# CHAPTER 2

# BACKGROUND

In this chapter, we will present the necessary background in this work. The chapter begins with the detail of structure and properties of diamond. Next, the diamond growth methods which are HPHT, CVD will be described followed by the CVD processes of diamond growth and MW-PECVD technique. In the last section of this chapter, the growth conditions which can affect to CVD diamond growth will be discussed.

## 2.1 Carbon Atom and Diamond Structure

Carbon atom has an atomic number of 6 with an electronic ground state configuration of $1s^2 2s^2 2p^2$. The valence electrons of carbon can form different chemical bonds by mean of three type hybridizations which are $sp$, $sp^2$, and $sp^3$. Prior to forming of chemical bonds in carbon atom, electron will be shift from $2s$ to $2p$ orbital in the excited state. If carbon atom cooporate into diamond structure, one electron in $2s$ and three electron in $2p$ orbital will redistribute into four new equal-energy level orbital, which is called fourfold ($sp^3$) co-ordinate. While, in the graphite structure, electron will redistribute into three new equal-energy level orbital, as called threefold ($sp^2$) co-ordinate. Fig. 2.1 shows the simple schematic electronic configuration of carbon atom in the ground state, excited stated, and hybridized to be fourfold and threefold co-ordinate.

Diamond is a crystalline in the cubic crystal system that consists of only carbon atoms. Carbon atoms of diamond form a covalent bond of $sp^3$ hybridization

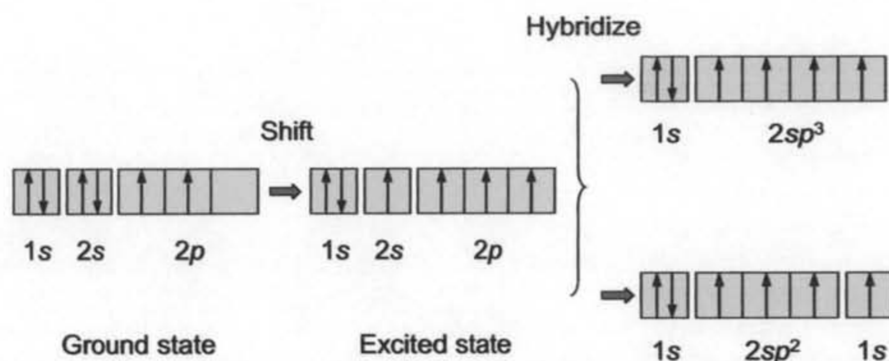


Figure 2.1: Schematic presentation of the fourfold coordinated $sp^3$ sites (top) and the threefold coordinated $sp^2$ sites (bottom) of carbon atom, adopted from [8].

with a lattice parameter ($a_0$) of 3.567 Å , a bond length of 1.54 Å and can be viewed as two face center cubic (FCC) structure displaced by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ $a_0$, as illustrated in Fig. 2.2.

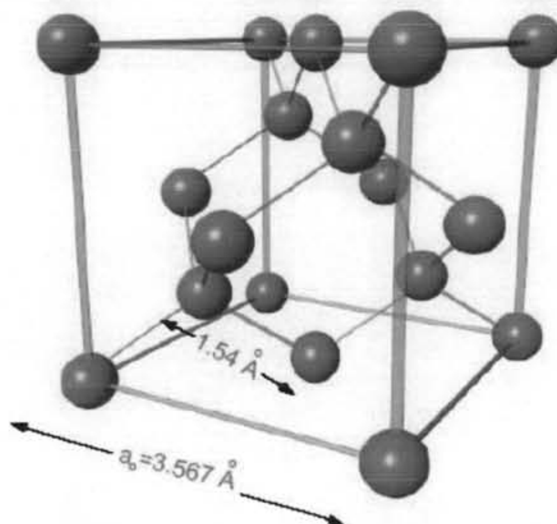


Figure 2.2: The conventional cubic unit cell of the diamond structures [9].

## 2.2 Diamond Properties and Applications

Several extreme physical and chemical properties such as high thermal conductivity, high electrical resistivity, high corrosion resistance, high optical transparency, and low thermal expansion coefficient etc, have made diamond an excellent material. In addition, the success of diamond growth by CVD methods to provide a diamond thin film to be used in widely applications. Properties of single crystal and CVD diamond are given in Table 2.1, we can describe some of their properties and applications as follows.

◇ Diamond has the highest thermal conductivity (approximately about five times of copper), low thermal expansion coefficient, and high electrical resistivity. Therefore, diamond is the best material to be used as a heat sink for integrated circuits [1].

◇ Diamond has a wide range of transparency from ultra violet (UV) to the far infrared (IR) in the electromagnetic spectrum, resistance to thermal shock and inert at room temperature and pressure. Therefore diamond can be used as a optical window in the hash environments [2].

◇ Diamond has a high carrier mobility, low dielectric constant and high electronic energy gap (5.45 eV). Therefore, diamond can be used in applications involving high frequency electronic devices [2, 10].

◇ Natural diamond is well known as a hardest material, low friction coefficient, high elastic properties, and high corrosion resistance. This suggest the usage of CVD diamond in coating of cutting tools, and milling tools as protective layer, which can improve efficiency and lifetime of tools [10].

◇ The biocompatibility property of carbon atom make diamond a superb coating materials in biological applications [11].

Table 2.1: Some properties of CVD and single crystal diamond, applied from [12, 13].

| Properties | CVD diamond | Single-crystal diamond |
|---|---|---|
| Density ($g/cm^3$) | 2.8 - 3.51 | 3.515 |
| Thermal conductivity (W$m^{-1}K^{-1}$) | 2100 | 2200 |
| Thermal expansion coefficient ($\times 10^{-6}K^{-1}$) | $\sim 2.0$ | 0.8 - 1.2 |
| Band gap (eV) | 5.45 | 5.45 |
| Electrical resistivity ($\Omega - cm$) | $10^{12}$ - $10^{16}$ | $10^{16}$ |
| Coefficient of friction in air | 0.035 - 0.3 | 0.05 - 0.15 |
| Young's modulus (GPa) | 820 - 900 | 910 - 1250 |
| Carrier mobility ($cm^2V^{-1}s^{-1}$) | | |
| electron (n) | 1350 - 1500 | 2200 |
| positive hole (p) | 480 | 1600 |
| Vickers hardness (GPa) | 50 - 100 | 57 - 104 |
| Dielectric constant at 45 MHz-20 GHz | 5.6 | 5.7 |
| ◇ Broad optical transparency from UV to IR | | |
| ◇Very resistive to chemical corrosion | | |
| ◇ Biologically compatible | | |

## 2.3 Diamond Growth

Because of the lacking and the high cost of natural diamond, it is difficult to utilize many properties of diamond. Many scientists have realized and understood these problems. Two prominent technologies, which are high-pressure high-temperature (HPHT) and chemical vapor deposition (CVD), are among the methods utilized in diamond synthesis.

### 2.3.1 High pressure high temperature growth

The diamond growth by high pressure high temperature (HPHT) method was first announced by General Electric (GE) group in 1955. This method can be achieved in three types of synthesis. (i) directed conversion using high pressure high temperature, (ii) high pressure high temperature conversion using metal solvents, and (iii) directed conversion using shock waves [14]. The main foundation of these methods are the transformation of graphite to diamond structure in the thermodynamic stable region of diamond using a high pressure (ten of thousands of atmospheres) and heated over 2000 K. Unfortunately, the high cost of production and technical limitation of HPHT method are the prohibiting factors for using this technique in wide applications.

### 2.3.2 Chemical vapor deposition

Chemical Vapor Deposition (CVD) is a process of chemically reacted volatile (the easiest is gas) compound of material to be deposited to produces a nonvolatile solid on a suitable placed substrate. The fundamental of CVD processes are schematically showed in Fig. 2.3. The process can be broken down to the different parts, as [15].

(1) Precursor gas flows from the gas inlet lines into the reaction zone.

(2) Within the reaction zone, gas is activated (e.g. by thermal processes, or plasma enhanced processes) and then, produces a new reactive species.

(3) A new reactive species are transported close to the surface substrate.

(4) The species of atoms or molecules will be either absorption (e.g. by chemical and physical absorption) or reaction occurring on the substrate surface, diffused close to the surface or desorbed back into the gas phases. These processes depend on the growth conditions and substrate materials.

(5) Nucleations form on the surface substrate and film starts to grow. The type of substrate, substrate temperature, and gas transport are the major CVD

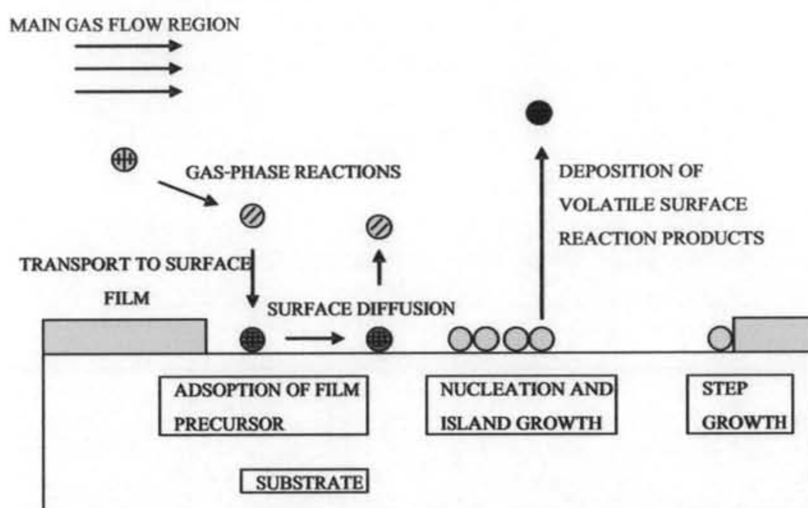


Figure 2.3: The fundamental in CVD process [15].

parameters that effected the surface morphology and quality of films. The growth conditions of CVD diamond will be described in section 2.4.

The first success of CVD diamond growth was disclosed by Eversole of Union Carbide Corporation in 1962 and was later confirmed by Augus et al. [3] in 1968. However, in their early experimental results, the low growth rate with a co-deposition of graphite are the problematic issues.

In the mid-seventies, Deryagin [3] of the Physical Chemistry Institute of Moscow added the hydrogen gas during the growth process. He found that the co-deposition of graphite was reduced while the diamond growth rate was increased.

The CVD diamond growth may be mentioned highly to be successful by the group of Japanese researcher of the National Institute for Research Inorganic Materials (NIRIM). The study by Matsumoto and Setaka [3] introduced the hot-filament reactor in 1981 and the microwave plasma reactor in the next year.

From that time on, CVD diamond researches have been focused on several issues; for examples, the nucleation mechanism [13, 16], the growth techniques, mechanism of gas phase [17], the simulation of electromagnetic field distribution [18] in order to improve and develop the CVD diamond reactor [19, 20, 21].

### 2.3.3 The CVD diamond growth

There are two types of diamond growth by CVD processes. They are homoepitaxy growth (using natural diamond as a substrate) and heteroepitaxy growth (using non-diamond material as a substrate) [1, 22]. For diamond growth on a non diamond substrate (i.e. silicon, or molybdenum), the diamond films have yielded only polycrystalline films which contain a randomly oriented crystals, as shown in Fig. 2.4.

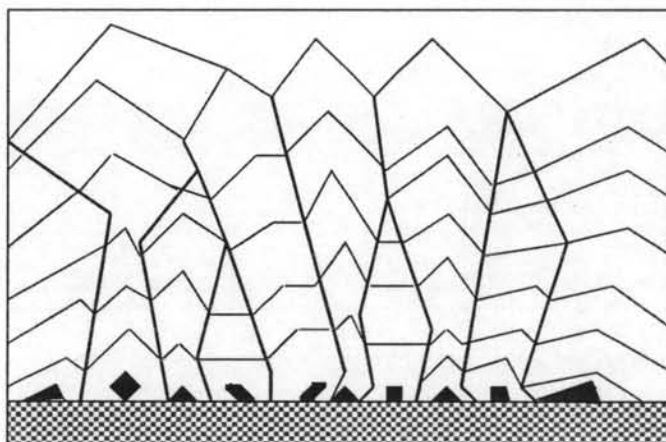

Figure 2.4: Side viewed of polycrystalline diamond films [3].

The growth of polycrystalline diamond film starts from a nuclei (black shapes in Fig. 2.4) in the initial stages. The black lines show a randomly morphology with times. Liu and Dandy [13] described that the nucleation sites in nucleation process are created on intermediate layers such as diamond-like amorphous, metal carbide, and graphite.

The growth processes of CVD polycrystalline diamond film consist of five distinguishable states, which are (i) incubation period for nucleation, (ii) three dimensional (3-D) nucleation of individual crystalline on the surface substrate, (iii) termination of surface nucleation and three dimensional (3-D) growth of nuclei to grains, (iv) faceting and coalescence of individual grains, and (v) growth of continuous film [13].

Table 2.2: Typical surface nucleation densities of diamond after different surface pretreatments, adapted from [13]

| Pretreatment method | Nucleation density ($cm^{-2}$) |
|---|---|
| No pretreatment | $10^3 - 10^5$ |
| Scratching | $10^6 - 10^{10}$ |
| Ultrasonic scratching | $10^7 - 10^{11}$ |
| Biasing | $10^8 - 10^{11}$ |

In addition, the substrate pretreatments are the necessary processes in order to increase nucleation density ($N_d$; the number of nuclei grown on unit surface substrate) and reduced the incubation times. There are various techniques used to enhance nucleation density, which include scratching, and substrate biasing, as showed in Table 2.2. The $N_d$ have been increased from $10^5$ $cm^{-2}$ on untreated substrate up to $10^{10}$ $cm^{-2}$ and $10^{11}$ $cm^{-2}$ for scratching and biasing methods, respectively. These high nucleation density also depend on the substrate materials and synthesis conditions.

Work by Paosawatyanyong [12] showed that the Si substrate was scratched with 1/4 $\mu$m powder with hand, before it is deposited. He found that this method can enhance the nucleation density to yield continuous diamond film.

Work by Lu et al. [23] showed that the diamond nucleations on silicon substrates are increased to the order of $10^9$ $cm^{-2}$ when substrate is applied with voltage during growth. In addition, they also found that the results of Raman spectrum ratio of $sp^3$ to $sp^2$ is increased when applied with -350 V ($sp^3$ and $sp^2$ spectrum are a characteristic of diamond and graphite structures, respectively, the details of Raman analysis will be described in section 4.2.1).

The study by García et al. [24] showed the results of biasing times to the nucleation of diamond films by set a negative voltage at 250 volt. In their work, the highest rate of diamond nucleation formed at biasing time of 20 mins. In

addition, they also found that the root mean square roughness (RMS) obtained by atomic force microscope (AFM) of diamond film has a minimum values when biased for 20 mins.

Therefore, in this study, in order to increase the nucleation density and reduced the incubation times of diamond films, two pretreatment methods which are hand scratching and ultrasonic agitation will be compared. The detail of substrate preparation will be described again in section 4.1.

### 2.3.4 Microwave plasma enhance chemical vapor deposition

Literatures of plasma-processing [?] referred to the *plasma-assisted chemical vapor deposition* (PACVD or PCVD) as a set synonym to *plasma enhance chemical vapor deposition* (PECVD). However, the source of excitation, i.e. radio frequency and microwave frequency are subdivided to be call with different name and abbreviation. For example, radio frequency plasma enhance CVD (RF-PECVD), or microwave plasma enhance CVD (MW-PECVD) etc.

In case of microwave discharge, plasma is created and sustained by coupling microwave energy to gases through the applicators of a various designs; for example, National Institute for Research Inorganic Materials (NIRIM) reactor, microwave plasma cavity reactor, ASTeX bell jar, ellipsoidal reactor, and surface-wave microwave reactor [19, 20, 21]. In MW-PECVD, the free electrons and ions are accelerated by electromagnetic field and transfer energy toward precursor gases via elastic and inelastic collisions and changed gases to the plasma. Plasma induced by this technique is called *cold plasma*, and the electrons have energy in the range of 1-10 eV [25, 26]. The original schematic diagram of NIRIM reactor or tubular reactor is shown in Fig. 2.5.

This NIRIM reactor was developed in the early 1980s by Kamo et al., which consists of a rectangular waveguide utilized to confine the microwave radiation

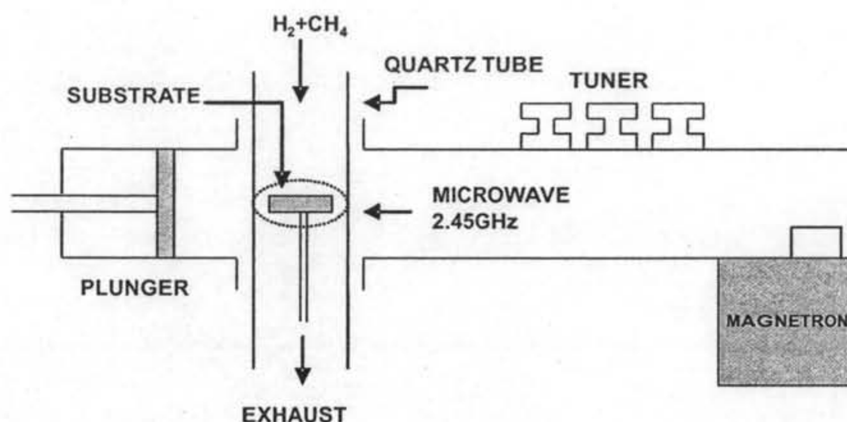


Figure 2.5: Schematic illustration of NIRIM microwave plasma CVD apparatus used for the growth of diamond films [3].

between microwave energy source (magnetron head) and quartz tube. The quartz tube (with diameter 4.5 cm or less) is placed in the path of the microwave in the rectangular waveguide while the substrate is placed at the point of maximum electric field. The plunger and the three stub tuners are used to adjust the short circuit part of the waveguide and to match the impedance, respectively. For MW-PECVD techniques, the traditional conditions of the diamond growth (as showed in Table 2.3) can be varied according to the specific reactor configuration and technology.

Table 2.3: General conditions for the growth of CVD diamond films [3].

| Gas Mixture | Total Pressure (Torr) | Microwave Power (W) | Substrate Temperature ($^oC$) |
|---|---|---|---|
| $CH_4$(0.5-2%)/$H_2$ | 5-100 | 100-700 | 700-1000 |

The common gas mixture for diamond CVD is methane ($CH_4$) diluted in hydrogen ($H_2$) in the range of 0.5-2 %. The pressure during growth is varied between 5-100 Torr (depending on the limitation of reactor), the microwave power and the substrate temperature are in the range of 100-700 W and 700-1000 $^oC$,

respectively. The influence of diamond growth conditions will be described in the next section.

## 2.4 CVD Diamond Growth Conditions

In general, the quality of CVD diamond film depends on the CVD parameters which include substrate material, gas precursor, substrate temperature, and deposition pressure. In this section, we will present these parameters that effect the CVD diamond growth.

### 2.4.1 The influence of substrate materials

The type of substrate material is an important factor to diamond growth, as mentioned in section 2.3.3. The melting point and the thermal expansion coefficient are the main factor in choosing the substrate for CVD growth. The high temperature during growth process is a limitation to low-melting point materials such as plastics or aluminium. In addition, the large difference of thermal expansion coefficient is a cause of film cracking [27]. Table 2.4 shows some physical parameters of materials (i.e. melting point and thermal expansion coefficient) to be used as substrates. From Table 2.4, the close thermal expansion coefficients of Si, Mo, W, Cr, and Ti to that of diamond are the main reason for these materials to be chosen as substrate materials or the intermediate layers for diamond growth and diamond coating, respectively.

Study by Mallika and Komanduri [28] showed the results of diamond films which is grown on a commercial silicon nitride ($Si_3N_4$) by ASTeX S-1500 MW-PECVD reactor. The results showed strongly adhered diamond coating on ($Si_3N_4$) substrate under the optimum growth condition.

Another study by Silva et al. [29] showed that the intermediate layers of Ti and Cr coated before the diamond film deposited on the ferrous substrate can reduce adhesion problem.

Table 2.4: The physical parameters, i.e. melting point and thermal expansion coefficient of some materials, adopted from [13].

| Substrate material | Melting point[a] ($^oC$) | Thermal expansion coefficient[b] ($10^{-6}K^{-1}$) |
|---|---|---|
| Diamond (cubic) | 3057 | 0.8 |
| Al (f.c.c.) | 660 | 23.5 |
| Au (f.c.c.) | 1064 | 14.1 |
| Fe ($\gamma$) | 1534 | >14.6 |
| Si | 1412 | 7.6 |
| Mo (b.c.c) | 2615 | 5.1 |
| $Si_3N_4(\beta)$ (hexagonal) | 2442 | 2.11 |
| W ($\alpha$) | 3387 | 0.55 |
| Ti ($\alpha$)<900 ($^oC$) (h.c.p.) | - | 8.9 |
| ($\beta$)>900 ($^oC$) (b.c.c.) | 1667 | 9.9 |
| Cr ($\alpha$)<1840($^oC$) (b.c.c.) | 1860 | 6.5 |

[a] at 1 atm, [b] at 20 $^oC$

However, the diamond films in this research are grown on the silicon wafer substrate, this is due to the high melting point and closely match thermal expansion coefficient with diamond.

### 2.4.2 The influence of precursor concentrations

The common gas mixture of CVD diamond growth is methane ($CH_4$) diluted in hydrogen ($H_2$). The $CH_4$ concentration is varied between of 0.5-2 % depending on the desired film quality (i.e. diamond purity, growth rate, and morphology). Many researchers [10, 12, 30, 31] reported that increased $CH_4$ concentration should reduce the film quality (based on Raman analysis) as well as change the surface morphology of films.

Work by Choi et al. [32] reported that in diamond growth on Si substrate, when increasing $CH_4$ concentration up to 5 %, the non-diamond phases are appeared based on Raman and transmission electron microscopy analyses. The exact mechanism of increasing $CH_4$ concentrations is not clear. However, a high concentration of $H_2$ is the basis of the processes. $H_2$ is believed to, (a) produce a radical molecules ($CH_3$) which are suggested as a species for nucleation and diamond growth, (b) etch graphite phase during diamond growth, and (c) terminate the *dangling* carbon bonds on the diamond surface [2, 27].

The influence of gas precursor is also reported by Bénédic et al. [33]. In their work, CVD diamond was grown with the additional of nitrogen ($N_2$) to the traditional $CH_4$ and $H_2$ gas mixture. They concluded that $N_2$ addition is a good addition to improve the diamond growth rate, surface morphology, and surface electric resistance.

### 2.4.3 The influence of substrate temperature

A substrate temperature effects on diamond growth are presented by many researchers [5, 19, 30, 34]. Diamond growth at temperatures above 1200 $^oC$ is found to lead to graphite while diamond growth at temperatures less than 500 $^oC$ is found to lead to DLC growth [3]. Therefore, the study of diamond growth is usually performed at the substrate temperature in the range of 700-1000 $^oC$, as shown in Table 2.3.

The study by Bühlmann et al. [31] showed that diamond film grown under $CH_4$ concentration of 2%, substrate temperature of 870 $^oC$ shows the well-faceted film while at temperature of 950 $^oC$, the film morphology was changed to balls or cauliflower-like.

Silva et al. [35] studied the correlation between substrate temperatures (400-700 $^oC$) and $CH_4$ concentration to surface morphology of diamond film. They found that these temperatures range with the low $CH_4$ concentration (<1%) made

the film very rough with (111) dominated morphology. At increased $CH_4$ concentration (>7%) and or decreased the deposition temperature (<550 $^oC$), the spherical ball was dominated.

In recent years, the CVD diamond film performed at low substrate temperature using $Ar/H_2/CH_4$ gas composition was proposed by Das et al. [5]. They found that the full width at half maximum (FWHM) of Raman peak of diamond characteristic was decreased from 7.94 to 6.81 $cm^{-1}$ while the substrate temperature was varied from 370 to 530 $^oC$.

It should be noted that in our experiment, no extra heater was utilized during the deposition processes. Thus, the samples were only heated by the microwave plasma.

### 2.4.4 The influence of deposition pressure

The pressure during the growth diamond film is a factor which depends on the CVD techniques including specific characteristic and reactor technology [7, 36]. In a review by Dandy [37], it was reported that the relations between deposition pressure and diamond nucleation density are reversible, because atomic hydrogen decreased the number of nucleation sites. Therefore, the deposition pressure is varied from 2-5 Torr for early growth of nucleation processes, and then deposition pressure is changed to 20-40 Torr for diamond growth processes. The influence of deposition pressure to CVD growth was studied by Borges et al. [19] in a surface-wave driven microwave plasma reactor. He found that the growth rate was maximum at the pressure nearly of 30 Torr by maintaining the $CH_4$ concentration at 0.75 %, substrate temperature at 950 $^oC$, and microwave power at 1.15 kW. Work by Li et at. [38] studied the effect of deposition pressure in the rang of 50-125 Torr to growth rate and quality of diamond films. By fixed $CH_4$ concentration at 5%, the growth rate was exponential growth with increasing pressure as well as increased the crystallinity indicated by Raman spectrum.