

CHAPTER 4

EXPERIMENTAL METHODS AND FILMS CHARACTERIZATION TECHNIQUES

In this chapter, the details of substrate preparation for CVD diamond growth and the experimental set-up will be described. The most widely characterization techniques of diamond films, Raman Spectroscopy, Scanning Electron Microscope (SEM), and Atomic Force Microscope (AFM) which have been used in this work will be presented.

4.1 Substrate Preparation for Diamond Growth

In this study, the diamond films are deposited on square pieces silicon (Si) with dimensions of $5 \times 5 \text{ mm}^2$. Before the Si substrates are loaded in the reactor chamber, they are pre-treated. The Si substrates are cleaned by rinsed with a detergent, scratched by hand (for the condition of hand scratching pretreatment methods) for 15 min with diamond power (virgin diamond power $1 \mu\text{m}$ type MB-1-um from EID), ultrasonically cleaned for 30 min in acetone, methanol, and de-ionized water respectively. Finally, they are dried with a nitrogen blowgun.

4.1.1 Conditions for diamond growth

As mentioned in section 2.4, there are many CVD parameters that effect the diamond growth, such as substrate temperatures, CH₄ concentration, deposition pressure, and microwave power. In order to acquire the optimum parameters for the CVD diamond growth, all conditions should be varied. In this study, CH₄ concentrations and deposition pressure are varied. The range of growth conditions using in this study are showed below in Table (4.1).

Table 4.1: Deposition parameters used for the diamond growth

Gas composition	CH ₄ :H ₂ = 0.5-5 %
Gas flow rate	H ₂ = 100 sccm CH ₄ = 0.5-5 sccm
Operation pressure	10-50 Torr
Microwave power	450 watt
Substrate temperature	370-470 °C
Deposition time	1-30 hour

The microwave power and H₂ flow rate are kept constant at 450 watt and 100 sccm (sccm refers to the gas flow in units of standard centimeters cubed per minute), respectively. The CH₄ concentration is varied in hydrogen (CH₄/H₂; %), defining as the ratio of CH₄ flow rate to H₂ flow rate in the range of 0.5-5 % and deposition pressure is varied in the range of 10-50 Torr. After the growth process finished, all substrates are cooled to room temperature within the reactor chamber under evacuating conditions.

4.2 Film Characterization Techniques

Various techniques have been used for the characterization of diamond films Electron Spin Resonance (ESR) [46], and X-ray Photoelectron Spectroscopy (XPS)

[47]. However, in this study Raman Spectroscopy, Scanning Electron Microscope (SEM), and Atomic Force Microscope (AFM) have been used for films characterization.

4.2.1 Raman spectroscopy

Raman spectroscopy is a technique which examines the type of bonding in carbon films. This technique involves photon, which can create or annihilate phonon [9] in the lattice. Essentially, this spectroscopy studies the interaction between electromagnetic wave and matter by absorption or scattering processes. The scattering processes may occur either elastically or inelastically. The elastic process is called *Rayleigh scattering* and inelastic process is called *Raman scattering* [48].

Raman scattering occurs when a photon (from monochromatic light source) interacts with the electric dipole of the molecule. Consequently, the molecule is excited to the virtual state and then, rapidly decays to vibrational energy levels above or below the initial state. The energy levels diagram of scattering is illustrated in Fig. 4.1. The heavy arrow line on the left of Fig. 4.1 shows the energy changed from the ground electronic state to virtual state with energy $h\nu$ when molecule interacted with the photon. The second arrow from the left shows the energy changed from the first vibrational level to virtual state. Two arrows in the middle and the right side of Fig. 4.1 show the changing that produce Rayleigh and Raman scattering, respectively.

In traditional Raman analysis, Raman spectrum is presented as a number of photons, (or intensities), versus Raman shift. Raman shifts occur either up or down shift relative to the incident photon frequency. The down-shift is called *Stokes lines* while the up-shift is called *anti-Stokes lines*.

Raman spectrum of natural diamond shows a sharp peak centered at 1332 cm^{-1} [1] and the Full Width at Half Maximum (FWHM) of the peak at 1.9 cm^{-1} . For diamond film grown by CVD process, the non-diamond phases (graphite or amorphous) may compound in the film. Raman spectrum of graphite shows a

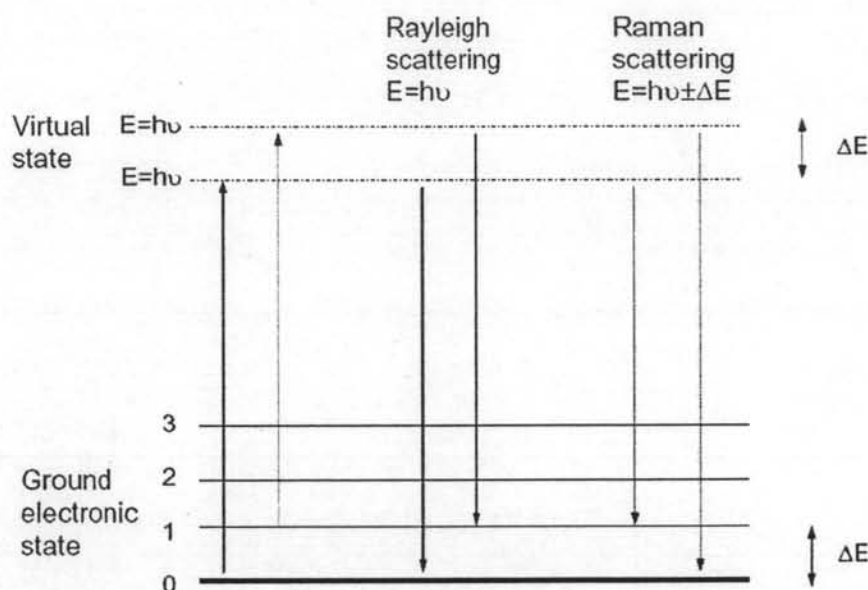


Figure 4.1: The energy levels diagram of Rayleigh scattering and Raman scattering [48].

broad peak centered at 1580 cm^{-1} [1]. Each type of carbon phases show Raman peaks at different position. The description details of their peaks are illustrated in Table 4.2.

It should be noted that the sensitivity of the Raman change depending on the different and the energy of laser used. For example, with 514 nm laser, the sensitivity is ~ 50 times for sp^2 (Graphite) [12, 49] and ~ 233 times for amorphous carbon [49], when compared with diamond phase. Hence, Raman spectrum of CVD diamond usually shows a broad hump around $1550\text{-}1580\text{ cm}^{-1}$. Raman spectrum of CVD diamond films in this study are recorded using Reinshaw model Rm1000. The 514.5 nm argon laser with $4\text{ }\mu\text{m}$ beam size is used for the excitation. The spectrometer resolution is set at 2 cm^{-1} over the $1000\text{-}1800\text{ cm}^{-1}$ range.

Table 4.2: The major Raman peaks from CVD carbon [1].

Peak Position	Type of Carbon	Description
$\sim 1140 \text{ cm}^{-1}$	small size ($< 0.1 \mu\text{m}$) cubic diamond	occasionally observed in diamond films small grain sizes
1315-1326 cm^{-1}	hexagonal diamond	broad band, observed in shock wave produced diamond
1332 cm^{-1}	cubic diamond	first order peak with FWHM of 1.9 cm^{-1} for natural diamond
1345 cm^{-1}	amorphous carbon	broad band
1355 cm^{-1}	microcrystalline graphite	observed in materials with small grain sizes
1550 cm^{-1}	amorphous or diamond-like carbon	broad band
1580 cm^{-1}	graphite	first order peak

4.2.2 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is a technique to examine the morphology of the specimen surface. Basically, the primary electrons are generated by thermionic emission from a tungsten filament and are focused on the specimen surface by the sets of scanning coils. The interactions between electrons and specimens are presented by the excitation volume. There are many processes occurred within this volume i.e. secondary electron, reflected or backscattered electrons, x-ray radiation, and Auger electron etc. The secondary electrons are a signal of SEM image. This signals are amplified and converted into image on a Cathode-Ray Tube (CRT) display. In order to prevent electrical charging during analysis, the surface of specimen must be electrically conducting. Therefore, a thin gold layer must be deposited on the film. In this study, the surface morphology of CVD diamond films are obtained by using JSM-6400 Scanning Electron Microscope

operating at a voltage of 15 kV.

4.2.3 Atomic force microscopy (AFM)

Atomic Force Microscope (AFM) is used to study the surface roughness of the diamond film. The root mean square (RMS) surface roughness is a standard deviation of the surface height within a given area, as defined by [50],

$$RMS = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{ave})^2}{N}}, \quad (4.1)$$

where Z_{ave} is the average surface height within the given area,

Z_i is the current surface height,

N is the number of data point within a given area.

In this work, the surface roughness of film is studied using Nano Scope IV with tapping mode over the range of $5 \times 5 \mu\text{m}^2$.