in Fig. 3.3 was deliberately chosen to show typical results for a film of fair quality; however, many researchers have grown excellent films with Raman spectra nearly indistinguishable from those of single crystalline diamond.

The various nano-emitter was qualitatively analyzed by laser micro-Raman spectroscopy (Renishaw Raman Microscope, Model 2000). In the Raman experiment, a He-Ne laser with the wavelength of 632.82nm was used as an exciting light source. The laser light with the power of 200 mW was reflected by a half-mirror, and focused on to the sample with an objective lens. The spectral slit width of the measurement system was 0.4 cm^{-1} . Most sp^3 rich amorphous carbon films contain a minimum of 5-15% bonded carbon. Since the Raman cross-section for sp^2 clusters is much greater than for sp^3 bonded structures, scattering from the former dominates the Raman spectrum, producing a broad Raman peak in the vicinity of 1500cm^{-1} , usually swamping the signal from the sp^3 bonded portion of the films. Therefore, small amounts of sp^2 bonded carbon in the diamond film can be readily detected.

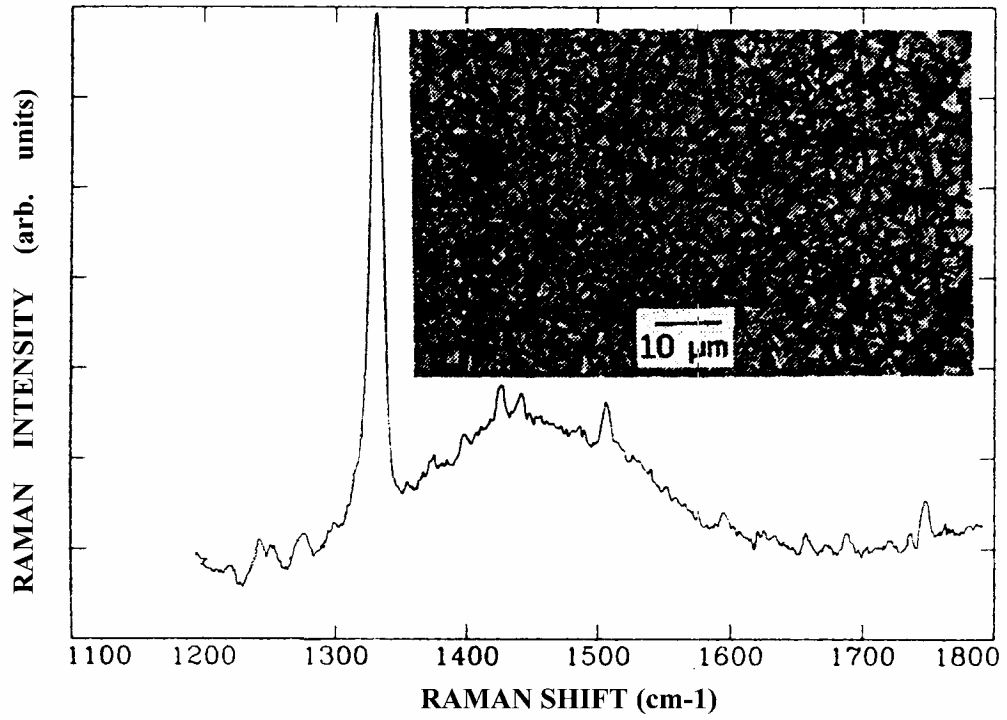


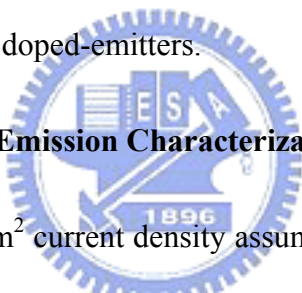
Fig. 3.2 Raman spectrum of the CVD diamond film grown on a Fused quartz substrate. Insert: optical micrograph displaying the morphology.

3.4.3. Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry, SIMS is the mass spectrometry of ionized particles which are emitted when a surface, usually a solid, is bombarded by energetic primary particles, which may be electrons, ions, neutrals or photons. The emitted or “secondary” particles will be electrons, neutrals species atoms or molecules or atomic and cluster ions. It is the process which provide a mass spectrum of a surface and enables a detailed chemical analysis of a surface or solid to be performed.

In this dissertation, secondary ion mass spectrometry, SIMS was used to identify the surface composition of the doped-emitters.

3.4.4. Measurement of Field Emission Characterization

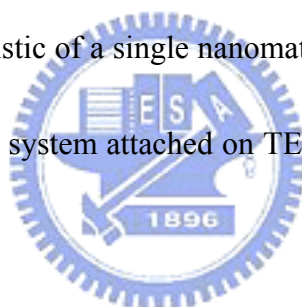


A display needs $\sim 0.1 \text{ mA/cm}^2$ current density assuming an anode voltage of $\sim 2 \text{ kV}$. The turn-on and threshold field for $10 \mu\text{A/cm}^2$ and 10 mA/cm^2 , respectively have been used as the merit parameters to distinguish various emitter materials [3]. Figure 3.3 presents 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 $100 \mu\text{m}$ above the Pt gate and was biased to $+800 \text{ V}$. 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 Kiethley SMU 237. The gate-to-cathode voltage (V_{gc}) was biased from 0 to 120V using a Kiethley 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.

3.4.5 Transmission Electron Microscopy (TEM)

One of the typical characters of nanophase materials is the small particle size. Although some structural features can be revealed by x-ray and neutron diffraction, direct imaging of nanomaterials is only possible using transmission electron microscopy (TEM). TEM is unique because it can provide a real space image on the atom distribution in the nanocrystal and on its surface. With a finely focused electron probe, the structural characteristic of a single nanomaterials can be fully characterized. Usually, the chemical analysis system attached on TEM system is the energy disperse X-ray spectroscopy (EDX).



3.4.6 Electron Energy Loss Spectroscopy (EELS)

EELS concerns the inelastic scattering of electron beam by solid and is carried out by directing an energetic (typically ~100 keV) beam of electrons onto a thin region of material (typically < 100 nm) and measuring the intensity of the transmitted beam as a function of energy loss (ΔE). The relative amount of sp^2 and sp^3 bonding in carbon can be inferred from such measurements. In the case of carbon, two energy regions are of interest:

(I) $\Delta E \sim 280$ to 300 eV: In this region, the energy loss is associated with the excitation

of an electron from the 1s carbon core to the Fermi level of graphite or to the conduction band of diamond. Differences in the 1s core level spectra between graphite and diamond permit one to distinguish between sp^2 and sp^3 bonding [4-5]. A comparison among EELS spectra for various carbon materials is shown in Fig. 3.5.

(II) $\Delta E \sim 0$ to 40 eV: In this region, the electron energy loss is due to the excitation of plasmons, identifiable as arising from the π electrons and the π and σ states of the carbon L shell, as shown in Fig. 3.4.



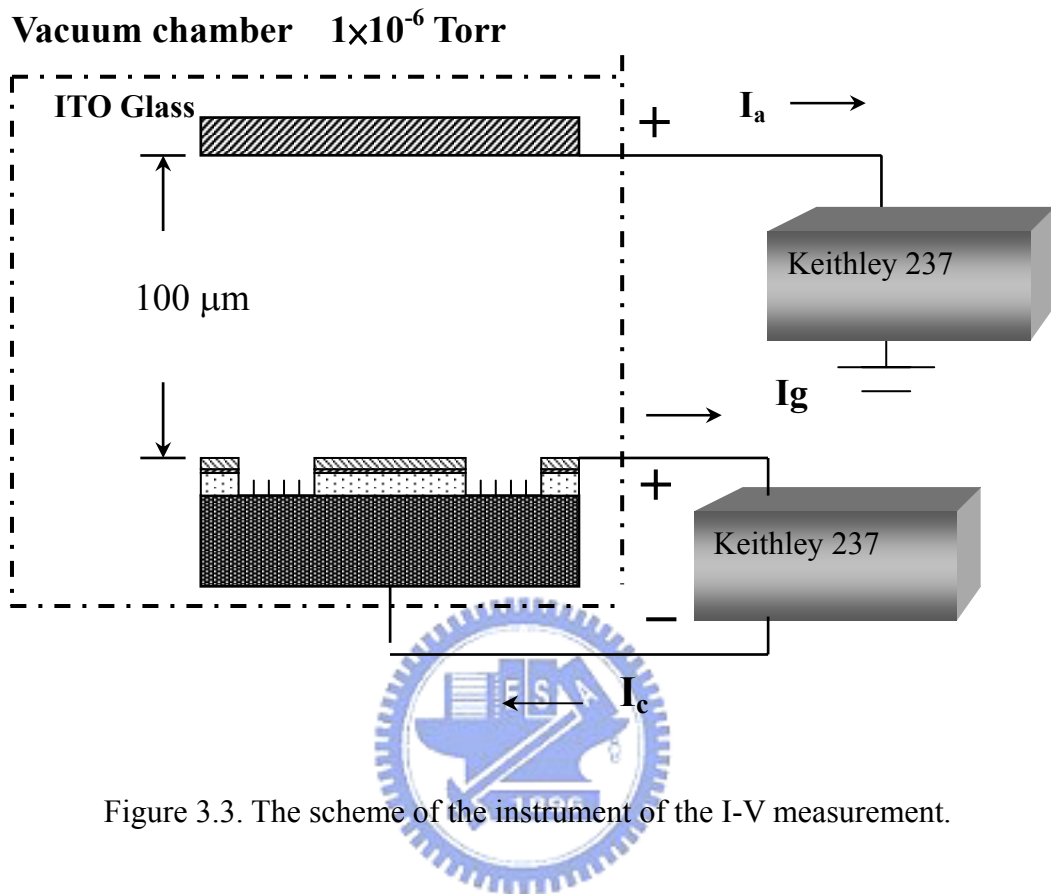


Figure 3.3. The scheme of the instrument of the I-V measurement.

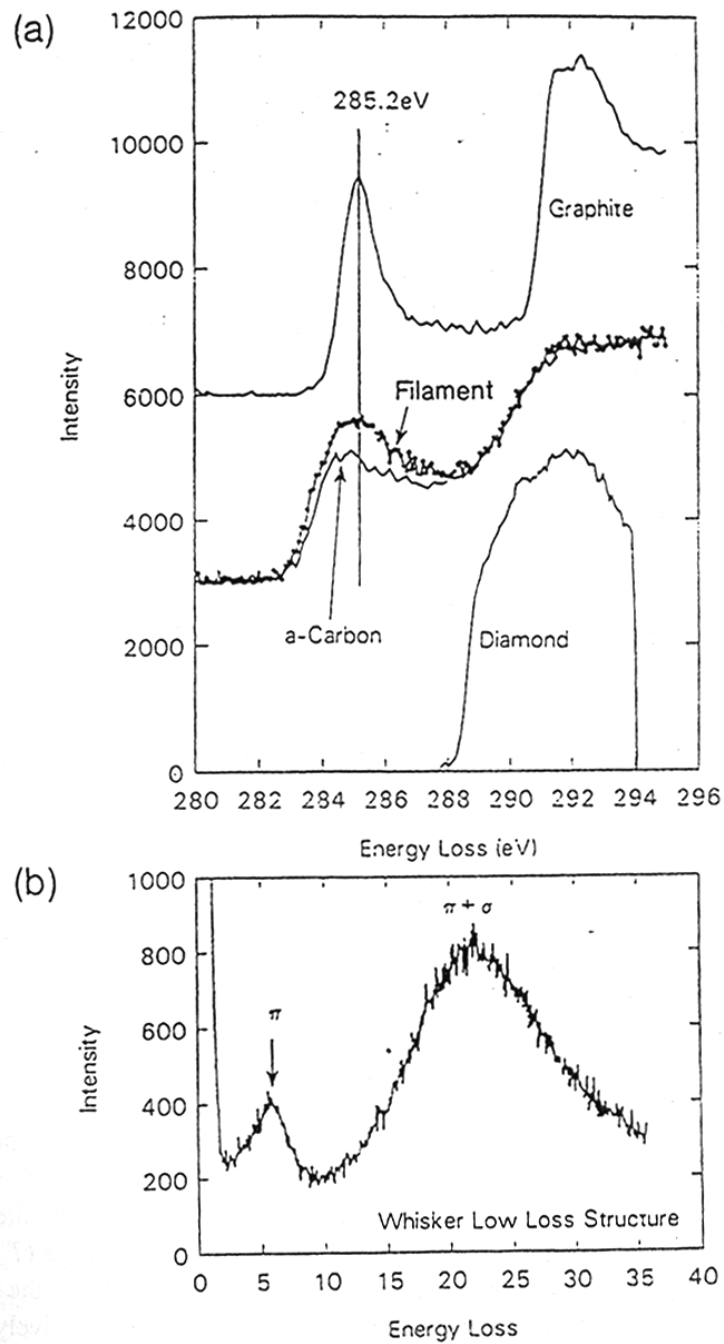


Fig. 3.4 (a) EELS spectra of graphite, diamond, amorphous (hydrogenated) carbon, in the 280-296 eV region; (b) the EELS spectrum for an ion-grown carbon filament in the 0-40 eV range.

3.5 Reference

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