# GROWTH AND CHARACTERIZATION OF LARGE, HIGH QUALITY SINGLE CRYSTAL DIAMOND SUBSTRATES VIA MICROWAVE PLASMA ASSISTED CHEMICAL VAPOR DEPOSITION

By

Shreya Nad

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#### ABSTRACT

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Single crystal diamond (SCD) substrates can be utilized in a wide range of applications. Important issues in the chemical vapor deposition (CVD) of such substrates include: shrinking of the SCD substrate area, stress and cracking, high defect density and hence low electronic quality and low optical quality due to high nitrogen impurities. The primary objective of this thesis is to begin to address these issues and to find possible solutions for enhancing the substrate dimensions and simultaneously improving the quality of the grown substrates.

The deposition of SCD substrates is carried out in a microwave cavity plasma reactor via the microwave plasma assisted chemical vapor deposition technique. The operation of the reactor was first optimized to determine the safe and efficient operating regime. By adjusting the matching of the reactor cavity with the help of four internal tuning length variables, the system was further matched to operate at a maximum overall microwave coupling efficiency of ~ 98%. Even with adjustments in the substrate holder position, the reactor remains well matched with a coupling efficiency of ~ 95% indicating good experimental performance over a wide range of operating conditions.

SCD substrates were synthesized at a high pressure of 240 Torr and with a high absorbed power density of 500 W/cm<sup>3</sup>. To counter the issue of shrinking substrate size during growth, the effect of different substrate holder designs was studied. An increase in

the substrate dimensions (1.23 – 2.5 times) after growth was achieved when the sides of the seeds were shielded from the intense microwave electromagnetic fields in a pocket holder design. Using such pocket holders, high growth rates of  $16 - 32 \mu$ m/hr were obtained for growth times of 8 - 72 hours. The polycrystalline diamond rim deposition was minimized/eliminated from these growth runs, hence successfully enlarging the substrate size.

Several synthesized CVD SCD substrates were laser cut and separated from the underlying seeds, and then polished to form CVD diamond plates. These plates were characterized with various techniques and were determined to be of type IIa quality or better with a high optical transmission. Etch pits were observed to occur at the edges of growth terraces after etching experiments. By exploiting such an observation along with long growth times, the electronic quality of the substrates was improved upon by reducing the etch pit density of the grown substrates by 1 - 3 orders of magnitude over the commercially available seeds.

This research has thus developed new process methods for enlarging the CVD SCD dimensions at high growth rates while improving their quality. These process methods were demonstrated by using electrically efficient, cost effective reactor designs. These process methods and reactor designs can now be used in the future for the synthesis of even larger and better quality substrates.

Copyright by SHREYA NAD 2016 To my family for standing by me at all times and to Dr. A, for believing in me.

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## CHAPTER 1 INTRODUCTION

## 1.1 Research motivation

Novel materials with better mechanical, optical, and electrical properties are the need of the hour for many applications in the real world. Diamond is one such material and has many exciting properties such as high thermal conductivity, chemical inertness, extreme hardness and electrical insulation. These properties have been exploited for several years in many different applications like optical elements [60], high energy beam detectors [61] and heat spreaders [62] among many others. For these and many more applications it is imperative to synthesize large single crystal diamond substrates which have very high quality and hence qualify as type IIa quality or better. Due to the absence of any grain boundaries, single crystal diamond substrates are more attractive for the aforementioned applications in comparison to polycrystalline diamond (PCD) substrates. But currently most applications suffer from the availability of high quality (< 100 ppb nitrogen impurity), thick (> 400  $\mu$ m), large (> 1 cm<sup>2</sup>), low birefringence and low stressed single crystal diamond (SCD) substrates. Recent experiments have demonstrated the high rate synthesis of high guality SCD substrates. The initial communications were reported in the late 90's and early 2000's ([63], [64]) and since then their results have been confirmed and extended by others ([12], [65]–[67]). All of the initial experiments employed single mode excited microwave discharges operating with H<sub>2</sub> and CH<sub>4</sub> gas mixtures at pressures of 100 – 180 Torr and with high microwave discharge power densities. They revealed the feasibility of high rate, homo-epitaxial SCD synthesis with growth rates of  $50 - 150 \mu m/h$ . Thus in recent years, interest in the synthesis of high quality SCD has dramatically

increased. Recent advances in producing large SCD substrates have been described in [35].

In order to produce large SCD substrates the most convenient deposition method thus far is the Microwave Plasma Assisted CVD (MPACVD) diamond synthesis process [68] which provides a suitable thermal and chemical environment for the growth of high quality SCD substrates at a high growth rate. With such a deposition process much work has been carried out by various research labs in order to synthesize high quality SCD substrates at a high growth rate. A mosaic wafer and tiled clone method employed by several groups sought to increase the dimension of the synthesized SCD substrates ([17], [21]–[23], [69], [70]). But problems concerning stress and impurities still inhibit the growth of large and high quality SCD substrates.

Thus, the main motivation of this research project is to overcome such issues in the synthesis of large and high quality SCD substrates and to successfully employ innovative growth strategies for this purpose. This research has been performed in the MSU developed microwave cavity plasma reactor (MCPR) which is referred to as reactor B here. Reactor B is one of the three designs of the MCPRs installed at Michigan State University. This reactor B was first designed and operated by K. W. Hemawan et. al. [42]. Later, a safe and efficient experimental operating regime and road map curves for reactor B was determined by J. Lu et. al. ([44], [45]). It is not only important to grow large and high quality SCD substrates but to also do so with an efficient setup. This thesis presents a careful analysis and more experimental details about operating regime of reactor B has been utilized to synthesize high quality CVD SCD substrates with optimized holder

designs. Additionally, in order to operate with higher power densities another microwave cavity plasma reactor was designed for high pressure levels. This reactor has been termed as reactor C here, which was designed and operated by Y. Gu et. al. ([41], [46]). Some SCD substrates grown with this reactor C have been analyzed here.
### 1.2 Research objectives

One of the goals of the thesis research was to investigate and to provide more experimental details about the operation of reactor B. While working in the high pressure diamond synthesis regime of 130 – 240 Torr, an objective was to demonstrate the synthesis of high quality SCD substrates and analyze the substrates grown in both reactors B and C under these high pressure conditions. The following tasks outline the main research objectives of this thesis work.

Task I – To extend the investigation of the experimental operating road maps to further extend the safe and efficient regime. An important part of this task was to place operating limits, both for the lower and upper operating power levels in order to prevent the creation of any unwanted hot spots and microwave plasmoids and to obtain discharge stability.

Task 2 – To study the reactor geometry variations and the associated experimental operating methodologies that enable the reactor to achieve high microwave coupling efficiencies and overall excellent diamond synthesis efficiencies over a wide range of input operating conditions.

Task 3 – To develop growth strategies which would enable us to enlarge the SCD substrate *in situ* in both reactors B and C.

Task 4 – To investigate the performance of different substrate holder designs on the synthesis of SCD substrates and to determine the optimized substrate holder design for fabricating large and high quality SCD substrates.

Task 5 – To synthesize high quality (type IIa quality or better) CVD SCD substrates with reactor B at the high pressure level of 240 Torr.

Task 6 – To characterize the synthesized SCD substrates with optical transmission measurements and imaging techniques among others.

Task 7 – To analyze the defect density of the synthesized SCD substrates by performing several etching experiments after establishing a technique for studying etch pit densities.

Task 8 – To investigate the flipped and beveled seed methods of SCD growth which would provide another mode of enlarging the synthesized substrate size while simultaneously reducing the defect density.

Task 9 – To start the exploration of a new forced flow reactor setup. This new reactor design would help in further increasing the growth rates by increasing the gas flow efficiency for the SCD deposition process while maintaining a stable discharge over the substrate.

## **1.3 Dissertation outline**

The tasks mentioned in the previous section have been performed and their description with some background and literature study have been described in the following 8 chapters in this dissertation.

An extensive literature review is described in chapter 2. This literature review provides a background to the progress made thus far in the synthesis of large and high quality CVD SCD substrates. The three different MSU reactor generations and the modifications made to them over the years are also discussed here. In chapter 2, the diamond growth process and mechanism are discussed providing the surface chemistry for deposition along with hydrogen etching of the substrate. This process is highly complicated and a much simplified set of equations are typically utilized to represent the chemistry occurring at high temperature, power and pressure levels during the deposition process. Some new methods to enlarge the SCD substrate are also briefly described. Their issues concerning such methods are also mentioned here. A discussion about the different types of defects and dislocations typically present in CVD SCD substrates has been included in this chapter.

Chapter 3 provides the details about the experimental setup of the main MCPR used for this research work i.e. reactor B. It describes the different input and output reactor variables which are important for the growth process. The different procedures performed in the reactor cavity before, during and after the growth process are also discussed here. Several substrate holder configurations were used in the different experiments conducted over the entire thesis research period. A complete list of the different holders and their designs is also included.

In chapter 4, experimental details regarding the methodologies to obtain the maximum microwave coupling efficiency within the reactor cavity and the process of controlling and sustaining a stable microwave discharge are discussed. Photographs of the plasma at different operating conditions describe its behavior over the entire processing time.

Chapter 5 extensively discusses the MPACVD SCD growth process in detail. This includes separate sections on the growth procedure and the effect of the growth process on the plasma – substrate holder boundary layer. This chapter also includes a comparison between the growth processes occurring in different substrate holder designs i.e. an optimized pocket holder design and the more conventional open holder design. These holder designs have been investigated thoroughly and their effect on the SCD growth has been described here. SCD substrates synthesized with different holders and the contrast in their growth patterns have been discussed here.

Chapter 6 discusses the analysis of the synthesized SCD substrates. This analysis relies on several different characterization techniques like growth rate measurements, UV/visible and infrared spectroscopy, volumetric analysis, atomic force microscopy for surface roughness measurements, etc. Etching experiments revealing etch pit densities of the SCD substrates indicate the defect density present in these samples. A complete discussion is included here.

The flipped seed growth method is described in chapter 7. This involves the initial growth of the CVD SCD substrates and the post growth processing of the substrates to initiate the flipped seed method. In addition to the flipped seed method, a beveled seed approach has also been investigated as a mode of growing better quality substrates. In

this chapter, an initial design of the forced flow holder setup is described along with some more new variations. A few experiments conducted with this first primitive reactor design are also discussed here.

Finally, chapter 8 gives the conclusions and summary of this thesis research work and provides several new avenues to explore for the fabrication of large and high quality SCD substrates in future experiments.

# CHAPTER 2 MICROWAVE PLASMA ASSISTED CVD SINGLE CRYSTAL DIAMOND SYNTHESIS: BACKGROUND AND LITERATURE REVIEW

## 2.1 Introduction

This chapter provides background information on the synthesis of single crystal diamond substrates and discusses some of the current research done in this field. Section 2.2 presents the reason for the interest in diamond as a novel material. Its different properties along with its internal structure description is discussed here. Diamond has been classified according to its crystal size and single crystal diamond substrates have been categorized based on their impurity levels in section 2.3. Section 2.4 discusses the microwave plasma assisted chemical vapor deposition method of diamond and provides the chemical reactions involved in both the growth of diamond as well as in its etching process. Later in section 2.5, a comprehensive literature review is provided which discusses the diamond research carried out at Michigan State University and by other different diamond groups. The current state of the art technology in the fabrication of large single crystal diamond substrates with a high growth rate has also been presented in this section. Finally, section 2.6 discusses the different types of defects and dislocations present in the SCD crystal structure. Different characterization techniques of analyzing these defects have also been elaborated here.

# 2.2 Why diamond?

The crystal structure of diamond consists of several  $sp^3$  hybridized carbon atoms. Each  $sp^3$  hybridized carbon atom has a tetrahedral structure with an angle of 109.5° between each of the hybrid orbitals [71] (figure 2.1).



Figure 2.1 An *sp*<sup>3</sup> hybridized carbon atom [1].

In this tetrahedral structure, each carbon atom is bonded with four other carbon atoms. The strong covalent bonds between the different carbon atoms ensure that the binding energy is very high (~ 347 kJ/mol). Hence, diamond is the hardest known material. Figure 2.2 shows the diamond cubic lattice structure. The unit cell shown in figure 2.2 displays two interpenetrating face centered cubic lattices which are displaced with respect to each other by 1/4<sup>th</sup> of the body diagonal [72].



Figure 2.2 Diamond cubic lattice structure.

The distance between two consecutive carbon atoms, i.e. the bond length is 0.154 nm and each unit cell contains 8 carbon atoms [4]. The lattice constant is 0.357 nm. The density of diamond at room temperature (298K) is 3.515 gm/cm<sup>3</sup> [4]. The high density of the diamond crystal leads to diamond having a very high thermal conductivity. The combination of diamond's high thermal conductivity, carrier mobility and breakdown voltage (figure 2.3) allows diamond to be used in electronic devices for harsh conditions.



Figure 2.3 The unique position of diamond. The size of the grey areas in circles show the proportional thermal conductivity of each material [2].

Owing to the high binding energy and the strength of the covalent bonds, diamond has a high band gap of ~ 5.45 eV. This accounts for diamond being an electrical insulator. Table 2.1 summarizes the important electrical, mechanical, thermal and optical properties of diamond ([2], [4], [5], [17], [73]).

Table 2.1 Important electrical, mechanical, thermal and optical properties of diamond.

Properties	Values	Application suitability
Wide bandgap, E <sub>g</sub> (eV)	5.45	Useful in high temperature operation

Table 2.1 (cont'd)

High electric breakdown field, E <sub>c</sub> (kV/cm)	10000	High power electrical devices	
High thermal conductivity, (W/cm-K)	24	Heat spreaders	
Electrical resistivity (Ω-cm)	10 <sup>14</sup> - 10 <sup>16</sup>	Good electrical insulator	
High bond strength	5.8 x10 <sup>19</sup> J per bond	Radiation detectors	
Wide spectral transparency	~ 71% from UV (225 nm) to far IR	Transmission components, high power laser windows	
Low loss tangent (tan $\delta$ ), High thermal conductivity	n = 2.60 @ 266 nm, n = 2.46 @ 405 nm	Output gyrotron windows	

Some other important properties of diamond include: chemically inertness, biological compatibility, exhibiting low or 'negative' electron affinity etc.

Figure 2.4 shows the phase diagram of carbon where depending on the pressure and temperature conditions the different phases of carbon: diamond, graphite, liquid and vapor, are marked ([3], [4]). As seen in figure 2.4, at high temperatures (> 3500 K) and at high pressures (>  $10^4$  atm) diamond is a stable state of carbon and is at a minimum energy level. But at normal temperatures, graphite is a more natural state of carbon. The black and grey lines display the equilibrium boundaries between the different phases. The diamond/ graphite/ liquid triple point lies at around  $10^5$  atm/ 5000 K. Once diamond is formed at high temperatures and pressures, at normal room temperatures it does not spontaneously convert to graphite. Rather it remains in the same  $sp^3$  hybridized form as a metastable state of carbon.



Figure 2.4 Phase diagram of carbon ([3], [4]).

Taking a closer look at the phase diagram shown in figure 2.4, figure 2.5 ([4], [5]) shows the regions in which the synthesis of artificial diamond has been conducted since the mid 1900's [74]. The synthesis process has been mainly categorized in three main sections: (1) natural genesis, (2) high pressure high temperature (HPHT) synthesis, and (3) chemical vapor deposition (CVD).



Figure 2.5 A closer look at the carbon phase diagram displaying the natural, HPHT and CVD synthesis regimes [5].

As the name itself suggests, the HPHT synthesis process involves large amounts of pressure and temperature to synthesize diamonds. The horizontal striped region in figure 2.5 indicates the pressure and temperature range used for this process. In contrast, the CVD synthesis process of diamond occurs at much lower pressure and temperature levels. The research presented in this thesis exclusively discusses the CVD synthesis process with a microwave plasma medium.

## 2.3 Classification of diamonds

Diamonds may be categorized according to their crystal dimensions. Single crystal diamond substrates may then also be classified according to the level and type of impurities present within the bulk of the crystal. The following two subsections discuss these two classifications.

#### 2.3.1 Diamond classification based on crystal dimensions

Synthesized diamond can be categorized according to its crystal size: (i) single crystal diamonds, and (ii) polycrystalline diamond. If the initial seed substrate used for CVD synthesis has a different lattice structure than diamond, the resulting synthesized diamond film is a polycrystalline film. Polycrystalline diamond can be further divided into three groups: (a) microcrystalline, (b) nanocrystalline, and (c) ultrananocrystalline diamond ([75], [76]). Table 2.2 lists these diamond classes and their respective crystal dimensions.

Table 2.2 Classification of diamond crystals	based on their dimensions.
--	----------------------------

Diamond class	Dimensions
(i) Single crystalline	5 – 10 mm
(ii) Polycrystalline	
(a) Microcrystalline	1 µm – tens of µm
(b) Nanocrystalline	15 – 100s of nm
(c) Ultrananocrystalline	2 – 15 nm

# 2.3.2 Classification of single crystal diamond substrates

Natural and artificial synthesized diamond substrates are also classified according to their different dopants as well as the level of doping. Table 2.3 summarizes the different types of diamond substrates ([5], [77]–[80]).

Diamond type	Impurities	Color	
(i) <i>la</i>	~ 2000 ppm N <sub>2</sub>	Clear to yellow	
(ii) Ib	1 – 1000 ppm N <sub>2</sub> Yellow, bro		
(iii) Ila	~ 1 ppm N <sub>2</sub>	Colorless clear	
(iv) IIb	~ 1 ppm N <sub>2</sub> , ~ 100 ppm B	Blue	
(v) III	< 100 ppb N <sub>2</sub>	Clear	

Table 2.3 Classification of diamond substrates based on the level of impurities.

## 2.4 Microwave Plasma Assisted Chemical Vapor Deposition (MPACVD)

### of diamond



Figure 2.6 Chemical vapor deposition of diamond.

Figure 2.6 shows a schematic of the chemical vapor deposition process of diamond with a microwave plasma. In this process, the substrate (shown in red) is placed over a cooled substrate holder. Depending on the different deposition reactor cavity designs, electromagnetic waves provide the required input energy to dissociate the typical mixture of gases used for CVD i.e. a mixture of methane (CH<sub>4</sub>) and hydrogen (H<sub>2</sub>) gases. A microwave discharge is formed directly above and adjacent to the substrate. The core of the discharge forms the activation region where the dissociation of the gases take place into the different important growth radicals. This region is shown in green in figure 2.6 as the gas activation region. Between the microwave plasma and the substrate is a boundary layer region. The important dissociated growth radicals diffuse through this discharge – substrate boundary layer and deposit on the substrate in the form of diamond layers.

Depending on the initial seed substrate used, an HPHT type Ib seed substrate yields a CVD single crystal diamond substrate, while other seed substrates which have a different lattice parameter than diamond like silicon substrates yield CVD polycrystalline diamond substrates.

The microwave discharge characteristics are altered with a change in the applied pressure [4]. At lower pressures (< few tens of Torr) the discharge fills up the discharge chamber with lower gas temperatures ( $T_g < 500 - 1500$  K) than electron temperatures ( $T_e$ > 10000 - 20000 K). As the pressure is increased (> 50 Torr), T<sub>g</sub> increases while T<sub>e</sub> decreases and the discharge separates from the chamber walls to take a shape that is dependent on the impressed electromagnetic field pattern and the reactor geometry. At even higher pressures, T<sub>g</sub> becomes > 1500 – 3500 K. The plasma, coupled with high microwave energy, becomes spatially inhomogeneous with a hot central core and a large radial thermal gradient extending up to the chamber walls. The MPACVD system, thus, not only provides a convenient chemical environment for the deposition of diamond, but also ensures a suitable thermal environment for the dissociation of gases in the form of a highly controlled, high pressure and temperature microwave discharge for the deposition of diamond. The core of the plasma is at a much higher temperature compared to the surrounding region as the temperature drastically decreases when moving from the central core region of the plasma to the edge of the plasma. The following are some of the advantages in utilizing a MPACVD method for diamond synthesis.

Microwave Plasma-Assisted CVD:

1) Ensures good control on single crystal diamond quality

- Helps in the synthesis of the best quality diamond (type IIa diamond or better as discussed in table 2.3)
- Has the potential for the single crystal diamond synthesis process to proceed with a high microwave power coupling efficiency
- Offers flexible design enabling improvements in plasma homogeneity, better growth rate (> tens of microns per hour) and large area deposition (few to hundreds of mm)

#### 2.4.1 Surface chemistry for the synthesis of diamond via MPACVD

The surface growth chemistry of diamond is a very complicated process. It involves several chemical reactions proceeding in the gas phase, on the surface of the substrate and in the bulk of the discharge, and in conjunction with the flow dynamics, diffusion, heat and mass transport etc. processes. The growth chemical reactions were investigated in the 1990's and many of these complicated processes have been tried to be simulated ([8], [81]–[83]).

For a gas mixture such as a mixture of hydrogen and methane gases, the microwave discharge plays the most important role in creating the necessary radicals for the growth process ([4], [84]). The microwave discharge provides a high gas temperature for efficient H atom production by thermal dissociation of H<sub>2</sub>. Atomic hydrogen [H] is required to begin the growth process. They remove the surface terminating hydrogen atoms on the substrate surface which helps in ensuring the growth of diamond and not of graphite.

The microwave energy input into the plasma helps in the dissociation of the hydrogen molecules by the free electrons. At lower pressures and temperatures (< few tens of Torr), the electron impact dissociation process dominates with the following equation.

$$H_2 + e^- \rightarrow H + H + e^- \qquad \dots (1)$$

At higher gas temperatures (> 3000 - 5000 K) and higher pressures (> 100 Torr), thermal dissociation of hydrogen molecules becomes the dominant process where the electrons lose energy by elastic collisions with heavier molecules (*M*).

$$H_2 + M \leftrightarrow H + H + M \qquad \dots (2)$$

While it is important to have atomic hydrogen to terminate the substrate surface in order to initiate the growth in the diamond phase and not in the graphitic phase, it is also important to have the necessary carbon containing growth radicals reaching the substrate surface. These carbon containing radicals are usually  $CH_3$ ,  $C_2H_2$ ,  $CH_2$ , CH etc. These gaseous phase reactions are as follows [84]:

$$H + CH_3 + M \rightarrow CH_4 + M \qquad \dots (3)$$

$$H + CH_4 \leftrightarrow CH_3 + H_2 \qquad \dots (4)$$

The complicated growth process has been simplified into several chemical reactions as discussed in the following discussion ([6]–[8], [81]–[83], [85]). The main chemical reactions include: (1) abstraction of hydrogen atoms, (2) adsorption of hydrogen atoms or hydrocarbon radicals, and (3) different growth paths like: thermal desorption and species integration.

The (100) surface, with the continuous impinging of atomic hydrogen on the substrate surface, becomes non – reactive to the incoming hydrocarbon radicals since it is now

almost completely hydrogen terminated. Thus the main reaction to open sites for the initialization of growth is the abstraction of hydrogen atoms from the (100) surface [4].

$$C_d H + H \rightarrow C_d^* + H_2$$
;  $R_{abs-H} = k_1[H]$  .... (5)

Here,  $C_d H$  is a hydrogenated site on the substrate surface;  $C_d^*$  is a radical site which has a hydrogen removed.  $k_1$  is the reaction rate constant for the flux of atomic hydrogen ([*H*]) on the surface and  $R_{abs-H}$  is the reaction and associated rate.

The open sites can now undergo adsorption of either more atomic hydrogens or hydrocarbon radicals like  $CH_3$ .

$$C_d^* + H \rightarrow C_d H$$
 ;  $R_{adH} = k_2[H]$  .... (6)

$$C_d^* + CH_3 \rightarrow C_d CH_3$$
;  $R_{adC} = k_3 [CH_x]$  .... (7)

Here,  $k_2$  and  $k_3$  are the reaction rate constants for the adsorption of an atomic hydrogen and a carbon containing radical on the surface.

Following the adsorption process, the process may now proceed through either of the two main mechanisms, i.e. either by thermal desorption or by species integration. Thermal desorption leads to the removal of the hydrocarbon radical and hence induces another open site, again leading to the equations (6) and (7).

$$C_d CH_3 \rightarrow C_d^* + CH_3$$
;  $R_{des} = k_4$  .... (8)

Here,  $k_4$  is the reaction rate constant for the thermal desorption of a radical from the surface.

In the second mechanism, the growth proceeds through the species integration process. The adsorbed growth species are now integrated to form the diamond structure and this begins with the abstraction of atomic hydrogen from the adsorbed species.

$$C_d CH_3 + H \rightarrow C_d CH_2 + H_2$$
;  $R_{abs-CH_{\chi}} = k_5[H]$  .... (9)

Here,  $k_5$  is the reaction rate constant for the abstraction of an atomic hydrogen from the adsorbed carbon containing radical.

With successive hydrocarbon adsorption and atomic hydrogen abstraction, the growth proceeds and completes the formation of the diamond crystal on the substrate surface. Thus, the growth process is a complex combination of the abstraction of terminal hydrogen atoms, adsorption of atomic hydrogen and carbon radicals and then desorption of these radicals.

Under steady state conditions, the above reduced set of growth equations can be combined to give a growth rate equation as was calculated by Goodwin et. al. [8]. The growth rate is directly proportional to the concentrations of the hydrocarbon radicals [ $CH_3$ ] and to the atomic hydrogens [H]. It is also a function of the different reaction rates mentioned in equations (5) – (9) ([4], [8], [83]).

$$G = k_3 \frac{n_s}{n_d} \left( \frac{k_1}{k_1 + k_2} \right) \frac{[CH_3][H]}{\frac{k_4}{k_5} + [H]} \qquad \dots (10)$$

Here,  $n_s$  is the surface site density (2.61x 10<sup>-9</sup> mol/cm<sup>2</sup> on 100 surface), and  $n_d$  is the molar density of diamond (0.2939 mol/cm<sup>3</sup>). The fraction of the reaction rates in equation 10 is the steady state radical fraction. The reaction rate constants are a function of temperature and are given by equation 11.

$$k_i = a_i T_s^{b_i} \exp\left(\frac{-c^i}{R T_s}\right) \qquad \dots (11)$$

Here,  $a_i$ ,  $b_i$ , and  $c_i$  are constants and R is the universal gas constant. At a surface temperature of 1200 K, Goodwin et. al. calculated the values of the reaction rate constants  $k_1 - k_5$  and are given in table 2.4 [8].

Reaction rate constant	Value (cm³/mol.s)	
k_1	2.9 x 10 <sup>12</sup>	
$k_2$	1.7 x 10 <sup>13</sup>	
k <sub>3</sub> 3.3 x 10 <sup>12</sup>		
$k_4$	1.0 x 10 <sup>4</sup>	
$k_5$ 2.0 x 10 <sup>12</sup>		

Table 2.4 Reaction rate constants for growth on the (100) surface at 1200 K.

With the simplification of the growth process, Harris and Goodwin [8] predicted the steady state radical fraction and simplified the growth rate equation 10 further.

$$G = 1.8 \times 10^{11} \frac{[CH_3][H]}{5 \times 10^{-9} + [H]} \qquad \dots (12)$$

Figure 2.7 (a) shows the growth steps occurring along the [100] growth direction. The numbers written alongside each atomic schematic shows the step number followed in table 2.5. Similar growth steps occurring along the [110] and [111] growth directions are schematically described in figure 2.7 (b) and (c) ([6], [7]).



Figure 2.7 Reaction sequences for growth along (a) [100], (b) [110], and (c) [111] growth directions [6], [7]. The dark grey circles are the surface diamond atoms ( $C_d$ ), light grey circles are the chemisorbed carbon containing radicals and the white circles are the atomic hydrogen.

Table 2.5 Reaction steps corresponding to the numbers written against each atomic schematic drawn in figure 2.7.

Step number	Reactions
1	$C_d H + H \leftrightarrow C_d + H_2$
4	$C_d + CH_3 \leftrightarrow C_d CH_3$
5	$C_d + C_2 H_2 \iff C_d C_2 H_2$
6	$C_d CH_y + H \leftrightarrow C_d CH_{y-1} + H_2$
11	$C_d. C_d \leftrightarrow C_d + * + C_d$
12	$C_d + * + C_d C_x H_y \rightarrow C_d + C_d C_{x-1} H_y + C_d$

The reactions occurring in steps 1, 4, 5, 6, 11 and 12, as shown in figure 2.7 are mentioned in table 2.5. In this table,  $C_d$  is the surface diamond atom, \* is a surface biradical and the species with a stop (.) in between is a dimer bonded specie.

The lack of atomic hydrogen on the surface results in the termination of the surface with  $sp^2$  hybridized hydrocarbon radicals. This graphitic or amorphous carbon phase incorporation within the diamond during growth leads to the formation of defects in the bulk of the synthesized CVD diamond substrate. A generic model for the defect formation was proposed by Goodwin et. al. [8], in which the fraction of defects formed in the diamond substrate may be given as:

$$X_{def} = \frac{G}{H^n} \qquad \dots (13)$$

Here, n is empirically derived. For the simplest model, usually n = 2 is chosen. In this case, the defect fraction can then be simplified and is directly proportional to the methane and hydrogen gases.

$$X_{def} \propto \frac{[CH_4]}{[H_2]} \qquad \dots (14)$$

$$X_{def} \propto \frac{[CH_3]}{[H]} \qquad \dots (15)$$

Thus the ratio of the flux of atomic hydrogen to methyl radical is an important factor to obtain low defect CVD diamond substrates with a high growth rate (figure 2.8). For such purposes, the ratio is normally maintained at 1000 – 10000 ([4], [84]).



Figure 2.8 A plot of methyl radical concentration vs. atomic hydrogen concentration ([8], [9]). The dotted contours show the  $sp^2$  defect fraction and the dark ones indicate the growth rates. The red outlined area shows the high power density, high pressure microwave CVD regime.

In figure 2.8, the flux of the methyl radicals is plotted against that of the atomic hydrogen. The dotted black lines show the constant graphitic/ amorphous defect fraction contours (equation 15) while the solid black contours indicate the constant growth rates on the (100) oriented diamond surface (equation 12). The different CVD diamond deposition techniques such microwave, hot filament, DC arc jet, RF torch and combustion torch are depicted in the plot according to their typical [*H*] and [*CH*<sub>3</sub>] concentrations. Currently the microwave plasma – assisted CVD (MPACVD) method is operating at high

pressures of > 320 mbar (> 240 Torr) and with high power densities as indicated by the red outlined region in figure 2.8. At such high pressures and power densities, the ratio of [H] and  $[CH_3]$  concentrations is appropriate for the growth of low number of defects in the substrates but with a suitable high growth rate (tens of  $\mu$ m/hr) for the synthesis process.

The absorbed microwave power density (in W/cm<sup>3</sup>) for a discharge is spatially dependent upon the impressed electric field  $(\vec{E}(\vec{r}))$ , electron density  $(n_{oe}(\vec{r}))$ , electron mass  $(m_e)$ , electronic charge  $(e = 1.6 \times 10^{-19} C)$ , electron – neutral collision frequency  $(\nu_m)$  and the angular frequency (i.e. the microwave excitation frequency,  $\omega = 2\pi f$ ). It is given by the following equation:

$$\langle P_{abs} \rangle(\vec{r}) = \frac{1}{2} \frac{n_{oe}(\vec{r})e^2}{2m_e v_m} \left( \frac{v_m^2}{\omega^2 + v_m^2} \right) \left| \vec{E}(\vec{r}) \right|^2 \dots (16)$$

Then the average microwave power density of a discharge (W/cm<sup>3</sup>) is given as:

$$\langle P_{abs} \rangle = \frac{P_{abs}}{V_d} \qquad \dots (17)$$

where,  $P_{abs}$  is the experimentally measured absorbed power (Watts) into the discharge and  $V_d$  is the experimentally measured plasma volume (cm<sup>3</sup>). As the absorbed power density into the discharge increases with increasing pressure, it also leads to an increase in the species concentration near the substrate, thereby enhancing the growth rate during deposition. As shown by the green outlined area in figure 2.8, all the SCD synthesis results discussed in this thesis have been carried out at such high deposition pressures of 240 Torr (i.e. 320 mbar) and with a high power density of 100 – 1000 W/cm<sup>3</sup>.

Diamond plates grown on (100) surface orientation have been found to yield the highest quality, smoothest grown surfaces along with the lowest defect densities as compared to substrates grown on (110) and (111) surface orientations ([86]–[88]). This

will be discussed in section 2.6. Thus, in this thesis all the synthesis steps of SCD substrates have been carried out on the (100) growth surface of the initial seed substrate.

#### 2.4.2 Hydrogen plasma etching of diamond substrate

One of the important pre-growth steps on the diamond substrate is the etching of the surface with the help of a hydrogen plasma. Etching experiments have been observed to not only remove impurities from the surface of the substrate but also to make the (100) growth surface smooth and hydrogen terminated. The termination of the growth surface with hydrogen ensures the growth of diamond and prevents the graphitic ( $sp^2$ ) phase growth of the carbon radicals. The etching mechanism, as is the case for the diamond growth process, consists of many chemical reactions [89]. The main equations have been discussed in [50] and are given in table 2.6.

Number	Reactions
1	$C_d \bullet C_d \iff C_d \dots \ast \dots C_d$
2	$C_d \dots * \dots C_d C_x H_y \rightarrow C_d \dots C_d C_{x-1} H_y \dots C_d$
3	$C_d C H_2 + H \iff C_d + C H_3$
4	$C_d \dots C_d H_2 \dots C_d + H \leftrightarrow C_d \dots * \dots C_d + CH_3$

Table 2.6 Reaction steps for hydrogen plasma etching mechanism.

In table 2.6,  $C_d$  refers to the surface carbon diamond atom and H is the atomic hydrogen in the gas. The species separated by (•) are dimer bonded and by (\*) are surface

biradicals. The species connected by (...) indicate neighboring surface species next to each other on the diamond substrate surface. In reaction 1 the dimer bonds between the atoms are first broken with the help of mechanisms like  $\beta$  – scission. Then in reaction 2, hydrocarbons are inserted in the open carbon sites with a dimer insertion mechanism. Reactions 3 and 4 show the etching mechanism on the surface. Here the surface carbon atoms are removed with the help of the atomic hydrogen. The investigation of the Gibbs free energy and enthalpy change in the different reaction rates for the 4 reactions given in table 2.6 indicate that the removal of carbon during this etching mechanism is irreversible [50]. This enthalpy change serves as an important factor for the surface to be smoothened by the etching process and hence for growth to proceed in the (100) plane of the diamond surface with a high growth rate by hydrogen terminating the surface.

### 2.5 Large area and high growth rate MPACVD SCD synthesis

#### 2.5.1 AIST and Osaka University, Japan

One of the pioneers in the CVD and HPHT synthesis of single crystal diamond substrates is the Diamond Research Group from National Institute of Advanced Industrial Science and Technology (AIST) and from the Osaka University in Japan. They have provided a major thrust in the development of the CVD technology and have achieved many significant improvements in the SCD growth process ([11]–[20], [22], [23], [69], [70], [90]–[103]). Their progress in the CVD SCD development over the past 20 odd years are discussed in this subsection.

### 2.5.1.1 High growth rate MPACVD synthesis

For any reactor design, the SCD growth rates and quality are influenced by several reactor variables. Some of these main factors are: (1) CH<sub>4</sub> concentration, (2) nitrogen concentration in the total gas flow, (3) substrate holder design, (4) substrate surface temperature distribution, (5) electric field intensity (and absorbed microwave power density) over the substrate holder and substrate surface, and (6) the gas flow into microwave reactor cavity.

The diamond synthesis work at AIST, Japan has been conducted with a 5 kW, 2.45 GHz microwave plasma SEKI AX6500 conventional reactor. The typical growth parameters for SCD synthesis on type Ib HPHT SCD seeds from Sumitomo Electric were: p = 160 - 180 Torr,  $[H_2] = 500$  sccm,  $[CH_4] = 50 - 60$  sccm,  $[N_2] = 0 - 3$  sccm, growth temperature = 900 - 1150°C, and the input microwave power = 1.5 - 2.6 kW ([11], [97]). Yamada et. al. have presented several experimental and numerical simulation data to

show the distribution of gas and electric field intensity within this reactor [10]. They have also provided a description on the effect of the nitrogen concentration on the different growth species in the reactor. This is shown in figure 2.9, which displays contours of the (a) gas temperature, (b) [H] concentration, (c) [CH<sub>3</sub>] concentration, and (d) [CN] concentration inside the reactor. These contours are symmetric with respect to the z axis.



Figure 2.9 Numerical simulation of contours of (a) gas temperature, (b) atomic hydrogen [H] density, (c) methyl [CH<sub>3</sub>] density, and (d) [CN] density, which are symmetric with respect to the z - axis [10].

New molybdenum substrate holder designs were also fabricated in order to increase the growth rate over time ([11], [12]) and were simulated to demonstrate the effect of different reactor variables, like substrate temperature, gas flow distribution, and electric field intensity, over the growth process ([15], [16]). The different utilized substrate holder designs are depicted in figures 2.10 [11] and 2.11 [12]. These holders are broadly classified as "open" and "enclosed" holders (figure 2.11). A high growth rate of ~ 30  $\mu$ m/hr and after optimization ~ 50  $\mu$ m/hr, was observed for a small radius projection on top of the bottom holder (figure 2.10). This helped in the focusing of the microwave discharge at the top of the holder thereby increasing the absorbed power density into the microwave discharge.

Holders	Numerical Results	Hydrogen Plasma (observed)	Diamond Growth Rates (observed)
Ø 8mm 5 mm → K ↓ 14 mm			~30 μm/h
¢ 16mm  <			~30 μm/h
<i>ф</i> 26mm ₩→			~10 μm/h
≪ 36mm >I			~5 μm/h

Figure 2.10 Schematic indicating the behavior of the hydrogen plasma, numerical simulation of the discharge and SCD growth rates for different substrate holder designs [11].

It was observed for the open and enclosed type holders, that the depth "d" of the seed surface with respect to the holder surface plays an important role in the quality (figure 2.12) and in the growth rate (figure 2.13) of the synthesized SCD substrates. The substrates grown in an enclosed holder have a smooth surface as compared to those grown in the open holders (figure 2.12). As the average depth of diamond (d<sub>ave</sub>) during

growth decreases i.e. as the diamond surface approached the holder surface, the growth rate approaches ~ 100  $\mu$ m/hr [12].



Figure 2.11 The open and enclosed substrate holder designs where "d" indicates the distance between the top of the seed and the top of the holder surface [12].



Figure 2.12 Quality comparison of the synthesized SCD substrates in an "open" vs. in an "enclosed" holder. As "d" decreases the surface smoothens out [12].



Figure 2.13 Plot of SCD growth rate vs.  $d_{ave}$ . As the average depth of diamond with time decreases the growth rates approach ~ 100  $\mu$ m/hr [12].

One of the important parameters for increasing SCD growth rate is the nitrogen concentration in the total gas flow. An appropriate trend for the different SCD growth rates as a function of nitrogen flow rate for the two different holder designs is presented is figure 2.14. As can be clearly seen, nitrogen helps in increasing the SCD growth rate. Although the quality of the grown SCD substrates is high for the enclosed holders as compared to the open holders (figure 2.12), the growth rate in the enclosed holders is lower than that in the open holders (figure 2.14) for the same nitrogen concentration. This is an example of how the local properties of the discharge can be influenced to modify the SCD quality and also the deposition rates. In this dissertation, an aim is to improve the quality and SCD growth rates simultaneously. This will be discussed in chapter 5.



Figure 2.14 Plot of SCD growth rate vs. nitrogen flow rate for open and enclosed holder designs [13].

Although this is a useful growth method for a high growth rate, but nitrogen inclusion in the gas flow also affects the optical quality of the grown substrate. This can be clearly seen in figure 2.15 which shows a freestanding CVD SCD plate separated from the underlying seed and has been grown at 180 Torr with 12% CH<sub>4</sub>/H<sub>2</sub>, [N<sub>2</sub>] = 0.6 sccm and substrate temperature =  $1130 - 1150^{\circ}$ C [14]. The dark brown discoloration of the plate indicates the high absorption due to the presence of nitrogen impurities within the crystal. Hence these substrates are not suitable for optical applications.



Figure 2.15 The separated HPHT seed (left) and a freestanding CVD SCD plate (right) grown with 0.6 sccm of  $[N_2]$  [14].

Along with nitrogen impurities, substrate temperature, gas and absorbed microwave power density distributions also affect the high quality growth of SCD substrates. Yamada et. al. simulated these reactor variables for holder designs shown in figure 2.16 ([15], [16]). For these same designs, substrate temperature, gas and absorbed microwave density distributions are displayed in figures 2.17, 2.18 and 2.19 respectively. When the substrate is placed within a hole then the temperature over the substrate surface is more uniform (figure 2.179(c)) as compared to when it is placed out of the hole (figure 2.17(a)). Also the farther away the walls of the hole are, the more non – uniform is the temperature distribution [16].



Figure 2.16 Substrate holder configurations used for simulations ([15], [16]).



Figure 2.17 Substrate temperature distributions for substrate holders shown in figure 2.16 [16].

It was also observed from the simulations that the direction of gas flow for the substrate placed out of the hole or in a wide hole were from the edge to the center (figure 2.18(a) and (d)) while for the substrate placed in the deep and narrow hole (figure 2.18 (b) and
(c)), the gas flow was directed from the center towards the edge [16]. These simulations provide important observations and the results have been utilized to explain the experimental research results described later in this thesis.



Figure 2.18 Gas distributions for substrate holders shown in figure 2.17 [16].

Numerical simulations for the absorbed microwave power density both with and without the substrate are shown in figure 2.19 [15]. The various plots of microwave power density versus substrate holder design shown in figure 2.19 demonstrate the importance of the substrate holder design. For such holder designs shown in figure 2.16, much of the absorbed power density is focused on the edges of the substrate holder itself or on the edges of the substrate. The high power density area of the discharge is located away from the surface of the substrate. Hence, the beneficial effect of the high power density is lost and is not utilized for the deposition process. A part of the research presented in this dissertation is focused on the optimization of a new substrate holder design and will be discussed in chapter 5.



Figure 2.19 Absorbed microwave power densities for substrate holders shown in figure 2.16 [15].

By using the various techniques of improving the SCD growth rate as discussed above, they were able to grow SCD substrate with high growth rates of ~  $50 - 120 \mu$ m/hr (with substantial amounts of nitrogen addition).

#### 2.5.1.2 Large area CVD SCD growth

One of the main problems in growing large area CVD SCD substrates is that during the growth process, the growing CVD substrate top surface area tends to constrict such that the final substrate has a much smaller smooth useful SCD surface area (figure 2.20). This is in contrast to the behavior seen during the growth of Si and SiC substrates (figure 2.20) which exhibit an outwards growth of the final substrate.



Figure 2.20 Outward growth of Si and SiC as compared to the constricted CVD SCD growth [17].

The Diamond Research Group at AIST have developed some methods to synthesize large area CVD SCD substrates with the help of the high rate growth techniques mentioned above. The three main methods are described here:

(1) High rate repetitive growth: By combining the enclosed substrate holder design with nitrogen addition during growth, they were able to repeat deposition runs on the same substrate many times to obtain a large CVD SCD substrate ([12], [18], [19], [98]). Figure 2.21 displays a 4.65 carat (1 carat = 0.2 grams), 10 mm thick SCD substrate which was grown with 24 repetitions at 68  $\mu$ m/hr for 150 hours with 1.8 sccm of [N<sub>2</sub>] [12]. The high nitrogen content enhanced the growth rate of the substrate but the amount of nitrogen present in the substrate varies with growth as is seen by the differing density of brown

lines in figure 2.22(b) [18]. Figure 2.22(c) shows an x- ray topography image. This image displays the dislocation lines, i.e. the dark black lines, propagating along the (100) growth direction and appear to originate mostly from the interface between the CVD substrate and the seed [19].



Side view





Figure 2.22 (a) A thick SCD block from figure 2.21, (b) A slice from the thick SCD block shows the varying nitrogen concentration in the substrate [18], and (c) X – ray topography image of the slice indicating large number of dislocations (black lines) propagating into the substrate [19].

There are some major issues with such a repetitive growth process. As seen in figure 2.21, the top view of the SCD surface shows that the useful SCD area is much smaller than the original seed area. Also, the side view indicates a thick polycrystalline diamond (PCD) rim growth around the SCD substrate (figure 2.21) and hence constricts its outward growth. Note that initially the grown surface area increases from 6 mm (HPHT seed dimensions) to 7 mm (figure 2.22(b)). Then the PCD growth takes over as a rim which increases with time and then constricts the growth of the smooth useful SCD surface area. It thereby limits the top SCD crystal size. The thicker the crystal becomes, the smaller is the area of the top surface. In addition, the intentional nitrogen input reduces the optical quality of the substrates grown (figure 2.22(b)).

(2) Side surface (100) growth: This method was developed as an alternative way of enlarging the SCD substrate by counteracting the SCD area shrinkage due to the PCD rim growth ([12], [18], [20]). Figure 2.23 shows a schematic of the steps for the (100) direction side surface growth [18]. Using the 3 steps described in this figure, a 6.6 carat block of SCD was synthesized (figure 2.23) although as can be seen clearly, the issue of PCD growth still persists.



Step1: Thick CVD layers grown on (100) seed by high rate growth

Figure 2.23 SCD substrate enlargement with a (100) side surface growth and the 6.6 carat SCD substrate produced [18].

The usual mechanical process of laser cutting and polishing of the grown substrate to separate the HPHT seed and the CVD plate results in a loss of diamond. In order to minimize these losses a new technique was developed by them called the lift off process ([14], [18]–[20], [96], [97], [99]). A schematic of this process is shown in figure 2.24 [18]. Here, the seed is first ion implanted with a high energy carbon ion source of 3 MeV with a dose of  $2 \times 10^{16}$  ions/cm<sup>2</sup>. This is followed by a high rate CVD SCD synthesis and then finally etching away the ion implanted layer which has turned to a graphitic phase layer during the high temperature growth process. In contrast to the laser cutting process which typically takes a few minutes, the etching of the graphitic layer takes 1 - 2 days.



Figure 2.24 Lift off procedure for separating the HPHT seed and the CVD plate [18].

Another (100) side surface growth method is depicted in figures 2.25 and 2.26 ([18], [20]). Here, first the CVD plate is separated from the seed with the lift off process and then it is grown along the original (001) direction. Then the side surface are grown along the (100) and (010) direction to result in a half inch substrate as seen in figure 2.26(a). This substrate was then sliced in half parallel to the original growth surface and then grown again along the (100) original direction on one slice. After the lift off process the half inch CVD plate, as seen in figure 2.26(b), was obtained. The high amount of nitrogen impurities again deteriorated the optical quality of the plate. More importantly, as seen in figure 2.26(c), the polarized light microscopy (PLM) image shows the high number of dislocation and defects along the interfaces (white arrows) between the different side surface growth and the original (100) direction growth. These dislocations in turn lead to a high amount of stress in the plate thereby leading to cracking of the plates.



Figure 2.25 Schematic of another (100) side surface growth method [20].



Figure 2.26 (a) Half inch SCD substrate obtained after step 4 in figure 2.24 (b) Half inch SCD plate (c) polarized light microscopy image of the half inch plate ([18], [20]).

(3) Mosaic wafer growth: This is the most popular approach for expanding the CVD SCD substrate area. It was first proposed by Geis et. al. in the early 1990's ([104], [105]) where they were able to orient 20 – 30 crystals and then grow a continuous 20 µm SCD film on top of them. Further progress in this direction was made by Posthill et. al. [106], Janssen et. al. [107], Schermer et. al. [108], and by C. Findeling – Dufour ([109], [110]) by different CVD processes like hot filament CVD and plasma enhanced CVD techniques.

Yamada et. al. have now expanded this work with the MPACVD growth method and prepared 1 - 2 inch mosaic wafers ([17], [21]–[23], [103]). The growth method is described in figure 2.27. First the normal procedure to prepare a CVD plate with a high growth rate and lift off process is followed. Then this process is repeated to form clones of the CVD plate. These clones are then arranged to form a tile which is then grown over to form a mosaic wafer, i.e. step 6 in figure 2.27 [21].



Figure 2.27 Schematic of the mosaic wafer growth [21].

A final 1 inch separated mosaic CVD wafer is shown in figure 2.28 [21]. The dashed lines in figure 2.28 indicate the boundaries between the four clones of the CVD plate. These interfaces can be clearly seen in figure 2.29.



Figure 2.28 A 1 inch mosaic wafer [21].

From the cross – sectional image of the tiled clone, shown in figure 2.29(a), the brown discoloration in the CVD crystal shows the nitrogen impurity incorporation within the substrate [21]. This affects the optical quality of the wafers and hence the transmission through the plates, as shown in figure 2.30 [17]. In addition, the critical factor in this mosaic wafer method is the precise alignment of the clones during the formation of the tile. Any misalignment results in dislocation and hence stress at the interfaces, as seen in figure 2.29(b). This stress then leads to cracking in the prepared mosaic wafers.



(a)

(b)

Figure 2.29 (a) A cross – sectional image of the interface in a tiled clone, (b) polarized light microscope image of the cross – sectional image [21].



Figure 2.30 (a) Optical transmission and (b) absorption coefficient of a 1 inch mosaic wafer in comparison to type IIa CVD plates and type Ib HPHT seeds [17].

By further investigating the misorientation and the alignment of the clones, it was observed an off angle growth on these clones helped in a smooth deposition of a mosaic wafers (figure 2.31) [22]. But even with these uniform growths, a non – uniform concentration in the impurities was observed which continue to create issues for this approach.



Figure 2.31 Effect of the misorientation of the interfaces and off – angle growth direction on the synthesis of a 1.5 inch mosaic wafer [22].



Figure 2.32 A 2 inch, 1.8 mm thick mosaic wafer grown over a tile consisting of 24 CVD SCD clones [23].

This mosaic wafer growth method was recently extended to 2 inch mosaic wafer growth, as shown in figure 2.32 [23]. This wafer comprises of 24 SCD clones. If the current issues of high impurity concentration, misalignment of interfaces, dislocations and hence stress along these interfaces are improved upon and/ or solved, then this method would definitely out–perform all other methods for the purpose of growing large and high quality CVD SCD substrates. But these critical factors continue to pose problems during growth and hence encourage research to develop other approaches for the growth of large and high quality SCD substrates.

## 2.5.2 Carnegie Institution of Science, USA

The Geophysicial Laboratory at the Carnegie Institution of Science, USA has been conducting research in the field of single crystal diamond synthesis since the early 2000's ([24]–[26], [64], [111], [112]). The system used for the first deposition experiments is a 6 kW, 2.45 GHz Wavemat MPDR313EHP MPACVD reactor. Since then they have expanded their laboratory which now includes several SEKI tubular and clampshell design reactors. The typical SCD growth parameters are: pressure (p) = 120 - 220 Torr, 0.2 - 5% N<sub>2</sub>/CH<sub>4</sub>, 12 - 20% CH<sub>4</sub>/H<sub>2</sub>, incident microwave power = 3 - 5 kW and substrate temperature =  $900 - 1500^{\circ}$ C ([24], [25], [64]). For colorless SCD substrates 0.2 - 10% O<sub>2</sub>/CH<sub>4</sub> was added to the gas mixture [24].

Yan et. al. [64] in 2002 redesigned the reactor cavity which allowed them to reduce the incident microwave power to 1 - 2 kW (3 times lower) with a stable microwave discharge and 10 times increase in the growth rate for SCD synthesis. They used 3.5 x 3.5 x 1.6 mm<sup>3</sup> HPHT type Ib seeds for growth processes whose growth surface is  $2 - 3^{\circ}$  off – axis

with respect to the (100) plane. By utilizing the above mentioned growth parameters, they were able to obtain large SCD growth rates of  $50 - 150 \mu$ m/hr and have successfully synthesized 5 carat SCD substrate. This substrate displayed some cracking at the corners and was brown in color due to high amounts of nitrogen incorporation. With the addition of oxygen in the gas mixture it was observed that the nitrogen, silicon and hydrogen related impurities and defects are lowered ([24], [64]). This although also reduced the growth rates to ~ 10 µm/hr. Figure 2.33 shows some examples of nitrogen doped light brown colored and near colorless brilliantly cut and polished SCD samples which are 0.2 - 2.2 carats in size [24].



Figure 2.33 0.2 – 2.2 carat brilliantly cut and polished nitrogen doped light brown colored and near colorless SCD substrates [24].

The optical transmission analysis of these nitrogen doped and colorless SCD substrates is shown in figure 2.34 [24]. As expected, the nitrogen doped SCD shows high

optical absorption due to substitutional nitrogen (270 nm) and nitrogen vacancy (NV) centers (370 and 550 nm) as compared to colorless and natural type IIa SCD substrates. Further analysis done by photoluminescence (PL) is displayed in figure 2.35 [24]. It shows the NV<sup>0</sup> (575 nm) and NV<sup>-</sup> (637 nm) centers and a wide luminescence region for the light brown colored nitrogen doped SCD. The natural type IIa and the colorless SCD show the first order (551 nm) and second order Raman spectra (between 575 – 600 nm).



Figure 2.34 Plot of absorption coefficient vs. wavelength for nitrogen doped, colorless and natural type IIa SCD substrates [24].



Figure 2.35 Photoluminescence (PL) spectra of a light brown nitrogen doped, a colorless and a natural type IIa SCD substrates [24].

They also observed that by low pressure (i.e. <1 atm.) high temperature (LPHT) annealing treatment of the synthesized nitrogen doped SCD samples, their optical measurements can be improved significantly ([24]–[26]). This was done in the same 6 kW, 2.45 GHz reactor with a redesigned reactor cavity at pressure levels of 150 – 300 Torr and high substrate temperatures of 1400 – 2200°C. Some results of this annealing treatment is shown in figure 2.36 [25]. The middle substrate in figure 2.36(a) is an as grown segment of a nitrogen doped SCD while the left and right cubes are annealed segments of the same SCD at 1900 and 1800°C for 2 and 3 mins respectively. Figure 2.36(b) top substrate is an as grown SCD, while the bottom is a 15 min annealed (1700 – 1800°C) substrate.



Figure 2.36 Examples of SCD substrates before (as – grown) and after annealing treatment [25].

The effect of the annealing treatment can be seen in figure 2.37 which shows the UV/Visible spectroscopy measurements for (A) an as – grown (i.e. before LPHT annealing) SCD substrate and for (B) a SCD substrate after LPHT annealing treatment (1800°C for 2 mins) ([24]–[26]). The inset photograph shows several annealed SCD substrates. As is clear from this figure, the annealing process helps reduce the absorption coefficient, depending on the annealing temperature, by a factor of 2 – 6. Thus, this process helps in removing the nitrogen based absorption bands. However, infrared absorption spectra (not shown in figure 2.37) indicate that the LPHT annealing treatment causes major modifications in the vibrational and electronic transitions related to hydrogen [24].



Figure 2.37 UV/Visible optical spectroscopy of (a) an as grown (not annealed) and (b) a LPHT annealed SCD substrates [24].

In figure 2.38, a white beam topograph [26] is displayed which was taken with the help of the Advanced Photon Source (APS) beam line 16BM-B at Argonne National Laboratory. The high density of dislocations in the crystal is clearly visible here as the dark black lines running parallel to the growth direction. Hence more work need to be done in order to reduce the defect density of the synthesized MPACVD SCD substrates.



Figure 2.38 A white beam single reflection topograph of a CVD SCD substrate [26].

This research work was then scaled up for large area growth with a microwave plasma size of upto 300 mm in a 915 MHz reactor [111] and microwave power of 70 kW on HPHT type lb seed substrates. These substrates were synthesized at 90 - 180 Torr with growth rates of  $10 - 30 \mu$ m/hr in a H<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> environment where the source of nitrogen input was gas leaks of 0.01 - 0.05 mTorr/min. Although this nitrogen impurity level still affects the impurity, the growth process too is inefficient due to the large levels of microwave power being utilized for synthesis process. In this thesis, the importance of the microwave power coupling efficiency and its effect on the diamond synthesis process will be discussed in detail in chapter 4.

# 2.5.3 LIMHP – CNRS, France

The Laboratoire des Sciences des Procédés et des Matériaux (LIMHP) – CNRS in France is another leading diamond research group. Their work has brought significant

contributions in the numerical modelling and spectroscopy characterization of the microwave CVD systems and diamond processes along with high quality diamond growth and analysis techniques. A schematic of their home – made, 2.45 GHz microwave plasma diamond deposition reactor and the attached optical emission spectroscopy (OES) setup is shown in figure 2.39 [27]. This is connected to a SAIREM (maximum power ~ 6 kW) microwave generator [113].



Figure 2.39 Microwave CVD reactor and the optical emission spectroscopy setup [27].

### 2.5.3.1 Continuous wave (CW) and pulsed microwave discharges

Several studies were conducted to study the effect of CW and pulsed microwave plasmas on the growth rate of SCD substrates ([28], [29], [32], [66], [114]–[116]). Since one of the main species for a high growth is [H], the variation of the repetition rate (f) and the duty cycle (%) of the pulsed mode microwave power was studied to find the effect on the [H] density [116]. It was observed that there is a 30% increase in the [H] density in the pulsed operation over the CW mode, as is shown in figure 2.40 [28]. This implies that a

pulsing discharge benefits the growth rate as compared to a CW mode discharge at the same average input power. Also by increasing the repetition rate and by decreasing the duty cycle, an increase in [H] density was observed.



Figure 2.40 Increase in atomic hydrogen density for the pulsed mode operation in comparison to the CW mode where the repetition rate = 500 Hz and duty cycle is 50% [28].

Simultaneously, the methyl radical density ([CH<sub>3</sub>]) at the surface of the substrate also increased with the pulsed mode operation [115]. [CH<sub>3</sub>] is one of the most important growth radicals and hence an increase in its density helps in the increase of the growth rate. By using these settings for the pulsed mode operation, the peak microwave input power increased as compared to that for the CW operation and hence the SCD growth rate was successfully increased to ~  $9 - 22 \mu m/hr$  for microwave power densities of  $95 - 190 W/cm^3$ 

([29], [32], [66], [114], [115]). Pulsed plasmas also helped in limiting the silicon contamination due to etching of the quartz dielectric windows ([32], [114]). Thus as a result, an increase of 40% in the diamond growth rate was observed over the CW mode at a constant average input power while maintaining the quality of the grown substrates [32].

#### 2.5.3.2 Numerical modelling and OES measurements of the plasma CVD reactor

Over the last 20 years, LIMHP – CNRS has developed several numerical models of a purely hydrogen discharge and a H<sub>2</sub>/CH<sub>4</sub> discharge for their reactor which have then been characterized by OES measurements ([9], [27], [30], [31], [113], [115], [117]–[123]). These studies can also be extended to other plasma CVD reactors. A brief description about the different models is presented in this section of the thesis.

Initially a 1 dimensional axial and radial model was developed for simulating different plasma parameters ([27], [29], [30], [113], [117], [119]–[121], [123]). The most important of these are the densities of the atomic hydrogen radical [H] and the methyl radical [CH<sub>3</sub>], and the gas temperature ( $T_9$ ). The variation of these variables is shown in figure 2.41. Figure 2.41(a) shows the axial variation of the gas temperature near and away from the microwave discharge and figure 2.41(b) shows the axial variations [H] and [CH<sub>3</sub>] densities [29].



Figure 2.41 Variation of (a) gas temperature ( $T_g$ ), and (b) [H] and [CH<sub>3</sub>] densities along the z – axis [29].

As has been mentioned before, the [H] species is critical factor in growth of high quality diamond substrates. It not only helps in saturating the dangling bonds on the diamond surface and hence stabilizing the surface for growth, it also etches away any graphitic  $(sp^2)$  deposition phase on the surface and opens up sites on the surface which helps in the incorporation of the carbon containing radicals leading to a smooth growth on the

diamond surface. Thus as seen in figure 2.41, a high  $T_g$  enables the dissociation of the hydrogen molecule and hence a high density of [H] is present in the microwave discharge and near the substrate surface. The main carbon containing radicals are typically CH<sub>3</sub> and C<sub>2</sub>H<sub>2</sub>. Figure 2.41(a) shows that the [CH<sub>3</sub>] radicals are formed for a  $T_g \sim 1250 - 2250$  K. The substrate is constantly cooled and is maintained at ~ 1000 K. This temperature gradient helps in sustaining a large [CH<sub>3</sub>] radical density near the growth surface and a large [H] density in the plasma core. For a high growth rate, a large amount of [CH<sub>3</sub>] radicals are required near/ at the surface and this is achieved by maintaining a high T<sub>g</sub>. Thus these are mostly thermal driven processes [29].

Figure 2.42 displays the effect of the microwave power density on the [CH<sub>3</sub>] and [H] densities [29] with 4% CH<sub>4</sub>/H<sub>2</sub>. With increasing microwave power densities from 65 – 125 W/cm<sup>3</sup>, the [H] density increases more rapidly as compared to the [CH<sub>3</sub>] radical density. It also leads to an increase in the gas temperature (not shown in figure 2.42). The [CH<sub>3</sub>] radical density was observed to be higher near the growth surface with increasing power density. This resulted in growth rate enhancement from 3.5 µm/hr at 150 hPa and 2.5 kW to 40 µm/hr at 380 hPa and 3 kW (simulated measurement).



Figure 2.42 Effect of microwave power density on [H] and [CH<sub>3</sub>] densities [29].

It was observed that acetylene [C<sub>2</sub>H<sub>2</sub>] radicals are important carbon containing radicals especially at high power densities and gas temperatures. The boundary layer between the hot microwave discharge and the substrate surface plays a crucial role in helping increasing growth rates. Methane gas in the feed gas mixture is converted to [C<sub>2</sub>H<sub>2</sub>] radicals in the hot core of the plasma (T<sub>g</sub> > 2600 K) and is then converted to [CH<sub>3</sub>] radicals on the surface thereby increasing growth rates [122]. In addition, by flowing methane gas directly into the boundary layer, it was observed that there is a direct conversion to [CH<sub>3</sub>] radicals in the boundary layer near the substrate surface due to lower surface temperatures (T<sub>s</sub> = 1100 – 2000 K). This would also help in increasing the growth rates ([113], [120]).

The microwave power density (MWPD), electron density ( $n_e$ ), electron temperature ( $T_e$ ), gas temperature ( $T_g$ ) and the atomic hydrogen [H] density has modelled extensively for a pure hydrogen discharge. Figure 2.43 shows the simulations for a pure hydrogen plasma at different operating pressures and at a constant plasma volume [30]. As seen

in figure 2.43, at a high pressure level of 300 mbar, the MWPD,  $n_e$ ,  $T_g$  and [H] density is maximum at the plasma/ substrate surface boundary. This indicates that the growth rate will be higher at high operating pressures. Thus, it is preferable to operate at high pressures of > 300 mbar.



Figure 2.43 Evolution of MWPD,  $n_e$ ,  $T_e$ ,  $T_g$  and [H] density with increasing operating pressures for 4% CH<sub>4</sub>/H<sub>2</sub> at a constant plasma volume [30].

Argon addition in the feed gas was also observed to enhance the growth rate of diamond [123] since it leads to an increase in the [H] density and a reduction in the [CH<sub>3</sub>] radical density. This suggested that the ratio of [CH<sub>3</sub>] radicals to [H] is critical and has to

be balanced such that the growth rate can be increased while simultaneously preventing the etching of the diamond surface.

Another 2 dimensional model was later developed to solve some of the issues faced with the 1 – D model ([31], [118], [119]). Figure 2.44 displays the 2 – D fluid model (left column) and the 2 – D self – consistent model (right column) for a pure hydrogen microwave discharge. The top and the bottom rows in figure 2.44 show the Ø symmetric gas temperature and [H] density variations for a hydrogen flow rate of 500 sccm at 200 mbar and at 3 kW [31]. Both the 2 – D fluid and self – consistent (LIMHP) model describe the axisymmetric variations appropriately.



Figure 2.44 Left column: 2 – D fluid model, Right column: 2 – D self – consistent (LIMHP) model, Top row: Ø symmetric gas temperature variation, Bottom row: [H] density variations for a pure hydrogen discharge [31].

The 2 – D fluid model also simulated the axisymmetric distribution of the methyl radicals, as shown in figure 2.45 [31]. It is clearly seen, that  $[CH_3]$  density forms a band around the plasma discharge where the gas temperature are ~ 1200 – 2200 K. This band

of high [CH<sub>3</sub>] density extends to within the microwave discharge – substrate surface boundary layer which helps in increasing the growth rate.



Figure 2.45 [CH<sub>3</sub>] radical density forms a band around the core of the microwave discharge [31].

When the plasma is ignited, it modifies the standing electromagnetic field within the reactor cavity. These fields are absorbed by the microwave discharge near the periphery of the plasma resulting in the EM coupling of power into the microwave discharge. The coupling technique, without the plasma generation in the cavity, is shown in figure 2.46 [30]. The electric field lines can be clearly seen by the arrows. They form the high electric field regions at the top, bottom and at the center of the cavity.



Figure 2.46 Generation of a  $TM_{012}$  mode and the EM coupling of microwaves within the reactor with an antenna/ coaxial probe [30].

This work was further applied to the reactors developed at Michigan State University (section 2.5.4). The coupling mechanism is shown in figure 2.47 for the TM<sub>012</sub> mode excitation [30]. The coupling probe excites the electric fields within the reactor cavity. By inserting a quartz bell jar, it helps in confining the flow of the hydrogen and methane feed gas only within this region. And hence finally allows the excitation of a microwave discharge directly above and in contact with substrate surface. This is shown in the last figure in figure 2.47 which shows the generation of a pure hydrogen discharge at 200 mbar.



Figure 2.47 TM<sub>012</sub> EM mode and a pure hydrogen discharge excitation within MSU developed reactors [30].

The evolution of the skin depth of the microwaves into the discharge for different pressure levels is shown in figure 2.48 [30]. Skin depth is given by the relation:

$$\delta = -1/Im(k)$$

Here, k is the wavenumber of the propagating wave in the plasma and is given by:

$$k^2 = k_0^2 (\epsilon_p / \epsilon_0)$$

Here,  $k_0$  is the free space wavenumber,  $\epsilon_p$  is the plasma permittivity and  $\epsilon_0$  is the free space permittivity. If the skin depth is too small, then the microwaves do not penetrate into the discharge and hence the power is not coupled into the entire plasma volume. If the skin depth is too long, then the microwaves pass through the plasma volume and no power is absorbed within the plasma volume.



Figure 2.48 Numerical modelling of skin depth variation for different pressures of 50 – 300 mbar [30].

# 2.5.3.3 High growth rate of SCD substrates

CVD SCD substrates were grown on ~  $3 - 3.5 \times 3 - 3.5 \times 1.5 \text{ mm}^3$  (100) oriented type Ib HPHT seed substrates in the home – made 2.45 GHz MPACVD reactor shown in figure 2.39. Typical growth variables for the deposition processes were: pressure = 70 – 260 mbar, microwave incident power = 1.3 - 3.2 kW, %CH<sub>4</sub>/H<sub>2</sub> = 2 - 7%, [N<sub>2</sub>] = 0 - 20 ppm, total flow rate = 500 sccm, substrate temperature = 700 – 1000°C, growth rate = 0.4 - 55µm/hr, and microwave power density =  $10 - 190 \text{ W/cm}^3$ . ([32]–[34], [114], [124]). Many different growth parameters were investigated to understand their effect on the growth of SCD substrates that were then characterized with several analysis techniques. These are detailed in references ([9], [29], [32]–[38], [114], [124], [125]). Some of these effects are discussed below.

(1) Effect of substrate temperature: When deposition was conducted at low substrate temperatures of 750°C and 4% CH<sub>4</sub>/H<sub>2</sub> with 95 W/cm<sup>3</sup>, the surface was found to have a

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large number of non – epitaxial crystallites in the form of square pits and the surface was rough with a low growth rate of 2  $\mu$ m/hr. At more than 1000°C, even though the growth rates increased to 6 – 7  $\mu$ m/hr, the surface showed large pyramidal hillocks (figure 2.49(a)) with a step flow growth. The optimum substrate temperature was found to be ~ 850°C where the surface has a very smooth surface morphology (figure 2.49(b)) [32].



Figure 2.49 CVD SCD substrates grown at 4%  $CH_4/H_2$ , and at (a) 1000°C and (b) 850°C ([32], [33]).

(2) Effect of methane concentration: For a constant microwave power density (MWPD) of 96 W/cm<sup>3</sup>, temperature of 850°C, and no intentional nitrogen addition, the methane concentration was varied from 2 - 7.2%. As shown in figure 2.50(a) the surface is covered with etch pits for 2% CH<sub>4</sub>/H<sub>2</sub> ([32], [33]). The low methane concentration combined with a large MWPD leads to a high etch rate instead of growth. Thus, a high MWPD must be coupled with a high methane concentration in order to mitigate the etching effects of the increased [H] density. Figure 2.50(b) shows a smooth surface for 4% CH<sub>4</sub>/H<sub>2</sub>. As

%CH<sub>4</sub>/H<sub>2</sub> increases from 2 – 7.2% the growth rate also increased 8 times i.e. from 2  $\mu$ m/hr to ~ 15  $\mu$ m/hr (figure 2.50(c)) ([32], [33]). If the methane concentration is increased to 8 – 10% then the synthesis process was seen to be limited by the production of soot and its deposition on the quartz windows ([35], [121]).





Figure 2.50 SCD surface morphology with (a) 2% CH<sub>4</sub>/H<sub>2</sub>, and (b) 4% CH<sub>4</sub>/H<sub>2</sub>. (c) Increasing growth rate with increasing methane concentration ([32], [33]).

(3) Effect of nitrogen addition: At 95 W/cm<sup>3</sup>, 4% CH<sub>4</sub>/H<sub>2</sub> and 850°C, the nitrogen concentration in the feed gas was varied from 0 - 10 ppm ([32]–[35], [125]). The surface morphology of the crystals grown before and after polishing are shown in figures 2.51 and 2.52 respectively [34]. Nitrogen incorporation reduces the formation of the non – epitaxial crystallites as seen in figure 2.49.



Figure 2.51 Surface morphology of as grown SCD substrates grown with (a) 0 ppm, (b) 6 ppm, and (c) 10 ppm of nitrogen [34].



Figure 2.52 Surface morphology of polished SCD substrates grown with (a) 0 ppm, (b) 6 ppm, and (c) 10 ppm of nitrogen [34].

As seen in figure 2.53, when the nitrogen concentration is increased from 0 ppm to 10 ppm, the growth rate also increased from 6 – 16 µm/hr. The inset photographs in figure 2.53 show the optical and photoluminescence images of the substrates grown with 0 and 2 ppm of nitrogen. The corners of these substrates clearly contain defects and polycrystalline deposition. When the methane and nitrogen concentrations were increased to 7% and N<sub>2</sub>/CH<sub>4</sub> = 286 ppm respectively, then the growth rate was 33 µm/hr, although the substrate had a brown discoloration due to the high nitrogen incorporation in the crystal [33]. This also affected the electronic quality of the substrate [35].



Figure 2.53 Increasing growth rates with increasing nitrogen concentration [35].

The nitrogen incorporation in the gas mixture modifies the (100) growth surface chemistry. It was also observed that when the substrate temperature was increased, then a larger concentration of the nitrogen radicals on the growth surface are desorbed and hence a lower nitrogen density is incorporated within the crystal, thus reducing the SCD growth rate [125].

(4) Effect of crystal orientations: The main crystal orientations of diamond substrates, i.e. (100), (110) and (111), were studied to understand their effect on the growth rate. The main parameters to investigate here are the  $\alpha$ ,  $\beta$ , and  $\gamma$  variables. A growth model was developed to study the growth of the different growth sectors, i.e. (100), (110), (111) and (113) faces, versus growth time ([9], [29], [35]–[37], [84]). These sectors are shown in figures 2.54 and 2.55.



Figure 2.54 The HPHT crystal is composed of the different sectors as shown in the bottom row. After cutting it a HPHT substrate oriented along (100) is produced whose corners and edges also have the same sectors [29].



Figure 2.55 (a) Simulated and (b) an SEM picture of a 500 µm thick SCD crystal synthesized on a (100) oriented HPHT seed [35].

The 3 growth parameters can be written down as a function of the growth rates of the different faces of the substrate (figure 2.55) ([35], [36]):

$$\alpha = \sqrt{3} \frac{V_{100}}{V_{111}} \qquad \beta = \sqrt{2} \frac{V_{100}}{V_{110}} \qquad \gamma = \sqrt{11} \frac{V_{100}}{V_{113}}$$

It was observed that the (110) plane has the fastest growth rate and hence the final CVD substrate did not have a (110) oriented plane. The (111) oriented faces, although have a slower growth rate, but there is also a high probability of defect ( $sp^2$ ) and impurity (like nitrogen) incorporation in these planes. These defects then lead to stress in the crystal which results in the cracking of the substrate. In contrast, the (100) oriented surface are most suitable for growth of CVD SCD substrates at high temperature to produce electronic and optical quality crystals [29].

For substrates with faces oriented along the (100) direction, three main results were obtained from the modeling studies [36]: (a) when  $\beta > 1$ , only then can the (110) faces be visible, (b) when  $\gamma > 11\alpha/(3 + 2\alpha)$ , only then can the (113) faces be visible, and (c) when  $\gamma > 11\alpha/(5)$ , only then can the stable substrate shape contain any (113) faces. Using these
results, the effect of methane concentration (figure 2.56), substrate temperature (figure 2.57) were studied. Both experimental (left) and simulated (right) results are shown in these figures ([35], [36]). With increasing methane concentration, the growth rates of the different faces can be seen to increase. Since  $\gamma > 11\alpha/5$ , so (113) faces are visible in the final crystal but they have the slowest growth rate. Whereas the (110) plane has the fastest growth rate and hence does not appear in the final substrate. The evolution of the (100) oriented substrate is shown in figure 2.56(b) for varying methane concentrations.



Figure 2.56 Effect of methane concentration on growth rates of the different sectors as seen (a) experimentally (left) and by simulation (right) ([35], [36]). (b) evolution of substrates grown on (100) oriented substrates [9].

A similar behavior, as explained above, is true for the effect of substrate temperature on the various growth sectors (figure 2.57).



Figure 2.57 Effect of substrate temperature on the growth rates of the different sectors as seen (a) experimentally (left) and by simulation (right) ([35], [36]). (b) evolution of substrates grown on (100) oriented substrates [9].

Thus, it was observed that by varying any of these different growth parameters it was possible to tailor the CVD SCD growth in order to enable a smooth large top surface. After investigating the different morphologies of the substrates obtained by geometric modeling, limits for the 3 variables were established to obtain smooth high quality top CVD SCD surface at high temperature, high pressure and with a high growth rate [9]:

$$1 \le \alpha \le 5/4$$
,  $\beta \le 1$ , and  $11\alpha/5 \le \gamma \le 11/4$ 

These numerical modeling studies are presented in figure 2.58 which shows the development of the CVD substrates grown on a (100) oriented SCD substrate with varying  $\alpha$ ,  $\beta$  and  $\gamma$  parameters [9]. The deposition time has been normalized with t = 1 being a 1 mm growth on the top surface of the SCD substrate. Hence, by choosing the  $\alpha$ ,  $\beta$  and  $\gamma$  parameters appropriately it is possible to obtain smooth, large top surface area.

Some results shown in this thesis experimentally investigate the effect of some of the growth variables discussed in this section.



Figure 2.58 Simulation of the development of the crystal structure of the final substrate grown on an initial (100) oriented SCD substrate with varying  $\alpha$ ,  $\beta$  and  $\gamma$  parameters [9].

Further, the misorientation of the crystal faces were studied where the top surface was cut/ polished to be at a few degree angle with respect to the (100) growth surface. Even though such a miscut on the top surface helps in the lateral growth of the substrate, it is only a short term effect. This miscut surface grows at a faster rate and enhances the

formation of growth steps. Once these growth steps are formed to completely align themselves to the (100) surface the growth rate decreases to that of the original (100) growth plane [29].

Type Ib HPHT substrates (figure 2.59(a)) were beveled at the 4 edges to form pyramidal substrates (figure 2.59(b)) [37]. The miscut angle for the 4 sides was 20° with respect to the <001> direction.



Figure 2.59 (a) Typical (100) oriented type lb HPHT seed, (b) beveled seed [37].

The beveled substrate was then grown with 100 W/cm<sup>3</sup>, 5% CH<sub>4</sub>/H<sub>2</sub> and at 850°C. The 3 rate parameters were:  $\alpha = 1.8$ ,  $\beta = 1.1$  and  $\gamma = 1.4$ . Figure 2.60 shows the evolution of the crystal faces after the growth was interrupted when the CVD substrate thickness was (a) 90 µm, (b) 270 µm and (c) 500 µm [37]. It is clear from this figure that the lateral and the edge faces disappear over time leading to a smooth, large (100) oriented surface. Figure 2.61 shows the surface morphology of this substrate [37]. With growth time the (110) face i.e. the lateral face obtains a fish scale like appearance with the steps propagating along the <110> direction.



Figure 2.60 Evolution of the beveled substrate with time after (a) 90  $\mu m,$  (b) 270  $\mu m$  and





Figure 2.61 Morphology of the beveled substrate after 300  $\mu$ m growth [37].

The growth rates of the lateral and the edge faces can be evaluated using the following two equations and figure 2.62 [37].

$$D_{lat} = \sqrt{D_{norm}^2 + d^2} x \sin(\theta_1 + \theta_2)$$
$$\theta_2 = \tan^{-1} \left( \frac{D_{norm}}{d} \right)$$

and,

Here,  $D_{norm}$  is the growth normal to the (001) plane, *d* is the lateral growth extension of the (001) growth face and  $\theta_1$  is the angle of misorientation i.e. 20°. Using these equations, the growth rate were measured to be 32.5 µm/hr (lateral face), 31.5 µm/hr (edge face) and 13.5 µm/hr (top face).



Figure 2.62 Growth orientations and angle inclinations for a beveled growth [37].



Figure 2.63 Plot of growth rate versus the misorientation angle. With increasing miscut angle the lateral growth of the (100) surface decreases [37].

In figure 2.63, the variation of the different growth rates on the top, edge and lateral faces are shown as a function of the misorientation angle along the (100) face [37]. Since the growth rate of the edges and the lateral faces increased with the miscut angle, the lateral growth of the (100) plane and the enlargement of the top surface reduced and a greater thickness was required to eliminated the edge and lateral faces. Using such a strategy and by maintaining the miscut angle to only  $\sim 20 - 30^{\circ}$  they were able to grow 1.7 mm thick SCD CVD substrates.

Some more examples of the substrates deposited by LIMHP, with the help of all the different growth variables mentioned in this subsection, are shown in figures 2.64 (inset) and 2.65. A Fourier Transform Infrared (FTIR) spectrum is shown in figure 2.64 which displays the typical 2 and 3 phonon absorptions of a 350  $\mu$ m thick diamond substrate with no major nitrogen peaks between 500 – 1500 cm<sup>-1</sup>.

Figure 2.65 shows a 5 multi – step, 3.3 mm thick SCD crystal grown with 3 – 3.8 kW, 200 - 270 mbar and 5 – 6% CH<sub>4</sub>/H<sub>2</sub> with no intentional nitrogen addition on a 3.5 x 3.5 mm<sup>2</sup> HPHT seed. Cracks are clearly seen in the laser cut crystal (figure 2.65(b)) due to the thick polycrystalline rim in the as grown crystal (figure 2.65(a)). Thus, this PCD rim is an important issue to investigate and minimize so as to improve the SCD quality and simultaneously increase its dimensions.



Figure 2.64 FTIR spectrum of a 350  $\mu$ m thick, 4 x 4 mm<sup>2</sup> SCD crystal (inset) grown at 400 mbar, 3 kW and with 7% CH<sub>4</sub>/H<sub>2</sub> [9].



Figure 2.65 A 5 step, 249 hour grown, 3.3 mm thick (a) 6.86 carat as – grown, (b) laser cut, (d) 0.44 carat polished SCD crystal [38].

#### 2.5.4 Michigan State University (MSU), USA

Diamond synthesis at high pressures and with high power density enhances the growth rate during the synthesis process. This has been discussed in several references ([12], [33], [63], [64], [69], [126]–[128]). New plasma reactors were designed to achieve the synthesis of single crystal and polycrystalline diamond substrates at high pressures and high power densities.

Single and polycrystalline diamond substrates have been synthesized at MSU via the MPACVD method in the different generations of the microwave cavity plasma reactors. Specifically, plasma reactors developed by MSU during the 1987 – 2002 period and more recently (2004 – 2014), with partial support from Fraunhofer USA, have been redesigned in order to enhance the growth rate. These reactors now enable the successful synthesis of SCD and PCD substrates at high pressure levels (180 – 300 Torr) and high microwave power densities (150 – 1000 W/cm<sup>3</sup>) ([41]–[46]). The MSU reactors are now classified as reactors A, B and C and are discussed in more detail in this section.

### 2.5.4.1 Reactor A design

Reactor A was designed to be operated at moderate pressure levels of 60 - 160 Torr. A cross – sectional view of the reactor A is displayed in figure 2.66 ([39], [42], [43], [126]). Here L<sub>s</sub> and L<sub>p</sub> refer to the short (i.e. the cavity) length and probe length respectively. L1 is the distance between the top of the substrate holder and the bottom short plate while L2 is the distance between the z = 0 plane and the bottom short plate. There is an abrupt radial discontinuity at the z = 0 plane. R1, R2, R3 and R4 are the other different geometrical variables of this reactor. In reactor design A, the molybdenum substrate holder position is fixed and the substrate holder is placed on a water cooled stage. The quartz dome has a radius of 13 cm and a height of 9.5 cm. Here R1 = 8.89 cm, R2 = 7.04 cm, R3 = 4.13 cm and R4 = 5.08 cm. In this reactor cavity, the short and probe lengths are adjusted to excite a single hybrid electromagnetic mode of  $TM_{013}/TEM_{001}$ . The produced electromagnetic mode is  $\emptyset$  symmetric within the cylindrical cavity and hence produces a  $\emptyset$  symmetric discharge hovering over the substrate.



Figure 2.66 Cross – sectional schematic of microwave cavity plasma reactor A.

Figure 2.67 shows the entire external microwave system setup of reactor A. It is connected to a (1) Cober power supply with an excitation frequency of 2.45 GHz and 6 kW variable power. The power supply contains a (2) magnetron, (3) circulator and a (4) dummy load and is connected to (5) rigid waveguides which are in turn is attached to a (9) flexible waveguide. A (10) transition unit connects the flexible rectangular waveguide to the coaxial waveguide which in turn couples the electromagnetic energy into the cavity with proper adjustment of the probe. The (6) dual directional power coupler, (7) incident and the (8) reflected power meters are connected between the flexible and the rigid rectangular waveguides.



Figure 2.67 The external microwave system for reactor A showing the connections to the microwave power supply and the external waveguides and transmission systems [39].

Reactor A was originally operated for moderate pressure levels for the deposition of polycrystalline diamond substrates. Table 2.7 lists the important internal and output microwave reactor A variables for the synthesis experiments typically performed [39]. These input reactor variables include substrate temperature (T<sub>s</sub>), pressure (p), total absorbed power ( $P_{abs} = P_{inc} - P_{ref}$ ; where  $P_{inc}$  is the incident power and  $P_{ref}$  is the reflected power), ratio of methane to hydrogen gases (% CH<sub>4</sub>/H<sub>2</sub>), total flow rate (ft), and deposition time. The linear growth rate, the growth rate by weight and the average absorbed power density ( $\langle P_{abs} \rangle$ ) are the output reactor variables mentioned in table 2.7.

Reactor variables	Values
Substrate temperature ( $T_s$ )	700 – 1150°C
Pressure (p)	60 – 160 Torr
Total absorbed power $(P_{abs})$	3 – 5 kW
% CH4/H2	1 – 8%
Total flow rate (f <sub>t</sub> )	100 – 1400 sccm
Linear growth rate	4 – 7 μm/hr
Growth rate by weight gain	27 – 50 mg/hr
$\langle P_{abs} \rangle$	32 – 43 W/cm <sup>3</sup>

Т	ab	le 2	2.7	Inpu	t and	outpu	it reactor	Αva	ariat	bles	for t	the t	ypical	synt	hesis	processes	
-																	-

## 2.5.4.2 Reactor B design

Over the last 30 years, reactor A has undergone many modifications in order to improve the growth rate for both polycrystalline and single crystal diamond substrates by increasing the absorbed microwave power densities. One important redesign is reactor B. It was redesigned to operate at moderate to high pressures of 60 – 240 Torr. A crosssectional schematic of the reactor B design is shown in figure 2.68.



Figure 2.68 Cross – sectional schematic of microwave cavity plasma reactor B [40].

The main differences between the reactor A and B designs are as follows:

1) The cooling of the stage and the dimensions of the molybdenum substrate holder were redesigned in order to improve operations at high pressure levels with greater absorbed microwave power densities. 2) The variables R3 (radius of the cooling stage) and R4 (radius of the molybdenum substrate holder) were modified. R3 was reduced to 1.91 cm and R4 to 3.24 cm. Thus, the substrate holder area was reduced by 4.5 times which increased the electromagnetic field intensity at the smaller region above the substrate holder by concentrating the electric field lines and hence increasing the displacement current density over the holder. This design modification allowed the reactor to be operated at high pressures and with high discharge absorbed power densities.

3) The variable length hybrid coaxial electromagnetic mode was excited. In this modified reactor design the variables L1 and L2 were made flexible such that the substrate position ( $z_s = L1 - L2$ ) could now be varied over +1 mm to -10 mm with respect to the z = 0 plane (figure 2.68).

4) A hybrid electromagnetic mode was excited in this modified reactor design. TM<sub>013</sub> was excited in the cylindrical cavity (z > 0 area) and TEM<sub>001</sub> was excited in the coaxial part of the cavity (z < 0 area).

Figure 2.69 [41] shows (a) the empty  $\emptyset$  symmetric cavity, (b) a coaxial probe insertion at the top of the cavity along the z – axis, (c) electromagnetic field excitation (TM<sub>013</sub>) with the help of the coaxial coupling probe. A quartz dome is placed at the bottom of the cavity to (1) confine the flow of gases, and (2) prevent the formation of more than one microwave discharge, and (d) the variable length coaxial region (TEM<sub>001</sub> mode) at the bottom of the cavity helps in the flexibility of the substrate position with varying L1 and L2.

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Figure 2.69 Hybrid electromagnetic mode (TM<sub>013</sub>/TEM<sub>001</sub>) excitation in reactor B [41].

This reactor was characterized and operational road map curves were obtained by K. W. Hemawan and J. Lu ([42]–[45]) for different substrate holder positions of  $z_s = -0.31$  cm and -5.7 mm respectively. These curves are shown in figures 2.70 and 2.71 respectively. These road map curves, i.e. operational field map curves, indicate the safe and efficient operating region of reactor B. For the characterization process of reactor B, a 2.54 cm diameter silicon substrate was used. Other reactor variables were total flow rate ( $f_t$ ) = 412 sccm with 3% CH<sub>4</sub>/H<sub>2</sub>, L<sub>s</sub> = 20.5 and 21.6 cm respectively, and L<sub>p</sub> = 3.6 cm.



Figure 2.70 Road map curve of reactor B with  $z_s = -0.31$  cm ([42], [43]).



Figure 2.71 Operational field map curves for reactor B at  $z_s = -5.7$  mm ([44], [45]).

Experiments to grow high quality polycrystalline diamond (figure 2.72 and 2.73) were conducted with this reactor design by K. W. Hemawan ([42], [43]). In these experiments the different reactor variables were:  $L_s = 20.3$  cm,  $L_p = 3.6$  cm, L1 = 5.65 cm, L2 is varied from 5.16 to 6.13 cm and thereby  $z_s = + 0.5$  cm to -0.5 cm. Polycrystalline diamond (PCD) substrates (figure 2.73) were synthesized on 2.54 cm diameter silicon substrates at varying pressures of 180 – 240 Torr, substrate temperatures of 950 – 1150°C and with 2 – 5 %CH<sub>4</sub>/H<sub>2</sub>. This modified reactor design increased the absorbed microwave power density to 150 – 475 W/cm<sup>3</sup> and hence improved the PCD growth rates above other research groups to 3 – 21 µm/hr.



Figure 2.72 Raman spectra and morphology of high quality synthesized PCD plate [42].



Figure 2.73 A freestanding, polished polycrystalline diamond plate synthesized with reactor B [42].

To further explore the operation of the reactor B, single crystal diamond (SCD) substrates were synthesized by J. Lu ([44], [45]). For single crystal diamond deposition, experiments were performed at high pressure levels of 240 Torr and with varying amounts

of nitrogen from 10 – 200 ppm. Nitrogen affects the growth rate and this was demonstrated in figure 2.74, which displayed that the growth rate increased from 8 to 45  $\mu$ m/hr with increasing nitrogen concentration in the feed gas mixture of hydrogen and methane. Secondary ion mass spectroscopy (SIMS) indicated the amount of nitrogen in the synthesized substrates. For a nitrogen concentration of < 10 ppm in the gas mixture, < 300 ppb nitrogen and silicon impurities was measured in the bulk of the substrates by SIMS and indicated that the substrates grown were of type IIa quality.



Figure 2.74 Growth rate of single crystal diamond substrates versus increasing nitrogen concentration from 10 – 200 ppm [44].

The growth rate of SCD substrates was also affected by the methane concentration (as discussed in section 2.2.4). With increasing methane concentration in the gas, the

SCD growth rate also increases. Experiments were conducted with varying [CH<sub>4</sub>] flow from 4 – 7% to study the increase in SCD growth rate in reactor B. The results of this study at 240 Torr,  $L_s = 21.6$  cm, and  $z_s = -3.34$  mm to – 5.73 mm, is shown in figure 2.75. As can be seen in figure 2.75, a high growth rate window is present for substrate temperatures between 1100 – 1200°C for reactor B. To further classify the synthesized substrates, Raman spectroscopy was conducted on them ([44], [45]). Figure 2.76 shows the growth rate and Raman FWHM data for substrates synthesized at 240 Torr and 6% CH<sub>4</sub>/H<sub>2</sub>. These substrates were compared to a high quality, low stress Element Six type IIa SCD plate and a commercially available type Ib HPHT diamond seed substrate. The synthesized SCD substrates indicated low stress especially in the high growth rate window between 1050 and 1250°C and were better than the HPHT seed substrates used for all deposition experiments (see figure 2.76).



Figure 2.75 A study of growth rate versus substrate temperature for varying methane concentration of 4 - 7% ([44], [45]).



Figure 2.76 Growth rate and Raman FWHM measurements of SCD substrates synthesized at 240 Torr and 6%  $CH_4/H_2$  and compared with a low stress Element Six crystal and a commercial type Ib HPHT diamond seed ([44], [45]).

# 2.5.4.3 Reactor C design

In order to even further expand the multi – variable operating and deposition region of the MSU microwave cavity plasma reactors, a new reactor C was designed. This reactor C was designed to operate at higher power densities (400 – 1000 W/cm<sup>3</sup>) with high deposition pressures (180 – 300 Torr) and was experimentally characterized by Y. Gu ([41], [46]).



Figure 2.77 Cross – sectional schematic of the microwave plasma reactor C [41].

Figure 2.77 shows a cross – sectional view of the reactor C design. There are some major configurational differences between this reactor C and reactors A and B. These are listed below:

1) The diameter of the reactor was increased from 7 inches i.e. 17.78 cm for reactor A and B to 12 inches i.e. 30.48 cm for reactor C. In addition, the diameter of the quartz bell jar was increased from 5.125 inches i.e. 13.02 cm for reactor A and B to 8.5 inches i.e. 21.59 cm in reactor C. This expansion in the quartz bell jar diameter provided a method

of moving the microwave discharge away from the walls of the quartz dome. This prevented any interactions between the intense plasma and the quartz dome walls and hence any contamination during the experiments. Thus, the process could now be run for longer deposition times with a stable plasma positioned above the substrate holder.

2) The radius of a section of the cylindrical cavity (section 3 in figure 2.77) was reduced from R1 = 15.24 cm to R5 = 12.07 cm. This smaller diameter section of the applicator region in reactor C helped in the concentration of the electromagnetic field lines over a smaller region and hence the absorbed microwave power density was increased to 400 – 1000 W/cm<sup>3</sup> for high deposition pressures of 180 – 300 Torr.

3) Due to the change in diameter in the different sections of the applicator, the electromagnetic mode excited in the cylindrical cavity is also different from that excited in reactors A and B. The cavity of reactor C is still Ø symmetric but the electromagnetic mode excited here is not a classical mode of operation anymore and hence is termed as a TM<sub>0</sub> mode. The mode in the coaxial region is still the TEM<sub>001</sub> mode since the cooling stage area and design are similar to those in reactor B.

The other reactor variables for this design included  $L_p \sim 3$  cm,  $L_s \sim 16.2$  cm, R2 = 10.16 cm, R3 = 1.84 cm, h = 10.86 cm, L1 and L2 ~ 6.12 cm, - 0.8 cm <  $z_s$  < 0.5 cm and L3 = 7.32 cm.

The road map curve for reactor C is given in figure 2.78 [41] for pressure levels of 75 Torr (100 mbar) to 240 Torr (320 mbar). The blue lines drawn in figure 2.78 indicate the safe and efficient operational limits of reactor C over a wide range of operating conditions. These measurements were conducted on a 1 inch silicon wafer as the substrate. The variables for the operational road map curve (figure 2.78) were: total flow rate ( $f_t$ ) = 400

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sccm with 3% CH<sub>4</sub>/H<sub>2</sub>,  $Z_s = -4.8$  mm, substrate temperature = 650 - 1250°C and the absorbed microwave power = 1.6 - 3.5 kW.



Figure 2.78 Road map curves of reactor C from 75 to 240 Torr. The blue lines indicate the limits of operation [41].

The advantage in the flexibility of the substrate position is displayed in figure 2.79 ([41], [46]). As the substrate position moves from z > 0 to z < 0 i.e. from z = + 4 mm to z = -6 mm from (a) to (e), the electric field intensity becomes more focused and increases directly above the substrate holder. This trend is also observed in reactor designs A and B. Thus for high power density and high growth rates during the deposition process, it is

advantageous to use such a flexibility in the substrate position and exploit the operating conditions for z < 0.



Figure 2.79 Varying electric field intensity with variable substrate positions of (a) + 4 mm, (b) + 2 mm, (c) 0 mm, (d) – 4 mm, and (e) – 6 mm with respect to z = 0 plane ([41], [46]).

A comparison between the absorbed microwave power densities versus pressure levels of reactors A, B and C are displayed in figure 2.80 [41]. As has been stated before, reactor A was designed for operation at moderate pressures (60 - 140 Torr), reactor B at high pressures (60 - 240 Torr) and reactor C at higher pressures (60 - 300 Torr). With the flexibility in the substrate positions and the smaller substrate holder areas, reactors B and C can be operated with high absorbed microwave power densities ( $\sim 100 - 1050$  W/cm<sup>3</sup>).



Figure 2.80 Comparison of the absorbed microwave power densities vs. pressure for reactor designs A, B and C [41].

The effect of these high absorbed microwave power densities and operating pressures levels is indicated in figures 2.81 and 2.82 ([41], [46]). Figure 2.81 displays the comparison between the single crystal diamond (SCD) growth rate variation versus temperature for reactors B and C. The higher power density for reactor C enables a higher growth rate as compared to reactor B for the same set of input variables of pressure (240 Torr), 5% CH<sub>4</sub>/H<sub>2</sub> and a fixed  $z_s$ . In figure 2.82, the single crystalline diamond growth regime is indicated for all three reactor designs A, B and C. Figures 2.81 and 2.82 shows

the diamond growth window for reactor B being between substrate temperature ( $T_s$ ) = ~ 1050 – 1200°C with a growth rate of ~ 25 µm/hr, and for reactor C being between  $T_s$  = 1150 – 1300°C with a growth rate of 38 µm/hr.

It is not only important to grow SCD substrates with a high growth rate but also with a high quality. Figure 2.83 shows the optical transmission measurements of the substrates synthesized with reactors A, B and C and also displays the effect of nitrogen on their optical quality ([44], [45]). Although it has been observed that nitrogen impurities within the total gas flow enhance the growth rate of SCD, they also increase the absorption of transmitted light through the crystals which deteriorates the optical quality of the synthesized SCD substrates. This fact is clearly visible in figure 2.83. Here, the operating conditions for substrates grown in (1) reactor A were p = 160 Torr, 5% CH<sub>4</sub>/H<sub>2</sub>, (2) reactor B were p = 240 Torr, 6% CH<sub>4</sub>/H<sub>2</sub>, and (3) reactor C were p = 240 Torr, 5% CH<sub>4</sub>/H<sub>2</sub>. The samples 1 and 2 shown in figure 2.83 exhibit high absorption in the UV/Vis wavelength range as compared to the samples 3 and 4 which have ~ 4 – 7 cm<sup>-1</sup> absorption even at the lower wavelength range. This high transmission behavior shown by the samples at ~ 225 nm indicate that the samples synthesized by reactors B and C are of high quality and can be classified as type IIa quality or better.



Figure 2.81 SCD growth rate vs. substrate temperature comparison for reactors B and C ([41], [46]).



Figure 2.82 Comparison of reactors A, B and C indicating the window of maximum SCD growth rate vs. pressure ([41], [46]).

In this dissertation, one of the goals is to improve the quality of substrates grown with the reactor B design and to increase the lateral growth of the substrates during the synthesis process itself. Further investigation of substrates grown over longer growth times and at high deposition pressures of 240 Torr are required to explore high power density operation of reactor B.



Figure 2.83 Optical transmission measurement comparison of samples grown in reactors A, B and C both with and without intentional nitrogen addition in the total gas flow ([44], [45]).

Most of the substrates discussed in this thesis have been synthesized in reactor B. This reactor has been discussed in greater detail in chapter 3. Some of the substrates analyzed and discussed in chapters 5 and 6 were deposited in reactor C. In this thesis only their analyses is presented in detail.

# 2.6 Defects in CVD grown SCD substrates

There can be different types of lattice defects in crystalline substrates. These are classified as: point defects (zero dimensional), line defects (1 – dimensional), planar defects (2 – dimensional) and bulk defects (3 – dimensional) [129]. The point defects can be either intrinsic: due to a self – interstitial atom or a vacancy, or can be an extrinsic defect: due to any impurities in the interstitial or substitutional sites (figure 2.84) ([47], [130]).



Figure 2.84 Point defects in a crystal lattice [47].

A self – interstitial atom is due to an extra atom being present in an interstitial site. A vacancy is created due to the absence of an atom from a lattice site. Foreign atoms (like hydrogen, boron or nitrogen) may be occupying a lattice site instead of a carbon atom, hence creating a substitutional defect (impurity atom) or they may occupy the empty

space between two lattice carbon atoms thereby creating an interstitial defect (impurity atom).

Line defects are mostly due to dislocations within the lattice structure of the substrate. These dislocations propagate through the bulk of the substrate and hence are termed as threaded dislocations. For the purpose of utilizing CVD SCD substrates in electronic applications, these threaded dislocations need to be minimized [131]. Dislocations are due to imperfections within the lattice structure which lead to dangling bonds along the central region of the line defect. These dangling bonds result in a significant local strain surrounding the central core of the dislocations are measured in terms of Burger vectors ( $\vec{b}$ ). By transcribing equal number of steps both left and right along the precise carbon – carbon bonds for a diamond lattice, the number of dislocations can be calculated around this loop if the start and stop positions are not the same. There are two main types of threaded dislocations: (a) screw, and (b) edge dislocations.

(a) Screw dislocations are formed due to the application of shear stress on an atomic plane (figure 2.85(a)). The plane ABCD is shifted by one set of atoms along the line of dislocation (AD) [48]. In this case the Burger vector ( $\vec{b}$ ) is parallel to the line of dislocation ( $\vec{l}$ ) [129].

(b) Edge dislocations are formed when an additional half plane of atoms is introduced within the diamond lattice structure. In figure 2.85(b), this half plane of atoms is shown by the ABCD plane where AD is the line of the half plane. The plane of atoms beyond AD is distorted due to the addition of the extra half plane [48]. In this case, the Burger vector  $(\vec{b})$  is perpendicular to the dislocation line  $(\vec{l})$  [129].

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Figure 2.85 (a) Screw dislocation and (b) edge dislocation in a SCD substrate [48].

In some cases, the dislocations are a mixture of both edge and screw dislocations and hence are termed as mixed dislocations. Here  $\vec{b}$  is at an angle since it has both a perpendicular and parallel component to  $\vec{l}$ .

Planar and bulk defects are caused by grain boundaries between different crystals and by vacancy clusters respectively [129]. Surface defects are also an issue since they result in twinning imperfections in the crystal and also stacking faults within different atomic planes [132].

It is important to employ different methods and study these dislocations in the synthesized CVD SCD substrates and then utilize them to minimize these threaded dislocations. The methods discussed here are: etch pit analysis of the surface, x - ray topography, and birefringence measurements.

## 2.6.1 Etch pit analysis of SCD surface

It has been observed that threaded dislocations in the SCD substrate arise due to inherent defects and bulk dislocations and also due to surface polishing. These threaded

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dislocations then propagate perpendicular to the (100) growth surface [133]. Local stress is created by these propagating dislocations throughout the bulk of the substrates. By etching the diamond surface, it was observed to be possible to reveal the terminated dislocations on the SCD surface. Initially dry oxygen etching was used for this purpose [134]. Later, a hydrogen plasma [135] and then a mixture of hydrogen and oxygen gases was used as the etching gas mixture ([29], [37], [49], [51], [52], [54], [58], [59], [124], [136]). The typical etching parameters were: 2% O<sub>2</sub>, 98% H<sub>2</sub>, 200 mbar, 3 kW and 850°C. Type Ib HPHT seed substrates have a large density of dislocations on its surface [38]. It was also observed that by plasma pretreating the HPHT seed surface, it is possible to reduce the imperfections and impurities on the seed surface (the etched growth sectors are seen on HPHT seed in figure 2.86) and to promote a consistent step flow growth throughout the surface ([49], [136]). This resulted in the growth of atomically flat CVD SCD substrates (figure 2.87) [49], although at the interface between the HPHT surface and CVD SCD substrate a large number of etch pits were visible [124].



Figure 2.86 Etched growth sectors on a H<sub>2</sub>/O<sub>2</sub> plasma etched (100) oriented HPHT seed [29].



Figure 2.87 SEM image of a laser cut and polished 600  $\mu$ m thick SCD substrate grown at 700°C with 10% CH<sub>4</sub>/H<sub>2</sub> after being pretreated with 4% H<sub>2</sub>/O<sub>2</sub> plasma [49].

 $H_2$  or  $H_2/O_2$  plasma etching preferentially etches the defects on the substrate surface. These defects may be impurities and/ or terminations of threaded dislocations on the surface. But as the etching time increased, the surface roughness increased along with the appearance of large etch pits on the substrate surface ([52], [136]). The etch pit crystallographic faces for both  $H_2$  or  $H_2/O_2$  plasma etching were found to be the same [50]. A typical etch pit is shown in figure 2.88 [50].



Figure 2.88 (a) A 3D AFM image, and (b) an AFM height profile of a typical etch pit on the SCD surface [50].
Some examples of the etched SCD surface are shown in figure 2.89 ([51], [52]).



Figure 2.89 SEM images of etch pits formed on the surface ([51], [52]).

LIMHP – CNRS provided a closer analysis of these pits and is shown in figure 2.90 ([51], [52]). The etch pit edges were observed to run along the <110> direction (figure 2.89) which suggested that the etching process tends to preferentially etch along the <110> direction. The crystallographic faces for the etch pits was also observed as the (113) planes ([51], [52]). They then described a stability criterion which is given as:

$$V_{E\{hkl\}} > V_{E\{100\}} x \cos \theta$$

Here,  $V_{E\{hkl\}}$  is the growth rate of the etch pit faces i.e. (113) faces,  $V_{E\{100\}}$  is the growth rate of the CVD growth direction, and  $\theta$  is the angle between the top and lateral face of the etch pit (figure 2.90). If this criterion is satisfied, then with time the etch pits become deeper (figure 2.90(b)) and their size increase. Thus to obtain smooth surfaces, the growth rate of the (113) face was increased by reducing the  $\gamma$  growth parameter (see section 2.2.7.3.3). This was achieved by the addition of nitrogen in the gas or by lowering the methane concentration. However, these techniques affect either the quality of the grown substrates or the SCD growth rate and since this doesn't eliminate dislocations,

other methods need to be found in order to minimize dislocations in the bulk of the substrate.



Figure 2.90 Etch pit development when the stability criterion (a) is not satisfied, (b) is satisfied [51].

While most of the pits had an inverted pyramid shape with a sharp point at the bottom (as seen in figure 2.90), some of the etch pits observed had a flat bottom face. It was suggested that the flat bottom pits were created when the etching process reached the end of the dislocation and hence the etch rate of the bottom dropped to be the same as that of the (100) plane [51].

In order to analyze the quality of the grown CVD substrates, the etch pit density of the substrates was calculated and compared to HPHT substrates over time (figure 2.91) [52]. The etch pit density was seen to reduce with etching time. Also, the observed etch pit density for CVD substrates ( $10^6 - 10^7$ / cm<sup>2</sup>) was found to be one order of magnitude higher than the initial HPHT substrates ( $10^5 - 10^6$ / cm<sup>2</sup>) [52]. The most number of etch pits were visible within 60 mins of etching.



Figure 2.91 Etch pit density of HPHT (sample A) and CVD (sample B) substrates [52].

To understand the effect of temperature on the etching process, Ivanov et. al. [50] masked a part of the SCD substrate with a polycrystalline diamond substrate and etched the surface with different temperature ranges. Figure 2.92 shows that with increasing etching temperatures, the etch rates increase as well.



Figure 2.92 Increasing (a) etching rate, and (b) etching depth with higher temperatures [50].



The misorientation of the top growth surface of the HPHT seed surface was found to have a significant impact on the shape of the etch pits ([37], [50], [52], [53]). Figure 2.93 shows the difference in the shape of the pits when the surface was misoriented (a) 10° and (b) 20° offset to <100> direction, and (c) 10° and (d) 20° offset to <110> direction [52]. Substrates misoriented along the <100> direction had a rougher surface after etching as compared to those along <110> direction [52]. The etch rate of the (100) surface also increased with the misorientation angle [50]. After the substrates in figure 2.93 were grown and then etched, it was seen that the offset angled substrates along <100> had a slightly larger etch pit density as compared to the ones with the offset along <110> direction.



Figure 2.93 Offset angle (a) 10° and (b) 20° to <100>, and (c) 10° and (d) 20° to <110> direction ([52], [53]).

Similarly, after a beveled substrate surface (figure 2.59) angled 10° and 20° offset to <100> was grown and then etched, it was observed that the grown beveled sides of the CVD SCD substrate had almost 2 times lower etch pit density as compared to the top (100) growth surface ([52], [53]). Figure 2.94 shows a 20° offset beveled substrate after growth and etching processes [52]. Figure 2.94(a) shows the entire substrate surface after growth. Figure 2.94(b) shows a magnified image of the central region of the substrate surface surface, with the top (100) surface having a higher etch pit density as compared to the side beveled substrate surfaces.



Figure 2.94 (a) A 20° beveled substrate offset to <100> direction, after growth (b) higher etch pit density on the top (100) surface [52].

In order to grow thick SCD crystals, it is important to utilize multi – step growth runs. But these growth interruptions introduce more defects at these interfaces due to the plasma pretreatment before each growth step ([37], [54]). This is shown in figure 2.95 [54].



Figure 2.95 (a) A phosphorescence image of the SCD substrate grown with 2 growth interruptions. The first is due to a decrease in substrate temperature and the second is due to plasma etching treatment (b) magnified view of the image marked in the red box in (a) [54].

Thus better methods are needed which would enable the growth of thick and large SCD crystals with a large growth rate while minimizing the number of growth interruptions.

#### 2.6.2 X – ray topography (XRT) and optical analysis of dislocations

XRT and optical analysis (like crossed nicol and polarized light microscopy (PLM), differential interference contrast microscopy (DICM) and birefringence imaging) of the SCD substrates are some non – destructive characterization techniques. Many of these techniques have been used to analyze the synthesized CVD SCD substrates and are discussed in references ([14], [35], [55]–[58], [96], [97], [131], [137]).

XRT helps in analyzing the extended dislocations, i.e. threaded dislocations, within the bulk of the substrate by determining the Burger vector ( $\vec{b}$ ) and the line of dislocation ( $\vec{l}$ ). These dislocations can either be edge, screw or mixed dislocations. These lattice defects appear as strain lines within the CVD substrate and hence appear dark. Figure 2.96 shows three freestanding CVD substrates which were grown on HPHT seeds with (a) high to (c) low surface damage due to polishing [55]. Bundles of dislocations are seen to be propagating along the growth direction and then diverging towards the top surface. These are analyzed to be <001> edge dislocations [14]. Figure 2.96 indicates that the many of the dislocations propagating into the CVD substrate originate due to mechanical polishing damage on the initial HPHT surface. Hence, high quality seeds with low degree of damage are needed to synthesize better CVD substrates.

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Figure 2.96 CVD substrates grown on high (a) to low (c) degree of surface damage on HPHT seed surface [55].

Diamond is a non – birefringent material. Hence, for a perfect crystal, the image obtained after passing light through two crossed polarizers should be dark as the polarizations are cancelled off. But dislocations and inclusions within the crystal lattice of diamond lead to strain and hence birefringence in the substrate which then appear either as bright spots or lines. Figure 2.97 shows a XRT and PLM image freestanding CVD plate [14]. The dark lines and spots seen on the XRT image correspond to the birefringent patterns seen on the PLM image. This indicates that the strain induced by the defects and dislocations in the bulk of the substrate can be determined by birefringent imaging.



Figure 2.97 A (a) XRT and (b) PLM image of a freestanding CVD plate [14].

The bundles of dislocations in the substrate along the (001) threaded dislocations are edge type dislocations. They also correlate to defects seen via XRT analysis. These bundles exhibit bright 4 petalled birefringent patterns in the crossed nicol polarizer image shown in figure 2.98. Typically the dislocation density measured by analysis of XRT and birefringence images for synthesized CVD SCD substrates is ~  $10^4 - 10^5$ / cm<sup>2</sup> ([56], [131]). Thus, birefringent imaging makes it possible to determine single isolated dislocations in the substrate.



Figure 2.98 Bright four petalled birefringent pattern correspond to bundles of dislocations [56].

In order to further analyze the grown substrates, quantitative birefringence studies were conducted [55]. For light passing through a birefringent material, the phase shift between the slow and fast polarizations of light, i.e. between the ordinary and extra-ordinary light rays is given by:

$$\delta = \left(\frac{2\pi}{\lambda}\right)(\Delta n)d$$

Here,  $\lambda$  is the wavelength of the monochromatic light (550 nm), d is the thickness of the sample and  $\Delta n$  is the birefringence in the crystal. Hence lesser the  $\delta$ , the lower is  $\Delta n$  and hence the birefringence. For an ultra – low birefringent crystal:

$$\Delta n \leq 1 \ x \ 10^{-5}$$

It was observed that birefringence images along the growth direction (figure 2.99(a)) exhibit high strain fields with  $\Delta n < 2 x 10^{-6}$ , as compared to the images perpendicular to the growth direction (figure 2.99(b)) where  $\Delta n < 5 x 10^{-7}$  [55].



Figure 2.99 Birefringence images (a) along, and (b) perpendicular to the growth direction [55].

At the low defect region, the dislocation density was measured as 400/ cm<sup>2</sup>. This behavior was then exploited to deposit low defect substrates by flipping the CVD substrates perpendicular to the original growth direction as the threaded dislocation propagate only along the original growth direction (figure 2.100) [57].



Figure 2.100 Three orthogonal growth steps to reduce dislocation density [57].

Nomarski images obtained by differential interference contrast microscopy (DICM) also provide a very useful surface analysis method to determine the dislocations in the substrate. Figure 2.101 shows the correlation between obtained birefringence, DICM and also etch pits obtained after etching the CVD surface [58]. It is clear that bundles of dislocations and etch pits (marked by point A red circle) result in a larger birefringence. Thus, the quality of the initial substrate is extremely important to grow high quality CVD substrates. By starting with nitrogen doped, type IIa and low defect density seed substrates, low dislocation density (~ 400 /cm<sup>2</sup>) CVD substrates have been synthesized [102].



Figure 2.101 (a) Birefringence image before etching, (b) Normarski (DICM) image after etching of the same spot, (c) Etch pit and birefringence analysis of the same spot after etching [58].

It has been observed with XRT and transmission electron microscopy (TEM) that with increasing film thickness, the dislocation density decreases ([37], [138], [139]) as they move towards the substrate edges. This has been done by angling the top surface. Surface features called "risers" were observed with step flow growth on homo- and hetero – epitaxial growth (figure 2.102) [59]. A CVD substrate grown on an 8° (100) offset HPHT substrate was etched and analyzed. The etch pits were formed at the tip of the V – shaped risers (figure 2.102(b) – red lined ellipses) according to the model (figure 2.102(a)).



Figure 2.102 (a) Numerical modeling of the development of the riser feature with the propagation of the dislocations, (b) Etch pits formed at the tip of the risers [59].

Figure 2.103 shows a cross- sectional view of the grown CVD substrate. The risers propagate (green lines) along the direction of step flow. Thus, the dislocations also propagate towards the edges of the substrate along the risers. Such a lateral displacement of the dislocations is an important observation and will be exploited in this thesis on flat (100) oriented HPHT substrates.



Figure 2.103 Cross – sectional SEM image of the propagation of risers with step flow growth [59].

# CHAPTER 3 MICROWAVE CAVITY PLASMA REACTOR B: MULTI – VARIABLE EXPERIMENTAL SPACE, EXPERIMENTAL SETUP, AND OPERATIONAL PROCEDURES

## **3.1 Introduction**

Most of the research in this dissertation has been conducted in the microwave cavity plasma reactor (MCPR) B design. This chapter provides a detailed description about this reactor configuration. First, the various components and connections of the entire system setup are figuratively shown and then described. The single crystal diamond synthesis occurs over a multi – variable experimental space. A comprehensive analysis of the different internal and external variables is also presented here. Several different operating procedures are implemented throughout the growth process. These include the pretreatment steps of cleaning the system and also the substrate itself. Different configurations of the cooling stage and additional shim sets have been utilized for the synthesis experiments and for the microwave coupling efficiency measurements (discussed in chapters 5 and 6). These configurations will also be discussed here. Finally, some of the initial measurement and analysis techniques are described here.

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# 3.2 Experimental setup

The schematic design of the entire setup for reactor B is shown in figure 3.1. The important components of the setup are divided into five main parts (separated by 5 sets of colored circles).



Figure 3.1 Schematic of the entire microwave cavity plasma reactor B setup.

#### 3.2.1 Microwave power supply and waveguide transmission setup

This comprises of a (1) 2.45 GHz, 6 kW Cober (S6F/4503) microwave power supply which consists of a (2) dummy load which absorbs the reflected power, (3) magnetron and a (4) circulator circuit. The magnetron tube and the circulator are internally water cooled (not shown in figure 3.1) via a house water line with input and output water pipes. This entire microwave power assembly is then connected to the waveguide and transmission system. It is first connected to an (5) S – band rigid rectangular waveguide which is air cooled, a (6) dual directional coupler and then finally to a (7) rectangular flexible waveguide. The rigid waveguide comprises of a straight copper waveguide (WR340) and a 90° bend which connects to the flexible waveguide. The other end of the flexible waveguide is connected to a (8) rectangular waveguide - coaxial line transition unit. Two power meters (60 dB) are connected to the rectangular waveguide line. These measure the (9) incident microwave power into the microwave reactor and the (10) reflected microwave power into the circulator. The power supply also has an arc detector in the front panel. This detects any arc or short circuit within the waveguide and shuts down the microwave power in the event that a microwave arc occurs within the waveguide system. The arc indicator light then turns on in the front panel of the power supply.

#### 3.2.2 Microwave reactor assembly and adjoining elements

The transition unit (mentioned above) connects the flexible rectangular waveguide and the (11) coaxial coupling probe. This probe consists of a central conducting coaxial probe running along the z – axis of the (12) Ø symmetric microwave reactor cavity. Figure 3.2 shows the design of the cylindrical cavity shell used for the experiments conducted in

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reactor B. It has two viewing ports at an angle to the front of the chamber. Figure 3.2(a) shows the cross – sectional view of the cavity from the bottom and figure 3.2(b) shows the front view of the cavity shell. Although this cavity shell shown in figure 3.2(b) was designed for some electric field measurements but the design is very similar to the design of the shell used for the PCD and SCD deposition experiments described in chapters 4 and 5 respectively.



Figure 3.2 (a) Top and (b) front view of the microwave reactor cavity design.



The top of the cavity is fixed with a (13) sliding short mechanism which helps in the tuning of the reactor cavity during operation. More about the reactor tuning is discussed in chapter 4. The reactor cavity consists of a (14) quartz bell jar in the lower part which confines the flow of the gases. The flange of the bell jar is affixed to a (15) stainless steel baseplate at the bottom of the cavity. During operation, the substrate and the substrate holder is placed over a (16) water cooled stage which is attached to the bottom of the cavity with the help of bolts. A (17) monochromatic pyrometer was setup on a tripod which was held in a fixed position for all experiments. This enabled a consistent measurement

of substrate temperatures. In a similar way, a (18) Canon EOS 60D camera was setup on another tripod to capture high resolution photographs of the microwave discharge during operation. During SCD synthesis, when the camera was not in use, a D – link webcam (cloud camera 1100) was set up at the same position for live monitoring of the microwave discharge. It was connected to the MSU engineering server via the Department of Engineering Computing Service (DECS) domain.

The base plate was placed on a (19) vacuum chamber, spaced by an o – ring in between. The vacuum chamber has a (20) front loading door for mounting the substrate and the substrate holder onto the water cooled stage which is then bolted to the bottom of the base plate.

#### 3.2.3 Vacuum system and connecting controls

The pressure of the vacuum chamber was measured with the help of two ((21) and (22)) pressure gauges (MKS 627B) connected to the side of the chamber. These are connected to 2 Baratron capacitance manometers to measure higher pressures (> 10 Torr) and lower pressures (< 10 Torr) respectively, within the vacuum chamber. A (23) pressure controller (MKS 651) controls the operating pressure inside the chamber during a process. The low pressure gauge is connected to a power supply readout (MKS PDR–C–RC). The vacuum chamber is also connected to a (24) vacuum pump via a (25) throttle valve which is in turn connected to the same pressure controller (23) as above. During reactor operation (typically 240 Torr), the throttle valve is kept open at 7 – 9% (as seen on the pressure controller) to maintain a constant operating pressure. For the entire length of this thesis, two mechanical roughing vacuum pumps were used: (a) Adixden 2021 SD,

which was later replaced by an (b) Alcatel 2010 SD. The pump was used to reduce the vacuum pressure to  $\sim 1 - 2$  mTorr after overnight pumping. In order to ensure that no hydrogen gas leaks out of the system during operation of the system, a (26) nitrogen gas purging line ( $\sim 10$  psi) was connected to the (27) exhaust line of the system to dilute the exhaust gas mixture. For the venting process, another (29) nitrogen gas line ( $\sim 60$  psi) was connected to the vacuum chamber through a (28) vent valve which is operated via the pressure controller. This nitrogen gas venting ensured that the mostly hydrogen gas was kept below the explosion limit.

#### 3.2.4 Gas flow lines and computer controls

The pressure controller is then finally connected to the (30) computer setup which runs a preset program, developed with a Labview software module, during the reactor operation. Three system recipes have been used in this dissertation. They are named as: "kwh\_scd1", "kwh\_scd2", and "zuo\_clean". More operational details are provided later in this chapter. The reactor is connected to four gas lines: (31) CO<sub>2</sub>, (32) H<sub>2</sub>, (33) Ar, and (34) CH<sub>4</sub>. These are in turn connected to four (35) mass flow controllers which are controlled by a (36) 4 channel main flow controller (MKS 247C). This controller has four channels: channel 1 (CO<sub>2</sub>), channel 2 (H<sub>2</sub>), channel 3 (Ar), and channel 4 (CH<sub>4</sub>). These gas channels can be controlled from the front panel or from the rear panel of the controller that has an analog interface for remote setting. It is important to minimize any impurities in the system during deposition experiments. Thus, research grade gases are used for both CH<sub>4</sub> and H<sub>2</sub> gases which are 99.999% (5N) and 99.9995% (5.5N) pure respectively. The carbon dioxide and argon gases are used for the cleaning of the quartz bell jar by oxygen plasma etching. Although they are not used for any synthesis experiments, the argon gas line is always kept open so that any gas leaks from the gas lines may result in only the leakage of an inert gas. All four gas lines are first mixed into one main line which is connected via a (37) main gas valve to the base plate. This main gas line splits into uniformly distributed entrant holes around the bottom of the quartz bell jar, such that the entry of the feed gas mixture is uniform throughout the volume of the quartz dome. The exhaust gases then flow out of the cavity through 16 holes drilled around the annular substrate holder, through the quartz tube parallel to the cooling stage and then out at through the holes at the bottom of the annular stage into the vacuum chamber.

All connections i.e. the gas flows, reflected and incident microwave powers, and operating pressure levels are controlled by and are in sync with the computer program. These variables run on preset values set according to the computer program. The safety of the system is also regulated by the automated computer setup. If the reflected microwave power reaches 25% of the incident microwave power, or if the operating pressure fluctuates by more than 1 Torr, then the computer automatically shuts down the microwave power supply. The entire reactor process from the process start up to process shut down is controlled by the computer.

#### 3.2.5 Cooling systems

Since the reactor runs at high deposition pressures and power levels it is important to have an efficient cooling system. The reactor is connected to a (38) Neslab CFT – 300 water chiller whose temperature can be maintained between  $15 - 22^{\circ}$ C, but is usually kept at 18°C. A main water line runs from the chiller to system and splits into two parts.

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The (39) first water line flows into the base plate and the water circulates within the grooves laid out inside the base plate. The (40) second water line enters the sliding short mechanism through a (41) water flow controller. This water line is also connected to the cooling stage (not shown in figure 3.1). Thus, the cooling stage temperature may be controlled by adjusting the water flow controller. Usually the cooling stage temperature is kept constant with no variation in the water flow controller. Under these settings, the water flow rate into the cooling stage is usually 0.52 - 0.6 gallons/min.

For further cooling of the reactor, an air blower is fixed to the back of the cavity. The air flows through an inlet into the (12) cavity shell in order to constantly cool the quartz bell jar/ dome during the reactor operation. Additionally, there are four fans on the system, of which one cools the microwave power supply and the other three cool the cavity during operation.

#### 3.2.6 Substrate holder stages

The water cooled substrate holder stage is an important component of the diamond system. The entire setup for the cooling stage inside the reactor is shown in figure 3.3 [43]. Here,  $L_s$  is the length of the cylindrical cavity or the short length. L1 and L2 are distances between the top of the substrate holder and the z = 0 plane and the bottom of the cooling stage respectively. The z = 0 plane (shown in figure 3.3 and figures 2.66 and 2.68) is defined as the plane of discontinuity between the cylindrical and coaxial parts of the cavity. Depending upon the experimental procedure, several different shim sets can be added to the setup in order to vary the distance between the substrate holder and the z = 0 plane. In this dissertation, L1 has been varied between 52.93 mm and 55.76 mm

(depending on substrate holder thickness), while L2 has been varied from 54.7 mm to 61.1 mm (depending on shim thickness). Thus, the substrate position, which is given by:  $z_s = L1 - L2$ , has been varied from -1.77 mm to -8.17 mm. The different  $z_s$  positions along with the varying L1 and L2 lengths are tabulated in appendix B.



Figure 3.3 Entire cooling stage setup inside the reactor cavity [43].

Figure 3.4 shows a more detailed cross – sectional view of the cooling stage ([43], [45]). The material used to design the cooling stage is stainless steel. In order to have an

efficient cooling system for the substrate holder and the substrate, the water lines run into the base of the holder. As seen in figure 3.4, a central water line runs into the stage and then there is one line for the water to flow out. Each of these pipes is 9.5 mm (0.375 inches) in diameter. The bottom of the stage is attached to a conducting plate that has a diameter of 15.24 cm (6 inches) and a thickness of 6.35 cm (0.25 inches). This stainless steel plate helps in the conduction of electromagnetic induced surface currents along the walls of the brass reactor cavity and thereby completes the electrical circuit for exciting the required electromagnetic modes. The walls of the cooling stage are 2.54 mm (0.1 inch) thick and the height of the cooling stage is 50.8 mm (2 inches). At the top of the cooling stage, there is a slight indentation (1.14 mm i.e. 0.045 inch) of the inner walls of the stage. This helps in the placement of the substrate holder and prevents it from being off – centered during the reactor operation. A circular groove, concentric to the cooling stage holds a quartz tube (figure 3.4) of thickness ~ 2.1 mm. This quartz tube directs the exhaust gases to flow out of the system through 8 holes drilled into the conducting plate. During the growth process, the temperature of the quartz tube increases, thereby expanding the walls of the quartz tube. Hence, an additional 1-2 mm space is provided in the width of the circular groove to allow for the expansion in the quartz tube. Similarly, the substrate holder sits slightly separated at the top of the tube (figure 3.4) to allow for the vertical expansion of the quartz tube.

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Figure 3.4 Drawing of the cooling stage used for reactor B operation ([43], [45]).



Figure 3.5 Schematic of a quartz tube.

During the cleaning of the quartz dome/ bell jar with an oxygen plasma treatment, a different substrate holder stage is used. This floating stage [140] stems from a reactor A design with a wider radius. It is not water cooled since it is used at a low pressure of 60 Torr. But similar to the cooling stage, it consists of a quartz tube to streamline the flow of the exhaust gas.

#### 3.2.7 Substrate holder configurations

Many different substrate holder designs have been used for the diamond synthesis experiments. All substrate holders utilized in this thesis have been fabricated from molybdenum obtained from Ed Fagan Inc. and fabricated by the machine shop in the Department of Physics at MSU.

#### 3.2.7.1 Substrate holder for polycrystalline diamond deposition

For the operational field map discussion, presented in chapter 4, polycrystalline diamond was deposited on a silicon wafer. For this purpose, a 2.55 inch substrate holder (SN–2inch–SCD) was used with holes drilled around the circumference (figure 3.6). These holes allow the exhaust gases to flow out of the system via the underlying quartz tube. Figure 3.6 shows the Solidworks drawing of the 2.55 inch holder. The inner concentric part of the holder (figure 3.6(b)) is placed directly above and in contact with the indentation in the cooling stage. For all polycrystalline diamond deposition discussed in this thesis, only this particular holder configuration has been used.



Figure 3.6 (a) Top view (b) bottom view – Solidworks drawing of a 2.55 inch substrate holder (SN–2inch–SCD). All units shown in the drawing are in inches.

#### 3.2.7.2 Pocket substrate holder for single crystal diamond deposition

For all single crystal diamond deposition experiments discussed in this thesis, the 2.55 inch substrate holder, shown in figure 3.6, forms the bottom piece of the entire holder configuration. The Solidworks drawing of a typical 1.5 inch diameter top piece (SN–1 inch–01–1.8) for SCD experiments is shown in figure 3.7. The diameter of this "pocket"

holder is same as the inner diameter of the concentric part of the 2.55 inch holder (figure 3.6) such that the two pieces fit directly above the cooling stage indentation. Figure 3.7 shows a substrate holder for SCD synthesis using a  $3.5 \times 3.5 \times -1.5 \text{ mm}^3$  HPHT type Ib seed from Sumitomo Electric. The seed is placed within the pocket during the deposition process. More details about this pocket holder design and its effect on the SCD growth process are described in chapter 5.

In addition to the two pieces shown in figures 3.6 and 3.7, an extra insert was used in several experiments to obtain the substrate temperature for deposition with only a required amount of incident microwave power. This insert is a flat molybdenum disk that has a diameter of 1.5 inch and a thickness of ~ 0.7 mm. Hence, the order of the holder components for SCD deposition is as follows (from the cooling stage upwards): (i) 2.55 inch substrate holder, (ii) flat insert, (iii) SCD 1.5 inch pocket substrate holder, (iv) SCD substrate.



Figure 3.7 Solidworks drawing of a 1.5 inch diameter "pocket" substrate holder (SN– 1inch–01–1.8) [45].

Figure 3.7 (cont'd)



In this dissertation, many different variations of the 1.5 inch diameter pocket holder have been employed for the SCD deposition experiments. A full list of these variations, which have been utilized in this thesis, have been given in appendix B. The difference in these substrate holder variations is that while the diameter of the holder is still the same, i.e. 1.5 inch, the (i) depth of the pocket ranges from 0.5 - 3.0 mm, (ii) length varies between 4 - 7 mm, and (iii) breadth varies from 3.7 - 7 mm.

One such variation is shown figure 3.8. For the flipped seed SCD experiments discussed in chapter 7, the dimensions of the pocket were changed. The Solidworks drawing for this holder (SN–1inch–side1) is shown in figure 3.8.



Figure 3.8 Solidworks drawing of a 1.5 inch "pocket" substrate holder (SN–1inch–side1) for side surface growth on flipped seeds.

#### 3.2.7.3 Open substrate holder for single crystal diamond deposition

In chapter 5, a few of the single crystal diamond deposition experiments have been performed in an "open" holder. Figure 3.9 shows a Solidworks drawing of the "open" holder.



Figure 3.9 Solidworks drawing of a 2.55 inch "open" substrate holder (SN-2inch-indent).

In contrast to the pocket holder shown in section 3.2.7.2, the open holder configuration consisted of only the substrate holder shown in figure 3.9. Also, this holder does not have a pocket. Instead, it contains only a slight indentation at the center to hold the diamond seed. So almost the entire seed penetrates into the microwave discharge during the synthesis process. The disadvantages of such a holder is discussed in length in chapter 5.

#### 3.2.7.4 Forced flow substrate holder for single crystal diamond deposition

In an effort for enhancing the CVD substrate surface area for growth, some initial tests were carried out with a new substrate holder design. This "forced flow" substrate holder was first designed in this thesis and then fabricated by the Physics machine shop. It comprises of 2 parts. Figure 3.10 shows the Solidworks drawing of the bottom part of the forced flow holder configuration with a slight indentation at the center to hold the seed.



Figure 3.10 Bottom part of the "forced flow" holder (SN–1inch–forced1).

Figure 3.11 shows the top section of the holder through which the gas flow is forced through onto the seed surface. The 8 projections/legs seen under the holder (figure 3.11) are placed on the cooling stage and help in the cooling of the top surface of the holder. The holder shown in figure 3.10 is placed directly under the central hole of this holder (figure 3.11) such that the flow of gases is directly onto the seed surface. For some of the

initial experiments, the insert (mentioned in section 3.2.7.2) was also used. Chapter 7 discusses these forced flow holder experiments in further detail. See figure 7.14 in chapter 7 which shows the entire forced flow holder setup for deposition experiments.



Figure 3.11 Solidworks drawing of top section of the forced flow holder (SN-2inchforced).

# 3.3 Multi – variable experimental space: input, internal and output variables

The chemical vapor deposition of diamond is dependent upon several experimental variables. These variables can be classified into 3 main groups: (a) input (U), (b) internal (X), and (c) output (Y) variables [4]. These 3 groups can then further be divided into subgroups which are shown in figure 3.12. Following is a discussion on the variables used in this thesis and the reactor parameter space that the microwave system was operated in.

### 3.3.1 Input variables (U)

The variables which can be defined and controlled by the person operating and designing the microwave plasma reactor are termed here as the input variables. They consist of the following different subs-sections. Only the actively utilized variables are mentioned in this section.



Figure 3.12 The multivariable experimental space for deposition of diamond in the microwave plasma reactor [4].

# 3.3.1.1 Reactor design variables (U<sub>1</sub>)

The reactor design parameters refer to the ones that are concerned with the overall setup and geometrical structure of the experimental reactor system. Table 3.1 displays the reactor variables utilized for optimization and synthesis experiments and its construction.

Table 3.1 List of reactor design variables used.

	eeed eeningeration
Reactor configuration	Reactor B
Type of power source	2.45 GHz Cober microwave power supply
Reactor wall material	Brass
Substrate biasing	None
Substrate cooling	Water cooled stage: 0.5 – 0.6 g/min
Substrate heating	Indirect heating: microwave discharge

# 3.3.1.2 Controllable input variables (U<sub>2</sub>)

Reactor design parameter

Table 3.2 lists all the controllable variables used in this dissertation. These variables refer to the parameters that are kept constant during a single experimental run by the reactor operator.

Table 3.2 List of input variables controlled by the operator.

Controllable	input	variable
Controllable	πipuι	variable

Set value

Used configuration

Substrate holder material	Molybdenum
Substrate holder configuration	Pocket (2 – 3 parts)/ open (1 part)/ forced flow (2 – 3 parts) holder
Table 3.2 (cont'd)

Gas chemistry	Synthesis: CH <sub>4</sub> /H <sub>2</sub> , etching: H <sub>2</sub> , dome cleaning: CO <sub>2</sub> /Ar
Hydrogen flow rate	400 sccm
Methane concentration	3 – 7%
Deposition pressure	130 – 240 Torr
Intentional nitrogen gas	None
Reactor optimization	Ls, Lp, L1, L2
Substrate position	$Z_s = L1 - L2$

# 3.3.1.3 Deposition process variables (U<sub>3</sub>)

The synthesis process variables are related to the growth duration and the substrate material characteristics. These are listed in table 3.3 below.

Table 3.3 List of deposition process variables utilized.

Deposition process variable	Utilized parameter
Deposition time	8 – 36 hours
Substrate material	<ul><li>(a) HPHT seed from Sumitomo Electric</li><li>(b) CVD plate from Microwave Enterprises</li></ul>
Substrate size	$\sim 2.3 - 7 \times 2.5 - 7 \times 0.4 - 1.45 \text{ mm}^3$
Substrate seeding	For PCD on Silicon wafer: 0.25 µm diamond powder
Input power	1.5 – 2.4 kW
Substrate temperature	1000 – 1150°C

#### 3.3.2 Internal variables (X)

The internal variables define the inherent plasma and system properties during a reactor process. Some of the variables are listed in table 3.4. Other parameters include gas temperature, electron temperature, gas residence time and microwave electromagnetic field strength.

In a process, when the pressure increases, the plasma volume decreases and hence the absorbed microwave power density increases for a constant absorbed microwave power level. Moreover, when the absorbed microwave power increases for a constant pressure, the microwave discharge volume also increases. But the absorbed microwave power density remains almost the same within the operating regime mentioned in chapter 4.

Internal variable	Used configuration
Absorbed microwave power	$P_{abs} = P_{inc} - P_{ref}$
Plasma volume	V <sub>d</sub>
Absorbed power density	$< P_{abs} > = P_{abs}/V_d$ : ~ 500 W/cm <sup>3</sup> at 240 Torr

Table 3.4 Some internal variables utilized in this thesis.

#### 3.3.3 Output variables (Y)

The system output variables are subdivided into 2 sub–sections. These describe the operation and the performance of the system itself and also the characteristics of the synthesized final CVD diamond substrate.

#### **3.3.3.1 Reactor performance (Y<sub>1</sub>)**

As has been discussed in section 2.5, the linear growth rate ( $\mu$ m/hr) of diamond deposition may be enhanced by operating at high pressures, high methane and nitrogen concentrations, appropriate high substrate temperatures and with a high absorbed microwave power density (figures 2.8, 2.42, 2.50, 2.53, 2.56 and 2.57). A high linear growth rate is one of the important operating output parameters and a major criterion for obtaining large CVD diamond substrates.

The total growth rate ( $\mu$ m/hr or mg/hr) includes the growth of any polycrystalline diamond rim on the substrate. This is calculated by measuring the total weight gain of the substrate that includes both the polycrystalline and single crystalline parts.

#### 3.3.3.2 Film characteristics

The uniformity of the CVD substrates was observed while measuring the linear growth rate (discussed in section 3.5.4). Normally for all substrates grown with reactor B, the uniformity was observed to be  $\pm 20 \ \mu m$ .

The surface morphology and texture was analyzed under a Nikon Eclipse ME600 optical microscope and by atomic force microscopy with a Cypher scanning probe microscopy respectively.

The CVD diamond quality was analyzed by UV/Vis and Fourier Transform Infrared (FTIR) spectroscopy, secondary ion mass spectroscopy (SIMS), birefringence imaging, Nomarski images taken by Differential Interference Contrast Microscopy (DICM), etch pit density analysis, x – ray topography (XRT), field emission scanning electron microscope (FESEM) and with energy dispersive spectroscopy/ x – ray analysis (EDS/EDAX).

For all experiments described in this thesis, the reactor design variables and the deposition process variables were kept constant throughout the reactor process. Depending on the experiment being performed, the controllable input variables were adjusted accordingly and then kept fixed for the entirety of the synthesis process. Some of the internal variables like the substrate temperature were measured during the experiment. Finally, after the conclusion of the process, the output variables were analyzed.

# 3.4 Microwave plasma reactor and its components: operating procedures

#### 3.4.1 Substrate and substrate holder preparation and cleaning procedure

#### 3.4.1.1 Pre – growth operating procedure

In this dissertation, two different substrates have been used to conduct deposition experiments. In chapter 3, microwave coupling efficiency experiments are discussed. These experiments were conducted with a 1 inch (2.54 cm) diameter silicon wafer as the substrate. A layer of polycrystalline diamond was deposited on top of the silicon wafer. In order to grow the polycrystalline diamond layer, it was important to first enhance the nucleation of the diamond islands on the substrate surface. For this purpose, 0.25 µm size natural diamond powder granules were used. These were sprinkled on the smooth and polished surface of the silicon wafer. Then with the help of a cleaning wipe and circular finger movements, the surface of the wafer was scratched seeded for atleast 10 - 15 minutes. The surface was observed under bright light to ensure that the entire surface was covered by an almost uniform distribution of scratch marks. This is a critical procedure since it is important that a uniform nucleation of diamond occurs over the entire surface thereby leading to a uniform growth of the PCD layer. The excess diamond powder on the substrate was then removed by wiping the surface with ethanol. Thereafter, the scratched silicon wafer was ultrasonicated in ethanol, rinsed with distilled water and then blow dried with nitrogen gas. Once the substrate was clean, it was loaded into the reactor for deposition.

The second type of substrate was used for single crystal diamond deposition studies (described in chapter 5 and 6). These substrates were HPHT type Ib diamond seeds i.e.

Sumicrystal UP cutting tool blanks (order number: UP353514) from Sumitomo Electric. The typical dimensions of these seeds were ~  $3.5 \times 3.5 \times 1.3 - 1.5 \text{ mm}^3$  (figures 3.13 and 3.14). As seen in figure 3.14(b), the top surface of the seeds is slightly larger (~  $3.7 \times 3.7 \text{ mm}^2$ ) than the bottom surface. Throughout the pre – growth procedure, the top larger surface is firstly carefully analyzed by taking weight and thickness measurements and then is thoroughly cleaned to remove any impurities.



Figure 3.13 HPHT type Ib diamond seed from Sumitomo Electric for SCD synthesis.



Figure 3.14 (a) Top view, and (b) side view with dimensions of a typical HPHT type Ib diamond seed from Sumitomo Electric.

For the cleaning procedure, the seed is first placed in a beaker with a mixture of nitric and sulfuric acids. The mixture of these acids contains 40 ml each of nitric and sulfuric acids, i.e. in a 1:1 ratio. The seed is heated in this acid solution at 350°C on a hot plate for 20 minutes. At this temperature, the acid mixture is at its boiling point, which helps in removing impurities (like oil) from the seed surface. This cleaning step is followed by another 20 minute acid cleaning step by boiling the seed in ~ 60 ml of hydrochloric acid. In between these acid cleaning steps, the seed was dipped in distilled water to remove any acid residue. For some of the initial experiments, the seed was also heated with 40 ml of ammonium hydroxide for 15 minutes. But due to safety issues in the lab fumehood and also since ammonium hydroxide did not improve the seed surface drastically, this cleaning step was eliminated from the seed cleaning procedure of all later experiments. After this, the seed was washed in distilled water and then ultrasonicated with 60 ml of acetone followed by 60 ml of methanol for 15 minutes each. The seed was then washed in distilled water to remove any solvent residue and then blow dried in nitrogen gas. Thereafter, the seed was immediately loaded into the reactor for deposition experiments.

Before the loading of the seed, the molybdenum substrate holders were cleaned with ethanol and then rinsed with distilled water. The water on the holder surface was wiped clean and then the holders were placed in an air drier for atleast 40 minutes.

#### 3.4.1.2 Post – growth operating procedure

After the entire deposition procedure, the substrate was unloaded from the reactor cavity. In order to clean any graphitic phase  $(sp^2)$  residue on the substrate, it was first boiled in a 1:1 mixture of nitric and sulfuric acids for atleast an hour or until the substrate surface was rid of any excess carbon deposition. The substrate was then washed in

distilled water and then ultrasonicated in methanol for 15 minutes after which it was washed again in distilled water and then blow dried in nitrogen gas.

For many substrates discussed in chapter 5 and 6, the CVD grown SCD plate was removed from the HPHT seed by laser cutting. The CVD plate was then polished on both the growth and the laser cut surface with the help of a Coborn PL3 planetary lapping bench [141]. At times, any polycrystalline deposition on the edges of the SCD surface was also trimmed off with the help of the laser.

After the deposition process, the holder surface has a layer of polycrystalline diamond. For future experiments, it was important to remove this layer to maintain consistent initial conditions. In order to remove this diamond layer from the holder surface, the holder was blasted with short bursts of glass beads at a high velocity. It was important that the sandblasting be done only for a very short amount of time in order to prevent the deterioration of the holder surface due to the high velocity particles. If the holder surface becomes too rough during sandblasting, the unwanted deposition of polycrystalline diamond on the surface becomes faster, thereby affecting the overall efficiency of the single crystal growth process. Following this sandblasting procedure, the holders were cleaned with ethanol to remove any residue of the sand, rinsed with distilled water and finally placed in a hot oven to be dried.

#### 3.4.2 Substrate loading into the microwave reactor

Once the seed was cleaned with acids and ultrasonicated in solvents, the system was prepared for loading the seed into the reactor for experiments. First, the appropriate substrate holder was cleaned with the process mentioned in section 3.4.1.1. The

substrate holder was chosen depending upon the spatial relationship between the top surface of the holder and top surface of the seed. This spatial relationship is discussed in much greater detail in chapter 5. The cooling stage and the bottom surface of the quartz dome were thoroughly cleaned with ethanol. The shim set and the quartz tube used for deposition experiments were also similarly cleaned. For the loading procedure, first, the shim set was aligned with the four screws at the bottom of the baseplate inside the vacuum chamber. It was adjusted such that it was in a stable position on the four screws. Next, the seed was placed in the pocket of the holder with the slightly larger surface being the top surface for growth. Depending upon the experiment being conducted, the substrate holder configuration was adjusted accordingly. The different holder configurations used for the experiments are listed in appendix B. The quartz tube was next placed on the cooling stage that was then held upright. The substrate holder with the seed was then gently positioned above the quartz tube. By slightly rotating the quartz tube and then the holder, it was verified that there was enough space between the two to allow for their expansion during the growth experiments at high temperatures. The entire cooling stage assembly was then slowly fitted onto the four screws under the shim set. Nuts were tightened at the bottom of the screws to fix the cooling stage in place. By shining a torch through the viewing ports into the cavity, it was also ensured that the seed was still placed inside the pocket. The door of the vacuum chamber was then tightened and the "open" button on the pressure controller was pressed to open the throttle valve and to allow the pumping down of the reactor cavity.

#### 3.4.3 Reactor leak test

Before beginning each synthesis experiment, it was important to first evaluate the leak rate of the reactor. From this leak rate, the nitrogen impurity in the experiment can be calculated. To start the leak rate, it was first ensured that the valve connecting the gas lines and the vacuum chamber, and the valve for the venting were completely closed. The throttle valve was then closed by pressing "close" on the pressure controller. After 1 hour of leak test, the throttle valve was reopened. The pressure on the pressure controller was noted before and after the leak test to determine the leak rate (section 3.5.1).

#### 3.4.4 Microwave reactor start up procedure

After the leak test, the different components of the reactor are opened in the following order:

- (a) Computer
- (b) Main gas valve
- (c) House water line to the microwave power supply
- (c) Fan and blower behind the reactor
- (d) Nitrogen purge line
- (e) Chiller
- (f) Incident and reflected power meters
- (g) Microwave power supply
- (h) The required gas bottles

It takes around 2 minutes for the microwave power supply to warm up after which the light bulbs on the front panel of the power supply turn on. The incident and the reflected power meters, and the pressure controller were then zeroed. The key on the pressure controller was turned 90° counter – clockwise to set the gas flow operation in its remote position. Depending upon the experiment, the appropriate gas channels were toggled to the "Rem" i.e. the remote setting in the MKS gas flow controller accordingly. The different gases then start flowing into the cavity according to the preset values. The Labview software module was turned on. By choosing the "create/edit mode" on the module, the different recipes can be chosen for the experiment. Variations in the preset recipe can be made in this mode of the software. For the growth process, the hydrogen (channel 2) and methane (channel 4) were turned on in the gas flow controller and the recipe "kwh scd1" was chosen. For an etching or conditioning process (discussed in the section 3.4.7), only hydrogen (channel 2) was flipped on and the recipe "kwh scd2" was chosen. Finally, for the plasma cleaning procedure of the quartz dome (section 3.4.9), the carbon dioxide (channel 1) and argon (channel 3) were flipped on and the recipe "zuo clean" was chosen on the software. Once the required recipe was chosen and adjustments in the values were made, the "Automode" was chosen where the same recipe was selected for the process to begin. The pressure then starts increasing which can also be seen on the graph on the software module. Once it reaches ~ 5 Torr, the microwave power supply indicator on the Labview module turns on indicating that the power supply can now be switched on and the "Ready" bulb lights up on the front panel of the power supply. The power supply was then turned "On" on the front panel and the power was slowly increased to ~ 1 kW. The microwave discharge can now be seen from the viewing port and it looks dispersed inside the whole dome with a light purple color. The microwave power was slowly increased at constant intervals of increasing pressure levels. After the ramp up

was complete and the required pressure level was reached, the other three fans were turned on and the web cam was positioned such that the microwave discharge can be viewed.

#### 3.4.5 Microwave reactor shut down procedure

Once the entire experiment was completed, the microwave discharge shut down automatically since the power supply turns off. The gas flow turned off as well except for the hydrogen gas line. The pressure decreases as was set by the preset values in the chosen recipe. It takes 10 - 15 minutes for the pressure to go to ~ 0 Torr at which point the components of the system were turned off in the following order:

- (a) Computer software was "Shutdown"
- (b) The gas flow switches were toggled off
- (c) The key on the pressure controller was rotated 90° clockwise
- (d) The throttle valve was opened to pump the residual gas out
- (e) All gas bottles
- (f) Microwave power supply
- (g) Main gas valve
- (h) House water line to the microwave power supply
- (i) Air blower and fan behind the reactor
- (j) Nitrogen purging gas bottle
- (k) Chiller
- (I) Incident and reflected power meters
- (m) All other fans

#### 3.4.6 Unloading of the diamond substrate

When the system is cooled down, the substrate could be unloaded from the chamber. First, the throttle valve was closed via the pressure controller. The front door of the vacuum chamber was also loosened. Then, the vent valve (green valve) in front of the vacuum chamber on the support table was opened very slowly while carefully monitoring the increasing pressure level on the pressure display. Nitrogen gas flows into the vacuum chamber during the venting process. The valve was opened only so much that the there is a steady slow rate of increase in the pressure level. Once the pressure reaches to ~ 720 Torr, the vent valve was closed partly and the vacuum chamber door was slowly pulled open. After the door was open, the vent valve was closed completely.

The four nuts holding the cooling stage in place were then unscrewed while holding the cooling stage constant with one hand. The stage was slowly lowered and the holder with the substrate were taken out of the chamber. Then the quartz tube and the shim set were removed from the cooling stage. These different components were then cleaned by the previous mentioned steps for future experiments.

#### 3.4.7 New substrate holder conditioning procedure

For the many different experiments discussed in this thesis, various substrate holder designs have been fabricated. A few of them have been displayed in section 3.2.7. After their fabrication, the contaminants on the surface need to be removed for experiments. In order to clean these holders, they were etched in the presence of a hydrogen plasma in the reactor. After cleaning the new substrate holder surface with ethanol and drying it in the hot oven, the new empty substrate holder was loaded into the cavity. The "kwh scd2"

recipe was selected for the conditioning process. Usually the holder conditioning process was carried out for 6 hours in a hydrogen plasma at 240 Torr and with 1.8 – 2.0 kW. During the system start up procedure, the hydrogen gas line (channel 2) was flipped to the "Rem" setting and from "ext.", i.e. the external or the computer setting, to the "flow" setting. The hydrogen "flow" rate is set at ~ 1000 sccm such that the pressure ramp up is faster. Once the required pressure level (i.e. 240 Torr) was reached, the hydrogen channel was flipped black to the "ext." setting which is fixed at 400 sccm for the rest of the experiment.

#### 3.4.8 Diamond synthesis procedure

Prior to the actual growth process, an additional step of hydrogen plasma etching the seed surface was conducted. This process was carried out to ensure that the surface was rid of any residual impurities, mechanical polishing damage and also to terminate the seed surface with hydrogen. The hydrogen termination of the seed surface is an important step to ensure the growth of diamond phase and to prevent any graphitic phase growth of carbon.

After the HPHT seed is loaded into the reactor, as mentioned in section 3.4.2, the computer software is set at the recipe "kwh\_scd2". Channel 2 (hydrogen gas) was switched to the "Rem" and "flow" setting. Now the pressure ramps up to 180 Torr with a 1000 sccm of hydrogen gas. Once a pressure of 180 Torr is reached, the channel 2 is flipped back to the "ext" setting i.e. at a flow rate of 400 sccm. The hydrogen etching of the seed is done for an hour with ~ 1.8 - 2.0 kW microwave power and at a substrate temperature of 1000 - 1050°C. The substrate and the plasma was monitored during the

etching process. After the etching process is complete, the system was shutdown using the procedure mentioned in section 3.4.5. The cavity was allowed to be pumped down for 30 minutes before the growth procedure was started.

For the synthesis process, a similar procedure like the etching was adopted. The recipe "kwh scd1" was chosen on the Labview module. The channels 2 and 4, i.e. the hydrogen and methane gas lines respectively, were flipped to the "Rem" setting and only channel 2 was flipped from the "ext" to the "flow" setting. The pressure ramp up then takes place with only a hydrogen plasma with the flow rate set at 1000 sccm. Once the required pressure (normally 240 Torr) was reached, the channel 2 was flipped back to the "ext" setting where the hydrogen flow rate as set by the computer is 400 sccm. During the ramp up process, the time, the input, incident and reflected powers, substrate temperature, water flow rate and the microwave power leak were all noted down. The microwave discharge was also monitored and checked to ensure that it did not interact with the walls of the quartz dome. At 240 Torr, the seed was again etched for 10 minutes at ~ 1100 -1150°C and with ~ 1.8 – 2.0 kW, before the flow of methane is started automatically at 20 sccm (for 5% CH<sub>4</sub>/H<sub>2</sub> concentration). Now the LEDs for both the hydrogen and the methane gas lines are on. The "display channel" can be rotated to view the flow rates for the different channels 1 - 4. Due to a calibration issue in the interface between the Labview module and MKS flow controller and readout, the methane gas flow rate needed to be changed accordingly. Table 3.5 shows the flow rate of methane set in the computer software and the actual flow rate that concentration represents for 400 sccm of hydrogen gas.

Table 3.5 Flow rate of methane as shown in the Labview module and in the MKS gas flow readout respectively.

3	1.182	12
4	1.576	16
5	1.97	20
6	2.364	24
7	2.758	28

%CH<sub>4</sub>/H<sub>2</sub> Flow rate on software (sccm) Actual concentration (sccm)

#### 3.4.9 Quartz dome cleaning procedure

After each deposition experiment, the dome was plasma etched to remove any soot and carbon deposition from the bottom surface. This helped in maintaining consistent initial conditions for the growth process. Here a floating stage [140] was used instead of the cooling stage (figure 3.4). This stage is not connected to any water cooling lines since the plasma etching is conducted for 1 hour at a low pressure (60 Torr) and power level (1.8 kW). No nitrogen purging or additional shim sets were used here. The floating stage was fixed to the bottom of the baseplate inside the vacuum chamber and then the cavity was pumped down. Only the carbon dioxide gas bottle was opened since the argon gas bottle was always kept open. The recipe "zuo\_clean" was selected during system startup. Channels 1 (carbon dioxide) and 3 (argon) were flipped to the "Rem" setting and only channel 3 was set to "flow". The argon gas flows at 400 sccm during ramp up and is switched back to 20 sccm after ramp up ("ext" setting). After the etching process, all components were shut down as previously mentioned in section 3.4.5.

#### 3.5 Some important reactor and substrate measurements

Before, during and after the deposition or etching experiments, several different sets of measurements were taken on substrate and on the system itself. In this section, the system leak rate before growth, microwave leak detection during growth, substrate temperature measurement, linear growth rate and growth rate by weight gain are discussed.

#### 3.5.1 System leak rate

For all SCD deposition experiments discussed in this dissertation, a vacuum leak test was performed at the beginning of the growth process. After the SCD seed was loaded into the reactor, the system was pumped down overnight (~ 12 hours) to the base pressure. Since the pressure controller is not calibrated, the base pressure reads ~ – 0.053 mmHg (1 mmHg = 1 Torr). Before the deposition run, the pressure on the power supply readout (MKS PDR–C–RC) was noted and then the throttle valve was closed with the help of the main pressure controller (MKS 651C) by pressing "close". On the readout of the pressure controller, the position ("pos") of the valve then reads "0%" which implies that the valve is now closed. The pressure is then noted after an hour of leak test following which the throttle valve is opened for the growth process. The leak rate is then calculated as follows:

$$Leak rate (mmHg/hr) = \frac{Vacuum \, pressure \, after 't' \, hours - Base \, pressure}{t}$$

$$Leak \, rate \, (mTorr/hr) = Leak \, rate \, (mmHg/hr) \, x \, 1000$$

Here, "t" is the number of hours for which the throttle valve is closed. For almost all experiments conducted, the leak rate was between 0.5 and 1 mTorr/hr. This corresponds

to a nitrogen gas leak of ~ 6 – 10 ppm in reactor B (this calculation is shown in appendix C).

#### 3.5.2 Microwave leak detection

Another important pre – growth measurement is the detection of any microwave leaks in the system. For this purpose, a microwave leak detector is used (2450 MHz model 1501 microwave survey meter) with a microwave sensing head. The sensor is protected with a styrofoam cover designed in a conical shape. The maximum permissible microwave exposure is ~ 5 mW/cm<sup>2</sup>. To ensure that the experiments were conducted safely, the microwave leak detector was used to sense any microwave leaks in the system during operation. Specifically, areas around the finger stocks, viewing ports and the water line into the sliding short were carefully monitored. The microwave leaks detected for all experiments were within the range of 0.2 - 1 mW/cm<sup>2</sup> which is well within the maximum permissible limit for microwave exposure.

#### 3.5.3 Measurement of substrate temperature (T<sub>s</sub>)

The substrate temperature was measured with the help of a one color monochromatic (0.96  $\mu$ m) IRCON Ultimax optical pyrometer. For all single crystal synthesis experiments discussed in this thesis (chapters 5 and 6), the emissivity setting of the pyrometer was kept constant at e = 0.1. In chapter 3, experiments to determine the microwave coupling efficiency were carried out on a silicon wafer that was first grown over with a polycrystalline diamond layer. For these polycrystalline diamond growth experiments, the substrate temperature was measured with an emissivity setting of e = 0.6. As shown in

figure 3.1, the optical pyrometer is set up in a way such that it is approximately 60° to the z - axis of the cavity. Even though the temperature was measured through the quartz dome, the infrared wavelength of the pyrometer enables accurate substrate temperature measurements. The cross – section over which the temperature is measured, i.e. the beam diameter, is ~ 2 mm. In order to obtain consistent surface temperatures, the pyrometer was mounted on a tripod (not shown in figure 3.1) next to the vacuum chamber. The angle of the three legs of the tripod were kept fixed throughout all the experiments in this thesis. The leg positions were marked on the table. The height of the three legs of the tripod were also marked.

For the temperature measurements, the pyrometer reading was scanned over the entire surface. Multiple readings were obtained at several places over the substrate surface. However, only the highest and most repeatable temperature measurement was noted down. A temperature gradient of  $\sim 100 - 150^{\circ}$ C was observed between the substrate and the substrate holder surface during experiments, with the substrate being at a higher temperature as compared to the substrate holder surface. This reduced the polycrystalline diamond deposition rate on the holder surface versus the diamond deposition rate on the substrate.

#### 3.5.4 Linear growth rate

In this thesis one of the diamond growth rates mentioned is the "linear growth rate" which is calculated based on the measurements of the thickness of the substrate before and after the synthesis process. This is an average growth rate where the thickness measurements have been carried out five times on each of the four corners and on the

center and then averaged out. The average linear growth rate is given by the following equation:

Average Linear growth rate 
$$(\mu m/hr) = \frac{Avg.d_2 - Avg.d_1}{t}$$

Here " $Avg. d_1$ " and " $Avg. d_2$ " refer to the average thickness measurements (in µm) on the corners and center of the substrate before and after the deposition process. "t" refers to the total deposition time in hours.

#### 3.5.5 Growth rate by weight gain

The other growth rate mentioned in this thesis is the growth rate calculation by weight gain. Five weight measurements are taken before and after the synthesis process and then averaged out to give the weight gain after the deposition. The weight gain is then calculated by the following equation:

$$Weight gain(g) = Avg.w_2 - Avg.w_1$$

Here " $Avg.w_1$ " and " $Avg.w_2$ " refer to the average weight measurements (in grams) before and after growth. The thickness of the synthesized SCD substrate is then calculated for an initial 3.5 x 3.5 mm<sup>2</sup> HPHT seed substrate and with density of diamond of 3.515 g/cm<sup>3</sup>. It is given by the following equation:

Thickness (mm) = 
$$\frac{(Avg.w_2 - Avg.w_1) x 10^3}{3.5 x 3.5 x 3.515}$$

Then the growth rate by weight gain for a growth time "t" is given by the following equation:

Growth rate by weight gain 
$$(\mu m/hr) = \frac{Thickness (mm) \times 10^3}{t (hours)}$$

## CHAPTER 4 MICROWAVE COUPLING AND OPERATIONAL EFFICIENCIES OF A MICROWAVE PLASMA ASSISTED CVD REACTOR UNDER HIGH PRESSURE DIAMOND SYNTHESIS OPERATING CONDITIONS

# **4.1 Introduction**

Recent experiments have demonstrated the high rate synthesis of high quality single crystal diamond (SCD). The initial communications were reported in the late 90's and early 2000's ([63], [64]). and since then their results have been confirmed and extended by others ([12], [33], [65], [67]). All of the initial experiments employed single mode excited microwave discharges operating with H<sub>2</sub> and CH<sub>4</sub> gas mixtures at pressures of 100 – 180 Torr and with high microwave discharge power densities. They revealed the feasibility of high rate, homo-epitaxial SCD synthesis with growth rates of 50 – 150  $\mu$ m/h. Thus in recent years, interest in the synthesis of high quality SCD has dramatically increased.

The high pressure microwave plasma assisted chemical vapor deposition (MPACVD) SCD synthesis method is able to synthesize high purity and high quality SCDs at high rates uniformly over large deposition areas [142]. Presently it is the most prominent plasma assisted SCD synthesis method [68]. Microwave plasma reactor designs that were initially associated with the early lower pressure diamond synthesis research experiments have now evolved and are being applied in research laboratories throughout the world ([9], [14], [24], [32], [34], [42], [44], [46], [69], [70], [90]–[92], [112], [114], [125], [127], [128], [143]–[148]). However, there is still a need to further improve the understanding and performance of MPACVD diamond synthesis reactors especially when they are operating in the high pressure (100 – 400 Torr) regime. Currently plasma reactor research activities are focused on: (1) the continued development of new,

efficient, high power density, high pressure, MPACVD reactor technologies and (2) the development and understanding of efficient, high quality, high growth rate diamond synthesis processes that take place within this high pressure regime ([9], [14], [24], [27], [30], [32], [34], [42], [44], [46], [69], [90]–[92], [112], [114], [115], [121], [125], [127], [128], [143]–[149]).

In diamond synthesis applications, a remaining important diamond synthesis process issue is the improvement of the electrical diamond synthesis efficiency. This efficiency is often expressed in kW-hr per carat and it must be minimized in any diamond synthesis process. Additionally, it is desirable that the reactor be experimentally flexible and capable of efficient operation over a wide experimental operating space. This chapter focuses on reactor design, matching techniques and associated process methods that allow very efficient diamond synthesis operation over a wide range of process variables; i.e. pressures ( $\sim 10 - 400$  Torr), input power levels, etc.

The MPACVD diamond synthesis process requires a focused and high intensity impressed electric field in order to create the intense, high power density discharges that enable the synthesis of high quality diamond at high rates. This is especially important when the diamond synthesis pressure is increased beyond 120 Torr. Currently MPACVD diamond synthesis reactors are single mode excited ([9], [12], [14], [24], [27], [30], [32]–[34], [42], [44], [46], [63]–[65], [67]–[70], [90]–[92], [112], [114], [115], [121], [125], [127], [128], [142]–[149]). These applicators have the advantages of being physically compact and capable of achieving efficient energy coupling into the dielectric and/ or plasma loads ([150], [151]). In contrast to traveling wave and multimode applicators, single mode cavity applicators impress high electric fields and the associated very high power densities into

dielectric and plasma loads ([150], [151]). It has been known for many years that the efficient operation of single mode applicators is limited to a narrow range of operating conditions thereby limiting their versatile application ([150], [151]). This is especially true when exciting a plasma load. That is single mode applicators are able to efficiently maintain and match a discharge only over a limited range of plasma densities and other experimental variable conditions [150].

However it was demonstrated that by varying the microwave excitation frequency [150] or cavity length and coupling tuning the applicator ([152]-[154]), the matching and process flexibility limitations of single mode applicators can be overcome. In particular, microwave plasma loaded applicators can be matched and coupling wall losses can be greatly reduced while the discharge is varied and maintained over a much wider range of plasma densities. High discharge plasma densities, i.e. well over 10 critical densities are produced, while still achieving a match and efficient discharge coupling ([152], [154]). In this part of the dissertation, these reactor design and operational techniques were applied to the MPACVD diamond synthesis process. Since at high operating pressures, greater than 150 Torr, the discharge shrinks away from the reactor walls and can move with respect to the diamond seed substrate, two additional internal applicator adjustments were added to increase the flexibility of the diamond synthesis process. These additional adjustments enable the in situ experimental tuning that is often needed to adjust the discharge to an optimal synthesis position with respect to the substrate. As the synthesis process is varied by, for example, changing the substrate holder size and/or as the diamond grows, these additional reactor size adjustments allow the applicator to be readjusted, matched and optimized during the process.

In view of the high power density, high pressure and high efficiency requirements for SCD MPACVD synthesis a new class of reactors was developed ([42], [44], [46]), as discussed in chapter 2. These new reactor designs incorporated four mechanically tunable geometrical variables that allow the internal reactor geometry to be varied in situ enabling the reactor to be adaptable to a variety of process conditions while still achieving high microwave coupling efficiencies. Since the four mechanical tuning adjustments are made inside the applicator they are referred to here as internally tuned applicators. These new reactor designs have already been applied to the MPACVD synthesis applications and their performance has been reported for polycrystalline diamond (PCD) [42] and SCD synthesis ([44], [46]). In this chapter of the thesis, the detailed reactor geometry variations and the associated experimental operating methodologies that enable the reactor to achieve high microwave coupling efficiencies and overall excellent diamond synthesis efficiencies over a wide range of input operating conditions are discussed for the first time.

### 4.2 Background

#### 4.2.1 An overview of MPACVD diamond synthesis

A cross section of a typical high pressure, high discharge power density MPACVD reactor and its associated microwave system is displayed in figure 4.1(a). The microwave plasma reactor consists of a phi symmetric cylindrical applicator (cavity or waveguide) attached to a matching system, the electromagnetic (EM) excitation region inside the cavity, a substrate holder/cooling stage and a microwave discharge. Ideally at high pressure the discharge, which is shown schematically and pictorially in figures 4.1(b) and (c) respectively, is separated from the reactor walls and is hovering above and is in contact with the deposition substrate. The microwave discharge heats the hydrogen and methane feed gas mixtures in the discharge activation zone to 2500 – 4000 K and thereby produces the appropriate growth radicals, i.e. [H] and [CH<sub>3</sub>] [82]. The important growth radical species must be abundantly present in the thin boundary layer which is adjacent to the substrate, as is shown in figure 4.1(b). In any reactor design at high pressures (above 100 Torr) the substrate and substrate holder must be cooled to the desirable, 850 – 1300 K diamond synthesis substrate temperatures.

When the pressure is increased from 50 Torr to 300 - 400 Torr the discharge shrinks in size and the absorbed power density increases from 5 – 10 W/cm<sup>3</sup> at low pressures to 1000 W/cm<sup>3</sup> at the higher pressures ([42], [44], [46]). Figure 4.2 displays how the discharge size shrinks as the pressure and input power are increased from 180 Torr to 260 Torr and from 2.0 kW to 2.5 kW respectively, thus increasing the discharge power density. Plasma densities for 2.45 GHz microwave diamond synthesis discharges are estimated to vary from 5 x 10<sup>11</sup> cm<sup>-3</sup> to 3 x 10<sup>12</sup> cm<sup>-3</sup> ([30], [121], [155]) when pressure (p)

is increased from 100 Torr to 240 Torr. Thus microwave discharges having over ten critical densities are created during the MPACVD diamond synthesis process ([152], [154]).



Figure 4.1 (a) A cross section of a typical single mode excited MPACVD diamond synthesis reactor attached to a matching system and a microwave power system, (b) the microwave discharge adjacent to the substrate holder, and (c) a typical photograph of a 5% CH<sub>4</sub>/H<sub>2</sub>, 240 Torr diamond synthesis discharge hovering over a one inch silicon substrate.

As pressure is increased, the plasma reactor design and operation challenges are to efficiently couple microwave power into the intense, high temperature discharge while still controlling its position to be above and in good contact with the substrate. The deposition species densities must also be able to be adjusted just above the substrate holder while still operating at high coupling efficiencies and without creating undesirable discharge – substrate holder reactions.



Figure 4.2 Photographs of the microwave discharge hovering over a silicon substrate as the operating pressure is increased from 180 Torr to 260 Torr [42]. The absorbed microwave power increases from 2.0 kW to 2.5 kW as pressure is increased.

#### 4.2.2 Microwave coupling efficiencies

Figure 4.1(a) displays the schematic of a typical MPACVD diamond synthesis microwave reactor. It consists of a microwave power delivery system, a matching system and the microwave plasma reactor cavity. The reactor cavity is connected to the external microwave delivery system at the reactor input plane. The output power from the microwave power delivery system is the incident power ( $P_{inc}$ ) and the total power coupled into the matching system at the input matching plane is given by:

$$P_t = P_{inc} - P_{ref}$$

where,  $P_{ref}$  is the power that is reflected from the input matching plane. The power coupled into the reactor cavity at the reactor input plane is given by:

$$P_c = P_t - P_w = P_{abs} + P_{loss}$$

where,  $P_{abs}$  is the power coupled into the discharge,  $P_{loss}$  represents the microwave power losses due to the conducting walls and any dielectric material losses inside the reactor cavity, and  $P_w$  represents any power lost in the matching system. The power reflection coefficient from the input matching plane is then given by:

$$R = \frac{P_{ref}}{P_{inc}}$$

Also  $P_c$  and  $P_{abs}$  can be expressed as:

$$P_{c} = P_{inc} - P_{w} - P_{ref}$$
  
and,  
$$P_{abs} = P_{inc} - P_{ref} - P_{w} - P_{loss}$$

Then the microwave coupling efficiency into the reactor is given by:

$$\eta = \left(1 - \frac{(P_w + P_{ref})}{P_{inc}}\right) x \ 100\%$$

The overall microwave coupling efficiency into the discharge is given by:

$$\eta_{coup} = \left(1 - \frac{(P_w + P_{ref} + P_{loss})}{P_{inc}}\right) x \ 100\%$$

Thus in order to efficiently couple microwave power into the discharge,  $P_{ref}$  should be minimized, i.e. the system should be matched and  $P_w$  and  $P_{loss}$  must also be minimized.

In this chapter of the dissertation, the coupling efficiency of internally matched microwave reactor system designs along with their associated operational techniques are explored to identify those that yield an excellent overall efficiency. When using internal reactor matching techniques the microwave power delivery system can be directly connected to the reactor (figure 4.3(a)). Then the input matching plane and the reactor input plane are the same plane and  $P_t = P_c$  and  $P_w$  is eliminated. An important question under these circumstances is whether internal matching techniques can be developed

which create and maintain stable discharges that are useful for diamond synthesis while also minimizing  $P_{ref}$ . If  $P_{ref}$  can be reduced to zero, then the major coupling losses only occur inside the reactor. The experiments discussed below investigate internal reactor matching techniques that enable the excellent matching of the discharge loaded reactor, as the reactor is varied over a wide range of experimental input conditions.

For the reactor B design shown in figure 4.3(a),  $P_w = 0$  and the efficiency of coupling microwave energy into the reactor,

$$\eta = \left(1 - \frac{P_{ref}}{P_{inc}}\right) x \ 100\%$$

If additionally, the reactor can be internally matched so that  $P_{ref} = 0$ ; i.e. the reactor is 100% matched and  $P_{inc} = P_c$ ; then the power coupled into the reactor,  $P_c$ , is divided between the power lost,  $P_{loss}$ , and the power coupled into the discharge,  $P_{abs}$ . Under these circumstances  $\eta_{coup}$  is given by:

$$\eta_{coup} = \left(1 - \frac{P_{loss}}{P_c}\right) x \ 100\% = \left(1 - \frac{P_{loss}}{P_{inc}}\right) x \ 100\%$$

Then  $\eta_{coup}$  can also be expressed in terms of the empty cavity quality factor ( $Q_0$ ), and discharge loaded cavity quality factor ( $Q_L$ ), i.e.

$$\eta_{coup} = \left(1 - \frac{Q_L}{Q_0}\right) x \ 100\%$$

where  $Q_0$  is defined as the Q of the reactor cavity without the discharge [156]. Measurements of a well – designed and a well maintained microwave cavity indicate that  $Q_0$  is dependent on the reactor design, construction and maintenance. In such a cavity,  $Q_0 \sim 1500 - 3000$ . When operating under diamond synthesis conditions, experimentally measured discharge loaded cavity  $Q_L \sim 70 - 100$  ([157]–[159]). Thus if internal reactor matching techniques are developed that are able to reduce the  $P_{ref}$  to zero or close to zero and  $P_w = 0$  then very high overall microwave coupling efficiencies of  $\eta_{coup} > 95\%$  can be achieved.



Figure 4.3 (a) Cross section of an internally tuned single mode excited microwave cavity plasma reactor: reactor B design ([42], [46]), (b)  $TM_{013} + TEM_{001}$  electromagnetic field patterns within the plasma reactor.

# 4.3 Microwave plasma reactor designs for a versatile and efficient high pressure operation

The microwave coupling and operational methods described in this chapter utilize the microwave cavity plasma reactor (MCPR) B ([42]–[45]) shown in figure 4.3(a). The MCPR B design employs several important design features: (1) single mode EM excitation, (2) internal applicator matching, and (3) the placement of the substrate on an independently mechanically adjustable substrate holder stage. Because of the unique applicator shape a single hybrid  $TM_{013} + TEM_{001}$  mode (figure 3(b)) is excited and it creates and maintains a discharge just above and in contact with the substrate holder. The input gases flow in through an annular ring located at the bottom of the TEM section of the reactor. The flow of gases is discussed in more detail in figure 5.1.

The MCPR B design has (1) two mechanically variable matching adjustments i.e. probe length ( $L_p$ ) and short length ( $L_s$ ) (figure 4.3(a)), and (2) two more mechanical variables L1 and L2 that enable a variable substrate position. By varying the four tuning adjustments, the MCPR (1) acts like an EM mode converter (2) acts like a variable impedance matching transformer and (3) allows the independent variation of the substrate position with respect to the discharge. The variable substrate position allows in situ adjustment of the plasma substrate boundary layer. As the substrate position changes the reactor geometry varies and the position and the shape of discharge also vary. This capability enables the optimization of the process growth rate and/or the growth uniformity. The benefits of this extra degree of freedom have already been demonstrated by improved PCD deposition uniformities ([42], [43]) and SCD growth rates ([41], [44]–[46]).

# 4.4 The experimental strategy for the measurement of coupling efficiency

The experimental measurement methodology is as follows:

(1)  $L_p$  and  $L_s$  (a) initially select, match and excite a desired EM mode, and (b) are further varied slightly to match the reactor to a desired optimum operating condition as the discharge is formed and process conditions are varied.

(2) L1 and L2 locate the substrate surface,  $z_s = (L1 - L2)$ , in contact with the discharge in order to adjust the discharge boundary layer for optimal diamond synthesis.

L1 and L2 also vary the size and shape of the discharge ([42], [43]). In this investigation,  $z_s$  was varied in discrete steps by inserting additional shim sets to vary L2. If  $z_s$  is varied then  $L_p$  and  $L_s$  may also have to be varied slightly to achieve excellent microwave coupling efficiency. The primary role of  $L_s$  and  $L_p$  is to maintain the desired EM mode excitation. L1 and L2 were adjusted (1) to position the discharge in contact with the substrate, (2) to achieve discharge stability (or to find a stable discharge operating regime) and (3) to adjust the size and shape of the discharge. Then when operating within the stable discharge operating space L1 and L2 were adjusted together with  $L_s$  to achieve optimal and efficient process conditions on the substrate.

### 4.5 Experimental methods

#### 4.5.1 The experimental measurement techniques

As is shown in figure 4.3(a), the microwave power delivery system consists of a 2.45 GHz variable power 800 W – 5 kW Cober power supply, a circulator, and calibrated incident and reflected power meters. All microwave coupling/ matching experiments presented in this section were performed using a 2.54 cm diameter silicon substrate as the benchmark diamond synthesis example. The silicon substrate was placed in a molybdenum substrate holder (figure 4.4) which in turn was placed on a water cooled stage (figure 4.3(a)). PCD was grown on the surface of the substrate as the various experimental microwave coupling measurements were made. The H<sub>2</sub> and CH<sub>4</sub> input gases used for all experiments had a purity level of 99.9995% (5.5N) and 99.999% (5N) respectively. The substrate temperature (T<sub>s</sub>) was measured with an optical emission one color pyrometer (IRCON Ultimax Infrared thermometer) of wavelength 0.96  $\mu$ m and with an emissivity of 0.6.

#### 4.5.2 The experimental variables

The experimental diamond synthesis system variables, which have been discussed in detail elsewhere [4], can be classified into internal, external input and output variables. The experimental variables discussed in this dissertation include the following:

(a) External input variables – (1) operating pressure, p (2) input power, i.e. the power coupled into the input plane,  $P_t$  (3) power reflection coefficient from the input matching plane,  $R = P_{ref}/P_{inc}$  (4) %CH<sub>4</sub>/H<sub>2</sub> (5) total input gas flow rate (ft) which is the sum of the

hydrogen and the methane flow rates, and the (6) reactor geometry variables  $L_s$ ,  $L_p$ , L1 and L2.

(b) Internal variables – (1) discharge volume,  $V_d$  (2) absorbed power density of plasma,  $\langle P_{abs} \rangle = P_{abs}/V_d$  (3) substrate temperature, T<sub>s</sub> and the (4) impressed EM field.

(c) Output variables – (1)  $\eta$  and (2)  $\eta_{coup}$ .



Figure 4.4 Substrate and substrate holder configuration

# 4.5.3 Identification of the experimental variable space for the coupling efficiency measurements

The experimental measurements described below are presented as representative examples of the reactor microwave coupling efficiency,  $\eta$ , behavior for reactor B. As is indicated in section 4.5.2 there are more than five important independent input variables. In this thesis  $\eta$  versus only a reduced set of input variables is presented. Here several input variables were held constant: (a) the total flow  $f_t = 412$  sccm, (b) %CH<sub>4</sub>/H<sub>2</sub> = 3%, (c) L1 = 5.3 cm, and (d) L<sub>p</sub> ~ 3.65 cm, which is a known optimum position ([42]–[45]). At this constant L<sub>p</sub> position high coupling efficiencies can be achieved and slight variations from this length do not appreciably change the coupling efficiency. The experimental variation of  $\eta$  was investigated versus four diamond synthesis variables: (1) pressure (2) power

input into the input plane,  $P_t$  (3) L<sub>s</sub> and (4) L2.  $\eta$  was then calculated as the input variables were varied over the following important diamond synthesis conditions: (1) 100 Torr < p < 240 Torr (2) 1.5 kW <  $P_{abs}$  < 2.8 kW (3) 22.2 cm < L<sub>s</sub> < 21.2 cm, i.e. discharge loaded reactor conditions that excite the hybrid EM mode and (4) – 8.17 mm <  $z_s$  < – 1.77 mm, i.e. conditions that position the discharge in good contact with the substrate ([42]–[45]). One very important internal diamond synthesis variable is the substrate temperature (T<sub>s</sub>). Typically diamond synthesis occurs when the substrate temperature (5) is 700°C < T<sub>s</sub> < 1300°C. The experiments discussed in this thesis display  $\eta$  only when the substrate temperature was within this range. While discharge volume, discharge shape and absorbed power density are important internal diamond synthesis variables their behavior was not discussed here since it does not change the measured microwave coupling efficiencies. The major measured output variable is the microwave reactor coupling efficiency,  $\eta$ . Diamond synthesis occurs during all coupling efficiency measurements.

### 4.6 Measurement of the microwave coupling efficiency

# 4.6.1 The Microwave coupling efficiency at a constant pressure and a constant substrate position

Considering first the case of a fixed reactor geometry, where the substrate position is held constant, a typical reactor experimental start up and operational scenario is as follows. The hybrid  $TM_{013}$  +  $TEM_{001}$  mode (figure 4.3(b)) is excited when L<sub>p</sub> and L<sub>s</sub> were initially adjusted to ~ 3.65 cm and ~ 21.5 cm respectively and a pure hydrogen discharge was ignited when the incident power was increased to 500 W and the pressure is 5 – 20 Torr. Then as the pressure was increased to 100 – 260 Torr, the incident power was increased to 1.5 – 2.5 kW. Once the constant operating pressure was reached, methane input gases were added and the reactor was matched by varying L<sub>s</sub>.

Figures 4.5 and 4.6 show the reactor matching behavior versus L<sub>s</sub> for a constant  $z_s = -8.17$  mm and a constant pressure of 180 Torr where  $P_{abs}$ , T<sub>s</sub> and  $P_{ref}$  are plotted versus L<sub>s</sub> for four different constant incident power levels of 1.8 kW, 2.0 kW, 2.2 kW and 2.4 kW. For the experimental behavior presented in figures 4.5 and 4.6, the reactor is defined to be operating in a "well matched" condition when  $P_{ref}$  is equal to or less than 10% of the  $P_{inc}$ . Thus microwave coupling efficiencies ( $\eta = (1 - (P_{ref}/P_{inc})) \times 100\%$ ) are > 90% and its normalized impedances all lie within the red circle (figure 4.7) and then the reactor is "well matched". When the reactor's normalized impedance lies inside the green circle in figure 4.7, the reactor is considered to be very well matched, i.e.  $\eta > 99\%$ .

The data in figures 4.5 and 4.6 indicates that independent of  $P_{inc}$ ,  $P_{abs}$  has a maximum,  $P_{ref}$  has a minimum and  $\eta$  has a maximum when L<sub>s</sub> = 21.55 cm. The reactor operates within the red circle of radius 1 on the Smith chart (figure 4.7) from about L<sub>s</sub> = 21.4 cm to
$L_s = 21.7$  cm, i.e. in a very well matched condition where  $\eta$  is > 90%. When  $L_s$  is between 21.5 - 21.6 cm,  $P_{ref}/P_{inc} < 0.01$  and then the normalized reactor impedance is within the green 0.1 radius circle in figure 4.7 and  $\eta$  > 99%. If  $L_s$  is adjusted to 21.55 cm the power reflection coefficient is equal to or less than 0.005, i.e. the reactor was almost perfectly matched, and  $\eta \sim 100\%$ . Thus at 180 Torr the reactor can be well matched over the incident power variation of 1.8 - 2.4 kW. When operating under these well matched conditions, EM standing waves exist only inside the reactor. Over the selected incident input power range of 1.8 - 2.4 kW the match improves slightly as  $P_{inc}$  increases. Excellent microwave coupling efficiencies of > 98% can be achieved with a careful adjustment of  $L_s$  with  $P_{inc} \sim P_c$ .

Figure 4.5(b) displays T<sub>s</sub> variation versus L<sub>s</sub>. When  $P_{inc}$  is increased T<sub>s</sub> also increases. For any given constant  $P_{inc}$  level, T<sub>s</sub> is a maximum when L<sub>s</sub> = 21.55 cm, i.e. when the reactor is best matched. T<sub>s</sub> decreases as L<sub>s</sub> is varied either above or below its best matched condition. The T<sub>s</sub> variation versus L<sub>s</sub> is repeatable. Thus, T<sub>s</sub> can be varied between 750 – 950°C while  $P_{inc}$  and L<sub>s</sub> are jointly varied between 1.8 kW and 2.4 kW and 21.7 cm and 21.4 cm respectively.



Figure 4.5 (a)  $P_{abs}$  vs. L<sub>s</sub>, (b) T<sub>s</sub> vs. L<sub>s</sub>. All other experimental variables are constant, such as 2.54 cm diameter silicon substrates, L1 = 52.9 mm, L2 = 61.1 mm, z<sub>s</sub> = - 8.17 mm, L<sub>p</sub> = 3.65 cm, %CH<sub>4</sub>/H<sub>2</sub> = 3%, p = 180 Torr and f<sub>t</sub> = 412 sccm.



Figure 4.6 (a)  $P_{ref}/P_{inc}$  vs. L<sub>s</sub> (b) a more detailed and expanded plot of the well matched reactor operating regime (shown in figure 4.5).

**Smith Chart** 



Figure 4.7 Smith Chart showing (1) a circle in red which represents a power reflection coefficient radius R = 0.1 and (2) a green circle which represents a power reflection coefficient radius of 0.01.

#### 4.6.2 Microwave coupling efficiency versus substrate position

After adjusting the reactor to a very well matched condition at a constant pressure,  $\eta$  versus  $z_s$  was investigated by varying L2.  $Z_s$  was varied in steps from – 8.17 mm to – 1.77 mm. At 180 Torr and at each constant substrate position a set of curves similar to those shown in figure 4.6 were measured. Figure 4.8 summarizes  $\eta$  versus  $z_s$  where the data was taken with p = 180 Torr,  $P_{inc} = 2.2$  kW, %CH<sub>4</sub>/H<sub>2</sub> = 3%, L<sub>p</sub> = 3.65 cm and f<sub>t</sub> = 412 sccm. At each constant  $z_s$ , L<sub>s</sub> was varied to determine the best matched reactor condition.

As  $z_s$  is increased from – 8.17 mm to – 5.7 mm to – 4.52 mm to – 1.77 mm the best matched position for  $L_s$  increases respectively from 21.55 cm to 21.65 cm to 21.71 cm to 21.85 cm (shown by the green curve in figure 4.8). As the length of the coaxial region was decreased the length of the cylindrical portion of the cavity was increased, albeit not in a linear fashion, in order to maintain the reactor in the excited hybrid resonance. The experimental data shows that as  $L_s$  is varied  $\eta > 95\%$  is still achieved. The best  $\eta$  varies from almost 100% at  $z_s = -$  8.17 mm to ~ 95% at  $z_s = -$  1.77 mm.



Figure 4.8  $P_{ref}/P_{inc}$  vs. L<sub>s</sub> for different z<sub>s</sub> positions at a constant incident microwave power of 2.2 kW, operating pressure 180 Torr and 3% CH<sub>4</sub>/H<sub>2</sub>.

#### 4.6.3 Determining $\eta$ over the reactor operating field maps

If the reactor geometry, substrate size, methane concentration and total gas flow rate are held fixed then the deposition process is a function of input power, pressure and substrate temperature. The relationship between these variables is nonlinear and given a specific reactor geometry it can be described by a set of experimental curves identified as the reactor operating field maps ([44], [45], [67]) which, at a given pressure, relates  $T_s$ to the input power and pressure. Figure 4.9 displays one such experimentally measured operating reactor map for a constant pressure of 180 Torr. This curve was measured by holding the input variables such as p,  $z_s$ , %CH<sub>4</sub>/H<sub>2</sub>, L<sub>s</sub>, etc. constant and as the input power was varied in 100 W steps from 1.2 kW to 2.5 kW, while recording  $P_{ref}$  and Ts. As the input power was increased from 1.2 kW to 2.4 kW the substrate temperature also increased from 700 – 1050°C. The photograph inserts in figure 4.9 display some examples of the discharge hovering directly over the 1" silicon substrate for different power levels. The cut edge at the top left corner of each photograph is due to the shape of the viewing window.

As the input power increased from 1.4 kW to 2.0 kW to 2.4 kW, the discharge size also increased from a size that is smaller than the substrate area leading to non - uniform deposition, to a more optimum plasma assisted diamond synthesis size which covers the entire substrate surface appropriately, to a discharge size that is much greater than the substrate area (figure 4.9) which leads to excess power utilization and hence system inefficiency. The lower green line intersecting the field map in figure 4.9 at about 1.6 kW defines the lower useful input power limit below which the diamond synthesis is non uniform over the substrate. If the input power is increased beyond the upper green line shown in figure 4.9 then the additional power is not needed and hence the diamond synthesis process becomes inefficient. This discharge behavior has been reported in reference [42], [43] and in figure 5 of reference [44]. The safe and efficient diamond synthesis regime for diamond synthesis ([44], [45]) was identified in figure 4.9 as the operating regime that lies between the upper and lower green lines intersecting the operating field map. Uniform, low loss PCD synthesis ([42], [160]) and high rate, high quality SCD synthesis ([41], [44]–[46]) has been achieved when operating in this region.

Also shown in figure 4.9 are the corresponding measurements of  $P_{ref}/P_{inc}$  and  $\eta$ . The  $P_{ref}/P_{inc}$  data in figure 4.9 was taken for a fixed L<sub>s</sub> of 21.55 cm and indicates that  $\eta$  is

close to or greater than 99% as the input power was varied from 1.6 kW to 2.4 kW. Thus when the reactor operates within the good diamond synthesis regime, as specified by the limits on the operating field map, then the magnitude of R lies within the green circle shown in figure 4.7.

Only when operating below 1.5 kW and above 2.4 kW does  $P_{ref}$  start to increase and then the coupling efficiency becomes less than 98%. However, even then R still lies within an acceptable well matched condition. Therefore, once the reactor is matched at 180 Torr the microwave coupling efficiency remains excellent as the input power varies from 1.5 – 2.4 kW. This implies that the diamond synthesis conditions such as temperature can be varied by varying the input power, as is shown in figure 4.9, within the safe and useful diamond synthesis regime without degrading the microwave coupling efficiency.

The experimental matching techniques that are presented in this section for a pressure of 180 Torr can be employed for any constant operating pressure. A separate unique operating field map was measured for each constant operating pressure. These curves were then combined into the resulting family of curves shown in figure 4.10. Note that even though the reactor was only optimized and matched at 180 Torr the reactor remained in a well matched condition over the entire 100 – 260 Torr operating regime. All coupling efficiencies are > 90%. Thus once the reactor was matched at 180 Torr, little reactor tuning was required as the reactor was varied over this large pressure/input power regime.

## 4.7 Placing limits on input power

The experimental data presented in section 4.6 indicates that when operating within the input power range of 1.5 - 2.5 kW,  $\eta > 90\%$ . In fact,  $\eta$  appears to improve as  $P_{inc}$  is increased (figure 4.6). This suggests that diamond synthesis rates at a given constant pressure may be even further increased with additional increases in the input power. However, there are, at any given pressure, reasons to place limits on the input power.

First, when operating at a constant pressure if the input power increases the discharge size increases and the absorbed discharge power density remains approximately constant or only slightly increases ([44], [45]). Thus as power is increased the discharge surface area in contact with the substrate holder expands beyond what is needed for the radical species to cover the substrate surface and thereby produce uniform deposition. This can be seen pictorially in figure 4.9 and can also be observed in figures 5, 6 and 7 in reference [44]. When this happens, diamond deposition also occurs on the molybdenum holder and thus an important amount of the input power is wasted. Therefore, there is a value of input power beyond which the synthesis process becomes less and less electrically efficient, i.e. carats/KW-h decreases. As indicated in figure 4.9 by the upper green line, in a given application and at a given pressure the input power should be limited to produce a discharge that just covers the substrate. Beyond this input power value any additional power input just increases the discharge size, and often an additional increase in input power even reduces the overall deposition efficiency.

An even further increase in input power (brown dashed line in figure 4.10) will increase the size of the discharge until it starts interacting with the reactor walls (figure 4.10(a)). These plasma wall interactions are either with the quartz dome walls or for other reactor

designs the discharge could also interact with the metal reactor walls. These microwave plasma wall interactions may lead to the formation of undesirable hot spots (figure 4.10(b)) [161] and microwave plasmoids (figure 4.10(a)) [162] and hence process contamination. Wall interactions may be reduced via wall cooling as is usually done for metal reactor walls.



Figure 4.9 Operating field map and matching, i.e.  $P_{ref}/P_{inc}$  and  $\eta$  vs.  $P_{abs}$ , for a constant pressure of 180 Torr. All other experimental input conditions are held constant, such as 2.54 cm diameter silicon substrates, L1 = 52.93 mm, L2 = 61.1 mm,  $z_s = -8.17$  mm, %CH<sub>4</sub>/H<sub>2</sub> = 3%, and f<sub>t</sub> = 412 sccm. L<sub>s</sub> and L<sub>p</sub> are also held constant at 21.55 cm and 3.65 cm respectively. The photograph inserts display examples of the discharge size as the input power varies from minimum to maximum input power.



Figure 4.10 Operating field maps and matching, i.e.  $P_{ref}/P_{inc}$ , versus absorbed power for three constant pressure conditions: 120, 180 and 240 Torr. All other experimental variables are constant [45]. Microwave plasmoids and hotspots may form in the grey area.

The cooling of metal walls will efficiently remove heat from the discharge and reduce the plasma wall material removal interactions. However, this is a counter – productive process since a hot discharge more efficiently produces the desired radical species. The removal of heat from the discharge via wall cooling requires additional input power to maintain the discharge temperature. Thus, the addition of more input power and the need for additional cooling results in an inefficient process. Operational input power limits were placed on the operating field maps (figure 4.10) where the reactor operates not only in the desired T<sub>s</sub> synthesis regime but also where it operates safely without wall interactions and without the formation of microwave plasmoids, and with high electrically efficiency.

#### 4.8 Some selected diamond synthesis results

The microwave reactor tuning and operational process described in the previous sections has been applied to both PCD and SCD synthesis. By using these operational techniques high quality PCD and SCD were efficiently synthesized over a wide input variable space, i.e. 150 - 350 Torr,  $P_{abs} \sim 2$  kW and T<sub>s</sub>  $\sim 950 - 1050^{\circ}$ C. All the experiments were carried out with the reactor operating in a well matched condition. Two results are described below: one describing PCD synthesis and the other describing SCD synthesis. PCD was uniformly synthesized over 1 inch by 1.5 mm thick silicon wafers. A typical experimental result is displayed in figure 4.11 which shows a 1.12 mm thick as – grown PCD plate grown on a 1 inch silicon wafer at 210 Torr, 3% CH<sub>4</sub>/H<sub>2</sub>, no added nitrogen for 100 hours with a growth rate of 11.2 µm/hr [41]. The typical growth rate and full width half maximum (FWHM) of the Raman spectra peak versus operating pressure are summarized in figure 4.12 [41]. Under optimized process conditions, uniform films were synthesized (uniformity of ± 10–15%) ([42], [43]). Further discussion on the uniformity of diamond films is given in reference [160].



Figure 4.11 A 1.12 mm thick unpolished PCD plate on a 1" Si wafer grown at 210 Torr,  $P_{abs} = 2.1$  kW with 3% CH<sub>4</sub>/H<sub>2</sub> and no nitrogen for 100 hours with a growth rate of 11.2 µm/hr [41].



Figure 4.12 FWHM of Raman spectra peak FWHM (cm<sup>-1</sup>) and growth rate ( $\mu$ m/hr) vs. pressure for PCD deposition with 4% CH<sub>4</sub>/H<sub>2</sub> and no added nitrogen [41].

High quality SCD substrates were synthesized by operating the reactor at the optimum coupling efficiency position. While keeping the short length and probe length fixed at

21.55 cm and 3.65 cm respectively, SCD plates were synthesized for varying growth times of 8 – 24 hours with a stable plasma discharge configuration. SCD material was grown up to  $350 - 500 \mu$ m thick and then a smooth, free standing, CVD, SCD plate was created by separating the CVD grown SCD material from the high pressure high temperature (HPHT) initial seed substrate first by laser cutting and then by polishing [141].



Figure 4.13 Smooth layered growth displayed by SCD substrate (SN059-01) grown at the optimum coupling efficiency position of reactor with 5%  $CH_4/H_2$  at 240 Torr and 1.98 – 2.05 kW for 8 hours with a growth rate of 30.15 µm/hr. The scale on each of the four optical microscopy pictures is 200 µm.

The growth rates, with residual nitrogen limited to less than 10 ppm, were  $16 - 32 \mu$ m/hr. The synthesized SCD substrates displayed a smooth layered growth throughout the surface without the formation of a major PCD rim. An example (sample SN059-01) is given in figure 4.13. A detailed experimental description about the SCD synthesis process will be provided in chapter 5. Secondary ion mass spectroscopy (SIMS) characterization of the synthesized SCD substrates indicates that these substrate have low nitrogen impurity concentrations (< 300 ppb) [45]. Thus, these substrates are type IIa quality or better.

Hence as demonstrated by these results we have synthesized high quality SCD substrates. The microwave tuning process is employed at the initial step where once the optimum coupling efficiency is achieved the length variables are kept constant throughout the synthesis step. Diamond synthesis efficiency was calculated for PCD deposited silicon wafer described in figure 4.11. For  $P_{abs} \sim 2.1$  kW, a PCD weight gain of ~ 2 gm and growth time of a 100 hours, the energy required to deposit a carat of diamond was calculated to be ~ 21 kW–h/Ct. Thus the reactor tuning and operational processes described above play an important role in obtaining low figure of merit (kW–h/Ct).

## CHAPTER 5 GROWTH STRATEGIES FOR LARGE AND HIGH QUALITY SINGLE CRYSTAL DIAMOND SUBSTRATES

## **5.1 Introduction**

Currently microwave plasma assisted chemical vapor deposition (MPACVD) is the most prominent method for synthesizing single crystal diamond (SCD) substrates ([17], [29], [64], [68]). Different diamond deposition methods utilizing the MPACVD technique have been employed for the purpose of investigating the synthesis of high quality, large area single crystal diamond plates. For example, Tallaire et. al., [35] have proposed controlling growth by controlling the evolution of the different crystal faces to produce a large defect free, top crystal surface. Mokuno et. al., ([12], [18]) have proposed to use alternative diamond growth steps on the top and the sides of the initial seed, first to enlarge the initial diamond seed surface and then ultimately to produce a large diamond substrate. They also observed that during growth on a single seed in an "enclosed holder", the SCD growth surface initially slightly increases during the first 1/2 to 1 mm of growth and becomes surrounded by a polycrystalline diamond (PCD) rim and the top SCD surface itself becomes enclosed by a thick PCD rim. Then as the diamond growth continues, the SCD growth surface continually deceases as the PCD rim thickness increases and encroaches into the SCD top surface. Thus the formation of the PCD rim limits the size and cross sectional area of the synthesized SCD. Yamada et.al. ([15], [16], [128]) numerically investigated the influence of varying the substrate geometry and discharge position on the local synthesis environment and the final SCD synthesis results. They found that if the microwave discharge is located close to substrate it is modified by the presence of the substrate and the substrate holder design. As a result, one can infer that the diamond synthesis process itself can be modified by varying the local substrate design/geometry. They also point out that the substrate temperature distribution on the top surface of the substrate most importantly controls the local diamond synthesis process. Recently Yamada et. al. ([23], [26], [163]) have combined the growth of "mosaic crystals", which was first proposed by M.W. Geis et. al. [105], with an ion implantation lift-off method to obtain over one inch single crystal diamond plates.

While much progress has been made in the synthesis of SCD substrates, each of these methods has problems such as limited growth size, growth process interruptions, stress and cracking, etc. When growing thick crystals, a limiting condition for all of these methods is the formation of non – epitaxial features on the corners, on the edges and on the top of the growing crystal surfaces. Ultimately, this leads to the formation and growth of a PCD rim which surrounds the top growing surface. Additionally, in order to be cost effective any process that is developed must deposit high quality SCD at a fast growth rate so that the growth can be carried out in a reasonable time and at a reasonable cost. This growth rate condition requires that MPACVD synthesis be carried out at high pressures (> 150 Torr) and with the use of a high power density microwave plasma ([42], [44], [46]). Thus, much development still remains in order to achieve the routine synthesis of large, thick and high quality SCD substrates suitable for industrial applications.

It was discussed in chapter 4 and as reported in the resulting publication, that when using high pressure and high power density microwave discharges, if efficient and repeatable MPACVD diamond synthesis is desired then it is important to design and operate the microwave reactor system in such a way that high microwave coupling

efficiencies are achieved [40] and then operate the reactor within a "safe and efficient" process regime ([42], [44], [46]). MPACVD experiments have been performed and these have also demonstrated that it is necessary to spatially control the "local" process environment around and in the vicinity of the substrate. One of the ways this can be achieved is by modifying the local discharge geometry conditions such as developing optimized substrate holder designs. In addition, as the process proceeds versus time it is also necessary to spatially control the "local" process conditions versus time adjacent to the plasma – substrate boundary layer in order to maintain the proper substrate deposition temperature and to avoid the formation of discharge hot spots [161].

In this chapter, the high pressure (130 - 240 Torr) and high power density microwave plasma assisted chemical vapor deposition (MPACVD) of single crystal diamond (SCD) substrates is investigated. Locally controlled growth strategies that enable the synthesis of large (~ 5 mm) and thick (200 µm - 2.5 mm) free standing CVD SCD substrates have also been discussed here. Two process control methods, i.e. control of the input power level versus time, and the precise control of the substrate holder geometry when combined play an important role in obtaining high quality free standing single crystal diamond (SCD) substrates. The performance of one distinct substrate holder design, the "pocket holder", is discussed in this chapter in detail and is compared to the performance of the more commonly used open holder. A comparison of these two holder designs operating in the high pressure SCD synthesis process environment revealed the advantages of the pocket holder. The pocket holder design not only aids in the growth of thick SCD substrates when operating within the reactor's safe and efficient operating regime, but also enhances their *in situ* lateral growth. Processes are described which

enhance the growth of the SCD surface area while simultaneously reducing the growth of the polycrystalline diamond rim that typically surrounds the synthesized SCD. Using such methods at 240 Torr MPACVD SCD plates and SCD cubes have been synthesized at high growth rates in reactors B and C.

## 5.2 The experimental microwave reactor and microwave system

The experiments presented here were performed with two different 2.45 GHz microwave cavity plasma reactors (MCPRs). These reactor systems are identified here as reactor B and reactor C, and have been described in more detail in chapter 2 and elsewhere ([44], [46]). In order to ensure high diamond growth rates and high discharge power density deposition conditions, all experiments were carried out in the high pressure deposition environment. Experiments were performed preferably at 240 Torr and the substrate holder was water cooled by a variable position cooling stage (figure 3.3). However, some experiments using the open holder had to be performed at reduced pressures of 130 – 160 Torr in order to prevent the formation of discharge hot spots and process runaway. The experimental results described here were obtained while the reactors were operated within the safe and efficient operating regime as discussed in chapter 4 ([40], [44]).

Figure 5.1(a) displays a cross section of the lower section of the reactor cavity. The substrate holder position is given by  $z_s$  where  $z_s$  is determined by the length variables L1 and L2 as:  $z_s = L1 - L2$  ([40], [42]).  $Z_s$  is adjusted to impress a mostly normal electric field at the discharge – substrate holder boundary and during a particular reactor operating process its length is typically adjusted to lie within – 8 mm <  $z_s$  < + 5 mm. As is shown in figure 5.1(b) the input feed gases flow into the reactor through an annular ring near the base of the quartz dome and then flow phi symmetrically up towards the substrate. The gases then flow around and through the discharge and then exit the reactor through a series of holes cut in the outer circumference of the substrate holder (as shown in chapter 3).



Figure 5.1 (a) Cross – sectional drawing of the lower portion of a typical MCPR cavity. The lengths L1 and L2 are variable and determine the substrate holder position slightly above or below the z = 0 plane. (b) Flow patterns within a typical MCPR.

The MCPR is connected to a Cober microwave power supply with an average power output level variation from 1 kW to 6 kW. This power supply has a poorly filtered DC supply voltage especially at the lower power levels used in the described experiments. This results in output power fluctuations at 120 Hz and slightly in microwave oscillating frequency around 2.45 GHz. This condition is mentioned in this section since it has been

observed that under conditions similar to these pulsed microwave discharges provide higher growth rates are obtained in comparison to continuous wave microwave discharges when operating at the same average input power and pressure levels ([28], [164], [165]). Therefore, these power variations at 120 Hz may enhance the growth rates over those reported with a continuous wave discharge. The photographs in figure 5.2 were captured with the manual exposure and high – speed continuous shooting mode (5.3 shots per second) of a Canon EOS 60D camera. The exposure time = 1/800 sec<sup>-1</sup>, aperture value = F/4.0, ISO = 1600, no flash, and color representation = sRGB. These pictures show examples of the maximum and minimum size variation of the discharge over time at a constant power level of 1.82 kW at 180 Torr with 3% CH<sub>4</sub>/H<sub>2</sub>. More pictures of the pulsing microwave discharge and the camera settings are discussed in appendix D.

In each of the photographs in figures 5.2, the top left corner appears to be cut due to the shape of the viewing window. A 1 inch silicon substrate is also visible directly adjacent and below the pulsed discharge. Operating at 2.2 kW or above, the microwave discharge size increases considerably beyond the size required to cover the entire substrate. This additional input power is not necessary and is essentially wasted. It is important to operate the reactor within the limits of the efficient region of the operating field maps in order to avoid power loss and also to prevent the formation of any hot spots and microwave plasmoids [40]. For this reason, the experiments described in this chapter have been performed within the power levels of 1.8 - 2.2 kW while still maintaining excellent microwave coupling efficiencies at high pressure levels of 130 - 240 Torr.



Figure 5.2 Photographs of the microwave discharge operating at 180 Torr with 3%  $CH_4/H_2$  and 1.82 kW.

#### 5.3 Experimental procedures

The experiments discussed here have been performed on <100> oriented 3.5 mm x 3.5 mm x ~1.4 mm HPHT type Ib seed substrates. All the seeds used in experiments discussed in this paper have a top surface area of  $3.7 \times 3.7 \text{ mm}^2$ . They were first cleaned with a mixture of nitric and sulfuric acids, then with hydrochloric acid and then were finally ultrasonicated in acetone and then in methanol before being loaded into the reactor. Once the substrate was loaded into the reactor, the system was pumped down for 12 hours to reach the base pressure of ~ 1 mTorr. During the deposition process a gas feed mixture of hydrogen and methane gases with a purity of 99.9995% (5.5 N) and 99.999% (5N) respectively was used. Any nitrogen that was present during the growth runs was due to the impurities in the feed gases and any slight leaks in the vacuum system. Nitrogen gas was determined to be limited to < 6 ppm in reactor B and ~ 10 ppm in reactor C.

Prior to and after the deposition process, the HPHT seed and the SCD substrate thicknesses were measured with a linear encoder. Several thickness measurements were taken at the four corners and at the center of the SCD substrate and which were then averaged out to calculate the growth rate. Similarly, for volumetric analysis an analytical weighing balance was used to calculate the weight gain after growth. During the growth process the surface temperature ( $T_s$ ) was measured with a 0.96 µm wavelength monochromatic optical pyrometer (IRCON Ultimax Infrared thermometer) with an emissivity of 0.1 and a minimum spot size of 2 mm. The setup of the pyrometer is shown schematically in figure 4.3 and has also been discussed in references ([40], [44]). It was setup 60° to the z = 0 plane and consistent temperature measurements were obtained by keeping it fixed on a tripod during the experiments.

# 5.4 Controlling the reactor versus time to achieve a constant substrate deposition temperature.

During all the SCD synthesis experiments described here, SCD grows on the single crystal substrate surface and a layer of PCD is deposited on the surface of the molybdenum substrate holder. The additional deposited SCD and PCD alters the plasma substrate boundary layer and the reactor behavior varies or drifts slightly versus deposition time, i.e. the reactor operating field map curves ([42], [44], [160]) vary versus time, as is shown in figure 5.3. Then the initial process temperature increases from A to B operating points. Thus, the substrate temperature increases versus time as the PCD layer grows and as the SCD substrate thickness increases. PCD is deposited on the molybdenum substrate holder and the seed surface temperature increases from  $T_s$  to  $T_s$ , where  $T_s' - T_s < 100^{\circ}$ C. The operating field map curves vary slightly as time increases from to to t<sub>1</sub> and the reactor operating point varies from A to B (see curves 1 and 2 in figure 5.3). However, for a typical SCD process it is desirable to hold the substrate temperature approximately constant over the entire synthesis cycle. This can be achieved by adjusting the reactor operating conditions and the reactor geometry versus time to compensate for these substrate and substrate holder physical changes and associated temperature changes.

As is shown in figure 5.3, the operating field map curves vary from curve 1 to curve 2 as the process evolves with respect to time. The substrate temperature can be held approximately constant by slightly adjusting the absorbed power versus time. For example, by reducing the absorbed power by just 50 - 100 Watts the substrate temperature can be held constant. The absorbed power may be adjusted by using any of

the three different ways. The most common way is to just directly vary the incident power by adjusting the microwave generator output. This is indicated in figure 5.3. The second and third methods of input power variation (not shown in figure 5.3) are by holding the incident power constant and by varying the operating pressure and/ or slightly varying L<sub>s</sub> to detune the reactor from a matched position. The variation of L<sub>s</sub> mismatches the reactor and slightly increases the reflected power ( $P_{ref}$ ). More details on the reactor tuning have already been discussed in chapter 4 and have been presented in reference [40]. In all the experiments described in this chapter, the method used to hold the substrate temperature constant versus time was by varying the microwave generator power.



Figure 5.3 Controlling the input power versus time to achieve constant substrate temperature versus time. The temperature is held constant at the initial temperature by moving the reactor operating point from A to C as the absorbed power is slowly and continuously reduced during the process cycle.

## 5.5 Single crystal diamond synthesis

#### 5.5.1 Open holder SCD synthesis

A series of diamond synthesis experiments were performed in reactor B using the open substrate holder design. In the open holder synthesis process geometry, the HPHT seed is placed directly on a flat, water – cooled molybdenum substrate holder as shown in figure 5.4(a). During synthesis the top, edges and the side surfaces of the seed are directly exposed to the active discharge and to the impressed microwave electric fields that exist in the substrate – discharge boundary interface. It is well known that at lower pressure operation (< 150 Torr) the open holder geometry synthesizes SCD crystals that are surrounded by a PCD rim and that the size of the rim increases with deposition time ([6], [7]). Figure 5.5 and 5.6 show a typical example of the results obtained using the open holder synthesis process. The open holder synthesis process is experimentally explored at the higher pressure range of 130 - 160 Torr. For the experiments in reactor B, the substrate holder position ( $z_s = L1 - L2$ ) was – 8.17 mm. The results were then used for benchmark comparisons for evaluating new and improved holder designs. These open holder experiments are briefly summarized below.

After pumping down the vacuum system for 12 hours, the seed substrate was microwave plasma etched for an hour with hydrogen gas at  $T_s \sim 1250^{\circ}$ C, to clean the surface and to prepare the substrate for deposition. A 3.7 x 3.7 mm<sup>2</sup> top surface area HPHT SCD seed substrate was placed on a flat open molybdenum holder as shown in figure 5.4(a) and MPACVD diamond synthesis was initiated. As the process evolved with time, the seed plus the synthesized diamond became thicker and protruded more into the discharge (figure 5.5(a) and (b)). Both the plasma substrate boundary layer and the local

discharge became more intense versus time and the seed substrate temperature increased. In order to hold the substrate temperature approximately constant, both the operating pressure and input power had to be varied with time. The operating pressure range for this example of open holder set of experiments was 130 – 160 Torr with 5%  $CH_4/H_2$  and with a total growth time of 35.5 hours. The experiment was interrupted at 8, 16, 19.5, 27.5 hours to take growth measurements and optical microscopy images and then finally after 35.5 hours the experiment was ended. The total growth at the end of 35.5 hours was ~ 671 µm and with a growth rate that varied with time between 11.28 -43.24  $\mu$ m/hr. In order to maintain T<sub>s</sub> between 1100 – 1180°C and to avoid process runaway, the pressure was decreased from 160 Torr to 130 Torr and the power (1.5 - 2.2)kW) was also adjusted to control the substrate temperature to lie between the desired deposition temperature range. Even at these low pressures and power levels, high temperatures of > 1100°C were obtained due to the substrate penetrating more and more into the plasma and hence leading to a non – uniform surface temperature. The detailed experimental measurements and observations are presented in figures 5.4 - 5.8.

The experimental observations of the open holder growth process are shown in figure 5.4(a – c). During the growth process, SCD (orange part in figure 5.4) was grown on the top surface of the seed substrate (yellow block in figure 5.4). Simultaneously PCD (grey region in figure 5.4) was also grown on the top edges and the sides of the seed. As shown in figure 5.4(b), an additional PCD layer was also grown on top of the molybdenum holder. As the synthesis process proceeded versus time (figure 5.4(b)), at t = t<sub>1</sub>, both synthesized SCD and PCD layers increased and a PCD rim completely enclosing the SCD top surface edges was formed. Eventually (figure 5.4(c)), at a later time t = t<sub>2</sub>, the PCD rim had grown

vertically upward, horizontally outward and radially inward into the SCD top surface. Thus, as the SCD top surface grew upward its SCD surface area decreased. The presence of the additional deposited diamond, i.e. the SCD on the seed, the PCD rim and the PCD deposition on the holder surface adjacent to the substrate, alters the plasma – substrate boundary and hence alters the local deposition process versus time. The photographs shown in figures 5.5(a) and (b) clearly show the growth of the PCD rim in an open holder configuration. The PCD rim can be seen to be glowing at a much higher temperature in these photographs, thus indicating a non – uniform surface temperature distribution.





Figure 5.4 A cross-sectional view of SCD synthesis versus time in an open holder. The yellow color denotes the HPHT SCD seed substrate, orange denotes the synthesized CVD SCD and the gray area identifies the deposited PCD material.



Figure 5.5 (a) An open holder growth process and (b) A side view of the discharge substrate boundary layer in the open holder configuration. (c) The discharge and seed substrate boundary layer just before discharge hot spot formation. The discharge is clearly separated from the holder and is concentrated on the top of the seed.

Figure 5.5(b) and (c) show the typical high pressure experimental observation, that when operating at higher power densities using the open holder configuration, the electric fields and the discharge can concentrate directly above an open holder. Initially when the process starts, the seed is directly exposed to the discharge. However, the presence of the growing substrate with its PCD rim changes the boundary layer between the substrate and discharge. As deposition proceeds, the plasma can dislodge itself from top of the substrate holder surface and moves towards, jumps onto, and as shown in figure 5.5(c) focuses on the top surface of the protruding substrate. This in turn dramatically changes the local growth conditions. Under these conditions discharge hot spots [161] can form on and adjacent to the diamond surface. Due to the non – uniform surface temperature created by the growth of the PCD rim, the growing rim provides a suitable region for the development of hot spots [161] and microwave plasmoids [162] with time and discharge runaway can also occur.

The optical microscope images (figure 5.6 (a – e)) show the increase in the thickness of the PCD rim with growth time. Figure 5.6(f) displays the appearance of the final substrate. The seed is still attached to the synthesized diamond after 35.5 hours of growth. The top SCD surface shown in figure 5.6(f) is surrounded by a thick polycrystalline rim while the top SCD surface area has decreased (figure 5.8) by 25% from ~ 13.7 mm<sup>2</sup> (initial seed area) to 9.75 mm<sup>2</sup>. The optical microscopy image of the SCD top surface shown in figure 5.6(a – e) indicates that the diamond growth on the top surface proceeds in an edge – center growth morphology. This is believed to be due to the non – uniform surface temperature of the diamond substrate, i.e. the sharp edges of the seed are at a higher temperature (figure 5.5(a)). As can be seen from the series of images in figure 5.6(a – e), the SCD surface begins with a smooth edge – center growth morphology, but as the deviation in surface temperature between the edge and center increases and as the substrate protrudes more and more into the discharge, the roughness of the SCD

surface also increases and the surface morphology deteriorates with time such that the result is a final smaller and uneven SCD surface area (figure 5.6(f)).



Figure 5.6 The evolution of the top surface of the SCD versus total growth time of (a) 8 (SN025–01) (b) 16 (SN025–02) (c) 19.5 (SN025–03) (d) 27.5 (SN025–04) and (e) 35.5 hours (SN025–05). (f) The final seed substrate plus the synthesized diamond after 35.5 hours of deposition time.

Figure 5.7 summarizes the growth measurements such as the linear growth rate, total weight gain and average rim thickness versus time. As the growth proceeds, it is clear to see from figure 5.7 that the average rim thickness is also increasing. This implies that the SCD surface area (figure 5.8) and also its linear growth is decreasing over time since most of the diamond deposition now occurs over the PCD rim. As a result, most of the diamond weight gain is due to the growth in the polycrystalline deposition on the edges of the seed which is contrary to original goal of obtaining large and thick SCD substrates.



Figure 5.7 SCD linear growth rate, PCD rim growth rate and total weight gain versus time. As growth time proceeds, the PCD rim thickness and the PCD weight gain increase while simultaneously the SCD linear growth rate decreases.



Figure 5.8 The synthesized CVD single crystal diamond area versus time for a 3.7 x 3.7 mm<sup>2</sup> HPHT seed crystal. As growth time proceeds, the useful SCD surface area reduces with an increase in the polycrystalline deposition.

Thus, it was observed that when synthesizing diamond at high pressures the open holder geometry hinders the development of a robust, high quality SCD synthesis process and must be improved upon. For this purpose, a different holder design was investigated which is referred to here as the "pocket holder design".

#### 5.5.2 Pocket Holder Synthesis

In order to improve and achieve localized control of the SCD synthesis process the open holder design geometry was modified. In a series of trial and error experiments the open holder configuration evolved into a new design that at first reduced the PCD rim and then finally completely eliminated the rim. The final result was the optimized holder designs discussed in the section. By placing the seed substrate in a pocket holder, a synthesis process was developed where the seed is placed within a recess or a "well" that is cut into the water – cooled molybdenum substrate holder (figure 5.9(a)). When the substrate was placed within this recess, the SCD substrate sides, edges and the top surface were no longer exposed to the intense microwave plasma and were also shielded from any microwave fields that may have concentrated on the hot edges of the substrate in the open holder configuration. The top surface of the substrate is located at a short distance, i.e. 0.5 - 2.0 mm depending on the exact synthesis process, below the top surface of the substrate holder.

Experiments were performed in reactors B and reactor C in a similar fashion to the open holder experiments. The substrate holder position ( $z_s$ ) for all synthesis experiments in reactor B was between – 5.38 mm and – 7.17 mm and in reactor C,  $z_s$  was – 4.6 mm. The seed was first hydrogen plasma etched for an hour with  $T_s \sim 1050$  °C at 180 Torr to remove any impurities and any polishing damage on the seed surface. The reactor was then pumped down to base pressure and then restarted for the growth procedure. The growth process versus time is described schematically and in the caption of figure 5.9. The operating pressure for the pocket holder growth experiments were carried out with varying growth times of 8 – 72 hours. The total new SCD growth thicknesses varied between ~ 200 µm to 1.3 mm and were produced with a growth rate of 16 – 32 µm/hr. For all experiments conducted,  $T_s$  was maintained within 950 – 1150°C by adjusting the incident power levels to be within 1.8 – 2.2 kW.





Figure 5.9 Cross – sectional schematic views of SCD growth versus time in a pocket holder. The color code is the same as in figure 5.4. As (a) SCD growth versus time proceeds (b) the new SCD grows without a PCD rim both vertically and horizontally. (c) Additionally PCD was deposited on the top of the substrate holder. (d) After the deposition cycle was stopped at  $t = t_3$  the newly grown SCD material was laser cut from the seed substrate and the PCD material was removed from the substrate holder.

Figure 5.10(a) displays a photograph of the discharge – substrate boundary layer that was located just above a pocket holder operating at 240 Torr with 5% CH<sub>4</sub>/H<sub>2</sub>. In contrast to the open holder boundary layer shown in figure 5.5, the substrate – discharge boundary layer was uniform above the pocket and molybdenum holder surface, and diamond synthesis was carried out without hot spots. The red – orange area in figure 5.10 was

produced by the glowing seed located within a pocket holder. Thus, the pocket holder design created, within the pocket, a suitable thermal environment (figure 5.10(b)) bounded by the walls of the recess. Such an environment aids in producing a uniform SCD synthesis process.



Figure 5.10 (a) A side view of the uniform discharge – substrate boundary layer at a 240 Torr pocket holder SCD synthesis process. (b) Pocket creates an appropriate thermal environment for uniform growth.

Figure 5.11(a) displays a typical pocket holder design. In this design, the side edges of the substrate are located at a short distance from the adjacent wall of the holder recess. The dimensions of the pocket are important, i.e. if the spacing between the edges and the surface is either too large or too small then a good, smooth SCD growth is not achieved. The optimum size of the pocket was determined after experimenting with several different pocket holder designs. As the SCD grows upward and horizontally (figure 5.11(b)), the substrate recess used in any additional growth steps had to be enlarged (both in depth and width) in order to maintain the appropriate spatial relationship between the substrate and the substrate holder.




Under these "pocket" growth conditions SCD growth proceeds either without producing a PCD rim or the PCD rim is greatly reduced. As shown in figures 5.9 and 5.11, during pocket growth the crystal grows both vertically and horizontally (figure 5.11(b)) and the top surface is smooth and has no PCD rim (figure 5.12). As growth proceeds, the crystal becomes thicker and the top surface area also increases. In fact, the enlarged top surface cantilevers out from all four sides over the original seed substrate. In order to achieve thick SCD growth the substrate surface and edges must be positioned appropriately within a recess in the substrate. The pocket holder location, shape and dimensions control the local synthesis process.

Some typical examples of the final substrates grown with the SCD pocket holder process are shown in figures 5.12 - 5.14, 5.16, 5.17, 5.19 and 5.20. During the diamond growth process, the substrate temperature versus time was controlled to achieve the appropriate vertical and horizontal SCD growth rates in the pocket. The growth conditions for all the experimental results were 240 Torr, CH<sub>4</sub>/H<sub>2</sub> = 5%, and T<sub>s</sub> ~ 950 - 1150 °C.

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Reactor B was used in results shown in figures 5.12 - 5.14 and 5.16 and reactor C was used in figures 5.17, 5.18, 5.20, 5.21. The input power was slightly adjusted with minor steps between 1.8 - 2.0 kW in order to keep the substrate temperature approximately constant versus time over the entire process cycle. The top surfaces of all the SCD crystals shown in figures 5.12 - 5.14, 5.16 and 5.17 display no PCD rim and have an increased top SCD surface area from the original seed surface area. The surface area for the 438 µm thick SCD shown in figures 5.12, 5.12, 5.13(a) and (b) has increased by 1.23 times while the top surface area of the thicker substrate shown in figures 5.17 has increased by  $\sim 2.15$  times. The SCD grown plates and cubes shown in figures 5.13(b) and 5.21(a) and (b) were laser cut from the seed, then laser trimmed and then finally were mechanically polished [141].



Figure 5.12 Top surface of a 438  $\mu$ m thick CVD grown SCD layer (SN075–01). The grown surface has increased ~ 1.23 times from 3.7 mm x 3.7 mm top surface area of the original seed to ~ 4.1 mm x 4.1 mm surface area. This final as – grown substrate was synthesized in a pocket holder with d = 1.5 mm and w = 0.5 mm and has no PCD rim.



Figure 5.13 (a) An as – grown SCD substrate (SN075–01) after a 24 hour growth at 240 Torr and with 5%  $CH_4/H_2$  and with no PCD rim (b) A 221 µm CVD SCD plate (SN067–01C) after laser cutting and mechanically polishing substrate SN067–01.

Figure 5.14 shows some more as – grown SCD substrates grown in a pocket holder for 24 - 36 hours in reactor B with 5% CH<sub>4</sub>/H<sub>2</sub> at 240 Torr. All these substrates indicate the reproducibility of the growth technique in a pocket holder design without the formation of any PCD rim while simultaneously enhancing the lateral surface area 1.284 – 1.344 times over the initial HPHT seed surface area.



Figure 5.14 Some more examples of as – grown SCD substrates deposited without any PCD rim. (a) SN082–01 (b) SN083–01 (c) SN091–01 (d) SN092–01.

The advantages in reducing PCD growth on the substrate edges have been observed in the synthesized SCD substrates. Figure 5.16(a) shows an as – grown SCD substrate synthesized on a <100> direction oriented HPHT seed. The top surface of the seed was cut at an angle (~  $2 - 5^{\circ}$ ) to the <100> growth direction (figure 5.15) to demonstrate the effect of the PCD rim. The left edge of the seed (red marked box in figure 5.16(a)) was 70 – 80 µm thicker than the right edge. The SCD substrate was synthesized at 240 Torr with 5% CH<sub>4</sub>/H<sub>2</sub>. The left edge of the substrate shows a PCD rim in contrast to the right edge. This difference is due to the fact that the left edge emerged out of the recess of the pocket holder with increasing growth time. The effect of the rim on the synthesized SCD plate is clearly visible in figure 5.16(b) which shows a birefringence image with an exposure time of 5 secs. The right edge of the CVD SCD plate exhibited very low stress as compared to that in the left edge. Thus, a conclusion can be made that such a reduction in the growth of the PCD rim in the synthesized SCD substrates not only enhances the substrate surface area but also leads to stress free high quality CVD SCD plates.



Figure 5.15 Side view of an HPHT seed with the top surface cut at an angle (~  $2 - 5^{\circ}$ ) with respect to the (100) growth plane.



Figure 5.16 (a) An as – grown SCD substrate synthesized in a pocket holder with d = 1.5 mm and w = 0.5 mm. (b) Birefringence image of the polished SCD plate with an exposure time of 5000 ms after laser cutting off the seed. The absence of the PCD rim on the right edge of (a) produces a stress free right edge of the SCD plate.

It was observed that with long growth times of 48 hours or more, the PCD layer on top of the surface of the molybdenum holder would tend to grow thick and acts as a secondary pocket holder (figure 5.17(a)) which increased the depth of the original holder. Eventually the PCD layer started to converge and attempted to join onto the SCD surface. This constricted the lateral growth of the substrate. At this point, the growth process needed to be stopped and the holder needed to be cleaned in order to enable a smooth growth process.



Figure 5.17 (a) The SCD growth process starts in a concave manner and then levels out with the PCD deposition on the holder surface. The growth process was stopped after the growth of a thick PCD layer on the holder surface. (b) An example of a thick PCD deposition on the substrate holder in reactor C.

Initially the CVD SCD substrate grows in a concave fashion (figure 5.17(a)) with a center to edge growth morphology (figure 5.12). As the growth proceeded with time, the CVD SCD top surface leveled out to align itself to the same plane as the adjoining PCD deposition on the holder surface. Figure 5.17(b) shows one such substrate where a thick layer of PCD was formed on the holder surface. The SCD substrate shown in figure 5.17(b) was grown by Dr. Yajun Gu using reactor C. The single growth step was carried out at 240 Torr, with 5% CH<sub>4</sub>/H<sub>2</sub> and with a growth time of 64.3 hours. When the synthesis step was completed, the PCD layer was separated from the molybdenum holder surface. The linear growth rate of the CVD SCD substrate was 24.9  $\mu$ m/hr which resulted in a total SCD thickness gain of ~ 1.6 mm. Figure 5.18 shows a close up of the substrate shown in figure 5.17(b). The underlying HPHT seed (yellow color) can be clearly seen in this figure. The CVD SCD substrate layer grown on the seed is transparent and is free of any PCD rim growth.



Figure 5.18 A close up view of the synthesized SCD in figure 5.17(b) (GYJ171) grown in a pocket holder with d = 2.6 mm and w = 1.0 mm and with the adjacent PCD layer on the substrate holder. This substrate was grown in reactor C by Dr. Yajun Gu.

Many CVD SCD substrates have been routinely synthesized using the pocket holder designs and have been laterally expanded to varying dimensions over different growth times (figure 5.14). Figure 5.19 displays a plot of the normalized lateral area gain versus the vertical thickness gain. The normalized lateral area gain for the MSU grown CVD substrates, referred to here, is the CVD lateral area gain over the initial HPHT seed area ( $3.7 \times 3.7 \text{ mm}^2$ ). These substrates have been grown over varying growth times of 10 - 72 hours and with 1 - 2 growth steps. All these substrates have no PCD rim around their top surface. There is a clear expansion in the final surface area of the CVD substrate. This demonstrates the advantage of minimizing/ removing the PCD rim with the help of the pocket holder design. These CVD substrates have then been compared to the substrate grown by AIST, Japan (figure 2.21) and the comparison is clearly depicted in figure 5.19. This substrate was grown on a 5 x 5 mm<sup>2</sup> HPHT seed with 24 repetitions for 150 hours but has a smaller final SCD surface area.



Figure 5.19 Plot of normalized lateral CVD area gain vs. vertical thickness gain for the MSU grown CVD substrates. The dotted horizontal line indicates the HPHT seed surface area. The red data spot shows the normalized lateral gain of the final SCD surface area of the substrate shown in figure 2.21 grown by AIST, Japan with 24 repetitions.

Experiments with multi – growth steps indicate an increase of the top SCD surface area by ~ 2.5 times (figure 5.20). Figure 5.20(a) shows the outward expansion of the CVD layers during growth in deeper pocket holders at 240 Torr and with 5% CH<sub>4</sub>/H<sub>2</sub>. This substrate was grown in 2 steps of 48 hours (1.17 mm thick) and 72.3 hours (1.6 mm thick). Figure 5.20(b) shows the top view of the grown substrate.



Figure 5.20 (a) Lateral expansion of the CVD growth for a 2 step as grown substrate synthesized in reactor C (GYJ161) (b) ~ 2.5 times expansion of the final CVD substrate over the HPHT surface area (grown in reactor C).

The synthesis growth steps described above were utilized to produce thick CVD SCD substrates with one or more growth steps (figure (5.21)). A multi – growth step CVD SCD cube has been shown in figure 5.21(a). This cube was grown with 4 successive growth steps of 48 - 72 hours each and with growth rates of  $25 - 30 \mu$ m/hr at 240 Torr and with 5% CH<sub>4</sub>/H<sub>2</sub> starting with a 6 x 6 mm<sup>2</sup> HPHT seed. The substrate holder surface was cleaned after each growth step to ensure that the growth proceeded without the formation of any hot spots on the holder surface at this high pressure growth regime. Also, as the substrate gained thickness, the pocket holder dimension (specifically the depth) was changed after each step to ensure that the substrate remained within the recess during the growth process. As shown in figure 5.21, the final SCD substrate was laser trimmed at the edges to form a 2.1 carat,  $5.3 \times 5.2 \times 4.5 \text{ mm}^3$  thick CVD SCD substrate. Similar growth and processing steps were followed for the production of the SCD cube shown in figure 5.21(b). It was grown in 1 growth step of ~ 95 hours at 240 Torr with 5% CH<sub>4</sub>/H<sub>2</sub>

and with a growth rate of 24.8  $\mu$ m/hr on a 3.7 x 3.7 x ~ 1.4 mm<sup>3</sup> HPHT seed. The final laser cut and trimmed CVD SCD cube obtained was a 2.3 x 2.5 x 2.7 mm<sup>3</sup> cube.



Figure 5.21 CVD SCD cubes after cutting and polishing. (a) A cube demonstrating the successful growth of a  $5.3 \times 5.2 \times 4.5 \text{ mm}^3$ , 2.1 carat thick SCD substrate in 4 successive growth steps (GYJ127 – G04) (b) A CVD SCD 2.3 x 2.5 x 2.7 mm<sup>3</sup> cube grown in 1 growth step (GYJ153).



Figure 5.22 CVD growth on a 7 x 7 x 0.4 mm<sup>3</sup> type IIa CVD seed from Microwave Enterprises (SN7x7cvd1–01). The scale on each picture is 500  $\mu$ m.

Similar SCD growth was carried out on optical quality type IIa CVD seeds from Microwave Enterprises (the as – grown substrate is shown in figure 5.22). This 227  $\mu$ m thick substrate was grown at 240 Torr, 5% CH<sub>4</sub>/H<sub>2</sub> for 10 hours at a growth rate of 22.76  $\mu$ m/hr. As is clear from figure 5.22, the surface of the as – grown substrate (SN7x7cvd1– 01) is smooth with no formation of any PCD rim. This implies that the pocket holder growth is convenient and suitable for the growth on large area substrates which may then be utilized for the enhancing the lateral dimensions of the substrate.

# 5.6 Discussion

When the empty cavity reactor is excited with electromagnetic energy then the impressed microwave electric field is primarily perpendicular to the holder surface ([42], [46]). If then a SCD diamond seed is placed on the open holder surface and the microwave discharge is ignited, the impressed electric field on the holder is modified by the presence of the diamond seed and the discharge (figure 5.23(a)). A substrate – discharge boundary is created at the substrate surface. The modification of the local electric field at the substrate holder – discharge boundary layer depends on the exact shape and material properties of the HPHT seed. At high temperatures, i.e. ~ 900 – 1100°C, required for diamond synthesis, diamond becomes a lossy dielectric [130]. Thus in the typical open holder diamond synthesis experiment the local microwave electric fields that exists in the substrate – discharge boundary layer differs greatly from fields that exist in the empty reactor.



Figure 5.23 Schematics of the (a) open holder and (b) pocket holder growth processes.

These fields are modified by the size, shape (especially by the presence of any edges and corners), and the lossy dielectric material properties of the diamond seed and are also influenced by the location and the intensity of the discharge. The electric field concentrates at the edges and corners of the seed which in turn increases the local electric fields and discharge power density around the seed substrate (figure 5.23(a)). This can lead to a process runaway that increases the temperature on the seed edges and corners and in turn causes further localization of the fields and the discharge and leads to the development of localized hot spots on the substrate edges.

The understanding about the importance of the "appropriate spatial relationship" (figure 5.11), between the top of the substrate surface and edges and the adjacent substrate holder surface and edges, is that by maintaining the correct distance between the substrate and the substrate holder and the plasma the following are the three consequences which are vital for an efficient SCD growth process. (1) The SCD substrate is shielded from the hot plasma species and the impressed microwave electromagnetic fields. (2) The diffusion and convective flows of the plasma and the radical species onto the SCD surface can be adjusted and controlled by varying the pocket dimensions, specifically 'd' and 'w'. For seed dimensions of ~  $3.5 \times 3.5 \times 1.4 \text{ mm}^3$ , depending on the growth time (8 – 72 hours), 'd' would be ~ 1.5 - 2.6 mm and 'w' ~ 0.5 - 1.0 mm. (3) The substrate is placed into an environment that is hot and relatively thermally uniform (figure 5.10 and 5.23(b)). The substrate surface, edges and the surrounding holder surfaces and edges are at locally uniform temperatures, thereby creating conditions that are essential for uniform SCD synthesis (figure 5.23(b)).

# CHAPTER 6 CHARACTERIZATION AND ANALYSIS OF SYNTHESIZED CVD SCD SUBSTRATES

# **6.1 Introduction**

Novel materials with better mechanical, optical, and electrical properties are the need of the hour for many applications in the real world. Diamond is one such material and has many exciting properties such as high thermal conductivity, chemical inertness, extreme hardness and electrical insulation. These properties have been exploited for several years in many different applications like optical elements [60], high energy beam detectors [61] and heat spreaders [62] among many others. Recently several diamond research groups have attempted to grow large area, high quality SCD plates/ substrates. Researchers from AIST, Japan have developed substrate lift – off, side surface (100) growth process, and a mosaic wafer growth process (described in section 2.5.1). These processes have shown good promise of enlarging the single crystal diamond surface area ([11], [17], [18], [21]–[23], [97]). Diamond growth studies performed by LSPM – CNRS, France by utilizing high growth rate, beveled HPHT diamond seeds and multi - step CVD diamond growth have also been successful in synthesizing large single crystal diamond substrates ([29], [33], [35], [37], [38], [114], [124]) (as described in section 2.5.3). The characterization and analysis of the substrates grown by these research groups indicate that they are of good guality. The absorption coefficient measurements by FTIR and UV/Vis spectroscopy show that the substrates have very low level of nitrogen content such that it is not detectable by these techniques ([32], [33], [35], [38], [114]). Photoluminescence spectroscopy of these substrates also indicate no luminescence due to nitrogen and silicon defects. But

while these growth strategies do deposit substrates with low impurity content, the synthesized crystals suffer from cracking and stress ([9], [38]). This is due to the fact that a major lingering problem in these deposition techniques has been the simultaneous growth of a polycrystalline diamond (PCD) rim around the single crystalline diamond (SCD) substrate. This not only leads to stress in the crystals but also reduces the final SCD surface dimensions due to the growth of non – epitaxial defects around the edges ([38], [12]).

In an effort to solve the polycrystalline rim issue, a "pocket substrate holder process" that prevents/ minimizes the growth of a PCD rim was investigated in chapter 5 and has also been published in reference [166]. This process includes the following steps: (1) placing the substrate in an optimized "pocket holder" geometry and then (2) applying the correct sequence of microwave plasma processing steps. As demonstrated in chapter 5, SCD synthesis occurs when the substrate is placed in a pocket and its edges and corners are shielded from the applied electromagnetic fields and the associated intense plasma, thereby producing rimless or almost rimless diamond. The question that remains then is what is the quality of the diamond grown by this method. Thus, the major objective of this chapter is to analyze the CVD SCD plates and as – grown substrates deposited in a pocket holder. Hence in this chapter, the characterization results of high quality SCD substrates synthesized in a pocket holder are presented. These substrates were deposited in a microwave cavity plasma reactor at high pressures (240 Torr) and high power densities (~ 500 W/cm<sup>3</sup>) ([44], [45]).

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# 6.2 The SCD experimental growth process

#### 6.2.1 SCD experimental system

The deposition processes of all single crystal diamond substrates discussed in this chapter have been carried out in a microwave cavity plasma reactor (MCPR) developed at Michigan State University. This reactor B design and the reactor variables are described extensively in references ([42], [44], [126], [160]) and also in chapter 3. In order to increase the growth rates, the synthesis process has been carried out at a high deposition pressure of 240 Torr. At these high pressure levels, the microwave discharge becomes extremely intense and the plasma volume decreases at high power levels of 1.8 – 2.2 kW. For 240 Torr, the microwave discharge power density was calculated to be ~ 500 W/cm<sup>3</sup> ([44], [45]). All deposition processes in reactor B were performed within the safe and efficient operating regime ([44], [45]). Additionally, in all experiments, the reactor and the associated processes were operating under optimized conditions, i.e. with microwave power coupling efficiencies of more than 95%. The details about the microwave power coupling process have been discussed in chapter 4 and in reference [40].

#### 6.2.2 Substrate holders used for synthesis

As discussed in chapter 5, it was observed that the design of the substrate holders played an important role in the deposition of large SCD substrates ([166], [167]). The more commonly used open holders, in which the substrate is placed in direct contact with the microwave discharge, lead to the formation of a PCD rim. This PCD rim not only reduces the useful SCD surface area but also leads to the formation of defects on the

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SCD surface especially at the edges. In order to increase the CVD SCD surface area and to improve the quality of the synthesized substrates, the pocket holder design shown in figure 6.1 was used, where the walls of the recess prevent or minimize the formation of any rim on the seed substrate. The growth process in these pocket holders (as shown in figure 5.9) has been discussed in greater detail in chapter 5 and in references ([166], [167]).



Figure 6.1 Pocket holder design for SCD synthesis. The yellow box indicates the cross section of a HPHT seed placed within a recess and away from the intense plasma region.

#### 6.2.3 Substrate cleaning process

All SCD growth steps have been carried out on  $3.5 \times 3.5 \times -1.5 \text{ mm}^3 < 100 >$  oriented HPHT type Ib seeds from Sumitomo. The growth process was preceded by careful chemical and plasma treatment procedures [40] in order to reduce the defects and impurities on the substrate surface prior to growth. These cleaning steps have been described in detail in section 3.4.1.1.

#### 6.2.4 Plasma etching of substrate

Following the acid and solvent pretreatment of the seed, it was loaded into the reactor and then the surface of the seed was plasma etched in a pure hydrogen plasma discharge at 180 Torr for one hour at  $T_s = 1000 - 1050$ °C. The reactor was then pumped down for half an hour. This hydrogen plasma pretreatment of the HPHT seed served two purposes: (1) it removed impurities on the surface of the seed which were then pumped out of the system, and (2) it reduced/ removed any polishing damage on the seed surface. This etching process thereby helped in preparing the seed for growth to proceed on a clean surface with less number of defects.

#### 6.2.5 SCD growth process

After the plasma pretreatment of the HPHT seed, the pressure was increased with the addition of hydrogen gas and a hydrogen plasma was reignited at ~ 5 Torr. The power level and the substrate temperature was then gradually increased with the increasing pressure. Once the required process pressure level was reached, the incident power was adjusted to maintain a constant substrate surface temperature. After 10 minutes of plasma etching in a pure hydrogen discharge at 240 Torr, methane gas was flowed into the quartz bell jar to begin the growth process. The SCD results discussed here have been synthesized at a pressure = 240 Torr, 5% CH<sub>4</sub>/H<sub>2</sub>, total flow rate ( $f_t$ ) = 420 sccm, no intentional nitrogen addition, substrate temperature  $(T_s) = 1100 - 1150^{\circ}C$ , incident power  $(P_{inc}) = 1.8 - 2.2$  kW and with a nitrogen impurity of ~ 6 ppm in the total gas flow due to gas impurities. As discussed in chapter 5, process control of the different input and output reactor variables during growth serves a crucial role in the synthesis of high quality CVD SCD substrates. The entire growth process in a pocket holder is described in detail in chapter 5 and in references ([166], [167]). In order to maintain consistent local growth conditions during the entire synthesis process, it was imperative to adjust the incident power level with time [166].

## 6.2.6 SCD post growth processing steps

At the end of the growth process, the final substrate was cleaned with a mixture of nitric and sulfuric acids and then rinsed by ultrasonicating it in methanol. After the initial characterization steps of linear encoder measurements for growth rate and weight gain measurements, optical microscopy, field emission scanning electron microscopy, atomic force microscopy and energy dispersive spectroscopy, the "as – grown" SCD substrates were laser cut to separate the CVD grown single crystal plate (in this chapter referred to as a CVD SCD plate) from the HPHT seed. Then the plates were mechanically polished to reduce the roughness on both sides of the plates [141]. The CVD SCD plates were then further characterized using UV/Vis and FTIR spectroscopy, secondary ion mass spectroscopy, birefringence imaging, differential interference contrast microscopy, x - raytopography and etching experiments were conducted to determine the etch pit density measurements.

## 6.3 Characterization results and discussion

#### 6.3.1 As – grown SCD substrate analysis

#### 6.3.1.1 Growth rate calculation

For the initial characterization, the weight gain of the as – grown substrate was measured by using a Metler Toledo XS105DU analytical balance. The weight of the substrate was measured five times and then averaged out to reduce the uncertainty in the measurements. The thicknesses of the as – grown substrates were then measured by using a Solarton DR 600 linear encoder. The thickness was measured over five points: one at each of the corners and one at the center of the substrate. Each thickness measurement was repeated five times and then averaged out to reduce the deviation in each measurement. For calculating the average growth rate of the SCD substrate the following equation was used:

Average growth rate  $(\mu m/hr) = \frac{Average thickness gain after growth (\mu m)}{Total growth duration (hr)}$ 

The substrates synthesized at a high pressure of 240 Torr and with 5%  $CH_4/H_2$  had high growth rates of 16 – 32 µm/hr over a range of varying growth durations of 8 – 24 hours.

## 6.3.1.2 Optical Microscopy

Reflection mode optical micrographs of as – grown substrates were captured with a Nikon Eclipse ME 600 optical microscope (figure 6.2).



Figure 6.2 The Nikon ME 600 optical microscope.

Figure 6.2 indicates the different components of the microscope. For the optical micrographs, the following settings were used:

- (a) Camera/ eyepiece switch turned on to camera
- (b) DIC polarizer out, i.e. inactive
- (c) Field and aperture stop off

(d) Filters – only a neutral density filter used. This gives a yellow discoloration to the micrographs.

- (e) DIC analyzer out, i.e. inactive
- (f) Dark field/ bright field switch set to bright field option

#### (g) Wollaston prism – out, i.e. inactive

Figure 6.3 shows the growth morphology of two representative, as - grown substrates grown at 240 Torr with 5% CH<sub>4</sub>/H<sub>2</sub>. It was observed that the surface morphology of the grown SCD substrates depends on the dimensions of the substrate holder. The HPHT seeds of these SCD substrates were placed within a pocket holder but depending on the thickness of the seed and the depth of the pocket of the substrate holder, the final SCD substrate may start to stick out of the pocket and penetrate into the plasma at the end of the growth duration. An edge - center growth morphology (figure 6.3(a)) was observed in the as - grown SCD substrates which in the final stages of the process growth cycle started to grow out of the pocket and penetrate into the plasma. Here the thickness measurements with the linear encoder indicated a slightly higher growth around the edges and corners of the substrate ( $\sim 20 \ \mu m$ ) in comparison to the center thereby resulting in an edge - center morphology. As is discussed in chapter 5 and in references ([166], [167]), when the substrate penetrates into the intense plasma, local growth conditions are modified with a slightly modified boundary layer and hence the electromagnetic field lines concentrate on the edges and on the corners of the seed. This leads to a non – uniform surface temperature since the sharp edges of the seed are at a higher temperature and hence results in an edge – center growth morphology with the growth of a polycrystalline diamond (PCD) rim. For this reason, a thin rim can be seen around the edges of the as grown SCD substrate (SN033-01) shown in figure 6.3(a). After the substrate edges penetrate into the discharge any additional diamond growth is similar to the growth in the more commonly used open holders ([166], [167]). In contrast, the as – grown substrates which remain embedded within the recess (figure 6.3(b)) throughout the growth duration

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and whose edges and corners remain shielded from the intense plasma exhibit a center – edge growth morphology (SN075–01). This implies that during the initial hours of growth, the center of the substrate grows at a slightly higher rate and is hence slightly thicker as compared to the region near the edges. This has experimentally been observed in short runs. Depending on the growth duration, after the termination of the deposition process, the top surface of the crystal smoothens out and becomes flat. Each experimental run is stopped before the top of the substrate surface penetrates the discharge. This pocket holder growth process is described in chapter 5 and in reference [166]. However, irrespective of the observed growth morphology, all synthesized as – grown substrates displayed a smooth step like layered growth morphology throughout the surface, as seen in figure 6.3.



Figure 6.3 Optical microscopy images of as – grown SCD substrates with (a) edge – center growth morphology (SN033–01) and (b) with center – edge growth morphology (SN075–01). The scale on each of the above images is  $200 \mu m$ .

## Figure 6.3 (cont'd)



## 6.3.1.3 Field Emission Scanning Electron Microscopy (FESEM)

To analyze the as – grown SCD substrates even further, the surfaces were observed under a Zeiss EVO LS 25 variable pressure scanning electron microscope (VP-SEM) at the Composite Center in Michigan State University. This SEM is equipped with an Energy Dispersive X – ray detector. The advantage of such a system is that it is possible to then observe the substrates with Field Emission Scanning Electron Microscopy (FESEM) without the need of coating the insulating diamond substrate surface. Figure 6.4(a) shows the surface of an as – grown substrate (SN054–01). This is similar to the as – grown substrate that were observed under the optical microscope (figure 6.3(a)). To take a closer look at the surface, the growth terraces (figure 6.4(b)) and the PCD rim (figure 6.4(c)) were also observed under FESEM. The dark spots seen in figures 6.4(b) and (c) are the residues of some solvents after the post growth cleaning process. Figure 6.4(b) clearly shows the growth steps on the substrate surface. In figure 6.4(c), the different faces and orientations of the crystals in the thin PCD rim are also clearly visible.



Figure 6.4 (a) Surface of an as – grown substrate (SN054–01) as seen under FESEM. Closer view of the (b) growth terraces on the surface and (c) the different crystal faces and orientations on the PCD rim.

# 6.3.1.4 Atomic Force Microscopy (AFM)

AFM analysis was conducted on the as – grown substrates to measure the surface roughness ( $R_a$ ) and to analyze the surface profile of the grown substrate. The instrument

used for this purpose is a Cypher<sup>™</sup> Atomic Force Microscope/Scanning Probe Microscope in the Department of Physics at Michigan State University.



Figure 6.5 Atomic force microscopy (AFM) analysis of an as – grown SCD substrate surface (SN075–01). (a) 2D AFM image, (b) 3D AFM image to display the growth steps, and (c) surface profile and roughness ( $R_a = 263.3$  nm) of the red line shown in (a).

Figure 6.5 (cont'd)



Figure 6.5 shows the AFM analysis of the as – grown substrate (SN075–01) shown in figure 6.3(b). Figure 6.5(a) shows a 2D image of 30  $\mu$ m x 30  $\mu$ m surface area. The red line over this image is drawn to determine the surface roughness (R<sub>a</sub>) as shown in figure 6.5(c). The blue spot and the red line in figure 6.5(a) corresponds to the blue spot and surface profile plot shown in figure 6.5(c). Figure 6.5(b) displays the 3D plot over the same surface area. The width and height of each growth step is clearly visible here. The surface profile is displayed in figure 6.5(c). The surface roughness (R<sub>a</sub>) for this as – grown substrate is ~ 263 nm. Careful observation of the different growth layers at different positions on the SCD surface indicate the growth layers are directed toward the edges and the corners of the substrate and originate near the central region of the seed substrate. This verifies the center – edge surface morphology for the SCD substrates grown in a pocket holder.

# 6.3.1.5 Energy Dispersive X – Ray Spectroscopy or Energy Dispersive X – Ray Analysis (EDS/EDAX)

The same instrument as used for the FESEM, discussed in section 6.3.1.3, was used for the purpose of Energy Dispersive X – Ray Spectroscopy or Energy Dispersive X – Ray Analysis (EDS/EDAX). This is a useful technique for analyzing contaminants in the substrate to a few microns in depth. Figure 6.6 shows the full area of the as – grown substrate (SN054–01) utilized for this purpose. The settings for the system were: 15 kV, live time = 30 sec, take off angle =  $33.4^\circ$ , amplitude time = 6.4 µsec and resolution = 125 eV.



Figure 6.6 Area of the as – grown substrate (SN054 – 01) scanned under FESEM for EDS/EDAX measurement shown in figure 6.7.

In figure 6.7, the elemental composition of the surface area shown in figure 6.6 is shown. As is clear from the graph shown in figure 6.7, the major element present in the substrate surface is carbon. There are also some traces of oxygen and aluminum. The

presence of oxygen may be explained by the possible termination of the surface with oxygen atoms when the substrate was exposed to air after deposition. Since there is no possibility of substrate contamination with aluminum during the growth/ etching or cleaning process, a possible reason for the presence of aluminum could be explained by any impurities on the surface during the fixation of the substrate onto the aluminum holder and loading it into the high vacuum chamber for FESEM and EDS measurements. Table 6.1 shows the data obtained for this substrate. They show the electrons being excited from the K – shell of each element when the high energy electron beam is incident on the substrate surface.



Figure 6.7 EDS measurement of different elements in the surface area shown in figure 6.6.

	Table 6.1 Elemental	analysis of as -	grown CVD substrate	(SN054-01	) via EDS.
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Element	Weight %	Atomic %	Net Int.	Net Int. Error
СК	97.23	97.94	3842.04	0

Table 6.1 (cont'd)

0 K	2.65	2	30.9	0.05
Al K	0.13	0.06	12.58	0.21

#### 6.3.2 CVD SCD plate analysis

In order to further characterize and analyze the synthesized substrates, they were first laser cut from the original seed substrate and then mechanically polished to form CVD SCD plates [141]. After polishing, the surface roughness decreased to 3 – 6 nm. This level of surface smoothness ensures efficient spectroscopy and stress analysis of the substrates with minimum unintentional reflection. Several PCD rim free substrates grown in a pocket holder design on (100) oriented HPHT seeds were cut into plates (figure 5.13(b) in chapter 5) and characterized. The UV/Vis spectroscopy measurements of such CVD SCD plates cut from (100) oriented HPHT seeds are displayed in figure 6.9. The laser cutting and polishing of the plates was done by Fraunhofer USA and Applied Diamond Inc.

In this section, the measurements shown in figures 6.10, 6.11, 6.12(b) and 6.13 were conducted on a 221 µm CVD SCD plate (SN067–01C). In order to emphasize the effect of the PCD rim, this plate was grown at 240 Torr with 5% CH<sub>4</sub>/H<sub>2</sub> and for 24 hours on a HPHT seed whose top surface was cut at an angle (a few degrees) offset to the (100) growth plane (figure 5.15). Figure 5.15 shows the side view of the angled seed. During growth, the left edge of the seed starts to grow out of the pocket and into the intense plasma while the right edge stays embedded in the pocket. As a result, the left edge

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develops a PCD rim but the right edge remains rim free (figure 5.16(a)). After growth, the CVD material was laser cut from the seed and was then polished to form a 221  $\mu$ m thick SCD plate (SN067–01C). The effect of this PCD rim on the quality of the CVD SCD plate (SN067–01C) is displayed in the birefringence images (figure 6.13). All UV/Vis, FTIR, SIMS and XRT measurements discussed in figures 6.10 – 6.12, and 6.15(b) have been conducted on this same CVD SCD plate.

#### 6.3.2.1 UV/Vis Spectroscopy

Ultraviolet and visible wavelength range spectroscopy measurements on CVD SCD plates were performed with a Perkin Elmer Lambda 900 UV/Vis/NIR spectrometer. The setup of the spectrometer is shown in figure 6.8. The spectrometer can scan from 185 to 3300 nm for the UV/Vis/NIR range. The monochromator consists of two holographic gratings of 1440 and 360 lines/mm for UV/Vis and NIR measurements respectively. The lamp was changed at 350 nm and the monochromator was changed at 810 nm. The expert mode of the computer software was used with a step size of 1 nm and a slit width of 2 or 5 nm. The integration time was set at 0.28 sec from 400 – 3300 nm and at 2 secs from 200 – 400 nm, to reduce the noise in the measurements and to avoid a deviation in the measurement during the lamp change. The spectral range that was scanned was from 200 – 800 nm.



Figure 6.8 Optical setup of the UV/Vis/NIR spectrometer.

The absorption coefficient of the sample was calculated with the help of the Sellmeier equation which is given as:

$$n^{2}(\lambda) = 1 + \frac{B_{1}\lambda^{2}}{\lambda^{2} - \lambda_{1}^{2}} + \frac{B_{2}\lambda^{2}}{\lambda^{2} - \lambda_{2}^{2}} + \frac{B_{3}\lambda^{2}}{\lambda^{2} - \lambda_{3}^{2}}$$

Here, *n* is the refractive index and  $\lambda$  is the wavelength. For diamond, the Sellmeier equation may be written as [168]:

$$n^{2} = 1 + \frac{0.3306 \lambda^{2}}{\lambda^{2} - (175 nm)^{2}} + \frac{4.3356 \lambda^{2}}{\lambda^{2} - (106 nm)^{2}}$$

The absorption coefficient is then given as:

$$\alpha = \frac{1}{d} ln \left[ \frac{(1-R)^2}{(1-R^2)} \frac{1}{T} \right]$$

where, d is the thickness of the sample, T is the transmission and R is the reflectance which are given as a function of the refractive index of diamond:

$$T = \frac{2n}{(1+n^2)}$$
,  $R = \left[\frac{(n-1)}{(n+1)}\right]^2$ 

The transmission was measured directly from the UV/Vis measurements while the reflectance was calculated with the help of the equation given above.

Figure 6.9 shows UV/Vis measurements for several CVD SCD plates and a type lb HPHT seed. Samples SN058–01C, SN065–01C, SN067–01C and SN075–01C were all grown in reactor B at 240 Torr, with 5% CH<sub>4</sub>/H<sub>2</sub>, no intentional nitrogen and for a growth duration of 15 – 24 hours. Samples SN058–01C, SN065–01C were grown on (100) oriented HPHT seeds, while samples SN067–01C and SN075–01C were grown on angled HPHT seeds whose top surface was offset to the <100> direction by a few degrees. All growth parameters for these samples are discussed in appendix F. In figure 6.9, samples SN7X7CVD1 and SN7X7CVD2 refer to type IIa CVD substrates obtained from Microwave Enterprises. From these measurements, it was clear that the synthesized CVD SCD plates are of much better quality than the type Ib HPHT seeds due to low nitrogen impurities and hence high optical transmission, especially at the lower wavelength range of 225 – 500 nm. It is also clear that the synthesized plates were of comparable type IIa quality similar to or even better than the Microwave Enterprises samples.

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Figure 6.9 A comparison of UV/Vis measurements of reactor B grown CVD SCD plates, type IIa Microwave Enterprises samples and a type Ib HPHT seed.

Figure 6.10 shows the UV/Vis measurements of the 221  $\mu$ m thick CVD SCD plate (SN067–01C). In figure 6.10(a), the transmission measurements of the plate are compared to that of a type Ib HPHT seed substrate. The difference between the two substrates is clearly visible, especially at the lower wavelength range of 200 – 450 nm (given by the green dashed box). In contrast to the HPHT seed which shows a high absorption at these lower wavelengths caused by large amount of nitrogen impurities, the CVD SCD plate shows high optical transmission. The transmission (%T) measurements for 400 – 800 nm of the CVD SCD plate is approximately 71% which matches the
theoretical value for these measurements ([169], [170]). The green dashed box shown in figure 6.10(a) was chosen to show the absorption coefficient versus wavelength for the plate at the lower wavelength range of about 225 - 400 nm (figure 6.10(b)). The wavelength of 225 nm is close to the fundamental cut off for diamond. As can be seen in figure 6.10(b), the average absorption coefficient is ~ 0.77 cm<sup>-1</sup> (as calculated with the help of the Sellmeier equation given above) for the wavelength range of 240 – 400 nm. This low absorption coefficient in the synthesized CVD SCD plates indicates the high quality (type IIa) of the grown plate and shows that any nitrogen impurity in the substrate is lower than the detection limit of the instrument (i.e. < 1 ppm).



Figure 6.10 (a) Comparison of UV/VIS spectroscopy measurements of a 221 µm thick CVD SCD plate (SN067–01C) and a HPHT type Ib seed substrate (b) Closer view of the absorption coefficient vs. wavelength plot of the plate at lower wavelengths.

Similar measurements were performed on multiple, pocket holder grown, laser cut and polished CVD SCD plates. Thus, these low impurity plates are reproducible. A comparison of these results with the previously published research ([17], [24], [38], [114]) revealed that the optical transmission for the CVD SCD plates is similar (~ 71% for the wavelength range of 400 – 800 nm) or even better (~ 65% in the lower wavelength region of 240 – 400 nm) than what has been reported before.

#### 6.3.2.2 FTIR Spectroscopy

Infrared spectroscopy measurements on the CVD SCD plate (SN067–01C) were performed by using a Perkin Elmer Spectrum One FTIR spectrometer. The spectroscopy measurement of transmission versus wavenumber is shown in figure 6.11. The absence of any major valleys between 1100 and 1500 cm<sup>-1</sup> implies very low nitrogen impurity concentration of <1 ppm in the CVD SCD plate. The intrinsic two phonon absorption features of diamond between 1900 and 2500 cm<sup>-1</sup> correspond with that given for type Ila quality diamond [171] within the uncertainty limits of the instrument. This FTIR measurement is similar to those observed for substrates mentioned in references ([9], [24], [35], [38], [114]). Similar to data presented in these references, the substrates grown in a pocket holder also do not show any peaks from nitrogen defects and impurities characteristically seen at 1332, 1344, 3123 and 3107 cm<sup>-1</sup>. This indicates that the growth process via the optimized pocket holder design [166] efficiently synthesizes substrates which are of type Ila quality and are comparable to high quality substrates grown by other MPACVD techniques.

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Figure 6.11 FTIR spectroscopy measurement of a synthesized 221 µm CVD SCD plate (SN067–01C).

## 6.3.2.3 Secondary Ion Mass Spectroscopy (SIMS)

In order to verify and evaluate the nitrogen impurity concentration in the CVD SCD plates, SIMS analysis was carried out by Evans Analytical Group. SIMS allows the elemental analysis of the grown diamond substrates and can measure trace amounts (sub ppm range) of impurities. Since nitrogen is one of the major factors in the deterioration of the optical quality of the substrates, all analyses on substrates was conducted to measure nitrogen impurities. The samples were first sputtered and coated with gold and bombarded with an oxygen/ cesium ion beam source. The probe size is 200  $\mu$ m x 200  $\mu$ m. The nitrogen depth profiles of an as – grown substrate (SN060–01) and a CVD SCD plate (SN067–01C) are shown in figures 6.12(a) and (b) respectively.

The as – grown substrate was synthesized at 240 Torr with 5%  $CH_4/H_2$  for 10 hours. The CVD SCD plate is the same plate as discussed in section 6.3.2.1 – 2.

The red line shown on the two figures depict the detection limit of the SIMS instrument which is 2 x  $10^{15}$  atoms/cm<sup>3</sup>. In order to convert this into ppb, the following steps were used:

$$[N] concentration (ppb) = \frac{2 x \, 10^{15} \, atoms/cm^3}{(3.515 \, gm/cm^3 \, x \, 6.022 \, x \, 10^{23} \, atoms \, / \, 12 \, gms)} \\ \approx \, 1.1338 \, x \, 10^{-8} \, = \, 11.338 \, ppb$$

Here, density of diamond = 3.515 gm/cm<sup>3</sup>, atomic mass of carbon = 12 gms and Avogadro's number (N<sub>A</sub>) =  $6.022 \times 10^{23}$  atoms.



Figure 6.12 SIMS analysis of nitrogen impurity concentration at different depths in (a) an as – grown SCD substrate (SN060–01), and a (b) 221  $\mu$ m CVD SCD plate (SN067–01C). The red line shows the detection limit of the instrument.

Figure 6.12 (cont'd)



For the as – grown SCD substrate, SIMS was carried out till a depth of  $5.9 - 10 \mu m$  and the nitrogen impurity concentration was similarly calculated as above to be ~ 88.4 ppb. SIMS analysis for the CVD SCD plate till a depth of  $6.6 - 12.9 \mu m$  revealed a nitrogen impurity concentration of 97.5 ppb. It is clear that the nitrogen impurity level is low at different depths in the SCD plate/ as – grown substrate and hence it was assumed throughout the bulk of the grown substrate. This is an important criterion to be fulfilled by CVD grown SCD substrates in order for them to be utilized in several optical applications. Even though there was no intentional nitrogen doping of all substrates mentioned here, the slight impurity in the feed gas mixture (~ 6 ppm) is the probable reason for nitrogen concentration to be > 80 ppb but < 100 ppb in the samples. Despite this level of nitrogen

impurity, the UV/Vis, FTIR and SIMS measurements discussed here indicate that the synthesized substrates are of type IIa quality or better.

#### 6.3.2.4 Birefringence Imaging

Birefringence imaging of the CVD SCD plates was performed with a Nikon Eclipse ME 600 optical microscope in conjunction with an external polarizer and analyzer setup designed from a couple of quarter wavelength retardation filters. The retardation filters are placed parallel to each other and are rotated perpendicular with respect to the other's polarization. The diamond substrate is then placed between the two filters. In the absence of anisotropy in the crystal structure of the substrate, the birefringence image appears dark. But stress and defects in the crystals affects the isotropy in the crystals such that the ordinary and the extra – ordinary rays in the collimated optical beam path travel at slightly different angles due to the difference in refractive indices "seen" by the two rays. This effect thus causes birefringence. For the birefringence images shown in figure 6.13, the dark field mode and the back light of the optical microscope (figure 6.2) with a beam collimator was used.

It has been shown that birefringence imaging provides a good indication about the correlation between dislocations/ defects in the crystal and stress regions seen in the birefringence images ([58], [137]). Figure 6.13 shows a series of birefringence images of the 221  $\mu$ m thick CVD SCD plate (SN067–01C) at different exposure times of (a) 500 ms, (b) 2000 ms and (c) 5000 ms.

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Figure 6.13 Birefringence images of a 221  $\mu$ m thick CVD SCD plate (SN067–01C) with exposure times of (a) 500 ms (b) 2000 ms and (c) 5000 ms.

As seen in figure 6.13, the birefringence analysis of the CVD SCD plate indicates low stress in the substrate. This can be seen especially at the center of the plate where the dark region indicates very low stress. With the exception of one edge, the other edges are also relatively low stressed. It has been discussed earlier ([56], [58]) that bundles of defects/ dislocations in the bulk of the CVD SCD plates create stress in the substrates and result in a four petal feature visible through birefringence imaging. In figure 6.13, it can be seen that even at high exposure times, the four petal features do not appear anywhere on the plate except on the left edge. Thus the number of dislocations also appear to be low in the synthesized plates since any major dislocation bundles are absent in the substrate and the dislocations present are probably isolated dislocations. The reason for stress in the left edge of the plate (figure 6.13) is that the original as – grown

substrate was synthesized on a HPHT seed with a top surface cut at an angle to the <100> direction (figure 5.15). This resulted, at the end of the run, in one edge protruding out of the pocket and as a result developed a polycrystalline rim at that edge (figure 12 in reference [166] and figure 5.16(a) in chapter 5). This PCD rim created the stress seen in figure 6.13. Such an observation implies that the presence of a PCD rim not only reduces the surface area of the grown SCD substrate but also reduces the quality of the grown substrate. Hence, it is imperative to eliminate the PCD rim completely in order to synthesize large and high quality SCD substrates.

## 6.3.2.5 X – ray topography (XRT)

X – ray topography is a very useful technique to analyze single crystal quality. This method is a non – destructive way of analyzing the defects and dislocations within the single crystal substrate. In this technique, the x – ray beam is incident at a fixed Bragg's angle on the substrate and then the diffracted beam is captured by a high resolution detector or an x- ray film. The difference in the intensity over the area of the projection of the substrate indicates the regions with defects and dislocations. It has been used by several groups to characterize SCD substrates to determine the quality of the grown substrates ([14], [54], [56], [57], [131], [172]).

In order to further analyze the synthesized CVD SCD plates, x - ray topography was conducted with a Rigaku XRT – 100 imaging system at the LeRoy Eyring Center for Solid State Sciences, Arizona State University. Figure 6.14 shows the setup for the XRT analysis and table 6.2 shows the settings used for the measurements. The system was used in the transmission mode. Figure 6.15 shows the XRT image of a {220} projection

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on the CVD SCD plate (SN067–01C). The projection was captured on an x – ray film at a resolution of 5  $\mu$ m. The system can measure substrates with a dislocation density of only < 10<sup>5</sup> /cm<sup>2</sup>. This indicates that the defect density of SN067–01C is < 10<sup>5</sup> /cm<sup>2</sup>. Section discusses 6.3.2.6 discusses a more specific way of calculating the defect density.



Figure 6.14 Setup of Rigaku XRT – 100 imaging system for XRT analysis.

Table 6.2 Settings of the Rigaku XRT – 100 imaging system for XRT analysis.

Setup component	Component setting
Entrance Slit	20.5 mm
Adjustable Slit Distance	20 mm, 30 mm
Camera Distance	40 mm, 50 mm
X-ray Source	Μο Κα1

Table 6.2 (cont'd)

Power	2 kW
Speed	2 mm/sec
Counts	35

Figure 6.15(a) shows a crossed polarizer image of a HPHT seed. For this image all settings for an optical micrograph are used except the DIC polarizer and the DIC analyzer are also active here. Figure 6.15(b) shows the {220} projection of the SCD plate. The black spots indicated on this projection show the distribution of the defects in the plate. Both figures 6.15(a) and (b) are marked by similar red dashed lines. This is to indicate the similarity of the defect distribution in the plate to the stress observed in the HPHT seed. This defect distribution displays the requirement of obtaining high quality initial CVD seeds in order to reduce the defect density further and thereby avoiding the use of the commercially available, high defect density (~  $10^5 - 10^6$  /cm<sup>2</sup>) type Ib HPHT seeds.



Figure 6.15 (a) Crossed polarizer image of HPHT seed. (b) {220} projection image of a CVD SCD plate (SN067–01C).

# 6.3.2.6 Etch pit density measurements with differential interference contrast microscopy and AFM

In order to determine the approximate defect density, etch pit density measurements were carried out on pocket grown CVD SCD plates and on as received and cleaned HPHT seeds. The substrates were etched in a 2.45 GHz microwave plasma reactor at 240 Torr for 1 hour in a pure hydrogen discharge. The surface temperature was maintained between  $1000 - 1050^{\circ}$ C by slightly adjusting the incident power between 1.8 - 2.0 kW. Since it is known that more etch pits are revealed with high pressures and temperatures ([45], [50]), this is assumed to be an aggressive etching technique and it was used for all etching experiments. The average etching rate is  $1 - 3 \mu$ m/hr. The etch rate was calculated from the weight loss (measured by volumetric analysis) for more accurate results rather than the thickness loss (measured by linear encoder). The following equations were used for this calculation:

$$Thickness \ loss \ (mm) = \frac{(Average \ weight \ loss \ after \ etching) \ x \ 10^3}{3.5 \ x \ 3.5 \ x \ 3.515}$$
$$Etch \ rate \ by \ weight \ loss \ (\mu m/hr) \ = \ \frac{Thickness \ loss \ (mm) \ x \ 10^3}{etching \ duration}$$

Here 3.515 g/cm<sup>3</sup> is the density of diamond and 3.5 x 3.5 mm<sup>2</sup> is the top surface area of the considered SCD substrate.

It has been shown that Differential Interference Contrast Microscopy (DICM) images provide correlation between etch pits formed on the SCD surface and threaded dislocations within the bulk of the substrate [58]. After the etching process, the etch pits have been similarly analyzed with DICM. For this purpose, the Nikon Eclipse ME 600 optical microscope (figure 6.2) was used. The bright field mode, Wollaston prism, DIC polarizer and the DIC analyzer are active in this technique. The Wollaston prism was set to "A" configuration. In DICM, the prism splits the polarized light beam into 2 parts. These two partial beams then strike the substrate at a slight lateral displacement with respect to each other. Now if there is some feature like a step on the surface between the two rays, then one of the rays has to travel an additional distance. Hence, the beam has a path difference between the two partial light rays. After these two beams pass through the prism and the lens they are again aligned in one direction with the help of the DIC analyzer and they then interfere with each other in the intermediate image. This path difference can now be seen through the camera. The images captured with the help of DICM are referred to as Nomarski images. This technique provides a good method of observing contrasting features on the substrate surface and hence the etch pits can be viewed with a high resolution. After the capturing of the Nomarski/ DIC images, the etch pit density was then calculated with the help of the Q – Capture pro 7 imaging software.

Figure 6.16 shows optical micrographs of an HPHT seed (SN086–01) before and after one hour of hydrogen plasma etching process at 240 Torr. Figure 6.16(a) shows the surface of the as – received seed. The seed surface before etching is smooth and polished. After the etching process, as is seen in figure 6.16(b), the surface of the seed becomes very rough. The damage due to the mechanical polishing on the surface may now be seen in the form of the polishing lines running across the seed surface. Most of the etch pits seen on the surface of the seed after the etching process are concentrated on these polishing damage lines. This is explained and displayed in figure 6.17(a).



Figure 6.16 Optical micrographs of an HPHT seed (SN086–01) (a) before and (b) after the hydrogen plasma etching process.



Figure 6.17 (a) Etched surface of a representative type Ib HPHT seed (SN086–01). The etched (b) center and (c) one edge of a representative 287  $\mu$ m thick CVD SCD plate (SN058–01C).

# Figure 6.17 (cont'd)



Some representative images from the etching experiments performed on a HPHT seed (SN086–01) and on a 287  $\mu$ m thick CVD SCD plate (SN058–01C) are shown in figures 6.17(a – c). This plate was grown at 240 Torr with 5% CH<sub>4</sub>/H<sub>2</sub> for 15 hours on a (100) oriented HPHT seed. During the growth of this plate the substrate had a center – edge

morphology but the process was stopped just as the substrate was starting to stick out of the pocket. Hence, the final substrate had only a very slight edge to center growth. These Normaski images have been taken with the same magnification. The difference in the color of the three images arise from the change in the rotation of the Wollaston prism which only changes the color of obtained images without affecting the actual features observed under the microscope. To provide an estimate of the etch pit density of the substrates grown in a pocket holder, first etching experiments were conducted on an as - received and cleaned HPHT seed to check the initial etch pit density i.e. possible propagating defects into the newly grown CVD substrate. In contrast to the plate (figure 6.17(b) and (c)), a large number of the etch pits on the seed (figure 6.17(a)) appear to be concentrated in and around the polishing grooves on the surface. But the etch pits on the plate are more randomly distributed over the surface. Even though the top surface of the plate was polished, after the etching process the top polished surface was removed and the underlying growth steps in the bulk of the plate were revealed (figure 6.17(b)). The etch pits were counted over several areas on the substrate surface with help of the 100x lens of the optical microscope. Then the etch pit densities were averaged out. The area of the typical Nomarski image obtained with a 100x lens is 1.1917 mm<sup>2</sup>. Thus then the average etch pit density was calculated to be 1.36 x 10<sup>5</sup> cm<sup>-2</sup> and 1.6 x 10<sup>4</sup> cm<sup>-2</sup> for the HPHT seed and the CVD SCD plate respectively. Hence the etch pit density was reduced by almost an order of magnitude. While analyzing the same etched CVD SCD plate under DICM, it was also observed that the edges of the plate (figure 6.17(c)) indicated almost 4 -5 times as many etch pits (~ 4.7 x 10<sup>4</sup> /cm<sup>2</sup>) as compared to the central region (figure 6.17(b)) of the plate (1.2 x  $10^4$  /cm<sup>2</sup>). In figure 6.17(c), the red dashed box indicates a high etch pit density at the edge region of the CVD SCD plate.

Figure 6.18 shows a 2.3 x 2.5 x 2.7 mm<sup>3</sup> CVD SCD cube (GYJ153) which was grown for 64.3 hours in 1 growth step at 240 Torr and 5%  $CH_4/H_2$  in reactor C by Dr. Yajun Gu. This cube was grown on a <100> oriented HPHT seed. After laser cutting off the HPHT seed and polishing the SCD substrate we obtained the SCD cube as shown in figure 6.18.



Figure 6.18 A 2.3 x 2.5 x 2.7 mm<sup>3</sup> cube grown in 1 growth step at 240 Torr with 5%  $CH_4/H_2$ .

The top grown surface of the CVD SCD cube was then etched (figure 6.19) using the same technique as described earlier and the etch pit density was calculated to be ~  $3.72 \times 10^3$  etch pits/cm<sup>2</sup>. This shows that the etch pits have reduced by almost 2 – 3 orders of magnitude.



Figure 6.19 DICM image of the growth surface of the cube shown in figure 6.18. The SCD surface was aggressively etched at 240 Torr for one hour in a pure hydrogen plasma but shows low number of etch pits.

The reduction in etch pit density from the initial seed surface may be due to several factors. Some of the probable reasons are listed here: (a) multiple dislocations coalescing to form one bundle of threaded dislocations, (b) threaded dislocations terminating within the bulk of the CVD substrate, and (c) threaded dislocations deviating towards the edges of the substrate. While factors (a) and (b) are equally likely, tedious analysis is required to study such a propagation of the etch pits threaded dislocations. For this reason, the main focus was on factor (c) in the discussion given in section 6.3.2.7.

#### 6.3.2.7 Etch pit distribution on CVD SCD substrates

A CVD SCD plate (GYJ153-side1-02) was synthesized with two consecutive 24 hour growth runs at a pressure of 240 Torr and with 5% CH<sub>4</sub>/H<sub>2</sub> in reactor B. Using the same etching technique mentioned above, etching experiments were performed on this CVD SCD plate. The polished top surface of the plate was etched for 1 hour. In order to further study the etch pits revealed after the etching process, AFM was conducted on this SCD surface. Figure 6.20(a) and (b) display a 3D and 2D AFM image of the etched surface respectively. Some of the deeper etch pits are clearly visible here. The surface profile of one of the etch pits on this plate's surface is shown in figure 6.20(c) which is ~ 100 nm deep and  $\sim 1 \,\mu m$  wide. The edges of the etch pits are aligned with the <011> direction. The faces of the etch pit are symmetrical with respect to the <100> growth direction in certain observed etch pits (figure 6.20(c)). However, in many other observed etch pits this is not true (figure 6.20(d)). For such uneven etch pits, seen in figure 6.20(d), there seems to be a combination of 2 or more etch pits. Such a coalesced etch pit formation would result in an uneven bottom edge of the resultant etch pit which may be due to the combination of several threaded dislocations. This is a possible interpretation of a flat bottomed etch pit. However, there may be other possible reasons for such an etch pit. Observations made from several other SCD experiments also indicated that the average width of the etch pits is in the range of  $0.5 - 7 \mu m$ .



Figure 6.20 AFM analysis of etch pits on a CVD SCD plate (GYJ153–side1–02). (a) 3D and (b) 2D image of an etched surface (c) Surface profile of an etch pit observed on the etched surface of a SCD substrate. Its depth is ~ 100 nm and width is ~ 1  $\mu$ m, and (d) surface profile of a non – symmetrical etch pit with respect to the <100> growth direction.

This etched CVD SCD plate was also observed under high magnification with DICM to observe any patterns in the etch pit distribution over the etched surface. The CVD SCD plate in figure 6.20 was chosen to show the etch pit distribution. This is displayed in figure 6.21(a) and (b). During the etching process, the polished surface is etched away and now the underlying growth steps are clearly visible in the polished CVD SCD plate as the wavy pattern (figure 6.21(a)). It was also observed that most of the etch pits tend to form at/ near the edge of each growth step (green dashed line in figure 6.21(a)). This observation gives the impression that during growth, defects propagate along the edges of the growth steps with deposition time. Similar observations have been made in hetero-epitaxial substrates as given in references ([59], [173]).

It has been discussed in other references that by modifying the shape of the seed to a beveled structure, the defect density of the grown CVD substrate may be improved upon [37]. References ([59], [173]) has shown that it is possible to tilt the dislocations by preparing the seeds in an off – axis direction. The TEM studies presented in these references show a distinct tilting of dislocations in the direction of the diamond layer growth. This was observed in substrates containing a low nitrogen concentration (a few ppm) within the first few tens of µm of growth.

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Figure 6.21 (a) and (b) High magnification DICM images to show the etch pit distribution over the etched SCD surface.

In the preliminary observations described here in this chapter, at the beginning of the deposition process the center of the seed was at a slightly higher temperature during

growth in a pocket holder. As a result, the growth rate of the center was slightly higher as compared to the edges of the seed. Hence, there is a center to edge growth morphology since the substrate during growth had the appearance of a primitive pyramidal structure (figure 5.11(b)). So instead of utilizing expensive cutting and polishing techniques to create beveled structures, the pocket holders employed here help in creating such a similar structure *in situ* via a much simpler method.

Thus a possible method of obtaining low defect CVD SCD substrates is that if the growth of the SCD substrate can be controlled and modified in such a way that the growth layers are steered/ deposited from the center of the HPHT seed towards the edge of the seed, then it is possible to obtain an almost defect free SCD substrate especially at the center. For such a growth process it is important to grow the substrate with a long growth duration. The CVD SCD cube shown in figure 6.18 has a center – edge morphology ([166], [167]) i.e. the growth progresses from the center of the HPHT seed towards the edges and the corners of the seed. The number of etch pits would then be reduced with more growth layers transgressing from the center to the edge of the substrate and as the thickness of the substrate increases. Hence we obtain a low defect density (~ 3.72 x 10<sup>3</sup> etch pits/cm<sup>2</sup>) on top of the CVD SCD cube as shown in figure 6.18. This etch pit conclusion requires further research, although the etching experiments performed in this chapter indicate that this may potentially be a good way of depositing low defect SCD substrates.

# CHAPTER 7 SOME OTHER APPROACHES TO LARGE AND HIGH QUALITY SUBSTRATES

## 7.1 Introduction

Apart from the growth strategies discussed in chapter 5, some different approaches for large and high quality SCD substrates may also be employed. This chapter deals with three such approaches, namely: (1) the flipped seed, (2) the beveled seed, and (3) the forced flow deposition approaches. In this chapter, details of some initial experiments and the corresponding system design for each of the three approaches are described.

The beveled seed experiments were conducted in both reactor B and C designs. The flipped seed and the forced flow deposition experiments have been performed with only the reactor B design. For the forced flow experiments, the system operation was modified since a new set of substrate holders (schematically shown in chapter 3) were designed to enable the forced flow.

While only some preliminary experiments for these methods have been discussed in this chapter, this investigation sets up a platform for future studies on these approaches.

## 7.2 Flipped seed growth method

The main motivation for this growth strategy stems from the method proposed in reference [55] which is briefly described in section 2.6.2. The electronic quality of the synthesized CVD SCD substrates is vastly affected by the threaded dislocations present within the substrate. These dislocations originate from the underlying seed substrate and propagate parallel to the growth direction which is typically the <100> direction for the (100) oriented seed substrates. But once the substrate is flipped orthogonal to the original growth direction i.e. either to the <010> or <001> direction, the threaded dislocations are prevented from growing along the new perpendicular growth direction. Such an approach would not only help in the reduction of the threaded dislocation density but would also help in increasing the synthesized CVD SCD substrate dimensions (figure 7.1).



Figure 7.1 Flipped seed growth methodology.

## 7.2.1 Some initial experiments

The purpose of utilizing this flipped seed method in our experiments was to investigate the effect of the pocket substrate holder designs on the flipped seed sample. Since such a substrate holder design has not been exploited before with the flipped seed method, the effort here was to improve the quality of the synthesized substrate by flipping the seed while simultaneously preventing the growth of a polycrystalline diamond rim and hence removing the probability of any edge defects.

For the initial experiments, first it was important to prove the feasibility of the proposed method with a pocket holder design. A  $3.5 \times 3.5 \times -1.5 \text{ mm}^3$  Sumitomo HPHT type Ib seed was bisected into 2 parts perpendicular to the top surface (figure 7.2) with the help of laser cutting. The approximate dimensions for the half seeds were ~  $3.6 \times 1.3 - 1.4 \times 1.5 - 1.8 \text{ mm}^3$ . The pocket holder used for the growth of these half seeds was a variation of the holder design shown in figure 3.7.



Figure 7.2 (a) Top view of seed before bisecting (b) side view of unpolished one half of the bisected seed.

The typical growth parameters for the flipped seed synthesis experiments were: p = 240Torr, %CH<sub>4</sub>/H<sub>2</sub> = 7%, substrate temperature = 1050 – 1100°C,  $z_s = -5.38$  to -6.78 mm. High growth rates of 30 – 40 µm/hr were obtained. Some examples of the synthesized CVD SCD substrate on half seeds are displayed in figure 7.3. Figure 7.3(a) shows a substrate after an 8 hour deposition run with a growth rate of 38.74 µm/hr and figure 7.3(b) shows a substrate after a 12 hour deposition run with a growth rate of 39.89 µm/hr. As is clearly seen from these substrates, the top surface is very smooth with no defects. But the edges do seem to have a small polycrystalline diamond rim. A possible reason for this PCD growth is the inappropriate dimensions of the holder used. The side surfaces of the flipped half seed were not protected from the intense microwave electromagnetic fields which thereby led to the growth of the PCD rim. For this reason, a new pocket holder was fabricated, as shown in figure 3.8 (SN-1inch-side1) for future half seed experiments.



Figure 7.3 Flipped half HPHT seeds grown for (a) 8 hours, and (b) 12 hours.

## 7.2.2 Flipped seed experiments on lab grown CVD substrates

More flipped seed experiments were performed on CVD substrates which were grown in reactor C. First, the HPHT seed was grown in reactor C at 240 Torr with 5% CH<sub>4</sub>/H<sub>2</sub> and then the CVD grown part was laser cut and separated from the HPHT seed. The CVD substrate was then polished on the laser cut side and also on two opposite side surfaces. Figure 7.4 shows an example of laser cut CVD substrate (GYJ153) with only the bottom surface polished. The two side surfaces shown in figure 7.4 were then polished. One of the polished side surfaces (figure 7.4(c)) was grown at 240 Torr for 10 hours with 5% CH<sub>4</sub>/H<sub>2</sub> and T<sub>s</sub> = 1100 – 1150°C. A new pocket holder (SN–1inch–side2) was fabricated for this purpose. The resultant substrate is displayed in figure 7.5, which shows the top surface, side surface and then closer optical micrograph views for the grown side surface. The surface is very smooth with no polycrystalline rim. The growth rate of the side grown substrate was 23.54  $\mu$ m/hr.



Figure 7.4 CVD part of sample GYJ153. (a) Top unpolished growth surface, (b) bottom laser cut polished surface, (c) unpolished side surface, and (d) unpolished second side surface.



Figure 7.5 (a) Grown side surface, (b) side view, (c) closer optical micrograph views of sample GYJ153–side1–01.

# Figure 7.5 (cont'd)



Figure 7.6 (a) Grown side surface and (b) side view of the CVD substrate grown with a second run of 24 hours (GYJ153–side1–02).

A second deposition run was conducted at similar operating conditions for 24 hours on the same side surface. Figure 7.6 shows the grown side surface and the side view of the substrate. It is clear from figure 7.6, that the substrate expands outwards with no polycrystalline diamond deposition around the edges and a smooth top surface with no defects. The growth rate of this second run on the side grown substrate was 17.87  $\mu$ m/hr. This side grown CVD substrate was then laser cut and separated from the underlying initial CVD substrate to form a ~ 664  $\mu$ m thick CVD plate.

A similar set of experiments was also conducted on larger CVD substrates. The 4 step grown, laser cut and polished CVD substrate (GYJ127) shown in figure 5.21 was bisected parallel to the growth direction with laser cutting. One half of the substrate (SN084) was flipped perpendicular to the original growth direction (figure 7.7) after polishing off the laser cut side and then grown on the side surface with two consecutive 24 hour growth runs at 240 Torr, 5% CH<sub>4</sub>/H<sub>2</sub>, T<sub>s</sub> = 1100 – 1150°C and growth rates of 21.56 µm/hr and 17.63 µm/hr respectively (figure 7.8). Figure 7.8(c) shows the final ~ 940 µm thick CVD substrate grown on the side surface of a flipped half CVD substrate. It is clearly seen that the surface has a smooth morphology and that there is no PCD rim around the substrate hence preventing any edge defect formation. Another pocket holder (SN–1inch–side3) was fabricated with appropriate dimensions for this flipped substrate.



Figure 7.7 Polished laser cut surface of bisected CVD substrate (GYJ127-side1).



Figure 7.8 (a) and (b) two consecutive 24 hour growth runs on a flipped large CVD substrate (GYJ127–side1–01 and 02 respectively), (c) ~ 940  $\mu$ m thick side grown CVD substrate with no polycrystalline rim.

## 7.3 Beveled seed approach

In the beveled seed growth approach, the edges of the seed are offset to the usual <100> growth direction by a few degrees. Thus the resulting seed has a smaller top (100) surface area and 4 misoriented edges offset by  $5 - 20^{\circ}$  to the <100> growth direction. The seed then looks similar to figure 2.59(b). The purpose of this beveled seed growth method is to exploit the center to edge growth morphology seen in the synthesized SCD substrates grown via pocket holders and combine this growth strategy with the tilting of etch pits at/ near the edges of the growth terraces. The initial idea for the beveled substrates was suggested by the research discussed in section 2.5.3.3 and shown schematically in figures 2.59 and 2.60. SCD growth on such misoriented seed substrates helps in the reduction of the etch pit density as seen in figure 2.94. The etch pit density was observed to be reduced on the beveled edges as compared to that on the top of the (100) surface after growth.

In the preliminary experiments conducted in this thesis, the effort was to investigate the effect of the pocket holder design on the beveled seeds and combine it with long term deposition runs. A (100) oriented HPHT seed was first laser cut and polished by Applied Diamond Inc. according to the dimensions provided in figure 7.9. A top  $1.7 \times 1.7 \text{ mm}^2$  was kept as the (100) oriented seed area, while the adjoining edges with a width of 1 mm were offset by  $\sim 7 - 10^\circ$  with respect to the <100> growth direction. For a typical as received HPHT seed, the top surface area is slightly larger ( $\sim 3.7 \times 3.7 \text{ mm}^2$ ) as compared to the bottom surface area ( $\sim 3.5 \times 3.5 \text{ mm}^2$ ).

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Figure 7.9 (a) Top view and (b) side view of the beveled HPHT seed to be laser cut and polished.

After laser cutting and polishing the surfaces, the beveled seed is similar in appearance to figure 7.10. Figure 7.10 (a) shows an optical micrograph of the (100) oriented top

surface and the offset edges of the seed. Figure 7.10(b) shows a photograph of the beveled seed.



Figure 7.10 (a) Side view and (b) top view of the beveled seed substrate.

After the careful preparation of the misoriented seeds, multiple experiments were conducted in both reactors B and C. For the experiments conducted in reactor B, the growth parameters were p = 240 Torr,  $T_s = 1100 - 1150^{\circ}$ C, growth time = 24 hours, % CH<sub>4</sub>/H<sub>2</sub> = 5%, and with ~ 1.6 - 1.75 kW microwave power. Figure 7.11 shows the top surface of a ~ 500 µm thick as grown SCD substrate (SN089–01) after a 24 hour growth run in a pocket holder with a growth rate of ~ 21 µm/hr. While the area coverage, as seen in figure 7.11(a), is uneven it is important to note that the CVD SCD top surface has a very smooth growth morphology (figure 7.11(c)). Figures 7.11(b) and (d) indicate the

lateral growth of single crystal diamond layers. The <010> and <001> propagation of the diamond layers is an important process for the enlargement of the single crystal substrate dimensions. It is also important to note that the grown SCD substrate is free of any polycrystalline diamond rim.



Figure 7.11 The top surface of SN089–01 grown in reactor B after a 24 hour growth experiment.

Similar studies were also conducted in reactor C. Figure 7.12 shows an ~ 1.9 mm thick as grown CVD SCD substrate (SN093–01) synthesized at 240 Torr, with 5% CH<sub>4</sub>/H<sub>2</sub>, T<sub>s</sub> =  $1000 - 1050^{\circ}$ C, 2.1 – 2.7 kW microwave power and for 50 hours. The growth rate of this substrate was ~ 24 µm/hr.





Figure 7.12 Top surface of SN093 – 01 grown in reactor C after a 50 hour growth experiment.

The SCD surface of the as grown substrate has a smooth morphology with no major defects. The substrate also has almost no PCD rim. In contrast to figure 2.60, it is seen from these synthesized substrates in pocket holders that the (113) and (111) surfaces can be completely grown over with higher growth rates and hence smaller deposition time, to enhance the (100) surface growth. This is another advantage of utilizing the optimized pocket holder designs as outlined in this thesis. More work in this direction is required to expand the substrate surface. In addition, etching experiments on such synthesized substrates will be useful in evaluating the etch pit density and hence the quality of the grown CVD SCD substrates on beveled seeds.

## 7.4 Forced flow growth

One of the main methods of obtaining thick single crystal diamond substrates is by improving the growth rates of the deposited samples. This can be done by forcing the flow of growth radicals onto the substrate surface at high pressures in order to increase the growth rate and also to adjust the pocket size during growth. The main thrust of the forced flow growth approach is to improve the gas flow efficiency and hence increase the deposition growth rate in a shorter time duration. This part of the research entailed the conceptualization of the forced flow idea, designing of new substrate holders and hence modifying the current reactor design, and finally performing some initial experiments.

## 7.4.1 Gas flow within the reactor

As has been discussed in section 5.2, the mixture of hydrogen and methane gases flow into the cavity through a series of holes drilled symmetrically around the base of the quartz bell jar. These gases flow into the dome (figure 7.13) uniformly, undergo chemical reactions within and around the core of the microwave discharge and then flow out through an annular ring consisting of 16 holes around the circumference of the 2.55 inch substrate holder (figure 3.6). The gas flow patterns directly above the substrate and in the vicinity are more complicated. The buoyant forces due to the hot plasma produce their own gas flow patterns. The hot and dissociated gas molecules above the substrate diffuse through the boundary layer and deposit on the substrate within a pocket substrate holder. While an accurate description of the exact gas flow within the quartz bell jar in the presence of a plasma is still under investigation, it is considered that a significant part of almost all the input gas concentration flows out as exhaust. This concentration of the gas
flowing around the boundary of the dispersed microwave discharge does not participate in the synthesis process and hence the gas flow efficiency is reduced.



Figure 7.13 Typical gas flow patterns in the quartz bell jar of the reactor cavity.

In order to counteract this issue and to enhance the growth rate, a modification in the gas flow pattern is proposed here. For this, a new substrate holder configuration was designed. The three parts of the new holder configuration are shown in figures 3.9 – 3.11. The arrangement of these parts of the new holder design is shown in figure 7.14. The bottom part is the SN–2inch–indent holder. The middle part is SN–2inch–forced1 holder and the top part is the SN–2inch–forced holder.



Figure 7.14 The entire forced flow substrate holder configuration.

In a forced flow reactor setup, the idea is to force part of the total flow of growth radicals through a small gap in a new substrate holder which is placed just over the original holder. Figure 7.15 shows the change in the gas flow pattern in the modified design. Figure 7.15(a) displays the entire setup while figure 7.15(b) shows a magnified view of the holder arrangement marked in red in figure 7.15(a). The central gap of the holder allows for some of the important growth radicals to flow at a faster rate onto the substrate surface and then flows out through the holes in the underlying holder, following the same pattern as before (shown in figure 7.13). The gas now flows through the central hole in the top part of the holder setup directly onto the substrate, then out through the gap between 8 legs of the top holder part and then finally out of the 16 holes drilled around the circumference

of the bottom holder. Both the middle and the bottom holder contain an indentation at the center to hold the seed. In a few of the tests, only a 2 holder (top and bottom holders) setup was used with no middle holder. With the help of the pumping out process, the gases flow over the substrate at a much faster rate as compared to the typical MPACVD reactor process. Since there are no holes in the top holder, more hot and diffused gas molecules are forced to flow through the gap at the center of the top holder.



Figure 7.15 (a) Entire modified system setup (b) Closer view of the holder configuration.

It is important that the boundary layer, through which the diffusion process takes place, should penetrate into the central gap in order to ensure the flow of growth radicals directly onto the substrate surface. If the boundary layer is detached from the substrate, then recombination of growth radicals may take place above the substrate surface leading to no or reduced deposition. Due to the change in gas flow pattern, the boundary layer between the microwave discharge and the seed is also modified (figure 7.15(b)). The boundary layer needs to be created such that it penetrates the central hole on the top holder and is positioned directly above the seed surface. In addition, the seed substrate should be at the right temperature for deposition to take place. A major challenge in this modified system setup is creating the appropriate thermal environment for the synthesis of SCD on the HPHT seed. This is a remaining challenge and one that needs further experimental investigation for the improvement of the forced flow process.

#### 7.4.2 Some preliminary experiments

A series of preliminary experiments were conducted with the substrate holder variation shown in figure 7.14. A stable plasma behavior was obtained for different pressure and power levels with such a configuration. Some initial experimental variables include: pressure = 120 - 200 Torr, 5 - 7% CH<sub>4</sub>/H<sub>2</sub>, growth time = 3 - 6 hours, substrate temperature =  $800 - 950^{\circ}$ C, incident power = 1.73 - 2.15 kW and a growth rate of ~  $1.3 - 2.3 \mu$ m/hr. From these initial experiments, it was concluded that more design variations are required to increase the substrate temperature to beyond  $1000^{\circ}$ C. A higher substrate temperature is required to improve the SCD growth rate to tens of  $\mu$ m/hr.

## 7.4.3 Possible variations of forced flow holders

This section describes some possible variations of the forced flow holder setup. Figures 7.16 – 7.18 show some of these possibilities. Figure 7.16 shows a slight modification to the normal substrate holder with the top holder having a series of holes drilled around the circumference to imitate the typical gas flow patterns (figure 7.13). While much of the hot and diffused gases flow directly on top of the substrate surface, the gas flow at the periphery of the dome volume follow the typical gas flow patterns. This helps in the constant influx of new gas mixture within the quartz bell jar.



Figure 7.16 One variation of the forced flow holder setup.

Figure 7.17 shows a slightly different design of the forced flow holder where the gas particles continuously diffuse onto the substrate. Here the inner legs of the top holder are completely closed off and due to the lack of any holes in the underlying holder, the gas particles concentrate around the area near the substrate. Now since the hot and diffused radicals are trapped within the enclosed space near the seed surface, the temperature of the substrate surface also increases. Although large carbon concentrations in this enclosure may lead to a fast rate of soot development, this configuration when combined with an adjustable stage allows the pocket holder to be adjusted as a function of time.



Figure 7.17 Another possible variation of the forced flow holder setup.

The earlier discussed forced flow reactor strategy works opposite to gravity but the buoyant force of the gases flowing through the boundary layer tends to shift the plasma away the appropriate position for deposition. Thus, an inverted reactor setup is also proposed here (figure 7.18), in which the gases flow in conjunction with the buoyant force. The hot and dissociated growth radicals are forced to flow directly through the small gap in the holder and onto the substrate. As compared to the earlier setup, the gas flow will

be higher through the center and hence prevent the shift of the plasma while simultaneously controlling the boundary layer directly adjacent to the substrate.



Figure 7.18 Inverted forced flow holder setup.

The main challenge here is that this design would require a major re – engineering effort for the reactor cavity. Innovative methods would be needed to keep the substrate fixed such that (1) it is flat on the holder surface, (2) it has an appropriate surface temperature for deposition, and (3) its bottom surface is cooled efficiently.

## CHAPTER 8 SUMMARY, CONCLUSIONS AND FUTURE DIRECTIONS

## 8.1 Summary and conclusions

#### 8.1.1 Microwave reactor coupling and operational efficiencies

It is important to develop an efficient and well matched reactor deposition process in order to increase the diamond deposition efficiency (i.e. low kW.hr/carat). One of the main reasons to do so is that in a commercial environment, an inefficient process increases the energy cost of producing CVD diamond substrates in bulk quantities. If the deposition process is electrically inefficient then both the size of the power supply and the cooling system are larger resulting in a larger initial system capital cost and in a larger footprint on the factory floor. Both the initial cost and the larger footprint would increase the cost of producing diamond.

In this thesis, an experimental methodology is described that enables the control and matching of a microwave discharge at pressures above 100 Torr. A unique aspect of the described technique is that it involves the variation of four reactor mechanical tuning length variables. These adjustments add considerable process flexibility and enable useful diamond synthesis process control and optimization. In this flexible operation, the reactor geometry can be varied to attain different process conditions and yet achieve efficient performance. Using this efficient reactor configuration, both high quality and high pressure PCD and SCD synthesis were demonstrated at high deposition rates. These experiments were all performed within the efficient and safe deposition process window of the reactors. These experimental results also demonstrated that high coupling efficiency can be attained over a wide range of process conditions that allow experimental

adjustment for the optimization of the process over large pressure regime (100 - 300 Torr), different methane concentrations (3 - 7%) and input microwave power levels (1.3 - 2.4 kW).

In order to realize the efficient, reliable and robust operation, input power limits must be placed on a given reactor design/ synthesis process application. The experiments presented in this thesis show that it is desirable at a given pressure to limit the input microwave power level. By increasing the input power, it is possible to increase the deposition rate, but at high input powers it also decreases the overall deposition efficiency (i.e. higher kW.hr/ carat). It is possible to increase both the deposition rate and the overall deposition efficiency by operating at higher pressures. These high pressure conditions help in increasing the absorbed microwave power densities. By preventing the loss of energy to the walls of the reactor cavity, the reactor can be operated in a reliable and stable regime. Even though coupling efficiencies may remain high (> 90%) as input power is increased, input power limitations are useful in order to achieve an efficient diamond synthesis process and simultaneously avoid discharge wall interactions and the formation of microwave plasmoids and substrate hot spots. Further work needs to be done to understand the formation of the hot spots/ plasmoids.

In particular, it was demonstrated that the employment of internal reactor matching enables a single mode excited, well matched, efficient reactor operation over a wide pressure/ input power/ substrate position regime while operating under diamond deposition conditions. If the reactor is adjusted to a very well matched condition at a midrange pressure, for example 180 Torr, then  $\eta > 90\%$  is achieved over the entire 100 – 260 Torr pressure and 1.5 – 2.4 kW input power regime without the need for additional

external matching. Additionally, when operating at a specific experimental operating condition within this pressure/ power regime, small additional internal tuning adjustments can be made to achieve  $\eta > 98\%$ . Virtually all of the available incident power can be coupled into the reactor over the entire 100 - 260 Torr operating pressure regime. Then  $\eta_{coup} \sim (1 - (P_{loss}/P_{inc})) \times 100\%$  and  $\eta_{coup} \sim (1 - (Q_L/Q_0)) \times 100\%$  and the problem of achieving high overall microwave coupling efficiencies into the discharge can be directed towards achieving and maintaining a high  $Q_0$ .

 $\eta_{coup}$  is improved if  $Q_0$  is increased, i.e. if the materials inside the reactor cavity are lossless, if the cavity metal joints are microwave tight, if microwave soot formation and carbon film deposition on the walls are eliminated, etc. If  $Q_0$  decreases from run to run then the overall system electrical efficiency will decrease from run to run. However, it is conceivable that a well-designed and maintained internally tuned MPACVD diamond synthesis system can achieve  $\eta_{coup} > 94\%$ .

In this thesis, this three to four variable experimental matching technique was applied to the CVD diamond synthesis application. However, this experimental methodology is applicable to most microwave sustained discharge applications operating above 100 Torr. Once the efficient and safe microwave coupling regime is established, this experimental methodology can be utilized in establishing efficient MPACVD processes within that operating regime.

#### 8.1.2 Pocket substrate holder variations and process control variations versus time

While operating at high pressures of 240 Torr, two local MPACVD SCD synthesis process control methods were combined and used to develop a process that synthesized

high quality SCD plates and cubes. The local synthesis conditions were controlled versus time over the entire process cycle by placing the seed in an experimentally optimized "pocket holder" geometric configuration. These holders enable the synthesis of SCD substrates without the formation of a PCD rim. Additionally, in parallel, the seed substrate temperature was controlled versus time to lie within 950 – 1150°C by slightly varying the input power versus time. By employing such growth strategies, thick (200  $\mu$ m – 2.5 mm) free standing diamond plates (in reactor B) and cubes (in reactor C by Dr. Yajun Gu) were grown when using one continuous process step and large (~ 2.1 carat) CVD SCD cubes (in reactor C by Dr. Yajun Gu) were grown when using as many as four growth steps.

The substrate holders employed in the MPACVD SCD synthesis were specifically (a) conventional open holder and (b) optimized pocket holder designs. It was shown that at high pressures the open holder synthesis process leads to a growth of PCD rim with time and also results in an edge to center growth morphology due to non – uniform surface temperature. This in turn leads to a decrease in the SCD surface area while simultaneously increasing the PCD rim width. In contrast to the open holder synthesis process, the pocket holder reduces the growth of any PCD rim while simultaneously increasing the SCD substrate size laterally as well as vertically. This leads to the synthesis of stress free CVD SCD plates especially at the edges. The SCD substrates grown in a pocket holder display a center to edge growth morphology in the initial stages of growth. This indicates that the central region of the substrate is growing at a slightly faster rate as compared to the edges of the substrate. As the substrate thickness increases the substrate temperature increases since the distance between the substrate surface and the intense microwave discharge reduces. In order to maintain a constant substrate

temperature in the high growth rate regime, the incident power levels were adjusted accordingly. It was experimentally observed that the growth rate of the substrates tends to drop as the substrate surface approaches the top holder surface. But if the substrate starts to grow out of the pocket and starts penetrating into the plasma, then it begins to imitate the open holder growth process and the growth rate increases with most of the deposition occurring on the polycrystalline diamond rim. Such a behavior needs to be prevented and hence the process was stopped at this juncture before the substrate completely penetrated into the plasma. This strategy was successful in reducing the PCD rim, in enhancing the as – grown SCD substrate area and in improving the synthesized SCD substrate quality by reducing the stress in the substrates.

By utilizing a combination of the pocket holder design and process control methods discussed in chapter 5, the SCD surface area was enhanced to 1.32 times (SN083–01 grown in reactor B and shown in figure 5.14(b)), to 2.14 times (GYJ171 grown in reactor C and shown in figure 5.18) for single step growth runs and to 2.5 times (GYJ161 grown in reactor C and shown in figure 5.20) with a 2 step growth process (figure 5.19). All these SCD substrates were synthesized without the formation of any PCD rim.

#### 8.1.3 The characterization of the grown diamond material

A detailed characterization of the as grown SCD material was presented in [174], was published in reference [175] and was discussed in detail in chapter 6. SCD substrates synthesized with MPACVD at high pressures with a pocket holder show smooth rimless growth morphology throughout the substrate surface. The characterization and analysis of both as – grown substrates and CVD SCD plates show that they are of high quality. Optical microscopy, FESEM and AFM indicate that the surfaces of the substrates have a smooth layered morphology. These growth steps were observed to be angled from the center to the edge of the substrate, thus verifying the center to edge growth morphology of the substrates. EDS measurements indicate that the elemental composition of the substrate is mostly carbon with trace amounts of oxygen. Birefringence imaging of the laser cut and polished CVD SCD plates display low birefringence. This implies that the grown plates have low stress and hence no cracks. UV/Vis and FTIR spectroscopy of the CVD SCD plates indicate that they have high (~ 71%) optical transparency with no detectable (< 1 ppm) nitrogen impurities. To quantify any trace amounts of nitrogen impurities, the SIMS analysis conducted by Evans Analytical Group shows that both the as – grown substrates and the CVD SCD plates have < 100 ppb nitrogen impurity concentration. This indicates that the synthesized substrates are of type IIa quality or better. To investigate the electronic quality of the grown substrates, etching experiments were conducted in reactor B. Starting with high defect density (> 10<sup>5</sup>/ cm<sup>2</sup>) HPHT seeds we have been able to reduce the defect density to ~  $10^4$ / cm<sup>2</sup>. It is also clear from the etching experiments that the etch pit density at the edges of the substrates are higher than the central region of the substrates. The etch pit density at the edge region is almost 4-5 times to that in the central region. For further reduction in defect density it is important to utilize type IIa quality CVD substrates as the initial seed. This fact was also confirmed with the XRT measurements done at Arizona State University. Despite the presence of a low nitrogen impurity concentration, the quality of these substrates is comparable to/ better than the previously published work presented by other groups ([9], [17], [24], [32], [33], [35], [38], [114]) and grown via other MPACVD methods.

The aggressive etching experiments, described in this research, on the synthesized SCD substrates have displayed interesting flow patterns on the etched substrate surface where the etch pits tend to coalesce at/ near the edges of the growth terraces. Such behavior was utilized in this thesis by instigating the growth of the SCD from the center towards the edge of the substrate and increasing the growth time of the synthesized substrates. Although the tilting of the etch pits is not a new observation, the creation of an *in situ* concave structured substrate during deposition in a pocket holder design shows a simpler method of obtaining the tilting in etch pits. By exploiting such a propagation of etch pits i.e. threaded dislocations, in combination with the center – edge morphology and long growth durations of the synthesized CVD SCD substrates, initial analysis of the etched substrates indicate that the defect density was further reduced to ~  $10^3$  etch pits/ cm<sup>2</sup>, i.e. a 1 – 3 order of magnitude lower than the initial commercially available HPHT seeds. More work needs to be done in this regard in order to understand the pocket holder growth process and to optimize this process to produce even lower defect SCD plates.

## 8.2 Resultant journal publications

This research has thus far been published in three journal publications and are given in references ([40], [166], [175]). Reference [40] discusses the optimization and characterization of the microwave cavity plasma reactor. The microwave coupling efficiency measurements and experimental methodology of the reactor are discussed in detail there. This publication also discusses the resultant SCD and PCD substrates grown with an efficient reactor setup with a high overall deposition efficiency. The growth of large SCD substrates and the investigation of the effect of different substrate holder designs are discussed in reference [166]. The open and pocket holder design growth processes are described here and the advantages of utilizing the pocket holder design over the more conventional open holders are also mentioned. The analysis and characterization of the synthesized SCD substrates was presented in [174] and has been discussed in reference [175]. The process technology resulting from a combination of these methods was filed in a US provisional patent (WO 2015/187389 A2) [176].

## 8.3 Future directions

The research presented here in this thesis opens up many possible avenues of exploiting the observations made and utilizing them in depositing larger and better quality single crystal diamond substrates.

The exploration and investigation of the reactor characteristics explained in chapter 4 can be studied even further. The data shown in figure 4.8 describes the evaluation of the microwave coupling efficiency as a function of  $L_s$  for different substrate holder positions (– 8.17 to – 1.77 mm). This study can be expanded further to understand the reactor performance below – 8.17 mm. This investigation is important in order to enhance the operational regime of the microwave reactor even further. Important questions about whether the reactor remains in a well matched regime at these lower substrate holder positions may then be possibly answered. This lower limit of substrate position can then be explored to map out the reactor behavior and deposit high quality diamond substrates at higher pressure levels and high absorbed power densities successfully.

An important future approach towards large SCD substrates would be to explore the extent to which the pocket substrate holders may be used for this purpose. To ensure uniform deposition for large SCD substrates at high pressures, there is an upper limit to which the pocket dimensions may be varied. This limit needs to be investigated. There are three ways by which this limit may be further expanded:

(a) By operating the reactor at even higher pressure (> 300 Torr), the growth rate may be enhanced further.

(b) By increasing the incident microwave power levels at a constant pressure level, the plasma volume may be increased. This increase in plasma volume would be

advantageous for uniform deposition over large SCD surfaces. But it is important to note here that such a reactor operation may be inefficient. It should also be carefully monitored to prevent any wall interaction and hence leading to process contamination.

(c) By adjusting the substrate position at higher pressures the focus and the shape of the plasma may be modified such that the entire substrate surface is covered for deposition. This would probably be the best approach to explore in order to expand the SCD substrate and enhance the lateral surface area with the help of an optimized pocket holder design.

Additionally, the lateral and vertical growth of SCD substrates in a pocket holder needs further study. Specifically, the deposition strategies and methods dealing with an extensive systematic investigation of the  $\alpha$ ,  $\beta$  and  $\gamma$  parameters may be explored. The SCD substrates discussed in this thesis display a lateral and vertical growth of the SCD surface. This indicates a growth of both the (110) and (100) crystal surfaces of the diamond lattice structure. Some of the synthesized SCD substrates also show a slower growth at the corners which indicate a slower growth rate of the (111) and (113) crystal faces. It is thus important to study and optimize operating conditions by which the growth along both the (111) and (113) crystal orientations may be enhanced. A systematic investigation of the  $\alpha$ ,  $\beta$  and  $\gamma$  parameters during the synthesis process for different experimental conditions is thus required in order to expand both the vertical as well as the lateral growth of the SCD surface area and hence synthesize large SCD substrates.

It would be useful to characterize and analyze the grown SCD substrates with techniques other than the ones discussed in this thesis. Methods like DiamondView, 3D x-ray topography projections, Raman spectroscopy, photoluminescence and

cathadoluminescence would provide valuable information about the defects and dislocations present in these substrates. SIMS analysis for other impurities like silicon would also be useful to understand the quality of the grown substrates. Initial analysis of the electronic quality of the substrates grown as a part of this thesis indicate that a reduction in etch pit density is possible by utilizing the center to edge growth morphology. It would thus be helpful for future experiments and process improvements to study this result further. More etch pit density measurements need to be conducted on thick (> 1 mm) CVD SCD substrates to fortify the observations made here. It would be interesting to study the quality of the edges of the substrates. By performing micro-Raman spectroscopy and etching experiments on the edges of the substrates, the quality of the expanding diamond substrate may be analyzed. It would also be important to understand whether the growth of the PCD rim around the SCD area is solely due to the substrate growing out of the recess or whether the etch pits tilting towards the edges are an additional factor in the formation of non – epitaxial crystallites at the edges which then result in a PCD rim. Such a study may be done before the trimming of the PCD rim for the preparation of CVD SCD plates and cubes.

A systematic study of the SCD growth process in a pocket holder as a function of time would provide valuable insight in the evolution of the SCD substrate. The growth rate of the central region in comparison to that at the edges may then be studied. By alternating such a study with etching experiments of the substrate surface, further knowledge about the tilting of etch pits may be obtained. This systematic study would then be very beneficial for further improvements in the process of growing large and high quality SCD substrates in optimized pocket holder designs.

The SCD substrate synthesis process discussed in this dissertation has been carried out on commercially available HPHT type Ib seed substrates. These diamond seeds have large defect densities and a high nitrogen impurity concentration as seen in chapter 6. This implies that these are not the most suitable initial substrates for depositing high quality CVD SCD substrates. It is thus imperative to use high quality CVD substrates as the initial seeds. The substrates grown and analyzed as a part of this thesis indicate a reduction in the etch pit densities. Such substrates may now be used for further reduction in defect densities with long term growth combined with the center to edge growth morphology (chapter 5). Such an approach would open up another avenue to grow large and high quality CVD SCD substrates.

The flipped seed and beveled seed growth approaches also provide good means of depositing large and high quality SCD substrates. A thrust in this direction would help in evaluating the quality of the substrates grown with these methods. Etching experiments on the grown substrate via these methods would indicate the behavior of the tilting in the etch pit formation. As suggested by the preliminary experiments performed in this thesis, the SCD surface may be enlarged without the formation of a PCD rim. Longer growth durations are required to analyze the substrates grown with the beveled seed approach.

# Growth direction



Figure 8.1 Cross – sectional birefringence image of a bisected one half (figure 7.7) of the 4 step grown CVD SCD cube shown in figure 5.21(a).

The process of depositing multi – step CVD SCD substrates help in the synthesis of thick substrates. But figure 8.1 indicates some issues with such a deposition strategy. Figure 8.1 shows a cross – sectional birefringence image of a bisected half (figure 7.7) of the CVD SCD cube previously discussed in figure 5.21(a). As is seen in this figure 8.1, the red box indicates the seams between consecutive growth layers. Each start and stop of the synthesis process leads to a different set of initial growth conditions, which in turn lead to a seam between the growth steps. These interruptions increase the probability of introducing more defects at these transitions for the next growth layer. Such a problem may be solved with a few possible solutions:

(a) By designing a new movable substrate holder and/ or a movable cooling stage. Such a movable substrate configuration would be automated and adjustable along the z – axis. This movement along the z – axis will then allow for the top surface of the substrate to be shifted below the top surface of the PCD deposition on the holder (figure 8.2). This will also ensure that the substrate remains embedded within the pocket and hence the growth times may be enhanced for large SCD substrate deposition.



Time: t = t1



Figure 8.2 Adjustable substrate position with the help of a movable substrate holder/ cooling stage.

(b) By designing a forced flow holder configuration, as discussed in chapter 7. The forced flow growth also indicates a promising conceptual idea for increasing the gas flow efficiency during the growth process. A challenge in this approach has been to increase the substrate temperature due to the separation of the boundary layer from the substrate surface during growth. A possible solution to this problem is a redesigning of the bottom

two holders in order to reduce the cooling of the substrate surface. This can be done by utilizing the existing flat insert (for SCD deposition) and pocket holder design by modifying their dimensions. The other variations in the forced flow holder and reactor setup, as discussed in chapter 7, may also be varied and used for increasing the growth rate of the SCD substrates. APPENDICES

## APPENDIX A

## Shim sets

## Shim set Thickness (mm) 1 0.75 2 1.10 3 1.38 4 1.55 (defective) 5 1.65 6 3.18 7 6.4

## Table A.1 List of shim sets used.

#### APPENDIX B

Substrate holder configurations and determination of substrate position.

In order to determine the substrate position ( $z_s = L1 - L2$ ), the 2 reactor variables: L1 and L2 first need to be determined. From figure 3.3, L1 is given as the distance between the top of the conducting plate to top of the substrate holder. For the case of the 2.55 inch substrate holder (from figure 3.4), the height of the cooling stage is = 2" = 50.8 mm. The height of the lip at the top of the cooling stage = 0.045" =  $\sim 1.1$  mm. The total thickness of the 2.55 inch substrate holder (figure 3.6) = 0.177" =  $\sim 3.23$  mm. Thus, L1 was calculated as: 50.8 - 1.1 + 3.23 mm = 52.93 mm. This configuration for L1 was kept constant for PCD and microwave energy coupling experiments discussed in chapter 4. Since the substrate holder configuration was changed for the SCD and etching experiments as discussed in chapters 5, 6 and 7, L1 was modified accordingly.

For the calculation of L2, the shim sets listed in table A.1 were used. As seen in figure 3.3, L2 is the distance from the top of the conducting plate to the discontinuity plane between the cylindrical and coaxial regions of the cavity, i.e. the z = 0 plane. For reactor B, the z = 0 plane is the top of the base plate (figure 3.3). Hence, L2 is calculated as: thickness of base plate (28.6 mm) + thickness of ledge (26.1 mm) (figure 3.3) + shim thickness = 54.7 mm + shim thickness. Table B.1 shows the L2 configuration for the different shim sets used in this thesis.

Shim set used (mm)	Base plate and ledge (mm)	L2 (mm)
None = 0	54.7	54.7
2 and 5 = 2.75	54.7	57.45
1 and 6 = 3.93	54.7	58.63
7 = 6.4	54.7	61.1

Table B.1 L2 configuration for different shim sets (from appendix A).

Table B.2 indicates the substrate holder position for all microwave coupling efficiency experiments discussed in chapter 4. For all PCD, SCD and etching experiments the shim set 7 was used, i.e. L2 = 61.1 mm. Since the substrate holder configuration was different for SCD experiments, L1 was also different. Table B.3 lists the different substrate holders used for all SCD and etching experiments discussed in chapters 5, 6 and 7. For convenience, the names of the substrate holders listed in parentheses in table B.3 indicate the same name as per the Physics machine shop fabrication records. The different holder configurations corresponding to the experimental data are mentioned in appendix F.

Table B.2 Substrate holder position for microwave coupling efficiency experiments (chapter 4).

L1 (mm)	L2 (mm)	$Z_{\rm s} = L1 - L2 \ (mm)$
52.93	54.7	- 1.77
52.93	57.45	- 4.52
52.93	58.63	- 5.7
52.93	61.1	- 8.17

Holder Number	Substrate holder		
1	Ø 2.55" PCD holder (SN–2inch–SCD) (figure 3.6)		
2	Ø 1.5" flat insert (thickness (t) ~ 0.7 mm)		
3	Ø 1.5" SCD pocket holder for 1 <sup>st</sup> runs (SN–1inch–01)		
4	Flat insert with central gap for pocketless expt. (t ~0.75 mm)		
5	Ø 2.55" open holder with indent (SN– 2inch–indent) (figure 3.9)		
6	Ø 1.5" SCD pocket holder for 2 <sup>nd</sup> runs		
7	Ø 1.5" SCD pocket holder for 3 <sup>rd</sup> runs		
8	Ø 1.5", 1.5 mm deep SCD pocket holder (SN–1inch–01– 1.5)		
9	Ø 1.5", 1.6 mm deep SCD pocket holder (SN–1inch–01– 1.6)		
10	Ø 1.5", 1.8 mm deep SCD pocket holder (SN–1inch–01– 1.8) (figure 3.7)		
11	Ø 1.5" SCD pocket holder for side seed growth (SN–1inch–side1) (figure 3.8)		
12	Ø 1" SCD pocket holder (GYJ–1inch–01–extd.side)		
13	Ø 1.5" SCD pocket holder for side growth (SN–1inch–side2)		
14	Ø 1.5" SCD pocket holder for side growth (SN–1inch–side3)		
15	Ø 1.5" SCD pocket holder for big seeds (SN–1inch–7x7)		

Table B.3 Substrate holder configuration for SCD and etching experiments.



Figure B.1 Ø 1.5" SCD pocket holder.

Table B.4 Dimensions for Ø 1.5" SCD pocket holder variations (d = d<sub>1</sub> + d<sub>2</sub>, w = (w<sub>3</sub> - w<sub>1</sub>)/2 or (w<sub>4</sub> - w<sub>2</sub>)/2).

Holder number	d₁ (mm)	d₂ (mm)	t (mm)	₩1 (mm)	₩2 ( <b>mm</b> )	₩3 ( <b>mm</b> )	₩₄ (mm)
3	0.72	0.7	1.96	4	4	5	5
6	1.0	0.86	2.96	4	4	6	6
7	1.52	1.14	3.05	4	4	7	7
8	0.72	0.78	1.96	4	4	5	5
9	0.72	088	1.96	4	4	5	5

Table B.4 (cont'd)

10	0.72	1.08	2.16	4	4	5	5
11	1.9	0.8	3.4	1.7	4	3.7	6
13	0.72	2.18	3.26	3	3	4	4
14	0.8	2.2	3.36	4.8	5.4	5.8	6.4
15	0.25	0.75	1.96	7.5	7.5	8.5	8.5

Since the substrate holder number 12 had a slightly different design as compared to the normal pocket holder shown in figure B.1, it has been shown in a different figure B.2.



Figure B.2 Ø 1" SCD pocket holder (holder number 12).

#### APPENDIX C

Calculation of nitrogen impurity concentration during the synthesis process

In all the experiments described in this thesis, no intentional nitrogen was added into the system since it deteriorates the optical quality of the grown substrates. But some unintentional nitrogen doping of the substrates may occur due to two possible sources: (a) due to some slight leaks in the system, and (b) due to impurities in the feed gas line. These 2 sources are discussed here.

(a) Concentration of nitrogen impurities from system leaks: The volume of the vacuum chamber and quartz dome of reactor B is ~ 78200 cm<sup>3</sup>. Typically for almost all the growth experiments listed in appendix F, the leak rate of the system is ~ 0.5 - 1 mTorr/hr. So for the case of 1 mTorr/hr leak rate and an atmospheric pressure of 760 Torr, the flow rate of air into the system may be calculated as:

$$\frac{1 x 10^{-3} Torr}{60 mins} x \frac{78200 cm^3}{760 Torr} = 1.715 x 10^{-3} sccm$$

The total feed gas flow rate of hydrogen and methane gases (say 5%) for growth processes is 420 sccm. The concentration of nitrogen in air is 78%. Thus, the concentration due to the leakage into the system may be calculated as:

$$\left(78\% x \ \frac{1.715 \ x \ 10^{-3} \ sccm}{420 \ sccm}\right) x \ 10^{6} = \ 3.185 \ ppm$$

(b) Concentration of nitrogen impurities from feed gases: The gases used for all deposition experiments are research grade hydrogen (5.5 N = 99.9995% pure) and methane (5N = 99.999% pure) gases. The hydrogen gas flow rate is 400 sccm (100%)

and typically for methane is 20 sccm (5%). Then the nitrogen impurity concentration from the gas mixture may be calculated as:

$$((1 - 0.999995)x 100\% + ((1 - 0.99999)x 5\%))x 10^6 = 5.5 ppm$$

Hence, the total nitrogen impurity concentration in reactor B is 3.185 + 5.5 ppm = 8.685 ppm, i.e. less than 10 ppm. So for a leak rate of 0.5 mTorr/hr, the nitrogen impurity concentration is 4.343 ppm, i.e. < 5 ppm. The leak rate for reactor C was calculated in section 5.2.4 of reference [41].

### APPENDIX D

### Pulsing of microwave discharge in reactor B

Pulsed microwave discharges help in enhancing the diamond growth rate as compared to a continuous wave mode plasma. This has been discussed in chapter 5 (section 5.2). While in this section, the discharge behavior at only 180 Torr is shown, the same pulsing of the discharge was also observed at other pressure levels of 100 and 240 Torr. Since the Cober power supply connected to the microwave reactor setup has poor filtering, output power fluctuations at 120 Hz were observed. Similar fluctuations were also observed in the microwave oscillating frequency, i.e. 2.45 GHz. Such power and frequency fluctuations result in the pulsing of the microwave discharge.

Table D.1 lists the camera settings used for capturing the photographs of the pulsing discharge at 100, 180 and 240 Torr during data acquisition of the microwave coupling efficiency measurements (detailed in chapter 4). Figures D.1 and D.2 show series of high speed mode captured photographs indicating the pulsing plasma behavior at 100 and 240 Torr respectively for different power levels. The photographs for 180 Torr are shown in figure 5.2. The settings for the PCD experiments on a one inch silicon wafer as shown in these figures have been discussed in chapter 4.

Camera model	Canon EOS 60D
Capture mode	High speed continuous mode (5.3 shots per sec.)
Aperture value	F/4.0

Table D.1 (cont'd)

ISO		1600	
Flash		None	
Color representation		sRGB	
Recording mode		Manual	
	100 Torr	1/320 sec <sup>-1</sup>	
Exposure time	180 Torr	1/800 sec <sup>-1</sup>	
	240 Torr	1/1250 sec <sup>-1</sup>	



Figure D.1 A series of high speed mode photographs of the pulsed microwave discharge in reactor B at 100 Torr, 3%  $CH_4/H_2$  with a constant average power level of (a) 1.45 kW, and (b) 2.01 kW.

### Figure D.1 (cont'd)



Figure D.1 shows a series of photographs taken for the pulsed microwave discharge at 100 Torr with a high speed setting at 1.45 kW (figure D.1(a)) and at 2.01 kW (figure D.2(a)). As seen from these figures, the microwave discharge is stable at low pressures irrespective of the power levels (1.4 - 2.1 kW). This implies that the plasma can be sustained at low pressures with very low power levels. This observation is in contrast to figure D.2. Figure D.2 shows a series of photographs taken for the pulsed microwave discharge at a high pressure level of 240 Torr with a high speed setting at 1.44 kW (figure D.2(a)) and at 2.0 kW (figure D.2(b)). As seen in figure D.2, the pulsing of the microwave discharge is much more apparent here, especially at 1.44 kW (figure D.2(a)).



Figure D.2 A series of high speed mode photographs of the pulsed microwave discharge in reactor B at 240 Torr, 3%  $CH_4/H_2$  with a constant average power level of (a) 1.44 kW, and (b) 2.0 kW.

## Figure D.2 (cont'd)


#### APPENDIX E

Experimental details of the SCD synthesis and etching process

Table E.1 Experimental variables for single crystal synthesis process.

Variable	Set value
Reactor design	Reactor B
Seeds used	(1) HPHT type Ib SCD seeds from Sumitomo
	from Microwave Enterprises (ME)
Pressure (Torr)	100 – 240
Time (hours)	2.33 – 36
Set power (kW)	1.1 – 2.4
%CH4/ H2	5 – 7
Intentional nitrogen addition	None
Substrate temperature (T <sub>s</sub> ) (°C)	1050 – 1170
Substrate position $(z_s)$ (mm)	– 5.38 to – 8.17
Shim set used	7
Short length (L <sub>s</sub> ) (mm)	21.55 cm
Probe length $(L_p)$ (mm)	3.65 cm

Variable	Set value
Reactor design	Reactor B
Pressure (Torr)	240
Time (hours)	1
Set power (kW)	1.55 – 2.15
H <sub>2</sub> flow rate (sccm)	400
Substrate temperature (Ts) (°C)	1000 – 1050
Substrate position (zs) (mm)	- 5.38 to - 6.78
Shim set used	7
Short length (L <sub>s</sub> ) (mm)	21.55 cm
Probe length (L <sub>p</sub> ) (mm)	3.65 cm

Table E.2 Experimental variables for single crystal etching process.

### APPENDIX F

### Experimental data of the SCD synthesis process

Table F.1 Set input and output experimental variables for single crystal synthesis processes.

Substrate	Press.	Time	Set	P <sub>inc</sub>	P <sub>ref</sub>	%CH4/	T <sub>s</sub> (°C)	t <sub>init.</sub>	t <sub>fin.</sub>	Growth	Zs	Holder
	(Torr)	(hrs)	power	(kW)	(kW)	H <sub>2</sub>		(mm)	(mm)	rate	(mm)	config.
			(kW)							(µm/hr)		
1 <sup>st</sup> half seed	240	8				7	1081	1.65	1.96	38.74	-6.78	1,2,3
2 <sup>nd</sup> half seed	240	8				7	1050 – 1100	1.88	2.36	39.89	-6.78	1,2,3
2 <sup>nd</sup> half see – 02	240	12				7	1050 – 1100	2.36	2.74	31.83	-6.78	1,2,3
3 <sup>rd</sup> half seed	240	10				7	1050 – 1100	1.66	1.67	1.23	-5.83	1,2,11
SN001-01	240	8				5		1.39	1.47	9.31	-6.78	1,2,3

SN001-02	240	8	2.0	1.894	0.121	5	959 – 1076	1.47	1.74	33.93	-6.78	1,2,3
SN001-03	240	8	2.0	1.875	0.112	5	1093 – 1108	1.74	1.86	16.17	-6.78	1,2,3
SN002-01	240	8	1.9	1.738	0.000	5	1096 – 1114	1.35	1.52	21.63	-6.78	1,2,3
SN002-02	240	8	1.8	1.654	0.042	5	1107 – 1174	1.52	1.73	26.07	-6.78	1,2,3
SN002-03	240	8	2.0	1.841	0.002	5	1040 – 1081	1.73	1.87	17.3	-6.48	1,6
SN003-01	240	8	1.9	1.767	0.000	5	1082 – 1114	1.41	1.64	28.88	-6.78	1,2,3
SN004-01	240	8	1.9	1.76	0.001	5	1068 – 1098	1.48	1.59	13.7	-6.78	1,2,3

SN005-01	240	8	2.0	1.765	0.000	5	1104 – 1151	1.34	1.56	27.08	-6.78	1,2,3
SN006-01	240	8	1.9	1.753	0.016	5	1107 – 1144	1.39	1.69	36.8	-6.78	1,2,3
SN007-01	240	8	1.9	1.743	0.017	5	1125 – 1141	1.4	1.643	30.48	-6.78	1,2,3
SN008-01	240	8	1.9– 1.95	1.792	0.000	5	1118 – 1156	1.40	1.487	10.55	-6.78	1,2,3
SN009-01	240	8	1.9	1.761	0.081	5	1133 – 1145	1156	1.332	29.8	-6.78	1,2,3,
SN010-01	240	8	1.9	1.74	0.062	5	1125 – 1155	1.37	1.585	25.65	-6.78	1,2,3
SN011-01	240	8	1.9	1.749	0.066	5	1108 – 1139	1.36	1.484	15.26	-6.78	1,2,3

SN012-01	240	8	1.9	1.773	0.070	5	1139 – 1147	1.37	1.63	31.7	-6.78	1,2,3
SN013-01	240	8	1.7– 1.9	1.619	0.103	5	1159 – 1175	1.37	1.622	32	-6.78	1,2,3
SN014-01	240	6	1.9	1.789	0.083	5	1133 – 1164	1.363	1.41	8	-6.78	1,2,3
SN015-01	240	8	1.9	1.722	0.110	5	1159 – 1180	1.41	1.592	23.17	-6.78	1,2,3
SN016-01	180	8	1.6	1.455	0.079	5	1151 – 1184	1.42	1.615	24.14	-8.17	1,2,4
SN022-01	240	8	1.8	1.672	0.170	5	1128 – 1157	1.41	1.498	11.13	-6.78	1,2,3
SN024-01	240	8	1.9	1.763	0.126	5	1108 – 1156	1.38	1.78	49.6	-6.78	1,2,3

SN025-01	160	8	1.9– 2.2	1.697	0.014	5	981 – 1175	1.387	1.733	43.24	-8.17	5
SN025-02	160	8	1.5– 1.8	1.458	0.054	5	1127 – 1176	1.733	1.856	15.48	-8.17	5
SN025-03	130	3.5	1.8– 1.9	1.577	0.005	5	1147 – 1165	1.856	1.855	-1.24	-8.17	5
SN025-04	130	8	1.45– 1.75	1.351	0.005	5	1136 – 1178	1.855	1.97	14.05	-8.17	5
SN025-05	130	8	1.1– 1.4	1.074	0.019	5	1165 – 1190	1.97	2.06	11.28	-8.17	5
SN026-01	240	8	2.2– 2.4	2.009	0.131	5	992 – 1108	1.4	1.69	36.36	-7.48	1,3
SN027-01	100	8	0.75– 0.9	0.79	0.003	5	1336 – 1452	3.66	Side	Growth	-8.17	5

SN028-01	160	4	2.05– 2.13	2.027	0.004	5	1119 – 1178	1.41	1.53	14.77	-8.17	5
SN029-01	240	12	1.5– 1.7	1.49	0.298	5	1125 – 1185	1.38	1.59	17.78	-6.48	1,6
SN030-01	160	8	2.0– 2.26	1.774	0.008	5	1018 – 1160	1.46	1.59	15.93	-8.17	5
SN031-01	240	2.33	1.65– 2.4	1.617	0.277	5	1013 – 1141	1.386	1.413	11.92	-7.48	1,3
SN032-01	240	8	1.6– 2.2	1.575	0.292	5	1097 – 1205	1.377	1.53	19.08	-7.48	1,3
SN033-01	240	8	2.1– 2.35	1.912	0.139	5	1104 – 1170	1.385	1.647	32.8	-7.48	1,3
SN034-01	240	8	2.3	2.079	0.122	5	1123 – 1144	1.393	1.638	30.67	-7.48	1,3

SN035-01	240	8	2.3– 2.42	2.137	0.11	5	1106 – 1157	1.412	1.495	10.36	-7.48	1,3
SN036-01	240	12	2.25– 2.4	2.136	0.103	5	1067 – 1120	1.345	1.441	8	-6.48	1,6
SN037-01	240	8	2.03– 2.1	2.916	0.143	5	1114 – 1144	1.424	1.535	13.94	-6.78	1,2,3
SN038-01	240	6.167	~ 2.4	2.145	0.085	5	1093 – 1112	1.422	1.476	8.76	-7.48	1,3
SN039-01	240	8	2– 2.03	1.842	0.134	5	1125 – 1156	1.408	1.568	20	-6.78	1,2,3
SN040-01	240	8	1.95– 2.07	1.806	0.111	5	1129 – 1158	1.383	1.487	12.9	-6.78	1,2,3
SN041-01	240	8	2.15– 2.18	1.958	0.083	5	1132 – 1157	1.393	1.58	23.4	-7.48	1,3

Table F.1 (cont'd)

SN042-01	240	8	2– 2.2	1.772	0.099	5	1126 – 1151	1.393	1.611	27.36	-6.78	1,2,3
SN042-02	240	15	2– 2.2	1.824	0.000	5	1107 – 1152	1.611	1.77	10.33	-5.69	1,2,7
SN043-01	240	8	1.8– 1.9	1.674	0.06	5	1129 – 1168	1.379	1.696	39.6	-6.78	1,2,3
SN044-01	240	8	1.9– 1.95	1.778	0.029	5	1133 – 1166	1.38	1.47	11.27	-6.78	1,2,3
SN045-01	240	8	1.87– 1.95	1.743	0.004	5	1130 – 1163	1.362	1.497	16.9	-6.78	1,2,3
SN046-01	240	8	1.72– 1.8	1.626	0.038	5	1125 – 1185	1.397	1.56	20.3	-6.78	1,2,3
SN046-02	240	12	1.85– 2.05	1.689	0.000	5	1112 – 1160	1.56	1.84	23.11	-6.78	1,2,6

SN046-03	240	8	1.78– 1.8	1.663	0.074	5	1136 – 1158	1.84	2.04	24.93	-6.78	1,2,6
SN046-04	240	12	1.98– 2.1	1.757	0.000	6	1129 – 1154	2.04	2.2	13.6	-5.69	1,2,7
SN047-01	240	8	1.73– 1.9	1.620	0.091	5	1118 – 1152	1.426	1.482	7.06	-6.78	1,2,3
SN048-01	240	10	1.96– 2.0	1.739	0.000	5	1113 – 1151	1.428	1.536	10.77	-6.78	1,2,6
SN049-01	240	8	1.88– 1.98	1.717	0.012	5	1115 – 1165	1.36	1.426	8.1	-6.78	1,2,3
SN050-01	240	10	2– 2.1	1.811	0.001	5	1112 – 1146	1.39	1.642	25.43	-6.78	1,2,8
SN051-01	240	10	2– 2.12	1.783	0.02	5	1115 – 1166	1.364	1.47	10.8	-6.78	1,2,8

SN052-01	240	10	2.01– 2.08	1.821	0.021	5	1122 – 1156	1.387	1.61	22.13	-6.78	1,2,8
SN053-01	240	10	1.98– 2.05	1.812	0.035	5	1127 – 1156	1.359	1.479	12	-6.78	1,2,8
SN054-01	240	10	1.92– 2.0	1.756	0.052	5	1111 – 1153	1.4	1.636	23.36	-6.78	1,2,8
SN055-01	240	10	1.95– 2.06	1.830	0.039	5	1102 – 1154	1.41	1.52	10.95	-6.78	1,2,8
SN056-01	240	10	1.95– 2.08	1.800	0.026	5	1078 – 1142	1.41	1.659	24.81	-6.78	1,2,8
SN057-01	240	10	1.95– 2.08	1.804	0.036	5	1097 – 1138	1.397	1.507	10.98	-6.78	1,2,8
SN058-01	240	15	1.98– 2.02	1.776	0.045	5	1112 – 1145	1.34	1.66	21.68	-6.78	1,2,8

SN059-01	240	10	1.98– 2.05	1.857	0.102	5	1080 – 1145	1.425	1.726	30.15	-6.78	1,2,8
SN060-01	240	10	2.04– 2.1	1.912	0.092	5	1109 – 1139	1.418	1.668	24.99	-6.78	1,2,8
SN061-01	240	12	1.99– 2.18	1.947	0.081	5	1107 – 1140	1.528	1.575	12.3	-6.78	1,2,8
SN062-01	240	15	1.94– 2.12	1.876	0.087	5	1105 – 1149	1.425	1.761	22.37	-6.78	1,2,8
SN063-01	240	15	2.01– 2.35	2.061	0.078	5	1093 – 1144	1.414	1.578	10.92	-6.78	1,2,8
SN064-01	240	18	2.03– 2.35	2.06	0.071	5	1080 – 1131	1.416	1.787	20.6	-6.78	1,2,8
SN065-01	240	22.57	2.1– 2.58	2.189	0.059	5	1083 – 1148	1.432	1.9	20.74	-6.78	1,2,9

SN066-01 or SN058-01SC	240	17.17	2.21– 2.5	2.183	0.092	5	1066 – 1140	1.13	1.6	27.33	-6.78	1,2,8
SN067-01 or SN059-01SC	240	24	2.1– 2.2	1.902	0.093	5	1125 – 1157	1.179	1.618	18.29	-6.78	1,2,8
SN068-01	240	4.5	1.95– 2.0	1.816	0.142	5	1091 – 1141	1.39	1.56	37.56	-6.78	1,2,9
SN069-01	240	18	1.83– 1.95	1.701	0.157	5	1123 – 1160	1.358	1.7	19.06	-6.78	1,2,9
SN071-01	240	24	1.9– 1.99	1.790	0.154	5	1113 – 1150	1.347	1.157	9.571	-6.78	1,2,9
SN072-01	240	24	1.9– 1.97	1.777	0.136	5	1114 – 1143	1.356	1.758	16.75	-6.78	1,2,9
SN073-01	240	24	1.81– 1.9	1.731	0.154	5	1089 – 1154	1.325	1.724	16.62	-6.78	1,2,9

SN074-01 or SN067-01SC	240	13.77	1.95– 1.98	1.791	0.150	5	1114 – 1151	0.969	1.094	9.06	-6.78	1,2,8
SN075-01 or SN065-01SC	240	24	1.88– 2.0	1.830	0.137	5	1109 – 1154	1.163	1.6	18.24	-6.78	1,2,8
SN076-01	240	12	1.9– 1.98	1.8	0.152	5	1125 – 1137	1.368	1.47	8.59	-6.78	1,2,9
SN077-01	240	24	1.9– 2.08	1.871	0.118	5	1115 – 1137	1.33	1.752	17.56	-6.78	1,2,9
SN078-01	240	15	1.9– 2.02	1.849	0.149	5	1108 – 1139	1.335	1.463	8.56	-6.78	1,2,9
SN079-01	240	23.32	1.93– 2.15	1.897	0.125	5	1095 – 1145	1.344	1.679	14.37	-6.78	1,2,9
SN080-01	240	24	1.86– 1.98	1.782	0.134	5	1111 – 1165	1.355	1.765	17.1	-6.78	1,2,9

SN081-01	240	24	2.02– 2.24	1.950	0.146	5	1056 – 1173	1.384	1.789	19.19	-6.58	1,2,10
SN082-01	240	24	1.95– 2.08	1.847	0.114	5	1102 – 1144	1.38	1.813	17.98	-6.58	1,2,10
SN083-01	240	24	1.95– 2.16	1.894	0.119	5	1102 – 1158	1.377	1.769	16.34	-6.58	1,2,10
SN084-01 or GYJ127-G04- CVD1-01	240	24	1.84– 2.03	1.827	0.113	5	1125 – 1181	2.419	2.937	21.56	-5.38	1,2,14
SN084-02 or GYJ127-G04- CVD1-02	240	24	1.74– 1.98	1.782	0.093	5	1106 – 1146	2.929	3.352	17.63	-5.38	1,2,14
SN088-01	240	10	1.92– 1.96	1.754	0.014	5	1121 – 1145	1.423	1.717	29.46	-6.58	1,2,10

SN089-01	240	24	1.62– 1.74	1.548	0.000	5	1106 – 1177	1.38 - 1.4	1.894	20.4 – 21.28	-6.58	1,2,10
SN089-02	240	24	2.01– 2.19	1.881	0.001	5	1175 – 1144	1.894	2.384	28.87	-7.28	1,10
SN090-01	240	24	1.87– 2.13	1.838	0.000	5	1104 – 1145	1.43	1.92	20.42	-6.58	1,2,10
SN091-01	240	36	1.79– 1.86	1.521	0.000	5	1080 – 1151	1.349	1.854	14.03	-6.27	1,12
SN092-01	240	24	1.57– 1.6	1.396	0.000	5	1135 – 1181	1.43	1.76	13.61	-6.57	1,2,12
SN7x7cvd 1–01	240	10	1.9– 2.0	1.754	0.169	5	1124 – 1197	0.453	0.68	22.76	-6.58	1,2,15
GYJ153 – side1 – 01	240	10	1.95– 2.02	1.84	0.114	5	1120 – 1176	2.45	2.69	23.54	-5.48	1,2,13

Table F.1 (cont'd)

GYJ153 – side1	240	24	1.89–	1.819	0.12	5	1124 –	2.69	3.11	17.87	-5.48	1,2,13
- 02			2.0				1162					

#### APPENDIX G

### Experimental data of the SCD etching process

Table G.1 Set input and output experimental variables for single crystal etching processes.

Substrate	Press.	Time	Set	P <sub>inc</sub>	P <sub>ref</sub>	H <sub>2</sub>	Ts	Avg.w <sub>1</sub>	Avg.w <sub>2</sub>	etch	Zs	Holder
	(Torr)	(hrs)	power	(kW)	(kW)	flow	(°C)	(mg)	(mg)	rate	(mm)	config.
			(kW)			(sccm)				(µm/hr)		
SN001-03	240	1	1.55–	1 506	0 1 2 1	400	1125–	03.02	03 78	3.25	-6 78	1 7 3
31001-03	240		1.6	1.500	0.121	400	1203	93.92	93.76	3.20	-0.78	1,2,3
SN001 02C	240	1	1.78–	1 654	0.074	400	1013–	16 52	16 52	0 222	6 79	1 2 15
31001-030	240		1.8	1.034	0.074	400	1014	10.55	10.52	0.232	-0.78	1,2,13
SN002 02	240	1	1.7–	1 671	0.020	400	1190–	08 30	09.14	57	6 79	1 7 2
311002-03	240		1.8	1.071	0.039	400	1339	90.39	90.14	5.7	-0.78	1,2,3
SN002-03C	240	1	1.78–	1 654	0.074	400	965 —	20.67	20.62	13	-6 78	1 2 15
011002-000	240		1.8	1.004	0.074	400	1030	20.07	20.02	1.5	-0.70	т, <b>∠</b> , тЈ

SN058-01C	240	1	2.1– 2.15	1.89	0.025	400	1003– 1014	13.35	13.31	0.975	-6.78	1,2,15
SN067-01C	240	1	1.78– 1.8	1.658	0.058	400	1002– 1025	10.096	10.03	1.533	-6.78	1,2,15
SN070-01 (HPHT seed)	240	1	1.73– 1.78	1.621	0.127	400	1039– 1079	65.75	65.73	0.464	-6.78	1,2,9
SN071-01	240	1	1.68– 1.7	1.575	0.129	400	1027– 1046	74.46	74.38	1.672	-6.78	1,2,9
SN072-01	240	1	1.6– 1.62	1.525	0.128	400	1025– 1050	86.29	86.18	2.18	-6.78	1,2,9
SN084-01 or GYJ127-G04- CVD1-01	240	1	1.45– 1.53	1.46	0.111	400	1009– 1045	236.2	236.1	1.567	-5.38	1,2,14

SN084-02 or GYJ127-G04- CVD1-02	240	1	1.84– 1.96	1.695	0.068	400	1025– 1050	276.3	276.13	4.23	-6.08	1,14
SN086-01 (HPHT seed)	240	1	1.78– 1.8	1.663	0.066	400	1028– 1047	62.532	62.526	0.139	-6.78	1,2,9
SN087-01 (HPHT seed)	240	1	1.64– 1.78	1.63	0.072	400	1010– 1052	64.042	64.028	0.325	-6.78	1,2,9
SN7x7cvd1 (CVD seed)	240	1	2.03	1.85	0.032	400	1018– 1030	79.63	79.49	3.34	-6.78	1,2,15
SN7x7cvd1 – 01	240	1	1.73– 1.75	1.603	0.094	400	1015– 1035	120.94	120.82	2.65	-6.78	1,2,15
GYJ153 (side 2)	240	1	1.63– 1.65	1.548	0.091	400	1031– 1050	51.63	51.56	1.81	-5.69	1,2,7

GYJ153 (as–	240	1	1 65	1 572	0.091	400	1020–	51 56	51 5	1 01	5 60	107
grown side)	240		1.05	1.575	0.001	400	1031	51.50	51.5	1.21	-5.09	1,2,7
GYJ153-side1-	240		1.65–	4 500	0.000	400	1028–	70.40	70.00	0.000	E 40	1 0 10
02	240		1.68	1.566	0.096	400	1032	72.42	72.38	0.928	-5.48	1,2,13
GYJ153-	240	4	1.58–	1 400	0 1 2 2	400	1019–	10.61	10.6	0.000	6 70	100
sideCVD-02	240		1.59	1.499	0.132	400	1038	19.01	19.0	0.232	-0.70	1,2,0

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