ELO GROWTH LARGE AREA SINGLE CRYSTAL CVD DIAMOND USING POCKET HOLDERS

By

Shengyuan Bai

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ABSTRACT

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Single crystal diamond is a promising ultra-wide band-gap material. Epitaxial lateral outgrowth using microwave plasma assisted chemical vapor deposition has shown promise towards synthesizing large size high quality single crystal diamond, but growth of this material is a continued challenge. This work explores the growth dynamics of single crystal diamond in a constrained system, namely a pocket holder, used to suppress the formation of polycrystalline diamond. Results demonstrate significant and reproducible effects of the pocket design on growth behavior and growth morphologies, with strong positive correlations observed between pocket dimensions and epitaxial outgrowth fronts. Enhanced growth rates at the leading edge of epitaxial lateral outgrowth are also observed. Internal structure of grown samples mapped by scanning x-ray rocking curve measurement reveal outgrown regions are consistently lower quality despite the smooth morphology. This result is compared with the growth rates of the top surface and edges which shows a strong correlation between growth rate and crystal quality. Traditional pocket holders are shown to constrain ELO in a 1st order exponential decay fashion in previous work and the lateral size of as grown diamond has an upper limit subject to its holder configurations. As an upgraded research project, this research will include the SCD grown by MPACVD in a series of angled holders designed to achieve better ELO and to maintain a good lateral growth rate. The growth using angled holders from wider pocket to narrower pocket, respectively results in larger size ELO with PCD growth, appropriate smooth ELO growth at constant lateral growth rate, and inward lateral growth. Constant lateral growth is reproduced by

iterative growth using regrowth angled holder. Larger area SCD are thus grown by MPACVD with constant vertical rate about 25 um/hr, 100 lateral rate about 18 um/hr, and 110 lateral rate about 12 um/hr.

All as grown samples are measured with x-ray rocking curve (XRC) mapping technique to reveal the crystallographic structural properties, and compared to the original substrates. Diamond 400 crystal plane curvature/flatness and morphology, XRC FWHM of 400/113/111 diamond peaks are plotted using self-made analytical software to compare the quality revolution before and after the growth. Quantitative birefringence (QB) maps and cross polar birefringence (CPB) photos are also taken to present the internal crystal structural defect within the CVD diamond. XRC mapping results show that growth using wider angled pocket, though with PCD rims, has better flatness (small curvature) and higher average structural quality (small FWHM); growth with intermediate pocket, with pure SCD growth, also has a good lateral growth behavior, with intermediate crystal morphology and intermediate structural quality; growth using smaller pocket results area shrink, but with larger crystal plane curvature, indicating the SCD is compressed due to the smaller size of the pocket. Thus, an intermediate choice would be the best way for iterative SCD growth to maintain the lateral growth rate and the crystal quality at the same time. In summary, the technique of growing CVD single crystal diamond using a pocket holder provides the possibility for the diamond to keep growing at a constant lateral growth rate in both 100 and 110 directions along with a constant vertical growth rate. The iterative growth strategies also illustrate this unlimited growth mode and crystal structural quality of such as grown CVD diamonds are characterized by novel established measurement techniques. Under such way, larger area and high quality single crystal CVD diamond can be grown by using Microwave Plasma Assisted Chemical Vapor Deposition.

Copyright by SHENGYUAN BAI 2022 To my parents for endless love and support To Fuming Yang, for all kinds of encouragement and understanding, wish her all the best in her graduate study

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Diamond growth has been attracting more and more attention, and many institutes and universities other than Michigan State University are setting up labs to discover new possibilities for lab grown diamonds. The specific research goals from this dissertation are investigated based on the previous hard work at MSU from the past decades. The author is proud to say the inherited of the DNA of research products and findings are expanded excitingly from previous and current researchers, Ph.D. and professors. The author mainly focuses on the research findings based on the start of Jing Lu, Yajun Gu, Shreya Nad, Amanda Charris Hernandes, Matthias Muehle and Ramon D. Diaz, and Professors Dr. Asmussen and Dr. Grotjohn, and their research groups, with the start of which may be traced back to 15 -20 years ago and even earlier. Other than the research findings from the above previous research groups, the author would also like to thank Dr. Garratt's diamond growth and measurement research group including Yun Hsiung, Karli Deutscher, Noelle Kurien, AJ Bensman, Madelyn Anderson, Xavier Lewis, Ben

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The author wishes to see further progress made by the community in the future and would also like to seek a future way to continue working together with all related scientists and engineers.

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Chapter 1

Introduction

1.1 Motivation

In past decades, single crystal diamond serves as a promising material in its optical properties, its outstanding physical properties like hardness, and rich in minerals all over the world[1]–[5]. Diamond is also outstanding for its promising electronic properties where diamond surpasses other wide band gap semiconductor materials such as SiC and GaN, etc.[3], [5]–[8]. Thus, diamond tops the promising ultimate materials for power electronics in high voltage, high temperature and high frequency applications, and as detectors for high energy physics[3]–[7], [9]–[15]. As technology is developing rapidly, 6G is already starting to form as a platform to network the world's most advanced technologies so far, such as VR/AR, IoT, quantum computing, and AI/ML, etc., even though 5G has dominated only a few years. Later technologies and applications are also found possible via diamond for near future applications since diamond can host color centers for quantum devices[5], [16]–[22].

The advent of modern technologies like 5G, hybrid and electric means of transportation, distributed local power networks, and more, drive continued interest in novel electronic materials. While most modern technologies are supported by traditional semiconductor materials like silicon, new materials with superlative properties are sought to enable solutions to current device capabilities, i.e. increased dynamic range in radar or increased switching speed and efficiency of high power rectification switches[1], [7], [17], [23]–[26]. Among new materials with superlative properties, diamond is one of the best for electronics applications. Compared to

1

other wide band-gap materials like SiC or GaN, it retains >4x the thermal conductivity, >2x the electron mobility (and >31x the hole mobility), and >3x the breakdown field[3], [5], [8], [9], [13], [22], [24], [25], [27]–[55]. Therefore, it is well positioned to serve in a variety of technological fields such as high power/high frequency electronic devices and optical applications (e.g. x-ray monochromators)[8], [28], [30], [39], [56], [57]. It is also promising for its multiple types of color centers in quantum information science applications. However, implementation of diamond in any of these technologies requires significant advances in crystal wafer quality and size.

It has been more than 30 years since the chemical vapor deposition (CVD) method was reported successful in diamond synthesis, however, there is still no clear path to reliably creating large area high quality diamonds[1], [3], [5], [7], [9], [28], [47], [57]–[60]. Approaches for enhancing the useable surface are of single crystalline diamond have been developed using both heteroepitaxial and homoepitaxial diamond growth. However, heteroepitaxial growth still carries a number of issues preventing large scale adoption, such as high dislocation densities due to lattice mismatch. Hence, homoepitaxial lateral outgrowth is the focus of multiple mainstream methods in today's literature as a way to extend the lateral area. Ways to increase the lateral area include: open holders (only substrate holder) where a diamond seed is placed on a large flat open holder surface, pocket holders, mosaic growth, and flipped seed growth[4], [7], [8], [20], [28], [30], [31], [59], [61]–[67]. Open holder designs tend to lead to non-uniform growth where a polycrystalline (PCD) rim is deposited and forms around the single crystal diamond (SCD) substrate, meaning a good quality in the center but rough diamond outwards. Mosaic techniques expand CVD diamond size by engineering offcuts and positioning diamond tiles precisely near

each other to induce overgrowth between tiles. In all techniques, the holder plays an important role in how temperature is regulated and gas precursors reach the growth surface.

Models of the of substrate temperature and gas flow indicate that conditions of growth at the diamond surface are non-uniform and directly affected by holder geometry. Simulations of growth surface conditions demonstrate that open holders do not regulate diamond temperature at all, with large variation in temperature radiating from substrate center to edge[22], [30], [31], [33], [42], [68]–[70]. In contrast, growing diamonds in a pocket have successfully demonstrated the growth of morphologically smooth diamonds[52], [58], [64]. Further, these studies have also demonstrated that growth from the (100) facet in a pocket leads to up to 2x expansion of the surface area. Simulations show that pockets suppress variation in temperature by shielding diamond form the plasma, but this depends on the dimensions of the pocket[27], [71]. Pockets exceeding 8 mm x 8 mm dimensions for 3.5 x 3.5 mm wide diamonds were found to lose the beneficial effects, and temperature distributions for wide holders mirrored those of open holder designs[52], [58], [64][71]. It is important to note, however, that maintaining a ratio below the 2.3 (8/3.5 mm) may maintain the beneficial effects of the pocket design, assuming other consideration like plasma shape and size are adjusted accordingly.

In this work we demonstrate examine the relationship between diamond lateral outgrowth behavior, pocket dimension, and reactor type. Pockets of increasing dimension in width and length, as well as depth, are studied for their effectiveness in producing high quality lateral outgrowth. Changes in growth rate as a function of proximity to the holder wall are modeled for one reactor type, and the differences between growth behaviors between reactors is analyzed.

3

To realize such applications, the followings are required for diamond: 1) scalable single crystal wafer, 2) excellent crystalline quality, and 3) accurate control of diamond doping.

As reported by Frost & Sullivan, synthetic diamond is starting to dominate over mined diamond in diamond market recently, and synthetic diamond is forecasted to dominate more global market supply in the next decades. Pathways to fulfill the requirements are proposed with synthetic diamond, containing both high pressure high temperature (HPHT) and chemical vapor deposition (CVD) growth of large area diamond and doped diamond, ways of measurements to characterize crystal structure and electronic properties of as grown diamond.

The market research report shows CVD diamond is starting to dominate the synthetic diamond market in the current decade, and it is obvious that CVD diamond is increasing in demand and supply.



Figure 1.1 Appearance of diamonds[72]

Since more diamond is synthesized in labs rather than mined naturally, and CVD is dominating the lab grown diamond, growing CVD diamond is in a great demand to realize the 3 requirements mentioned above. MPACVD has been showing it promising unique kinds in growing large size high quality single crystal diamond over the past decade[5], [8], [9], [23], [29]–[31], [36], [52], [63], [64], [73], [74].

CVD diamond is approved in above efforts to show lateral growth behavior in pocket holders and are promising to grow both in larger area and thicker. This will make a major breakthrough for CVD diamond that is earlier thought only grow in 1 dimensional (thicker). Such effort needs to be put in to grow bigger CVD diamond with larger area and high qualities.

Traditional straight walled pocket holders are proved to be promising in growing larger area SCD but constrain the lateral growth size to have an upper limit. The angled pocket holders are recently discovered in this dissertation with previous experiment results to show constant lateral growth rates for SCD large area growth.

For better understanding SCD growth quality, crystal structural characterization is necessary. Structural defect is also required to shoe quality of CVD SCD.

Thus, the dissertation focuses on creating an advanced CVD diamond growth technique in growing large area singe crystal CVD diamond and establishing crystal structural quality characterization standards for large area high quality SCD in the future.

1.2 Research Objectives

This research project mainly focuses on the deposition of high quality, large area single crystal diamond SCD by using MPACVD where advanced pocket holders are investigated. This research project fully considered all products and findings from the previous works done for CVD diamond growth at Michigan State University. The overall objective of this investigation is to develop experimental methods that enable the fast and stable growth rate of high quality, large area single crystal CVD diamond using the designated pocket holder configurations. Feedbacks from the novel established characterization techniques, such as the growth profile analysis, the XRC mapping, and the crystal plane morphology, provide better understanding of the growth. For the ultimate goal of this research project, it is desired to achieve large area high quality single crystal CVD diamond growth in a stabilized long process using the advanced pocket holders in microwave MPACVD system. A series of experiments were carried out for such research goals to explore the growth of CVD SCD over a wide range of input experimental variables centering the holder configurations. Core research experiments are described below, and are divided into two parts: A) single crystal CVD diamond growth, and B) single crystal CVD diamond measurements. Both parts are listed below as the basic components.

Core research activities:

A) Single Crystal CVD Diamond Growth

In the single crystal CVD diamond growth part, this research project collected all historical CVD diamond growth data from previous growth that using pocket holders. Scientific understanding is achieved as the backbone support of the CVD growth. Further diamond growth using traditional

pocket holders and advanced newly designed pocket holders are carried out for better diamond growth results.

The main research goal can be split into step by step objectives here:

- 1. To better analyze the historical growth with pocket holders
- 2. To complete the CVD diamond growth with pocket holders
- 3. To understand what effects pocket holders are applying on to the deposition processes
- 4. To reveal how scientifically pocket holder geometries are influencing the deposition results
- 5. To design and make new pocket holders based on historical growth data
- 6. To complete the dataset for CVD diamond growth using pocket holders by adding newly growth results and historical growth results
- To draw a conclusion for how the pocket holder geometries are influencing the growth behavior
- 8. To design advanced next generation pocket holders based on the conclusion drawn above
- To conduct larger area CVD diamond growth using newly designed advanced pocket holders
- 10. To analyze the growth behavior in advanced pocket holders
- 11. To compare growth behaviors between those in advanced pocket holders and those in traditional pocket holders
- 12. To reveal what growth results are optimized by using advanced

B) Single Crystal CVD Diamond Measurements

In the single crystal CVD diamond measurements part, the research project focuses on the outline growth profile generate using data point grab software, X-Ray Rocking Curve mapping, 400 crystal plane morphology, and birefringence measurements.

Above focuses with bullet points are listed in details as follows:

- Acids cleaned as grown CVD diamond side view pictures are taken under the stereo microscopes.
- 2. Lateral growth outline profiles are collected for analysis using data point grab software.
- 3. Apply theoretical diamond growth model to mathematically fit the outgrowth data collected in the previous method.
- 4. Establish XRC mapping methods using Rigaku SmartLab XRD for diamond 400 peaks for phi angles at 0°, 90°, 180°, and 270°, diamond 113 peaks, 111 peaks and 220 peaks.
- Build up house made data analysis software for collecting and analyzing XRC peak location maps and FWHM maps.
- Build up house made crystal plane morphology illustration software to reveal the morphology and its related properties based on the 4 peak locations maps from phi angles at 0°, 90°, 180°, and 270°.
- Using necessary tools to understand simple cross polar birefringence properties by using Nikon microscopes
- 8. Using newly established quantitative birefringence tool to understand quantitative birefringence properties

Each of the above research steps and focus bullet points will serve as one of the core research objectives and are interspersed in the whole dissertation from Chapter 3 to Chapter 7.

1.3 Dissertation Outlines

The dissertation of this research project is composed of 8 chapters. The core content of the dissertation is summarized in the paragraphs as followings.

Chapter 1 Introduction

Chapter 1 presents a short introduction and the overview of this dissertation's research project. It includes research motivations, research objectives, and dissertation outlines. The major dissertation research objectives are divided into two major parts where each of the research steps and focus bullet points will serve as the core research objectives and are interspersed in the whole dissertation from Chapter 3 to Chapter 7.

Chapter 2 Background and Literature Review

Chapter 2 covers important key background information related to singe crystal diamond and a literature review, including the structure and properties of the diamond material and a historical overview of the CVD diamond growth process. The physical and the chemical aspects of the CVD diamond are introduced in Chapter 2. The diamond growth processes of HPHT diamond and CVD diamond growth are also discussed. Although the mechanism for diamond growth by CVD is still complicated, Chapter 2 also describes in detail important factors that have to be

considered in order to grow diamond by the CVD process. The effect of the experimental growth variables, such as methane concentration, atmosphere pressure, substrate temperature, and the growth behavior over time are also described. Lastly, a review of SCD growth by using MPACVD using a pocket holder is presented at the end in Chapter 2.

Chapter 3 CVD Reactors and Diamond Growth

Chapter 3 describes CVD diamond growth set up and experimental procedures, and provides detailed description of the MSU DS4 Microwave Plasma Assisted CVD configuration that was used in this dissertation research project. In Chapter 3, detailed and comprehensive descriptions of the experimental equipment are illustrated. The experimental procedures including sample preparation such as substrate images, properties, and cleaning steps, diamond loading, ramping up, conditioning, deposition, cool down are presented. Also, a description of the pocket holder configuration that was used in the dissertation is presented. The techniques used to characterize the grown diamond samples are also presented. A comprehensive description of using microscopes to collect a complete set of images is also described in Chapter 3.

Chapter 4 Diamond Characterizations

Chapter 4 investigates the SCD measurement process. Chapter 4 described the discovery and establishment of X-Ray Rocking Curve mapping techniques to understand as grown CVD diamond crystal structural properties. Diamond 400 peaks are measured using the XRC techniques at phi angles at 0°, 90°, 180°, and 270°, and diamond 113 peaks, 110 peaks, and 220 peaks. Detailed steps of collecting XRC data using Rigaku SmartLab XRD system on the same

diamond sample over locations from rough measurements to fine measurements and finally to mapping measurements are described in Chapter 4. Detailed calculations and individual peak fittings are presented for 400 diamond peaks, 113 peaks, 111 peaks, and 220 peaks. The house made XRC mapping data analysis software is introduced and presented to show how to produce XRC peak location maps and XRC FWHM maps, and other essential properties for 400, 113, 111, and 220 peaks. House made crystal plane morphology software is also built for illustrating 400 crystal plane morphologies for as grown diamond since diamond substrates are 100 oriented. The morphology is illustrated and calculated by the peak location data achieved from the 400 peaks at phi angles at 0°, 90°, 180°, and 270°. The related properties like curvatures are also calculated and plotted using the morphology software. At the end of Chapter 4, descriptions of birefringence images taken by cross polar birefringence and quantitative birefringence are also presented together with all other necessary characterization tools.

Chapter 5 Traditional Pocket Holders

Chapter 5 presents the results of an investigation that explored the SCD growth using MPACVD which uses traditional pocket holders that has a straight up wall with the substrate diamond in the center. The substrate temperatures are compared mainly at two levels, 980 °C and 1020 °C, and a constant pressure of 240 Torr. Historical data are collected from previous work and compensate experiments are also carried out to complete the dataset for the use of traditional pocket holder. Variables are set to be different pocket width, depth and total deposition time, and different reactors. Results revealed that the deeper pockets do not contribute to grow larger area SCD crystals significantly but different pocket width provide different limitations for growing wider SCDs. Lateral outgrowth profiles taken using the method introduced in Chapter 3 are compared

between historical growth data and new designed growth data. Scientific understanding of lateral growth behavior in the traditional pocket holders are analyzed based on the theory of kinetics of phase change which successfully applies to the diamond growth environments where plasmas phase changes to diamond crystal phase during deposition. Shallow pockets have enhanced lateral growth rates and larger area gains. Also, in Chapter 5, the importance of stopping the diamond growth process before it grows out of the pocket plays a key role in the deposition part, and is described in detail.

Chapter 6 Angled Pocket Holders

Chapter 6, in order to promote the lateral outgrowth of CVD diamond, presents a set of experiments in which advanced pocket holders are designed to understand growth behavior in newly designed pocket holders. Under the new pocket geometries, pocket depth is held constant at 2.6 mm in total while the pocket shapes and angles are varied. The results showed for a single experimental run the lateral diamond surface area could be up to 24 mm² in size. The results of the SCD growth using a series of angled holders with different angles are shown. Lateral growth results are clearly illustrated by using the outline profile data point grab method mentioned in Chapter 3. Results show narrower pocket limits lateral growth heavily, wider pocket loses protection to the diamond sample and PCD may form on the rim of the sample, proper size of the angled pocket holder allow constant and smooth lateral growth of SCD. Laser cut and polishing allows the top part of as grown samples can be considered as new substrate for iterative diamond growth. Iterative angled pocket holder is also designed for growing larger CVD diamond with constant lateral growth rate. Thus, more diamond growth steps are shown promising to be added to the smooth and large diamond top surfaces of earlier growth steps. In these iterative growth

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experiments, the diamond top surface was further enlarged up to around 36 mm². Core results for growing CVD diamond in angled pocket holder are proper distance between sample and pocket, and proper angle of the pocket allows constant lateral growth rate for CVD diamond for both 100 and 110 in lateral directions. Under such conditions, CVD diamond can be grown with constant lateral growth rates 18 μ m/hr in 100 direction, 12 μ m/hr in 110 direction and 25 μ m/hr in vertical direction, which allow the iterative growth strategy to keep growing large CVD diamond.

Chapter 7 ELO Growth Results and Analysis

Chapter 7 presents ELO growth results comprehensively from the above experiments especially from the traditional pocket holders and advanced pocket holders like the angle holders. XRC mapping results and structural quality analysis are also carried throughout all samples in the series of experiments to show the trend of the growth behavior and to draw final conclusions for this dissertation.

Chapter 8 Summary and Future Work

Chapter 8, finally, presents the conclusions and summary of this thesis research. Also, different future activities are suggested to continue to make further potential progress in the future.

The above bullet points summarizes the basic outlines of each chapter of this dissertation titled with *ELO GROWTH LARGE AREA SINGLE CRYSTAL CVD DIAMOND USING POCKET HOLDERS*.

Chapter 2

Background and literature Review

2.1 Diamond Material

Diamond is a solid form of the element carbon with its atoms arranged in a crystal structure called diamond cubic[75].

As natural materials, diamond is one of the minerals that are far from evenly distributed over the earth. Diamonds are extremely rare, with concentrations of at most parts per billion in source rock[75]. As in **Figure 2.1** shows, diamond is normally formed under deep earth which requires extremely high temperature and extremely high pressure for an extremely long time.

As one of the best-known and most sought-after gemstones, diamonds have been used as decorative items since ancient times. Diamond has the highest hardness of any natural material, along with its high dispersion of light, makes itself useful for industrial applications such as cutting and polishing tools, and desirable as jewelry. As the most highly traded gemstone, famous four Cs standard has been created by diamonds trading organizations that color, cut, clarity and carat are the 4 major factors to grade and certify diamonds[76].



Figure 2.1 Diamond Formation under deep earth[77]

Graphite is another form of carbon which is the chemically stable form of carbon at room temperature and pressure[78]. However, diamond converts to graphite extremely slowly at room temperature and pressure. Thermodynamically, diamond transitioning to graphite are well calculated both theoretically and experimentally, of which the triple phase's point of diamond/graphite/liquid is at 12 GPa at 5000 K. The temperature and the pressure of the triple phase point are extremely high compared to room temperature and pressure, which is the reason that can explain why diamond requires extremely long time (forever) to convert to graphite. All of the above factors and many other interesting but unclear properties for diamond as a useful material makes it desired to be valuable in research, applications and investigation. All related aspects of diamond material are discussed part by part in this section below.

2.2 Diamond Properties

Diamond is famous of its hardness among all natural materials. Other than its hardness, diamond is also famous of its shiny appearance for people to use as decorating items. The scientific research activities have been focusing on diamond materials for hundreds of years and many other aspects of diamond's properties are also revealed to show its splendid nature among all kinds of materials. This section covers the diamond properties over crystal structure, thermodynamics, phase diagram, mechanical, electrical, chemical stability, optical, etc.

2.2.1 Diamond Crystal Structure

Diamond is a crystal form of carbon atoms[79]. Diamond crystal lattice unit cell is illustrated in **Figure 2.2**. The lattice cell is directly called diamond lattice structure with a cubic structure with lattice parameter a_0 of 3.567 Å. The cubic structure is a repeating pattern of total 8 atoms that make up diamond solid. Each of the 8 atoms at the corner is counted as 1/8 atom since each atom at the corner is shared with 8 adjacent lattice. Each of the 6 atoms at the center of the 6 faces is counted as 1/2 atom since each atom at the face is shared with 2 adjacent lattice. There are 4 carbon atoms (labeled as green in **Figure 2.2**) that are located at the 4 of 8 tetrahedral sites, each

located at 1 tetrahedral site. Therefore, there are in total 8 x 1/8 + 6 x 1/2 + 4 = 8 atoms in the unit cell.



Figure 2.2 Diamond Cubic Crystal Structure

Diamond cubic unit cell is in the $Fd\overline{3}m$ space group (space group 227) and all carbon atoms are positioned according to the face centered cubic Bravais lattice[79]. On top of the face centered structure which contains the 8 corner atoms and 6 face centered atoms, the tetrahedral bonded atoms (labeled green in **Figure 2.2**) are separated by 1/4 of the width of unit cell in each dimension (including x, y, z, and the diagonal direction). Carbon atoms are the most close packed in the body diagonal direction, i.e. 111 direction. As **Figure 2.2** presents, 6 carbon atoms labeled as blue are on the same plane, and the other 6 atoms labeled as red are on the other plane. Both planes formed by the blue atoms and the red atoms are parallel and the normal direction of
both planes is the body diagonal direction which directs from the atom labeled as white (bottom front corner) to the atom labeled as grey (top far corner).

Mathematically, the location of each atom can be described using 3 dimensional (x, y, z) coordinates within the unit cell when consider the lattice parameter as a unit and the shift from the current position to the next unit cell basically adds ± 1 to the coordinates. The corner atom can be described as (0, 0, 0), i.e. the original, for example, the carbon atom labeled as white. The face centered atoms have coordinates (0, 1/2, 1/2), (1/2, 0, 1/2), and (1/2, 1/2, 0). The 4 tetrahedral bonded carbon atoms labeled as green each have unique coordinates (1/4, 1/4, 1/4), (3/4, 3/4, 1/4), (3/4, 1/4, 3/4), and (1/4, 3/4, 3/4).

Based on the above mathematical expression, along with Miller indices expression of diamond cubic lattice unit cell, the distance between atoms and the distance between atom planes can be derived regarding to the lattice constant a_0 as the base. The first nearest carbon atoms have distance $\frac{\sqrt{3}}{4}a_0 = 1.545$ Å. The second nearest atoms have distance $\frac{\sqrt{2}}{2}a_0 = 2.522$ Å, and the third nearest atoms have distance $\frac{\sqrt{11}}{4}a_0 = 2.958$ Å. The most closed packed crystal plane is (111) plane which has the d-spacing between the nearest plane $d_{111} = \frac{\sqrt{3}}{3}a_0 = 2.059$ Å. Since 4 tetrahedral bonded atoms are inserted at the 1/4 width in each of the dimensions, (400) crystal plane as shown in **Figure 2.3** shows its unique property with d-spacing $d_{400} = \frac{1}{4}a_0 = 0.892$ Å. 400 diamond crystal planes are important in the measurement sections in the following dissertation chapters.



Figure 2.3 Illustration of diamond 400 crystal planes in repeated diamond lattice unit cells.

The atomic packing factor (APF) describes the efficiency of space occupation for carbon atoms as a form of diamond, where the atoms and the bonds between are considered in rigid ball model, meaning the surface of atoms are contacting each other. In this rigid ball model, the radius of each atoms is constant and is calculated as $r = a_0/2 = 0.77$ Å.

The APF is thus calculated,

$$APF = \frac{(8)4/3\pi r^3}{a_0^3} = \frac{\sqrt{3}}{16}\pi = 34\%$$

The density of diamond ρ can also be derived below based on the atomic packing factor APF, where *n* equals to 8 atoms in the unit cell, *A* is atomic weight for carbon 12.011 g/mol, V is the volume of the unit cell and NA is the Avogadro constant 6.023 x 10²³/mol.

$$\rho = \frac{nA}{VN_A} = 3.515 \text{ g/cm}^3$$

This well calculated result of density of diamond shows a great agreement with experimental results from pure diamond materials.

2.2.2 Diamond Thermodynamics

As introduced in previous section, including diamond, carbon atoms can also be formed into graphite under certain conditions (mainly certain temperature and pressure). **Figure 2.4** illustrates both appearance and crystal structure of diamond and graphite. Diamond structure is discussed above in section **2.2.1**. Structure of graphite forms layered structure with annulus of 6 carbon atoms as the base within each layer. Thus, graphite is a crystalline form of carbon with a hexagonal structure. For the unit cell of graphite, since it has a hexagonal structure, it is in space group P6₃mc with lattice constants a = 2.461 Å, and c = 6.708 Å. Normal d-spacing for 200 graphite is $d_{200} = c/2=3.354$ Å. Density of graphite ranges from 2.09 to 2.23 g/cm³.



Figure 2.4 Crystal formation of diamond and graphite

Under normal conditions, diamond is converting to graphite thermodynamically, as the free energy expression states below[80]:

$$C(s, diamond) \rightarrow C(s, graphite)$$
 $\Delta G^{\circ} = -2.9 \text{ kJ/mol}$

However, there is an enormous activation energy barrier about 370 kJ/mol for this process which limits the conversion from diamond to graphite under normal conditions to be extremely

slow[81], [82]. Some thermodynamic values of carbon related materials are listed in **Table 2.1**, where free energy, enthalpy and entropy are compared.

Substance	$\Delta H_{f^{o}}$ (kJ/mol)	S ^o (J/mol/K)	$\Delta G_{f^{o}}$ (kJ/mol)
Graphite (s)	0	5.6	0
Diamond (s)	1.8	2.4	2.9
$CO_2(g)$	-393.5	213.7	-394.4
$O_2(g)$	0	205.1	0

Table 2.1 Enthalpy, entropy, and free energy values of carbon related substance[83]

2.2.3 Carbon Phase Diagram

Under certain conditions, carbon can form diamond, graphite, liquid, and vapor[84]. The carbon phase diagram in **Figure 2.5** illustrates general conditions required for diamond and graphite to convert to each other. In the phase diagram, it can be seen that, under relatively low pressures, graphite is the most common form of carbon and is stable from room temperature up to its melting temperature at approximately over 4000 K. While, diamond is relatively meta-stable at low pressure low temperature region, and is only stable at very high pressures, ~ 10 GPa.



Figure 2.5 Carbon Phase Diagram, graphite - diamond[85]

2.2.4 Diamond Mechanical Properties

Diamond is famous of its super hardness. It is the hardest on both Vickers scale and Mohs scale among all natural materials. Mechanical properties of diamond are listed in **Table 2.2**.

Property	Symbol	Value	Unit
Hardness	Н	$1.0 \ge 10^4$	kg/mm^2
		115	GPa
Vickers	HV	10000	1
Mohs	HM	10	1
Tensile Strength	Т	> 1.2	GPa
Friction Coefficient	μ	0.03	1
Density	ρ	3.515	g/cm ³
Bulk Modulus	В	440	GPa
Young's Modulus	E	1.22	GPa
Sound Velocity	u	$1.84 \ge 10^4$	m/s
Thermal Expansion Coefficient	E	$1.1 \ge 10^{-6}$	1/K
Thermal Conductivity	С	900 - 2320	W/mK
Debye Temperature	T _D	2000	К

Table 2.2 Mechanical, structural and thermal properties of diamond[86][64]

The structural, mechanical, and some of the thermal properties of diamond are listed above to show diamond's outstanding physical properties. Thus, diamond is always promising in many industrial applications when higher strength materials are pursued. Different coatings and depositions of multiple types of diamond films and bulk crystals ranging in size from ultra-Nano crystals, to nano-crysatllines, to polycrystalline, eventually to single crystal diamond have been showing their promising sides in industrial and engineering applications, as shown in **Figure 2.6**.

The thermal conductivity is high for diamond compared to other electrical materials, which makes diamond a great potential materials for making devices that are required to work under extreme weather conditions, or devices that can show better performance under the same environmental conditions.



Figure 2.6. Scale of diamond as of crystal sizes

2.2.5 Diamond electrical properties

Not only have diamond shown promising properties in its physical structural, mechanical, and thermal properties discussed above, but diamond also started to draw a lot more attraction in tis electrical properties. Advanced technologies are making rapidly progresses in the second decade in the 21st century, which pushes all science and technology communities eager to search for novel electrical materials for better performance as the challenge of different current devices in multiple applications are much clear over years[1], [3], [8], [21], [87]–[89]. Diamond happens to be proven to be the promising electrical material due to its outstanding properties in both its physical properties listed in **Table 2.2** for mechanical, structural and thermal properties, and its valuable electrical properties that are also listed in **Table 2.3**.

Property	Symbol	Value	Unit
Electrical Resistivity	R	10 ¹³ - 10 ¹⁶	Ω•cm
Dielectric Constant	3	5.7	1
Electron Mobility	μ_e	4500	cm ² /V 's
Hole Mobility	μ_h	3800	cm^2/V 's
Electron Saturation Velocity	u	$2.7 \ge 10^7$	cm/s
111 Work Function	W	negative	eV
Energy Bandgap	E	5.50	eV
Breakdown Field	E	10	MV/cm

 Table 2.3 Electrical and electronic properties of diamond[64][86]

Higher values of the listed electrical properties are the base that bring diamond promising in showing better performance than traditional electrical materials that are based on Si, or SiC.

2.2.6 Diamond Electronic Properties

Electronic-wisely, diamond show the same outstanding properties as listed in **Table 2.3** that have outperformed traditional semiconductor materials Si, SiC or even the new generation semiconductor material III-V materials.

Especially, diamond has an ultra-wide bandgap of 5.45 eV which is extremely higher than that of Si (1.12 eV) and SiC (3.27 eV). While carbon element is in the same group above Si element in the periodic table, diamond, silicon carbide and silicon share the same crystal structure but only with different lattice constants, as **Figure 2.7** presents.



Figure 2.7 Lattice constants of diamond, silicon carbide and silicon

Diamond is made up of all smaller carbon atoms while Si is made up bigger Si atoms. Therefore, the size of Si unit cell is bigger than the unit cell of diamond. The silicon carbide uses the same structure while all Si atoms are at the corners and face centers positions, 4 carbon atoms are at 4 of the tetrahedral sites center to make up 4 carbon atoms and 4 Si atoms in the unite cell of SiC. It can also be seen as, when shifting 1/4 in all x, y, and z directions of the lattice constant, all carbon atoms are at the corners and face centers, and 4 Si atoms are at 4 of the tetrahedral sites in the unit cell. The structure is thus symmetric for both Si and carbon atoms. The way how both Si and carbon atoms make up SiC makes both elements contribute equally in most of the structural environment and therefore most properties of SiC are an average of that of Si and diamond.

2.2.7 Diamond Chemical Properties

Diamond is a chemical substance of form of carbon. Both diamond and graphite are allotropes of carbon. To best understand the forms of carbon, the allotropes other than diamond and graphite are also important to be aware of. Allotropes of carbon are listed in **Table 2.4**.

Carbon atoms are bonded differently in each of the allotropes, thus chemical properties are as a result differently since bonding and bond breaking will require different energies in each of the allotropes.

Diamond carbon atoms are bonded to each other in Sp³ type for each carbon atom is connected to 4 carbon atoms in a tetrahedral structure as diamond structure shows. Each of 4 outer electrons of the center carbon atom is bonded to one electron from one other carbon atom, and in such way the primitive structure can be repeated and covers the whole diamond substance. All non-diamond substances mostly are made up of carbon atoms bonded with each other in using Sp² bonds, where one carbon atom is bonded with 3 other atoms in the plane with a 120° angle between any 2 bonds. Thus, the famous ring structure is built of six carbon atoms as the primitive structure. 3 of 4 outer electrons are bonded within the plane, while the other electron is formed into a big pi bond with the adjacent layer. The layers, in this way, are bonded together with a cloud of pi bonds. Less Sp3 bonds makes graphite more active than diamond for reacting with other substances, and resulting in smaller density.

Table 2.4 Allotropes of carbon[90]

Substance	Description
Diamond	Hard, transparent, Sp3 bonded
Graphite	Soft, black, Sp2 bonded
Lonsdaleite	Hexagonal structure
Graphene	Laminar structure
Linear acetylenic carbon	carbyne
Amorphous carbon	amorphous
Fullerenes	including buckminsterfullerene, a.k.a buckyballs, such as C_{60}
Carbon nanotubes	CNT, having cylindrical nanostructure
Schwartzites	-
Cyclocarbon	-
Glassy carbon	-
Superdense carbon	Proposed allotropes

At room temperature, diamond do not even react with strong acids of bases sue to its well-built Sp^3 structure. Diamond has an ignition point ranges from 690 C° to 840 C° in pure oxygen and the smaller the diamond is, the easier it burns, meaning diamond can be burned into CO₂. It increases in temperature from red to white and burns in a pale blue flame, and can continue to burn when the source of heat is removed.

2.2.8 Diamond Optical Properties

As the most general understanding, diamond is transparent and colorless. This is due to its wide band gap of 5.5 eV which corresponds to the deep UV wavelength of 225 nanometers.

GIA	Status: current	
grade and description		
D		
Е	Colorless	
F		
G		
Н	Near	
Ι	Colorless	
J		
Κ	Foint	
L	raint Vellow	
М	Tenow	
N		
0		
Р	Very Light Yellow	
Q		
R		
S		
Т		
U		
V	Light	
W	Yellow	
X		
Y		
Z		

Table 2.5 Diamond color grading by GIA[91]

Color is one of the 4C of diamond, and colors in the diamond are generated from the crystal lattice defects and impurities. Nitrogen, boron, are phosphorous normal elements that can be introduced into diamond structure during diamond growth. The Gemology Institute of America (GIA) grades the yellow color diamonds in a normal color range listed in **Table 2.5** which is used commonly to compare colors between diamonds. Clarity is another of the 4C regarding optical properties. GIA develops clarity scales as shown in **Table 2.6** that is normally used for

comparing diamonds. The scales range from flawless (FL) to included (I). Sub grades are used for finer classified in categories such as Very Very Slightly Included (VVS), to Included (I).

Clarity Category	Clarity Grade
Flawless	FL
Internally Flawless	IF
Very Very Slightly Included	VVS1
	VVS2
Very Slightly Included	VS1
	VS2
Slightly Included	SI1
	SI2
	I1
Included	I2
	I3

Table 2.6 Clarity Scales by GIA[92]

At room temperature, reflective index of diamond is measured with n = 2.417 taken at the standard 589 nm wavelength using Fraunhofer D lines of sodium yellow doublet. Thus, velocity of light in diamond can be calculated based on the reflective index and the velocity of light in vacuum, using $v = c/n = 3 \times 10^8 \text{ m/s} / 2.417 = 1.24 \times 10^8 \text{ m/s}$. Due to its structure, this optical property is isotropic, that makes perfect diamond barely has no birefringence.

2.2.9 Diamond Spectrum Properties

Imperfections are complex in diamond structure and since imperfections like defects and impurities are key to all properties of diamond, such information are discussed below.



Figure 2.8 Diamond types[93]

Diamond is classified into four main types according to how the imperfections are exist. The simplest classification of diamonds are based on the existence of certain element as the main impurity. Nitrogen and boron are chosen to be the key considering factors due to their frequently present in mined diamond.

As Figure 2.8 illustrates:

- ◆ Type I diamonds include nitrogen atoms as the main impurity
 - o Inside type I diamonds, type Ia diamonds include aggregated N atoms
 - Type IaA diamonds include pairs of nitrogen atoms, which doesn't affect the color of this type diamond

- Type IaB diamonds include large even-numbered nitrogen atom aggregates, and the color shows from yellow to brown
- Type Ib diamonds include single distributed nitrogen atoms, and they often show light yellow to brown in color
- Type II diamonds don't have nitrogen impurities
 - Inside type II diamonds, type IIa diamonds don't have nitrogen or boron, so they are rare. And they can be colored pink red, or brown.
 - Type IIb diamonds include boron as the main impurity, so they appear from light blue to dark blue in color

Type I diamonds absorb in both the infrared (IR) and ultraviolet (UV) region, from 320 nm. While type II diamonds, unlike type I diamonds, absorb in a different region of the IR, and transmit in the UV below 225 nm.

Main impurities are discussed above, however, many other defects of impurities usually make diamonds presenting unique properties. Color centers are found recently to show their potential in quantum computing. Defects can be detected by absorption spectrums from, for example, electron paramagnetic resonance (EPR), photoluminescence (PL), cathodoluminescence (CL), IR, visible, and UV. Defects can be identified, and the concentration can also be estimated. This can also be used to differentiate synthetic diamonds from natural diamonds.

Substitutional impurities like nitrogen normally create several main centers that have notations: A center, B center, and C center, and N3 centers, as illustrated in **Figure 2.9**.



Figure 2.9 Nitrogen substitutional centers in diamond[94]

Nitrogen vacancy center (NV center) is the most studied color center in diamond so far. As shown in **Figure 2.10**, the nitrogen atom N as the impurity substitutes one of the tetrahedral site carbon, and creates a vacancy site V.



Figure 2.10 Color centers in diamond[95]

Though many color centers exist in diamond, creating perfect conditions for each single color center like NV center is still far from simple[96]. NV centers in diamond are recently to show its performance in realizing fully functional qubits at room temperature, where electrically readout the NV spin state at the level of a single center is required for improving better performance of NV center productions. NV centers in diamond thus become promising qubits for basic quantum computing. The more qubits the system has, the faster computing speed it has, and the speed of which increases by power.

2.3 Diamond Applications

Diamond has been used for a variety of applications since thousands of years ago when it was firstly mined[8], [20], [58], [64], [75], [89], [97], [98]. As gemstones, diamonds are rare and attract people's allure. While natural rough diamond gemstones may not look prettier, after polishing and certain processing, it shows shiny surfaces, just like the illustration in Figure 2.11.



Polished Diamond

Figure 2.11 Illustration of rough diamond and polished diamond[99]

Other than its appearance, in ancient times, people have already started to use diamond as cutting tools[100]. For example, ancient Chinese people sued diamond as a jade cutting knife sue to diamond's super hardness. Till current century, multiple diamond applications are applying diamond's hardness to either directly become cutting tools, or as the film coated on to the original material that harden the product for better mechanical products.



Figure 2.12 Illustration of mechanical uses of diamond: **a**) as cutting materials[101], **b**) as indenter for hardness measurement[102]

Due to diamond's high hardness, good thermal diffusivity, and good performance of the sharpness of the cutting edge, it's been used as cutting knives as **Figure 2.12 a**) presents the mechanics of how diamond cuts metals. During the modern industrial uses over years, diamond is also famous for its using as an indenter for Vickers hardness testers. In the Vickers hardness tester, the indentation uses a 136 degrees squared-based diamond pyramid sharp conical, as shown in **Figure 2.12 b**), pin to the samples and the load varies from 1 kgf to 120 kgf for typically 30 seconds. Length of the diagonals shaped on the surface of the materials are used to calculate the hardness of the samples.

Other than well-developed industrial engineering applications, advanced applications of diamonds are also used in research activities. **Figure 2.13** introduces the recent use of diamonds as anvils in Mao group to providing a combination of both flat surfaces for extreme high pressure and transparent media for X-ray through the samples between diamond anvils.



Figure 2.13 Diamond anvil cell used by Mao Group, where samples can be pressed to very high pressures between the flattened tips of two diamonds[103].

Thus, optical applications are also important for diamonds. In ancient times, people once used diamond to observe the dispersion of light[104]. Modern technical results show the dispersion, also called as fire, in diamond the red ray (Fraunhofer B line, 687 nm) has a refractive index of 2.407, the blue ray (Fraunhofer G line, 430.8 nm) has a refractive index of 2.451, and the violet ray (Fraunhofer H line, 397 nm) has a refractive index of 2.465. The difference between refractive indices of red and blue rays is 0.044.

Till current decades, diamond, due to its transparency and hardness, has been made into vacuum windows, laser windows, and microwave and terahertz windows[105]. Diamond windows are used for low thermal mechanical stress, a wide range of operation temperatures, pass through of lasers or beams[106]. Certain optics are also made with diamond, such as beam splitters, total reflector, and liquid cells. The broadband transparency and the high refractive index make diamond an ideal material for infrared beam splitters as required by Fourier transformed infrared (FTIR) spectroscopy[107]–[109]. Diamond liquid cells can be used for the spectroscopic analysis of liquids where two windows with well-defined spacing are used. Diamonds are also used for X-ray optics and targets[105]. Diamonds are transparent for X-ray and can handle high power levels. Conventional X-ray beam position monitors interrupt the X-ray beam and motorized stages are required to move them. Diamond X-ray beam monitors well optimized this area, and diamond filters are also used to attenuate the X-ray beam in synchrotron facilities. Other parts are preferable for modern synchrotron radiation sources using diamonds such as polarizers (phase plates) and monochromators[110]. Other than above mentioned functions, diamonds are also used for X-ray detectors in pixelated transmission-mode, or pixel detectors. Due to its extremely low charge carrier density combined with high radiation hardness and high thermal conductivity, diamond has been considered as the perfect materials for high energy particle detectors. Silicon sensors are required to be substituted very often since they are easily damaged by the high energy radiation [17], [108], [111].

Figure 2.14 presents one of so many aspects that diamonds are used in synchrotron applications where small scale crystal atoms and crystal structures can be analyzed by high energy beams like X-rays at the atomic scale at high pressure and high temperature. Synchrotron beams are

generated at a very high speed so the beam heats the sample to extreme high temperature that diamond anvil cells are good at dissipating the heat and maintaining a stabilized environment for the samples[112].



Figure 2.14 To measure crystal structures at the atomic scale at high pressure and temperature, a diamond-anvil cell is used at ASU with a sample is aligned with an X-ray beam (blue line) and laser beams (orange areas). The laser beams heat the sample to thousands of kelvins in temperature. The small red/gray rectangle sandwiched between diamond anvils is the sample[112].

Diamonds is an insulator due to its ultra-wide band gap of 5.5 eV, higher than other novel materials like GaN (3.44 eV) and SiC (2.36 eV). The very wide band gap of diamond makes it out performed other electrical materials in the high power high energy engineering field[113].

Both electrically and electronically, diamond shows it outstanding properties as the previous section discussed. Combining its high electron/hole motilities, which gives high electrical current, its wide band gap, which gives high power, its high speed, which gives high frequency, diamonds are favorable for applications such as high voltage unipolar devices, high frequency unipolar switches, high frequency power transistors and high speed switches. In industries, functional applications such as bipolar transistors, Schottky diodes, FETs, MOSFETs, LEDs, and many novel quantum devices are all at a very high developing speed[1], [1], [16], [17], [89], [95], [96], [109], [114], [115]. With applications in broadcasting stations, radar systems, and other RF technologies, diamond could be the first solid state device to handle communication satellites where the operation requires 120 W at 10 GHz[1], [16], [114].

Computing materials are attracting the science and technology communities' attentions over the past years[16], [89], [95]. Among a variety of computing, quantum computing is the brightest star in the research field. Negatively charged nitrogen-vacancy center NV-, shows it potential to accelerate the development of quantum technologies such as ultra-sensitive nanoscale quantum sensors, quantum repeaters for long distance quantum networks, simulators of complex dynamical processes in many-body quantum systems, and scalable quantum computers[116].

Figure 2.15 presents recent works done illustrating a single qubit of NV- diamond color center, and an overview imaging the quantum communication network in the future. Rapid progress are coming soon in the near future as it is happening now, the more optimized functional quantum network will bring many novel applications from our imagination to reality, such as distributed quantum computing, accessing a quantum server in the cloud with full privacy, and stabilizing quantum clocks[16]. Many large and small startup companies are also raised up to dedicate their

research and development effort in coming up with a viable diamond based quantum computer in the next decades[117].



Figure 2.15 a) Quantum qubit[116] and b) Future quantum network[16]

Ultra nanocrysatlline diamond (UNCD) has been reported for multiple bioengineering appilcations such as eye enviormental fluid protecttion, biomarker, bio-chips[53][118][119]. MPACVD single crystal diamond has also been reported in using as doismeter in radiotherapy treatments for cancer[119]. UNCD films are recently being reaserched in detecting viruses like COVID[120]. Enviormentally, diamond films are developed to treat waste water[121][122]. BDD electodes clean some of the organic pollutants and oxideze them to CO₂, or can be used as catalytes to transfter CO₂ to other chemicals[123].

2.4 Diamond Synthesis

Natural diamonds are firstly mined in a modern way in the past centuries. However, diamonds are only mined in about 25 countries and on every continent except Europe and Antarctica. Major diamond trading centers are pointed in **Figure 2.16**, and so as the mining sites[124].



Figure 2.16 Diamond trading center and mining sites[125]

Diamond mining, in the past decades, has been raising issues in environmental concerns[126]. In a De Beers mine, on average, the ore that needed for final production to polish a one-carat diamond is up to 250 tons. In percentage, averagely every year, 80 % of mined diamonds would go to be used in industries, while 20% of them are satisfied for gems. In amount, 80 tons of synthetic diamonds are produced from industries every year. The Kimberley process is set up by the countries mining or trading natural diamonds. With consideration of no more mining, diamond synthesizing has been raised over the last century[125].

2.4.1 History of Synthetic Diamond

Synthetic diamond, also referred to as lab-grown diamond, or man-made diamond, is the diamond that is produced by manufacturing process, but not like natural diamond, which is produced by geological process and extracted by mining[127].

To synthesize diamond, scientists firstly made efforts to reproduce and mimic the natural conditions deep underneath the earth, where the extreme high pressure an extreme high temperature is required[127]. **Figure 2.17** presents the phase diagram for carbon which helps understand what conditions are required for carbon atoms to form and crystallize into diamond. It shows diamond as a crystal form of carbon, is metastable only at low pressure and low temperature. Since natural conditions are mostly reproduced, HPHT method synthesizes diamond at around 15 GPa and in a range from 3000 to 3500 K. Even catalytic HPHT method synthesizes at 5-10 GPa, and with a temperature ranges from 1250 K to 2250 K. Though catalytic HPHT can synthesize diamond at more mild conditions, the pressures and temperatures are still too extreme. CVD method, instead, synthesizes diamond metastablly at relatively low pressure and low temperature, compared to the conditions used for HPHT methods.



Figure 2.17 Pressure - Temperature phase diagram of carbon for diamond synthesizing[128]

The earliest confirmed reproducible synthesis of diamond is reported in 1953, before which, diamond synthetic research activities are already started in US, Sweden, and the SU[127]. These earliest research resulted in the initial discovery of 2 main diamond synthesizing processes, the high pressure high temperature (HPHT) method and the chemical vapor deposition (CVD) method.

2.4.2 HPHT Synthesis



Figure 2.18 HPHT method for synthesizing diamond[129]

As discussed above, from the phase diagram, it can be seen that HPHT method, no matter if catalysts are used or not, requires high pressure and high temperature when synthesizing diamond. Thus, the anvils are established to create an enclose environment that can hold high pressure up to 10-15 GPa and temperature up to several thousands of Kelvins[127]. A seed is placed in the capsule with 6 inner anvils made of graphite tungsten, and 8 outer anvils made of steel surrounding from inside out, and outsides are covered rubber and oil between the pressure

vessel for the purpose to maintain the temperature, and at the mea time, keep the pressure inside of the capsule[127].



Figure 2.19. Type Ib HPHT diamond by Sumitomo[130]

The success in synthetic diamonds made the prices far lower than polished and mined diamonds in the market[131]. De Beers opened up its limits of synthetic diamond brand into the market in 2018 and the overall costs of their synthetic diamonds are 1/10 of that of natural diamonds in the market[132]. These movements accelerated the development in synthetic diamond and drops the costs in both mining and industrial using of diamonds. Sumitomo is one of the vendors who provide type Ib HPHT diamonds as **Figure 2.19** shows. Other manufacturers, such as Element 6, ADT, NDT, etc. are also conducting similar businesses.

Nitrogen are normally added during HPHT growth since it helps diamond to crystallize and grow faster. Nitrogen also makes the color of as grown HPHT diamonds yellow[133]. Generally, the seed in HPHT capsule also dissolves molten metals such as Fe, Ni, or Co for lowering the

temperature and pressure required for the diamond growth in HPHT process[132]. The crystallization process is slow and normally takes from several days to weeks for even one crystal.



Figure 2.20 Growth sectors in HPHT diamond[134]

As **Figure 2.20** shows, HPHT synthetic diamond crystals tend to have cubic faces onto octahedral faces. Growth rates and patterns are different to natural diamonds, the HPHT synthetic diamonds show different growth sectors, and as the ability to contain nitrogen concentration and type is different, different sectors will appear different colors, i.e. light yellow to almost clear, which can be seen easily under microscopes for a cross shaped growth sector structure. Most HPHT substrates are cubic, and are cut from bulk as grown samples as a reference from **Figure 2.20** with 100 as both top facets and side facets. Some other times, due to the growth and cutting craft, the cubic HPHT substrates are cut to have 100 top facets (in which it is called 100 oriented) and 110 side facets, which are a 45° rotation from the first scenario. In another scenario, 111 facet is cut to be top facets and 112 and 110 facets are thus to be side facets. Geometrically, the physical surface of any bulk diamond doesn't have to be exactly

parallel to the indexed crystal plane, while the tradition is used for indicating the surfaces. Cutting and polishing diamond samples with its indexed crystal planes is convenient for everyone to have a good understanding of the diamond.

Colorless HPHT synthetic diamonds are also produced after some effort, where nitrogen needs to be cleared when growing diamond[135]. The result duration would be longer without nitrogen and accurate controlling are required for it. Big colorless HPHT diamonds, such as 10 carats and bigger, are produced and reported in 2018[136]. The sample shown in **Figure 2.21**, is graded with I clarity and H color.



Figure 2.21 15.32 carat HPHT synthetic diamond graded by GIA[136]

2.4.3 CVD Synthesis

To avoid creating extreme conditions for HPHT synthesis process, CVD process is viable since it requires low pressure and relatively ow temperature as the more mild conditions in which diamond is synthesized metastablly, as discussed above and as shown in the **Figure 2.17**, the phase diagram of carbon.



Figure 2.22 CVD diamond growth, a) mechanism of MPACVD diamond growth, and b) a photo of CVD diamonds during growth[137]

Figure 2.22 illustrates the mechanism of CVD growth process in a) and shows a photo of CVD diamonds during the deposition in b). Generally speaking, the CVD method uses certain types of input energy to generate hydrocarbon gas mixture, which are key precursors for diamond growth. Since the conditions required for CVD process are mild, diamond growth are undergoing chemical reactions to hydrocarbon species and substrate surface carbon to form carbon-carbon Sp³ bonds[138]. Though diamond is metastable at relative low pressure and low temperature, the gas atmosphere is ignited to plasma clouds and surface of substrate is also chemical active, i.e. the activation energy barrier is broken by the input energy, such as radio frequency (RF), Microwave Plasma Assisted (MPA), hot filament (HF), etc., which brings sufficient conditions for precursors and substrates to form diamond[9], [19], [65], [139].

CVD processes are not fixed to certain types, but always follow the following series of essential steps[86]:

- 1. Transport of reactants from gas inlets to the reaction zone.
- 2. Activating chemical reactions in the gas phase producing new reactive species.
- 3. Transport of reactants and new products to the substrate surface.
- 4. Adsorption of reactive species on the substrate surface.
- 5. Surface reactions leading to film formation.
- 6. Desorption of volatile by-products from surface reactions.
- 7. Transport of by-products away from the reaction zone.

During the CVD processes of any type CVD for diamond growth, chemical reactions are the essential component, understanding what chemical reactions are core mainly helps in understanding of how diamond is grown during a CVD process.

Precursors for gas mixtures of carbon based chemicals are analyzed and set to use hydrogen H_2 and methane CH_4 as the main gas precursors with methane CH_4 concentration to hydrogen H_2 at around 5 %, meaning CH_4 : $H_2 \sim 5 \% [64]$, [86].

Reactions of hydrocarbon species with chemically active substrate surface carbon are illustrated in **Figure 2.23**, where a series complex reactions are combined for the purpose for diamond growth. Harris-Goodwin's work proposed the model that describes a mechanism for epitaxial growth where CH_3 is the only significant species generated from its original substance methane CH₄.[140], [141] H₂ molecule is also separated into plasma status, as described, in H^{\bullet} . In the plasma status, the electron that is freely moving around its principle body without forming a bond with another is highly active and possible to form bonds. As mentioned, the surface of diamond substrate is also chemical active under the input energy like discharged plasma with CH₄ and H₂, thus the surface is noted as $C_d - H$. Using these notations, the reactions in **Figure 2.23** can be derived into reaction expressions[1]:

$$C_d - H + H \cdot \xrightarrow{K_1} C_d \cdot + H_2$$
 (2.1)

...



Figure 2.23 Chemical reaction mechanism of methyl adsorption and dehydrogenation for diamond growth[142]

Expression are listed from (2.1) to (2.6), where k denotes the reaction rate. 4 main steps can describe the reaction expressions[1][142].
In Harris-Goodwin model[33], [140], [141], the surface is first activated and become hydrogen terminated. Some carbon atoms are reacting with hydrogen species and some are reacting with hydrocarbon species as they both exist in the atmosphere and are chemically active.

$$C_d \cdot + H \cdot \stackrel{K_2}{\to} C_d - H$$
 (2.2)

Secondly, in the adsorption process, chemically active hydrocarbon species attaches to the carbon on the substrate surface, thus a new carbon - carbon Sp^3 bond is formed.

$$C_d \cdot + CH_3 \cdot \stackrel{K_3}{\rightarrow} \quad C_d - CH_3$$
 (2.3)

Reverse process also happens since the conditions are favorable for both directions with different rates of the reaction expression, thus the desorption is removing the end part of the formulae, i.e. the surface atoms of the substrate. This process, by itself, is also the well-known etching.

$$C_d - CH_3 \xrightarrow{K_4} C_d \cdot + CH_3 \cdot$$
 (2.4)

Finally, diamonds grows in the process of incorporation where the hydrocarbon species is attached to the surface and Sp3 bonds ae well-formed for the next cycle of epitaxial reactions. During the processes, atomic hydrogen promotes the incorporation process by assisting the removal of byproducts in the gas phase so that incorporated part of the carbon species together form a new epitaxy layer of diamond film.

$$C_d - CH_3 + H \cdot \stackrel{K_5}{\to} C_d - CH_2 \cdot + H_2 \tag{2.5}$$

Layer by layer on the location where it starts the reaction as the original growth point, diamonds are deposited on top of the substrates.

$$C_d - CH_2 \cdot + H \cdot \xrightarrow{K_6} C_d - C_d - H + H_2$$
(2.6)

Using the above reactions proposed by Harris and Goodwin, the growth rate can be derived by using the concentrations and the reaction rates of the above expressions. The growth rate is derived as:

$$G = k_3 \frac{n_s}{n_d} \left(\frac{k_1}{k_1 + k_2}\right) \frac{[CH_3][H]}{\frac{k_4}{k_5} + [H]}$$
(2.7)

Where n_s is the surface site density about 2.61 x 10⁻⁹ mol/cm², and n_d is the molar density of diamond 0.2939 mol/cm³.

After the plugins of the above values, and the reaction rates provided by Goodwin, the growth rate is simplified to:

$$G = 1.8 \cdot 10^{11} \frac{[CH_3][H]}{5 \cdot 10^{-9} + [H]}$$
(2.8)

For reactor type C at MSU, the concentration of hydrogen [*H*] is about 10^{-8} mol/cm³, and methane is used for 5%[86]. The rough calculated result shows $G_{100} = 50 \mu$ m/hr, which is in agreement with what the CVD usually provides.

Growth types are different in the numerous types of deposition techniques. In CVD processes of diamond growth, chemically active hydrocarbons are bonded with the chemical active surface carbon bonds and deposited into a new layer of diamond. Though Harris Wood model describes the CVD growth of diamond, the growth mechanism of diamond films is still lack of understanding because it is difficult to conduct in situ measurement during the deposition process[64]. While the substrates are selected to be singled crystal HPHT type Ib diamonds, or other single crystal diamonds, the growth are happening homoepitaxially. Homoepitaxial diamond growth is summarized in **Figure 2.24** for a better illustration[89]. In this homoepitaxial diamond growth model, surface steps are shown as a mesa structure on top of the substrate for the as received diamond substrate due to its natural misoriented angle (also called offcut angle or miscut angle) and the polishing surface.



Figure 2.24 Diamond homoepitaxial growth illustrated using mesa model[143]

After bonded onto the surface, the homoepitaxial growth of diamond becomes a 2 dimensional nucleation behavior on terraces. Energetically favored by deposition and diffusion, newly deposited atomic step grows along the terrace starting at the step front. According to the complexity of the surface environment, the homoepitaxial diamond growth model is classified into 3 main categories: step free lateral growth, 2D island growth, and 3D growth as shown in **Figure 2.24**. Since polishing a single crystal diamond to make its surface step free or with zero misoriented angle, the 2D and 3D growth are the most common realities[89]. Though split into 3 categories, homoepitaxial diamond growth would expect all three categories happen the same time on one specific sample due to the complexity of the surface environment. The rough 3D growth can be seen as a combination of endless tiny step free growth with little space. Due to the growth direction is influenced by the misoriented angle (the angle between crystal planes and the horizontal plane) of the surface, final morphologies after growth would have to be expected to be

different. Ideally, each step will grow laterally along the upper side of the misroiented angle, and the step free surface would be formed. In 2D island growth, the intervals between formed islands are wider than the terrace width estimated from the misroiented angle. Vertical growth also happens in 2D island growth. In 3D rough surface growth, the intervals are narrower and the surface is rough, which allows much heavier vertical growth happens on the homoepitaxial diamond growth.



Figure 2.25 Final morphologies using different methane ratio during the growth[89]

Methane ratio is also reported to make important role in final morphologies of diamond growth, as **Figure 2.25** shows, less ration of methane, which provides less carbon source and keeps the growth at a nice and slow growth environment, finally provides the best as grown surface morphology for homoepitaxial CVD diamond growth. Very low percentage of methane (0.005 – 0.025 %) results a step free as grown 111 surface morphology, which corresponds to the step free

growth mode. Based on the same theory, medium percentage of methane would give 2D island growth and heavy methane concentration would provide 3D rough growth results.



Figure 2.26 Behaviors of adspecies[144][145]

Figure 2.26 illustrates what can happen to the adspecies during the homoepitaxial CVD diamond growth. The energy differences between terraces steps are the driven forces for directing the movement of adspecies. Under a steady state condition, a net lateral movement represented as a drift force resulting from energy differences which drives the adspecies drifting, and diffusion. A complete model of behaviors of adspecies during deposition includes adsorption, incorporation, diffusion and nucleation. These behaviors are all related to energy preference of the change between the after movement and before movement.

All of the above results illustrates that surface morphology including roughness and oriented angle, and growth conditions including methane concentration which decides the carbon atomic nucleation density and enough time and enough space for atomic diffusing, are key factors for growing ideally better homoepitaxial CVD diamond. Adsorption rates, diffusion/drift speed and nucleation rates would influence each other during the CVD diamond growth process. Defects are usually formed during the CVD growth process due to its complex processes and environments. Sp² bonds, substitutional sites, interstitial sites, vacancies, dislocations are typical defects formed during the CVD diamond growth.

In Goodwin model, defect formation is also discussed as the reaction of defect formation is expressed as[140], [141][33]:

$$C_d - A + C_d - A \xrightarrow{k_{def}} HC_g - C_g H$$
 (2.9)

Thus, the fraction of defect of the as grown surface, x_{def} , can be expressed as:

$$x_{def} = \frac{k_{def} [C_d A]^2}{k_i [C_d A] [H]}$$
(2.10)

Where $k_{def}[C_d A]^2$ is defined as the rate of defect formed in the deposition process, and $k_i[C_d A][H]$ is defined as the rate of diamond formed in the duration.

When applying the growth rate derived in **equation 2.7**, the defect percentage can be thus written as:

$$x_{def} = \frac{k_{def} n_d G}{k_i^2 [H]^2}$$
(2.11)

 Sp^2 bonds are formed during the CVD diamond growth process, when an adsorbate and the adjacent adsorbate react with each other first before they are fully incorporated into the lattice. Sp^2 bonds formed at the beginning will turn into Sp^2 defects during the growth process.

A mixture substance of both SP² and SP³ is a kind of amorphous called Diamond-Like Carbon (DLC)[146]. Properties and applications of DLC compared to diamond, and graphite are illustrate in **Figure 2.27**. DLC basically have properties that are in between with diamond and graphite, which also makes many applications promising. CVD diamond growth using single crystal diamond as substrates so far is easily to grow good quality diamond, but sometimes may show amorphous carbon formation on the other type substrates or pocket holders used in historical research.



Figure 2.27 DLC structure [146] and properties compared to diamond and graphite [147]

Substitutional, interstitial, and vacancy are main point defect types created during the CVD diamond growth[10], [16], [148]–[150]. Structure of diamond lattice remains unchanged while some physical, optical and electrical properties may be changed. Doping as one of the most common used CVD related technique, is the most well understood method to create substitutions, interstitials and vacancies in as grown diamond using CVD process.



Figure 2.28 Point defects in diamond crystal[151]

Point defects are the basic defects formed during the CVD diamond growth. As **Figure 2.28** illustrates, without doping, meaning if defects are formed by only carbon atoms (empty circles in **Figure 2.28**) in the crystal structure, there are single vacancies, group vacancies, self-interstitials, and Frenkel pairs (a pair of self-interstitial and a since created single vacancy). When doping, foreign atoms (color circles) are introduced to either substitute carbon, take the interstitial site or create a XV pair such as NV, SiV pair.

All point defects formed at the growth front/surface during the CVD process will be the source of further defect growth. Dislocations are such one dimensional defects formed during the CVD growth. Dislocations are categorized into two types: edge dislocation and screw dislocation[152].

Figure 2.29 illustrates edge dislocation in diamond crystals and the way how it moves due to the plastic deformation. Dislocation can be moved perpendicular to the dislocation direction, due to the shear stress applies along the same movement direction. It is clear to see that a unit step of slip is moved from the inside of the crystal out to the surface of the bulk. Further dislocations movements may cause bulk defects like crack in diamond crystal.



Figure 2.29 Edge dislocation in diamond crystal and the movement due to shear stress[153]

Screw dislocation is the other main type dislocation that is often formed in the CVD diamond growth process[154]. As **Figure 2.30** illustrates, a cubic lattice screw dislocation with a Burger's vector B shown in **a**) colored in red. A diamond lattice screw dislocation along 110 direction is shown in **b**). The two diamond sublattices are shown as yellow and white spheres. A cutting plane P that was used to generate the dislocation is shown, orthogonal to the strength nearest neighbor bond along (1, -1, -1).



Figure 2.30 Screw Dislocation in diamond: a) bulk illustration, and b) 110 direction screw dislocation[155]

Further to one dimensional defects, dislocations, 2D defects are also often formed in the duration of CVD diamond growth. 2D defects contain but not limited to stacking faults, crystalline domains, grain boundaries, and twins, etc[148], [156]. These defects are often seen not in single crystal diamond, but polycrystalline diamond (PCD), nano-crysatllines diamond (NCD), or ultra nano-crysatllines diamonds (UNCD), in which crystal sizes are smaller and smaller. Bulk defects of diamond are the macro 3D defects formed in diamond crystals[157]. CVD diamond growth often end up in seeing different bulk defects such as large inclusion, cracks.

From point defects scale up to 3D defects, lattice defects in diamond crystals can be characterized using different type of spectroscopic techniques, such as UV-Vis-NIR, IR, Raman, PL, CL, EPR, and NMR[158]. The types, detected features and defects, advantages and disadvantages of these techniques are listed in **Table 2.7**, are summarized for characterizing defects in diamond[159].

Technique	Type of	Typical	Commonly detected features	Test	Advantages	Disadvantages
	speedoseopy	range	and derects	conditions		
UV-Vis- IR	Absorption (transmission)	250- 800 nm	ND1,N3,N2,H3,H4,595 nm, GR1	~77 K	Evaluation of color causing defects; relatively inexpensive	Large samples absorb too much light, causing detector saturation; difficulty quantifying results from faceted stones because of the uncertain path length of light travel
IR	Absorption (transmission)	400- 11000 cm ⁻¹	A and B aggregates centers, C centers, hydrogen related defects, H1a, H1b, H1c, H2, amber centers	Room temperature	Determination of diamond type; relatively inexpensive; defect concentration can be quantified by normalization	Large samples absorb too much light, causing detector saturation
Raman	Luminescence	100- 2000 cm ⁻¹	Diamond Raman line 1332 cm ⁻¹	Room temperature	Identification of diamond; analysis of internal strain	Expensive; yields little information regarding treatment; difficulty analyzing strongly fluorescent Samples
PL	Luminescence	350- 1000 nm	N3, 490.7 nm, H4, H3, NV ⁰ , NV ⁻ , GR1, H and Ni related defects	~77 K or lower	Detection of HPHT treatment; characterization of low- concentration defects; small analysis area allows for detailed investigation	Expensive; difficulty analyzing strongly fluorescent samples; variety of laser excitations required to activate various defects; requires carefully controlled cryogenic test temperatures

 Table 2.7 Characterization techniques using spectroscopes for diamond lattice defects[159]

Table 2.7	(cont'd)
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CL	Luminescence	400- 700 nm	A and B band, n3, H3, H4	Room temperature	Evaluation of internal structure; detection of defects causing luminescence	Requires an electron beam and a vacuum; provides little information about color treatment
EPR	Resonance absorption in a changing magnetic field	-	C centers, NV defects	Room temperature	Detection of very low- concentration defects; evaluation of specific defect structures and charges	Very expensive; long sample run times; provides little information about color treatment

Dislocations are shown to be able to be measured using X-ray topography (XRT) technique in the past decades[97], [98], [139], [149], [150], [160]–[167]. The depth and position of dislocations are projected from the 3D diamond sample to 2D films, and thus the type of dislocations can be analyzed, as shown in **Figure 2.31**.



500µm

Figure 2.31 Detected dislocations of a type Ib diamond[168]



a) Homoepitaxy





Figure 2.32 Diamond homoepitaxial and heteroepitaxial growth[169]

The above discussed defects of CV diamond growth are mostly corresponding to homoepitaxial diamond growth. However, heteroepitaxial growth is also another important form of the CVD

process. Heteroepitaxial diamond growth uses non diamond single crystals as substrates so there exist more unique features during CVD diamond growth process. Single crystal CVD diamond has also been grown into large scale suing heteroepitaxial diamond growth technique, as show in **Figure 2.32**. The homoepitaxy illustrates diamond grown on diamond in **a**), and heteroepitaxy illustrates diamond grown on diamond in **a**), and heteroepitaxy illustrates diamond growth on diamond in **a**). **c**) shows a large freestanding single crystal diamond synthesized by heteroepitaxial diamond growth[170].

Many other type of imperfections and defects are usually happening to CVD growth process. Not for only single crystal diamond grown using homoepitaxy technique, but also for other techniques. As illustrated in **Figure 2.33**, imperfections such as curving/warping, mosaic spread, dislocation density are often seen in both homoepitaxy and heteroepitaxy of diamond growth.



Figure 2.33 More defect types and imperfection of as grown diamond

Mismatches of lattice parameters to cause stress and strain for either distorted or relaxed as grown diamond lattices are common in heteroepitaxy diamond growth. Orientation tilt is also an

interesting feature due to the geometry relationship between the lattice parameters of the as grown diamond crystal and the substrate crystal materials.



Figure 2.34 AFM image of a typical hillock.[171]



Figure 2.35 SEM pictures of hillock on a) 100, and b) 111 facets[89]

One other major defect is hillock. A hillock may be originated from the source of non-epitaxial crystallite, close grouping of penetration twins, graphitized bundle, or a surface contaminant[172]. After the nucleation of the source for hillock, the growth part next of the source has higher rate than the surrounding atoms, which causes hillock, a geometrical rise up in the location. Hillocks are usually categorized into pyramidal hillocks (PC), flat hillocks (FC), and unepitaxial crystals (UC), simply based on their geometry[173].

In **Figure 2.34**, the hillock is capture in an AFM image in which it can be described as a spiral growth propagating as a triangular screw dislocation when observed on 111 oriented surfaces[172][173]. **Figure 2.35** presents pictures of hillocks under SEM for **a**) 100 oriented surface, and **b**) 111 oriented surface[89]. It can be seen clearly, due to the crystal structure geometry, a pyramidal hillock appear on 100 oriented face, as quadrangular pyramids with sides facing along 110 directions. On the other hand, hillocks on 111 faces show triangular shapes, with side of the triangle in 112 direction, and along 110 direction.

2.4.4 Current Challenges and Requirements

Thanks to diamond's outstanding properties, it is believed to be promising for applications mostly in electrical engineering. CVD diamond was proposed to be a new technology for the future decades ago[174]. However, many progresses are made from different research groups and institutes all around the world, there are many unknown or unclear processes remaining for scientists. Challenges are mostly focused on how to grow large size high quality single crystal CVD diamond[8][17][19].



Figure 2.36 Improvement on sizes of different crystals[175]

The most top challenge of synthetic diamond is to make large size single crystal diamond substrates. Since no matter what applications diamonds are used for, lack of size always limits the developments of all applications on diamond. When it comes to wide bandgap materials for electrical applications, it is very clear that other crystals are being improved in their sizes, but diamond is not over the past decades. As **Figure 2.36** illustrates, Diamond hasn't changed too much in its size compared to Si, SiC, GaN, Ga₂O₃, or AlN. New development are carried out in the recent years though, recently reported results show diameter of CVD diamond is up to 200 mm at the research scale[176]. However, commercially, 15 mm -25 mm cubic shape CVD diamond is now commonly the biggest[177].

Wafer size single crystal substrates are eagerly required from the market in recent years. **Figure 2.37** presents a photo of diamond wafers. However, growing large size single crystal using CVD methods still faces many challenges. Multiple types of CVD diamond growth techniques are emerged under this circumstances. Such techniques include direct diamond growth using multiple types of pocket holders, flip seed technique, heteroepitaxy, and mosaic technique[5], [10], [57], [58], [139]. Many further techniques such as ion implantation[24], [178], [179], liftoff[31], [139], [178], and diamond slicing techniques[180], are also emerged for reducing defects in as grown diamond during the above mentioned growth techniques.



Figure 2.37 Image of diamond wafers[181]

2.5 Single Crystal CVD Diamond

In this section, single crystal CVD diamond growth progresses made in recent decades are summarized.

2.5.1 Direct Single Crystal Diamond Growth

The method that always comes first in mind as for CVD growth, is the simply direct growth. Direct growth requires the conditions are controlled that the overall area of top grown surface is larger than that of the seed substrates. Many research institutes have made progresses in direct diamond growth over the past years using both open sample holder[9], [10], [15], [74], enclosed sample holder and pocket sample holder[29], [63]–[65], [67]. In the open holder geometry, the sample is always placed on top of a flat surface in which the whole sample may be exposed to the charged plasma. In the pocket holder geometry, the sample sits in the center at the pocket of the holder, and the sample is surrounded by the caved pocket. The charged plasma in the pocket holder geometry doesn't fully cover the entire sample, but shapes uniquely on top of the surface of the substrate. Simulation works are also done a lot to illustrate and explain the process of diamond growth for better understanding the CVD diamond growth process. Though many new institutes are joining the community, works in this aspect are mostly done at Laboratorie des Sciences des Procédés et des Matériaux, CNRS in France, National Institute of Advanced industrial Science and Technology (AIST) in Japan, Xidian University in China, Harbin Institue of Technology (HIT) in China, and Michigan State University (MSU), etc. over the past decades.

The French group reported their work on the growth of singled crystal diamond with large dimensions, including increasing growth rates, thick growth, and large area growth[74], [182]. They also worked on investigating how to control and even decrease the defect densities. They reported and summarized that diamond growth rates increase with higher concentration of nitrogen, and diamond growth rates increase with higher power density, and higher methane concentration, as **Figure 2.38** illustrates[14]. The results suggest that within the proper range of nitrogen concentration from 0 to 10 ppm, and microwave power density from 60 to 130 W/cm³, and methane concentration from 0 to 10 %, the growth rates is linearly increased as $\Delta R/\Delta C_N= 1$ µm/hr/ppm, $\Delta R/\Delta P=1.43$ µm/hr/(W/cm³), and $\Delta R/\Delta C_{CH4}=3.67$ µm/hr/%. Increasing of substrate

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temperature also will increase the growth rates. The growth rates roughly scale as the square root of CH₄ concentration, and also increases with the increasing of the pressure.



Figure 2.38 Diamond growth rates change with conditions[14]

Figure 2.39 (a) shows predicted morphology of a 500 µm thick CVD film grown on a 100 HPHT substrate where 100 faces are colored in white, 110 faces are colored in pink, 113 faces are colored in blue, and (111) faces are colored in green. (b) shows scanning electron microscope (SEM) image of a typical CVD film on its HPHT substrate. (c) and (d) show evolution of the growth rates of different crystal planes as a function of CH₄ concentration and surface temperature. Higher methane concentration provide more active carbon sources for diamond crystal nucleation, thus increases the growth rates, and higher temperature inputs higher energy required for the nucleation which also increases the growth rates.

It is clear to see that the predicted growth morphology is in a good agreement with the actual experimental growth with the SEM picture. Thus growth mode limits the growth of the entire

diamond substrate since it is obvious that the formation of 111 facets are formed and due to its close packed property and the slow growth rates compared to 100 faces, which makes the as grown CVD diamond achieves smaller as grown area.



Figure 2.39 Diamond growth morphology and related growth rates[14]

To predict the final geometries of the as grown single crystal diamond, the ratios between growth velocities between each facet are derived in α , β , and γ for the growth parameters as below[183]:

$$\alpha = \sqrt{3} \times \frac{V_{(100)}}{V_{(111)}}; \quad \beta = \sqrt{2} \times \frac{V_{(100)}}{V_{(110)}}; \quad \gamma = \sqrt{11} \times \frac{V_{(100)}}{V_{(113)}}$$

From the expression of the parameters above, it is easy to identify that to form ideal cubic shape larger square shaped area as grown diamond 100 top surface, the 3 parameters should all be set to 1. In this case, the (111), (113), and (110) facets would be collapsed in the final morphology. That is to say, ideally to form cubic morphology, where (111), (113), and (110) facets will not emerge at all.

Many other final morphologies re also predicted based on the growth parameters as shown in **Figure 2.40**. As an example, the 100-111 coexistence domain is made up of 3 topological subdomains, which are [8, 3, 0, 0], [4, 3, 0, 0], and [4, 6, 0, 0], according to whether 100 faces are octagonal or square and 111 faces are triangular or hexagonal. In such way, 55 different final morphologies are illustrated based on 15 face coexistence domains covering the whole (α , β , γ) parameter space.



Figure 2.40 Predicted as grown diamond morphologies with different combination of growth parameters[183]

Among these morphologies, the large area growth are only possible under the specific parameter combinations. Since the substrates are 100 oriented, the top surface area is aimed to get larger

100 facets in size for the final growth morphology. Thus, only certain area in the parameters map could lead to larger 100 top surface as shown in **Figure 2.41**.



Figure 2.41 Selected parameters for large area top surface diamond growth[183]

As illustrated in the **Figure 2.41**, a linearly increased 100 top surface area is proposed at a combination of $\alpha = 2.0$, $\beta < 2 \alpha / 3$, and $\gamma = 3.0$. In this case, the initial seed starts from a half cube 100 plane top and side facets measuring 3 mm on each edge, plotted under three different geometric growth parameter combinations.

Recently, the simulations on diamond growth on (100) surfaces has been reported using 3D kinetic Monte-Carlo method, where processes such as adsorption, desorption, etching, and surface migration are taken into account[70].



Figure 2.42 3D Monte-Carlo simulation of diamond growth on 100 surface[70]

The 3D Monte-Carlo simulation results are shown in **Figure 2.42** as detailed step edge of only three atomic layers of diamond growth on 100 surface at the conditions of 850C°, 4% methane, 200 mbar, and 3kW. The first layer grows quickly, and a step flow growth is obtained with two atomic layers high step, which reproduces experimental results[70].

To grow high quality single crystal diamond, the French group obtained a low dislocation sample from a substrate with a large square hole in the center[74]. As shown in **Figure 2.43**, in that particular sample, dislocations are found to propagate vertically and horizontally from the substrate and to terminate at the top surface or at the sides of the hole, thus leaving the center part with a strongly reduced dislocation density. Some comments are added for the particular sample: The hole created in the center makes the sample partial grow laterally inward, and each

side of the hole can be seen as the pocket wall to the opposite side of the sample edge, which brings that lateral growth using pocket holders are promising in growing large area high quality single crystal diamond. The use of pocket holders are discussed in the following sections.



Figure 2.43 Decreasing dislocation density using a hole in the center of the substrate[74]

Diamond growth using pocket holders are carried out at multiple institutes. Both growth efforts and simulation works are done for better understanding how to grow larger area single crystal diamond.



Figure 2.44 growth results in an open holder[64]

Open holder growth illustration is discussed in **Figure 2.44**, where PCD deposition happens on top of the Molybdenum holder as single crystal diamond deposition happens on its substrate[58]. Thus, the PCD surroundings are dangerous to the edges of the as grown single crystal diamond, and PCD rims will form after growth, as illustrated in **c**) and seen with a real photo of **d**).



Figure 2.45 Growth results in a pocket holder[64]

On the other hand, the pocket holder provides a protection of the substrate as the substrate sits in the center and the top surface of the pocket holder is higher than the top surface of the substrate. During the deposition process, as shown in **Figure 2.45**, PCD deposition happens on the surface and the edge of the pocket holder, and only single crystal diamond deposition happens on its substrate. Once the growth last long over time, the protection disappears and as grown single crystal diamond is close enough to the PCD on the pocket edge, the deposition should stop and the CVD diamond and the PCD can be lift off for further process[64].



Figure 2.46 Simulated flux flow in a) open holder vs in b) pocket holder[184]

The simulation of the comparison of open holder and pocket holder from AIST diamond growth group suggests that the gas flow goes bypass the sample edge I one certain direction as the gas flows bottom up, as shown in **Figure 2.46** (**a**). And it shows in (**b**) that the protection of the pocket actually maintains the flux cycling around the substrate with in the geometry of the pocket holder. The cycling of the gas flow create the environment for as grown sample to keep growing single crystalline but not to form PCD[184].

Research group at AIST have also conducted many direct single crystal diamond growth using their CVD systems[5]. Very thick single crystal diamond samples are grown with multiple steps of repetitive growth process[185]. The substrates are selected to be HPHT Ib 3 mm x 3 mm x 0.5 mm. Hydrogen etching is set for 30 min before deposition. Gas flows are 500 sccm H₂, 60 sccm CH₄, 0.6-1.8 sccm N₂. Pressure ranges from 130 to 220 Torr, with input power ranges from 1 to

3.7 kW. The power density is thus 50 -150 W/cm³. Substrate temperature ranges from 1000°C to 1300 °C. Growth rates are estimated to be $30 - 100 \mu$ m/hr[185].



Figure 2.47 Large CVD diamonds grown by AIST (**a**) 10 mm thick, 4.7 ct, (**b**) 9.9 mm thick, 3.5 ct, (**c**) 8.7 mm thick, 4.4 ct[185]

As seen **in Figure 2.47**, the grown SCD area is significantly smaller than the original HPHT seed due to the thick polycrystalline rim around the SCD grown surface. This indicates that the thicker the grown SCD crystal, the smaller is the area of the top surface.

Another simulation has been analyzed using COMSOL recently to show difference between pocket holders and open holders[71]. As **Figure 2.48** illustrates, the electrical field distribution is simulated by COMSOL with flat holders and grooved holder. Both (a) regular corner, and (b) round corner with radius of 0.7 mm are proposed for pocket holders. Side views of (c) samples on an open holder and (d) samples in a 0.7 mm radius rounded corner pocket holder illustrate the difference of electric field distribution between the two holder designs.



Figure 2.48 COMSOL simulation of influence of pocket holders[71]

The simulation results suggest the pocket holders are really crucial to the growth of high quality single crystal diamond. The electric field distribution is much smoother in the pocket holder, where the electric field directly above the holder can be concentrated in the area above substrates, rather than excessively distributed on the surface of the holder in the non-substrate area. The intensity on the edges are weaker in rounded corner pocket holder where the electric field is no longer concentrated on the edges, and the PCD formation can be effectively

suppressed. Other than previous gas flow simulation of difference between open and pocket holders, the COMSOL simulation approves the protection from the pocket holder on another point of view.



Figure 2.49 Temperature distribution over the space for different sample holders.[71]

The temperature distribution is also measured with a related experiment to show the temperature profile is less curved in the pocket holder design, which enables better crystal growth performance. As shown in **Figure 2.49**, in the same temperature range, the difference between the maximum and minimum temperatures on substrate surface was 171.8 C° for the flat holder and 83.6 C° for the grooved holder.
2.5.2 Flip Seed Growth

Flip seed method is also used for growing large area and high quality single crystal diamond. The direct growth methods always return a fast growth rate at the vertical directions than lateral growth directions. The flip seed method grows diamond at the 100 surfaces, where it basically has three steps.

As Figure 2.50 shows,

- Step 1: the growth results into thick CVD diamond
- Step 2: rotate 90 degree and grow on side 10 surfaces
- Step 3: repeat of step 2.

The ultimate goal of this method is that the top surface area is increased, in such way, compared to its original top surface area. As seen in the photos of experimental sample, though the top area decrease in step 1, the side growth in step 2 increases the area on the side. Many other experiments also used the flip seed method to achieve larger areas.



Figure 2.50 Steps of flip seed growth method[186][187]

The flip seed method also suggests a way for how to suppress the propagating dislocations during the growth. As **Figure 2.51** illustrates, the threading dislocations are limited from the seed after two steps of the growth using the flip seed method. X-ray topography (XRT) is used to characterize and display dislocations, and it is clear to see that dislocations are dark lines which are lessen in color, i.e. numbers in the second block and the third block. The dislocations in each block are perpendicular to each other, which allows the higher quality surface is always used as the deposition surface during the growth.



Figure 2.51 X-ray Topography (XRT) of CVD diamond using flip seed method[161]

The flip seed method is believed to require extremely long growth times, resulting sample uniformity is also needs to be improved. Ways of improving this method contain ion implantation and lift off processes. **Figure 2.52** introduces a CVD plate achieved by multiple side surface growth by flip seed method and a lift off process. The CVD diamond is resulted in as grown 12.6 mm x 13.3 mm x 3.7 mm in size as the photo shows. The plate is then lift off by ion implantation, with (a) a transmission photo, (b) polished plate, and (c) birefringence picture, shown in **Figure 2.53**, where it is clear to see the features are different at locations due to the flip seed growth method.[178]



Figure 2.52 Growth done by multiple flip seed steps and CVD plate achieved by lift off process[178]



Figure 2.53 Pictures of the CVD plate achieved in Figure 2.52[178]

2.5.3 Mosaic Technique Growth

Mosaic growth is also used wide commonly for larger area single crystal diamond synthesis. Many preliminary researches are conducted at AIST and MSU, etc. The mosaic method is used by tiling different substrates together during the growth for large area CVD plates, as **Figure 2.54** illustrates.[188]



Figure 2.54 Schematic steps of mosaic growth method[189]

Each step of the above illustrated steps of mosaic growth requires actual careful treatment in selections, alignment, and lift off process or laser cutting process, and polishing. For the final CVD plate to be identified as a single crystal diamond, each of the substrates need to have nearly zero misorientation with the others. As the substrate has diamond crystal structure, the best way for alignment before the growth is to have all substrates have the same orientations in bath crystal structures and physical bulk surfaces. Mostly, there should be one substrate, typically the center tile, who serves as the reference for the other substrates, if polishing works are required to

lessen the misorientation values between other substrates and the reference substrate. In this way, crystal structural orientation measurement is required in the selection and aligning steps.

To decrease the difficulty in the steps of substrates selection and aligning, several ideas are taken into account. One idea is to create a perfect alignment with zero misorientation between two substrates, one single substrate is cleaved into two pieces, and the two pieces are grown into one single crystal diamond plate as **Figure 2.55** shows. This idea though doesn't truly make the as growth plate larger, but proves the mosaic method is promising. The intersection between the two pieces A and B joined together after the growth and the intersection was able to show smooth transition from two substrates to one single crystal. Such phenomenon is established due to the two substrates A and B are well aligned.



Figure 2.55 Mosaic growth on two pieces cleaved from one substrate[187]

It is important to point out the two pieces cleaved from one substrate may not be easily controlled as for edge qualities for A and B. The reproduction may face challenges and plus it is not truly expanding the area, the idea so far only approves the method is promising.





Another effort, called cloning technique, was made by AIST to work on reducing the difficulty for substrates selection and alignment in the mosaic method. Cloning technique works based on the mosaic technique but realized the repeating growth from the same substrate will create the CVD plates with the same orientations which can be used as clones for mosaic growth substrates, just as **Figure 2.56** shows. Highlight steps in this cloning technique is the repeating initial growth procedures for identical mosaic seed substrates, and the following step on connecting the clones.

Expanding the growth efforts from single substrates and using the mosaic growth diamond plates for further mosaic growth, the AIST group finally successfully achieve the final product measured up to $20 \times 40 \text{ mm}^2$. Further efforts are made towards a 2 inch wafer, where a final mosaic substrate measured up to $40 \times 60 \text{ mm}^2$ was assembled by joining together twenty four 10 x 10 mm² cloned single crystal diamond plates. The results of their work also show difference in temperature over locations, and cracks at the edges are formed probably due to the internal stress. They reported the size of the sample almost hit the limit of the CVD system. Results also suggested better crystal structure orientation is required for the technique with respect to mosaic boundaries and to prevent cracking.

The most recent systematical mosaic growth efforts are made at MSU, in which crystal structure orientations are characterized accurately by newly developed measurement procedure. The mosaic samples are prepared in a more careful manner and the pocket sample holders are designed and used specifically according to the mosaic substrate sizes. As discussed above, the misorientation angles are key factors in the mosaic growth process. The works done by MSU made a clear illustration on all possible misorientation angles between samples.

These misorientation angles include:

- Misorientation angle between crystal planes and their bulk surfaces with in the same substrate
- Misorientation angle between crystal planes of the adjacent substrates
- Misorientation angle between bulk surfaces of the adjacent substrates

The above listed misorientation types can all be taken care of by polishing technique in which the designated misorientation angles can be achieved at a really high accuracy within 0.01°. In such way, the misorientation angles between crystal planes of adjacent substrates are categorized into three types, as **Figure 2.57** illustrates, according to the relative orientation with respect to the interface, the touching edges of the substrates. The three types of the misorientation are called Twist, Tilt, and Torsion, so the TTT alignment. In the definition of the TTT alignment notation, the x direction is defined to be parallel to the interface, parallel to the top surface, the y direction is defined to be perpendicular to the interface, parallel to the top surface, and z direction is defined to be perpendicular to the top surface. The misorientation between crystal planes around x axis is defined as Tilt. The misorientation between crystal planes around y axis is defined as Torsion. The misorientation between crystal planes around z axis is defined as Twist. Each "T" misorientation behaves differently during the growth as for mosaic growth technology.



Figure 2.57 Mosaic growth set up for TTT alignment[86]

Once the relative misorientation is defined, the mosaic substrates are prepared with almost zero misorientation angles from all aspects. The bottom surfaces of mosaic seeds are polished together to present stable settings, and to enhance the flatness, a polished PCD plate is placed underneath the mosaic substrates. In such way, the base of mosaic substrates are taken care of.



Figure 2.58 A photo of mosaic seeds before place in the reactor for growth[86]

The top surfaces are also measured to identify misorientation angles between substrates, and top surfaces are also polished together to present smooth physical bulk surface with barely no change across the interface to enhance the rapid growth at the interface. A PCD frame is used to center the mosaic substrates in the center of the pocket holder and prevent the substrates from moving off the optimized position, as shown in **Figure 2.58**, before the substrates are loaded for mosaic growth. The result worth to notice is the gap between the two substrates across the interface is controlled to be less than 5 μ m, which enhances faster mosaic growth at the start of deposition process.

X-ray rocking curves are carried on the sample for study of evolution of misorientation angles. Peak separation of XRC profiles will be observed for mosaic samples when the measured area:

- has a crack
- contains a small angle grain boundary
- PCD emerges from the seed
- covers more than one mosaic seed

XRC results are analyzed by house made analysis software and the threshold for identifying single crystal for peak separation is set to be less than 1 Full Width Half Max (FWHM). Evolution of changes in relative misorientation as of TTT alignment for mosaic growth results are reported in the above discussed method, as shown in **Figure 2.59**. The mosaic CVD diamond is grown in the sequence of A, B, C, D, and the misorientation angles of their Twist, Tilt and Torsion are illustrated for understanding the growth mechanism for mosaic technique. It can be seen the peak separations are clearly reduced over the mosaic growth from A to D which suggests the growth process can easily smooth the difference of the misorientation in Tilt, which is perpendicular to the interface. Such results suggest the misorientation perpendicular to the interface of the deposited film. The reduction of torsion and Twist is little after growth. While the movement of boundary is substantial in y direction of around 0.5 mm, this result also indicate the growth mechanism makes the perpendicular to interface as the favorable moving direction, which coherent with the reduction of misorientation in Tilt.



Figure 2.59 Evolution of relative misorientation of TTT alignment in mosaic growth[86]

As further improved measurement technique is used and a smart analysis software is built, the understanding of misorientation angles between tiles is also further improved. Line scans of XRC results are shown in **Figure 2.60** with 0.1 mm intervals between adjacent measurement points on a 2 x 2 mosaic sample. It can be seen that little peak separations are achieved between each adjacent tiles, where $\Delta \omega$ ranges from 0.0465° to 0.2331°. The growth front is easy to be

seen by naked eye where lateral step flow growth dominate the as grown top surface of the mosaic sample.



Figure 2.30 Linescans XRC over a 2 x 2 mosaic as grown sample[86]

Change in peak locations and lattice curving are also analyzed in the mosaic growth work. A summary of the mosaic growth effort done is also discussed in this recent work, in which the state of the art geometric, crystallographic, growth, and scaling results are clearly stated for optimized mosaic growth technology.

2.6 Direct MPACVD Single Crystal Diamond Growth at MSU

Direct growth using MPACVD at MSU has been started in the past decades from designing and building the initial CVD system, conducting single crystal diamond growth, to nowadays, large area diamond growth using pocket holders. The recent research activities that focused on single crystal growth are many research products that are standing on the shoulders of giants. In the most advanced results, the deposition of high quality PCD rimless single crystal diamond SCD via MPACVD is investigated. Many tasks are accomplished over the past years. Growth of SCD are conducted mainly using pocket holder with width of 6.0 mm and depth of 2.3 mm, 2.9 - 1.9 kW microwave power, 240 Torr, 5% methane, and 985 – 1040 °C. Different depths of the pocket are used from 2.0 mm to 2.9 mm with process time from 12 hours to 60 hours, and methane of 4% to 7%. The width of pockets are also varied from 6.0 mm to 7.6 mm as investigation on large area regrowth of diamond.

As shown in **Figure 2.61**, the conventional pocket holder design has an inner pocket for centering the diamond substrate with proper gap distance between each edge and pocket wall. The HPHT type Ib 3.5 mm x 3.5 mm x 1.4 mm diamond substrates with 1.25 mm to 2.05 mm gap distances from the starting of the growth. The outer pocket is the useful pocket for protecting the sample with better electric field distribution and better gas flow for single crystal diamond synthesis.



Figure 2.61 Conventional pocket holders designed and used at MSU for single crystal growth[64]

Growth result of a photo of a typical as grown sample is shown in **Figure 2.62**. Both the side views and top views are shown in pictures and schematic drawings. In the drawings, it is easy to see that the top surface of the substrate is a little higher than the inner pocket step, and as grown

CVD diamond has wider width. Though PCD deposition on Molybdenum holder decreases the possible area, with clear circle between relatively large crystal size PCD and the outside, as grown top surface is smooth.



Figure 2.62 Growth results and illustrations of growth using a pocket holder[64]

However, the increase of the area is suppressed by the pocket and the PCD deposition on the pocket. The growth in the lateral direction also shows difference between the side (100) orientation and the corner (110) orientation. Smooth edges on the sides are observed with interesting intersection between corners and sides. Such phenomenon is believed to be caused by growth sectors of diamond.



Figure 2.63 Highlight of single crystal growth using a pocket holder[64]

Highlight of this work focuses on the long growth and regrowth of SCD with multiple seeds and with different pocket geometries. The statement of how the regrowth between each other is not

clear, while the results show the influence of the difference in pocket sizes on sizes of as grown CVD diamonds. As shown in **Figure 2.63**, it can be seen that the normalized area gain are all increased before the mark of 50 hours growth time. The increase is fast in first 12 hours for all, and increased slowly between 12 and 50 hours. Most samples are decreased in sizes beyond 50 hours but ACH67 gets a little increased in sizes with pocket dimensions of 7.0 mm width and 2.9 mm depth. The data represents 4 dimension sizes of pockets, and results suggest the wider the pocket is, the larger the increased size is during the growth. Combining together this result with the PCD rim of diamond grown in open holders, it is simple to draw a rough conclusion that the gap distance between the sample and the holder is important, it cannot be too narrow or too wide. As analyzed above, the fast increasing in size is due to the apace between edges and pocket walls, and the increasing rate slows down between 12 and 50 hours because the holder geometry is increased to 2.9 mm depth. The decrease in size of all samples beyond 50 hours are believed that the CVD samples are grown out of the pocket already so the protection of the pocket disappear.

All of the above discussed information are key basic understandings and theories to this dissertation for the research project. Many historical data and preliminary results for SCD growth and discussed optimized measurement techniques in the previous results are used for reproduce or better and more systematically analysis in the following chapters of this dissertation.

Chapter 3

CVD Reactors and Diamond Growth

3.1 Experimental Setup

The microwave plasma assisted chemical vapor deposition technique is the main technique being used in diamond growth at MSU. In this research, main growth efforts are carried out using the diamond system 4 (DS4), which is a type C reactor corresponding to previous notation. Some of the growth are carried out using diamond system 2 (DS2), which is a type B reactor. Both reactors have really similar designs as the precious designers described, and the main introduction in this dissertation would focus on DS4. The diamond system generally contains microwave generator, power supply, a vacuum chamber connected with useful process gases and pumps, cooling systems, and controlling computers and related hardware.

In general, DS4 uses a hybrid mode of electromagnetic filed with TM_{001} and TM_{01n} , with short Ls=16.25 cm, and probe position Lp=3.0 cm. DS2 uses the hybrid TM_{013}/TEM_{001} electromagnetic mode with short distance Ls=21.3 cm, and probe position Lp=3.8 cm.

More details of a diamond reactor are shown in **Figure 3.1**.



Figure 3.1 Cross section view of schematic components of a diamond system[64]

3.1.1 The Diamond System

Generally speaking, the diamond system is made up of a diamond reactor and its bundled equipment, hardware and software, as **Figure 3.2** illustrates. Categorized by functions of all parts, the diamond system can be divided into six divisions.

The six divisions, by functions, are[86]:

- 1) Microwave power supply and trasmission structure
- 2) MPACVD reactor and vacuum chamber
- 3) Feedgas flow and control system
- 4) Vacuum pumping and pressure control
- 5) Temperature control
- 6) Computer aided semi-automated control

The microwave power supply and trasmission structure division is used in DS4 in which it contains a Muegge Power Supply (model MS015KE-110DL), and a Megnetron head (model MH015KS-312CN). The operating frequency of the microwave generator is at 2.45 ± 0.01 GHz, which is capable of generating a maximum power output of 10 kW. The transmission structure is followed with a waveguide to transmit eh generated microwave to the probe inserted vertically above the reactor cavity. The output of the magnetron power supply is connected to a circulator that isolates and protects the power supply from any power that may be reflected from



Figure 3.2 Six divisions of a diamond system, modified from[86].

microwave reactor. The reflected power is led to a water-cooled dummy load which is impedance matched.

Both forward power P_f and reflected power P_r are measured during the process, and the absolute power Pabs can b ederived: $P_{abs} = P_f - P_r$. Microwave power measurements are made using dualdirectional power couplers inserted in the waveguide between the circulator and microwave reactor. Typical microwave power used for diamond grwoth an drelated proesses are controled to be in the range from 1.8 kW to 3.4 kW. The reflected power P_r is typically controlled around 10% of the forward power P_f . With the representative values, the reflected power P_r could range from about 120 W to 400 W.

The reactor and vacuum chamber diviosion mostly fouceses on the cylindrical reactor cavity, as presented in **Figure 3.3**. A hybrid TM₀₁₃ and TM₀₀₁ electromagnetic resonant mode is applied in type B reactor. The cylindrical cavity has a height that can be adjusted to $1.5 \lambda_g$, where λ_g is the incident wavelength. The height of the coaxial cavity corresponds to half of the wavelength in air λ_0 for the microwave frequency. Due to different electromagnetic modes could be applied, and several discahrge zones could be gerneated, as shown in **Figure 3.4**, the process gases are limmited in the specific zone by the quartz dome. In thi sway, the sample is placed at the level between the cylindrical cavity and the coaxial cavity, where the quartz dome limits the gases for only the zone surrounding the placed sample.



Figure 3.3 The hybrid electromagnetic mode used in DS4[64].



Figure 3.4 Three typical discharges (in green) that generated from a TM₀₁₃ mode[64].

The electromagnetic power distribution in the TM01 modes is constant in the annular direction around the vertical axis of the cavity and has a center maximum in the radial direction. The

microwave radiation is coupled into the cylinder via an antenna (probe) reaching a quarter wavelength through the top plate of the cylinder and the region of concentrated power on the very bottom of the cavity is selected for the plasma formation. The TM_{013} mode offers a larger distance between the near-field of the probe and the discharge region.



Figure 3.5 Separate TM modes used on DS4[64]

Two transverse magnetic (TM, no magnetic field in the direction of radiation propagation) modes that are useful for the purpose of establishing a localized plasma discharge are shown in **Figure 3.5**. The two electromagnetic fields are TM_{012} on the left and TM_{013} on the right.

The electromagnetic modes for different diamond systems are defined based on the above background information for different purposes of diamond growth. These two parameters are key

adjustment for selecting the electromagnetic field modes, 1) The short position, defined as Ls defined as the distance between the sliding short and the base plate, and 2) The probe position, Lp defined as the distance between the point of the probe and the sliding short, as shown in **Figure 3.1**. The DS4 configurations are designed with dimensions of $R_1 = 15.24$ cm, $R_2 = 10.16$ cm, $R_3 = 1.84$ cm, $R_5 = 12.07$ cm, $L_1 = L_2 = 6.12$ cm, and fixed dome dimensions of $2R_D = 21:6$ cm, and h = 10.86 cm. The probe and sliding short lengths are variable parameters set around at typical values of Lp ~ 3.0 cm and Ls ~ 16.25 cm. This modified Type C reactor design with a larger dome, and larger cavity employs a "non-classical" electromagnetic TM₀/TEM₀₁₁ plasma excitation applicator mode. This hybrid approximation allows finest control of plasma position, size, shape and intensity. The diamond substrate is placed in the center of a pocket holder while in the process, as **Figure 3.6** shows.

In the gas flow control division, typically a mixture of hydrogen gas H_2 and methane CH₄ are fed into the chamber for diamond growth. Airgas research grade H_2 gas cylinder size 300 with purity 99.9995% is used. Airgas research grade CH₄ gas cylinder size 300 with purity 99.999% is used. The other gases are normally not used, and need to be discussed if necessary. During the processes related to diamond growth, flow rate of H_2 is set to be 400 standard cubic centimeter per min (sccm), and the CH₄ flow rate is usually set to be 20 sccm, which is a 5% ratio to that of H_2 . The flow rates of gases are controlled using MKS type 1179A mass flow controllers. In addition to reacting gases, nitrogen gases are used to purge the lines and the chamber and to vent up the chamber. Airgas research grade N₂ gas cylinder size 300 was once used for first partial of the research, and now the supply of N₂ is from the houseline N₂ gas supply from liquid nitrogen.



Figure 3.6 Illustration of how to load the sample holder[64]

 N_2 gas is also used to compensate the exhaust gases output from the chamber with N_2 as 10 times of the amount of reacting gases in order to dilute the flammable concentration of the exhaust gases, i.e. flow rate of N_2 is usually set to be around 4,200 sccm. When ramping up the pressure, H_2 flow rate is typically set to be 1,500 sccm, and thus the N_2 flow rate for ramping is set to be 15,000 sccm. There is only one fan for exhausting all output gases as a combination of all reactors from the building.

In the pumping and pressure control division, the pressure is usually set to be from 10 Torr to 300 Torr as for fulfillment of diamond growth and related process conditions. The pressure is kept at a dynamic balance for the vacuum chamber while both the reacting gases are flowing at a constant rate and the pumping set is vacuuming gases. The rough pump used in DS4 is type TRIVAC D 16 BCS, a two-stage rotary vane mechanical pump. A throttle valve type MKS 152D/1253D is used to regulate the pressure level. The gas pressure is measured with three pressure gauges at different measuring ranges. A MSK type 141A Baratron Absolute Pressure capacitive based sensor measures at 0.1 - 1000 Torr. A MKS type 623 Baratron Capacitance Manometers measures also at the range from 0.1 Torr to 1000 Torr. A MKS Series 910 Dual Trans Micropirani/Absolute Piezo Transducer measures at a widest range from 10⁻⁵ Torr to 1,500 Torr. Thus, the base pressure of the system is measured using the value of 10^{-5} Torr. Experience shows, at a good sealing condition of the vacuum chamber, the pressure can drop to the base pressure from the atmosphere in ~ 1.5 hour. The leak rate of the vacuum chamber is teste frequently to make sure the system is at a good sealing condition. Typical leak rate is measured at 5 - 10 mTorr/hr. Anywhere of the connection parts of the vacuum chamber should be taken care of for better sealing conditions, including using rubber O-ring for sealing the quartz dome, tighten the assembly of the connection of valves and the pump, chamber door should be closed. Keeping the system at vacuum is the important practice for maintain the lifetime of the system.

In the temperature control division, the reactor doesn't include a direct temperature measurement like a thermal couple inside the chamber due to the special circumstance of the conditions required for diamond growth in the system. The microwave input is the source of energy which heats up the gases in the chamber. The system is thus cooled by air and by well-designed water cooling system. The balance is then created between the input microwave energy and the cooling air and water. The substrate temperature during diamond growth and related process is measured using an IRCON Ultimax monochromatic infrared pyrometer operating at 0.96 um, which is fixed in place from one of the portals of the cavity pointing towards the center of the pocket holder across the quartz dome. The emissivity of the pyrometer is set to 0.1 for DS4's diamond growth and related process. The cooling system cools several key components including the dummy load, the magnetron head, the probe, the sliding short, and the base plate. The sample is in contact with the sample holder, and then substrate holder, the conducting short plate, and finally the base plate. So the sample is cooled indirectly. This means the design of the pocket holder requires the specific thickness at the bottom of the sample holder for the heat transfer. All of the components mentioned are cooled to maintain the temperature around 20 °C. The water cooling system of DS4 is operated under a main cooling facility servicing multiple reactors and other machines in the building. It needs to mention there is only one main pump for the main cooling service in the building. Additional air cooling is added using two air blowers to cool the quartz dome bell jar through an inlet in the cavity portals and a fan is used for lowing wind to the whole system from the front. Another air blower cools the magnetron head. The temperature is monitored within a threshold and safety operations will be triggered if the temperature is too high, an interlock can be tripped shutting down any active process.

In the computer aided semi-automated control division, a computer is connected to the biases through a Beckoff I/O buses to send orders to the system. The operating system is a Windowsbased closed-source software designed to monitor and control all components. The hard drive is updated in 2021 and reinstalled to the system with an updated operating system. The user can input the values of data digitally, such as short position and probe position, which are mechanically adjusted by stepped motors. In the same manner, all parameters including temperature, pressure, microwave power and gas flow rates can be monitored and adjusted. Values of all the parameters are stored in the text file with a sampling rate of 3 seconds. The user can only follow the hard coded physical limits which allows multiple digital interlocks for safety. The use can operate the system manually and can also operate the system with pre-programmed recipes. The recipes can be edited a head of time before running the process. The user can still operate the system manually at any time during a recipe when necessary. Recipe steps cannot be modified or extended during an active process.

3.1.2 Controlling of the system

To more accurately control the system which is required for growing diamond under a more stable conditions with less fluctuation in parameters, certain monitoring and controlling features are added on with a closed loop control mechanism. This offers a great help for the user to keep the system in a better growth conditions for long times. The first reason for using this add on control is the need to frequently active lowering the power to maintain the temperature at a constant value. Then the pyrometer can be set to continuous mode.



Figure 3.7 Schematic drawings of all add-on components with the system[86]

Figure 3.7 shows the entire operation of the DS4 system with the add-on control. Most components are logged through the main computer, and the temperature measured by the pyrometer can be constantly logged in the Raspberry Pi with an analog-to-digital (ADC) module. The Raspberry Pi is also relayed to the Beckoff bus with a digital-to-analog (DAC) module. The Raspberry Pi monitors the temperature with pre-entered temperature limits and adjust the power



Figure 3.8 Overview front look of DS4

when necessary. The power control from Raspberry Pi can be sent to the computer through an Arduino Leonardo. Real time camera pictures are taken during processes with a Raspberry Pi camera (RPi). Both the main computer and the Raspberry Pi have separate monitors and keyboard inputs. Data from the Raspberry Pi can be uploaded to external cloud servers for real-time monitoring during long runs. **Figure 3.8** presents an overview of the current front look of DS4.



Figure 3.9 Example of full temperature profile and set power profile

The temperature measured from a pyrometer is stored in Raspberry Pi with a resolution of 1.4 °C. The Raspberry Pi is encoded with some Python scripts for better monitoring and controlling automatically. The power is usually adjusted at a 40 W difference to have the temperature present a noticeable change. The temperature is usually dropped by 6 °C once the power control is effectively on. When it goes over longer time and goes to lower temperature and lower power, the change of power is more sensitive to the change of temperature. The temperature may start to change before the power changes 40 W and the temperature may be dropped more than 6 °C, and up to 14 °C. **Figure 3.9** shows an example of a full temperature profile (red) and set power profile (green), with the upper limit of the temperature being 990 °C.

The add on Raspberry Pi camera takes a photo of real time growth every 30 seconds. The time intervals can be changed on Raspberry Pi. Before using Raspberry Pi, a stand-alone DSLR camera is used to monitor the inside of the chamber. The DSLR camera is now mover to monitor the gas pressure. The Raspberry Pi camera is a Module v2, based on a Sony IMX219 8-megapixel sensor paired with a Pixco 50 mm F1.4 lens to limit the field of view to a small range that is able be see through the small hole of the observation portal. The pictures taken by RPi camera are stored in RPi during the diamond growth and related processes. Pictures can later be assembled into time-lapse in GIF pictures by RPI in the later part of the process to present the real time process for the users. The user would be able to identify any tiny changes happening to the sample during the process. As **Figure 3.10** shows, one representative growth of the sample provides 4 pictures of different times during the process. PCD deposition and substrate growing larger are being monitored clearly. The green colored sphere also stands for the concentrated methane plasma covering right on the top of the sample. The pictures are not so focused over

time due to deposition increases the thickness of the sample and changes the depth of the field for the RPi camera. This features proves better camera setup is helpful for real time analysis for diamond growth.



Figure 3.10 RPi pictures of a representative sample growth over time

3.2 Sample Preparation

Sumitomo high pressure high temperature (HPHT) single crystal diamond type Ib 100 oriented substrates with size of 3.5 mm x 3.5 mm in area are used in the dissertation research project. Some of the substrates are in full thickness 1.4 mm or 1.0 mm, some others are recycled by laser cutting and polishing with typical thickness of 0.35 mm, 0.4 mm, 0.6 mm or 0.8 mm. HPHT seeds have a golden-yellow color because the diamond contains 1.0 - 10 ppm nitrogen in the crystal, and since, they are classified as type Ib diamond. These diamond seeds typically have defect densities of $10^4 - 10^5$ cm⁻², which is considered high[64].

3.2.1 Sample Cleaning

No matter to grow diamond or characterize the diamond itself, the diamond sample itself should be as free from surface impurities as possible. Procedures of wet chemical cleaning of diamond sample cane remove metallic, graphitic and organic contamination. Strong acids and normal solvents are used in this procedures. For different purposes, the cleaning steps are standardized for (1) pre-deposition cleaning, to remove all contaminants, and (2) post-deposition cleaning, to remove graphitic residues deposited during the ramp-down process.

(1) Pre-Deposition Cleaning sequences:

- Nitric Acid (40mL) and Sulfuric Acid (40mL) mixture boiling at 380°C for 20 minutes.
- Rinse in DI water.
- Hydrochloric Acid (40mL) boiling at 380°C for 20 minutes.
- Rinse in DI water.
- Use DI water beaker to transport sample to solvent fume hood.
- Ultrasonic cleaning with sample in Acetone (30mL) for 5 minutes.
- Ultrasonic cleaning with sample in Methanol (30mL) for 5 minutes.
- Dip sample in Isopropanol (30mL). (Store in isopropanol jar if the sample will not be loaded into the system within a couple of minutes.)
- Dry sample with nitrogen gas gun.
- Transport sample using a new covered Petri dish for immediate loading into the deposition system.

(2) Post-Deposition Cleaning

- Nitric Acid (40mL) and Sulfuric Acid (40mL) mixture boiling at 380°C for at least 1 hour, and up to 3 hours. The acid mixture can be discarded and replaced as needed until the sample is free from graphitic residue.
- Rinse in DI water.
- Use DI water beaker to transport sample to solvent fume hood.
- Ultrasonic cleaning with sample in Methanol (30mL) for 5 minutes.
- Dip sample in Isopropanol (30mL).
- Dry sample with nitrogen gas gun.

3.2.2 Diamond Polishing

Rough diamonds are necessary for polishing to present shiny and smooth surfaces. Sample surfaces are required to be smooth for diamond growth, since a smooth surface provides the environment for good step flow deposition. As grown samples which may contain rough surfaces or contaminants, are also needed to be polished for later characterization process or even for simply illustration by photos. Diamond polishing at Fraunhofer USA (now Fraunhofer CMW) uses purely mechanical process, where diamond grit over a rotating cast ion disk called scaife is used. The diamond surface that needs polishing is pressed with a flat surface with more than 10 N force, and the rotating angular speed of the scaife is up to 3000 rpm, which makes the linear velocity up to 50 m/s. The sample holders of the diamond is equipped with micrometers which helps the polishing process to control the polishing result within a small angle with a resolution of 0.01°. Such accurate polishing process helps sample preparation and the following growth and characterization steps a lot.

3.2.3 Laser Cutting

Sometimes rough diamonds are too rough for polishing, for example, when as grown samples are full of rough edges. Some other times diamonds need to be cut into pieces for size requirement or recycling, either horizontally or vertically. Either growth directly from HPHT type Ib substrates or regrowth from well prepared CVD plate or recycled HPHT seeds would require the sample to present flat edges and smoot surfaces. PCD frames and inserts, and Si inserts are also usually laser cut to required sizes in the research project. When above situation happens, the laser cutting technique comes before diamond polishing. The laser cutting system, also located at Fraunhofer CMW, is a Bettonville Ultra Shape 5xs-IR system, with a continuous wave Nd:YAG Laser system from CSI Group operating at 1064 nm. The laser spot size on the sample is below 20 μ m in diameter, and the output power is 18 W. Roughness of cur surfaces result in have values of R_a = 180nm, and R_{zdin} = 1100nm. The above values can be reduced to R_a = 2.5nm, and R_{zdin} = 17nm after polishing, as measured by a profilometer. Both values for polished samples are in the typical range measured for commercial substrates.

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3.2.4 Pocket Holder Cleaning

Samples are taken care of by the above mentioned procedures and methods. However, the sample holder is one other part the goes into the vacuum chamber for carrying out a diamond growth.



Figure 3.11 Sample holder photos: a) clean holder before loading to the chamber, b) as grown sample holder with PCD deposition

New sample holders are machined to have good polished top surfaces to eliminate PCD or graphite growth at its best. However, the pocket holder needs to be cleaned so that no irregular shaped remnants should exist from machining or from last growth, as **Figure 3.11** shows. Any abrupt shape from the holder surface will attract the growth of non-diamond and influence the temperature distribution surrounding the entire sample. A Molybdenum tool is used for removing PCD or other machining remnants at a first without producing further contamination.

Sandblasting is also necessary when large PCD or graphite are hard to remove. Methanol solvent cleaning in ultrasonic for 20-30 min would be useful for cleaning tiny contaminants, and the following steps in drying the holder with nitrogen gas gun and preheat the holder in the oven for at least 3 hours at 100 °C before loading to the chamber are taken. Thus, the sample holder is ready for in CVD process.

3.2.5 Sample Holder Conditioning

The sample holder may be contaminated during the sandblasting step and other surface attached contaminants might not be removed physically easily. The sample holder is thus firstly undergoing a conditioning step when it is loaded into the chamber. In the conditioning step, the holder is exposed to microwave hydrogen plasma in the CVD system at conditions similar to diamond growth, around 2800 W for at least 3 hours and can be up to 20 hours. The temperature of the pocket normally goes to 700 - 880 °C for different type of holders. The successful conditioning happens when temperature profile reads a flat temperature for at least 1-2 hours. During the conditioning process, the plasma color observed might be blue or orange. The orange plasma is observed when contaminants such as sand remnants or graphite deposition are being etched by the hydrogen plasma. The temperature is raised in this process due to the reaction of hydrogen etch. The temperature gradually drops since less and less etching reactions are happening over time. The plasma color is then faded to blue, which is the normal color of hydrogen flame color. The conditioning process is considered finished once the purple color is achieved and the temperature is held flat.

3.2.6 Substrate Etching

The sample is usually etched with hydrogen plasma in the CVD before actual deposition process, or as a separate single process for other purposes. The main goal of hydrogen plasma etching is to use hydrogen plasma to clean the sample for having a smooth surface and free of contamination. The etching process is performed at 10 - 60 min due to different surface conditions, at around 950 °C. The removing rate is about 5 um/hr. Some RIE etch are performed on some samples but are not included in the main projects. The purposes of etching of the samples are similar to purposes of conditioning sample holders. Some other purposes of hydrogen plasma etching include removing surface materials, and creating hydrogen terminated top surface. The etching process that is arranged directly before deposition process also ramps up the vacuum chamber and puts the substrate surface is an active situation which allows for a smooth and immediate start of methane deposition.

3.3 Sample Holder Design

Pocket holders are used throughout this research project and have been used in previous researches approving growing good quality single crystal diamonds that uses HPHT type Ib diamond substrates. Data from historical samples are analyzed and feedbacks are made for better understanding and applying pocket holders in epitaxial lateral outgrowth of single crystal diamonds. Thus, new pocket holders are designed based on theoretical derivation and scientific understanding to push forward the effort in single crystal diamond growth in MPACVD. Details of analyzing data and novel designed holder performance are discussed in the later chapters.

3.3.1 Use of SolidWorks

Design drawings are made using SolidWorks for making sample holder geometries. The reference dimensions are used from the substrate holder dimensions with a one inch diameter circular space for the sample holder. A representative novel designed angled pocket holder (SBH20, short for name initials holder #20) is illustrated in **Figure 3.12**, in which pocket sizes are the key components which are calculated purposely for specific diamond growth.

3.3.2 Pocket Holder Geometries

As shown in the **Figure 3.12**, the inner pocket is square and shaped with about 0.154 inch (3.9 mm) sides. The outer pocket is also square and shaped with 0.592 inch (15 mm) sides. A 0.04 inch (1 mm) depth of the inner pocket is used for centering and holding the majority part of the sample. The difference in the thickness from the top of the inner pocket to the top of the outer pocket is 0.163 inch (4.1 mm). In such way, the pocket is wider and wider as it goes from bottom to top. A slope is then formed a teach side, with an angle from the horizontal planes. As traditional straight walled pocket holder is considered to have 90° pocket, the new type of sample holder is named angled pocket holder. The angle can be calculated using the above information, for example for this specific angled pocket holder, $tan(\theta)=0.163/((0.592-0.154)/2)$, which returns

to $\theta = 36.66^{\circ}$. Typically this holder is called a 37 degree angled pocket holder. Other than the angles with respect to the horizontal plane, the dimensions of sides and depth (thickness) are also considered for how to place the sample. Following chapters will cover details of how each angle of the angled sample holder is derived for different purposes.



Figure 3.12 A representative novel designed angled sample holder designing

Sometimes there is a step transition from the inner pocket and the outer pocket, and the circular treatment of the four corners are left for the machine shop to make batter corners, (1) providing

enough space for the corners of the sample to get in touch with the plasma, (2) limiting weird pocket geometry attracting the plasma that influences the sample growth.

3.3.3 Machining

The sample holders are machined at the physics machine shop with a Molybdenum bar with 1.15 inch diameter as the raw material at MSU with the SolidWorks drawing script.

3.4 Diamond Processing Procedures

Typical diamond processes used in this dissertation research project are discussed above. To have a bigger scope of what diamond processes and want are the related diamonds work in this dissertation, an overview of diamond processes and a diamond works cycle are discussed step by step in this part. It is worth to notice that this is the current steps and update of the steps and works cycle are expected at anytime of the future work.

3.4.1 Overview of Full Diamond Growth Steps

- 1) Design sample holder
- 2) Send design to and get sample holder from machine shop
- 3) Clean sample holder
- 4) Load holder for conditioning
- 5) Run conditioning with SOP as a short simple run

- 6) Substrate laser cutting, polishing as necessary
- 7) Clean sample
- 8) Load sample to DS4
- 9) Wait for system to achieve base pressure
- 10) Follow the SOP of running the system
- 11) Set up data logging and recipe in the main computer
- 12) Set up monitoring and power control system in Raspberry Pi
- 13) Synchronize Raspberry Pi monitoring with recipe start time in main computer
- 14) Wait for plasma ignition
- 15) Align pyrometer to point to the center of the sample
- 16) Wait for system to achieve programmed operational pressure
- 17) Hydrogen etching, adjust power to achieve 950 °C
- 18) Wait for activation of methane gas input
- 19) Adjust power to set deposition temperature between desired range
- 20) Activate power control system in Raspberry Pi
- 21) Monitor system during the deposition
- 22) Stop manually when conditions are no longer satisfied if necessary
- 23) Wait for deposition to close to the end
- 24) Deactivate power control from Raspberry Pi before deposition finishes
- 25) Wait for ramp down process as programmed in the recipe
- 26) Shut down power supply, gas and cooling systems
- 27) Unload sample
- 28) Clean sample

29) Move to next process

3.4.2 Diamond Works Cycle

A full cycle of diamond works is proposed as the following:

- 1) Projects establishing
- 2) Sample holder design, and preparing
- 3) Diamond substrates preparation
- Sample characterization before and after each process including microscopes, XRD, QB, etc.
- 5) Polishing and laser cutting
- 6) Sample growth
- 7) Data from all processes upload to database
- 8) Data analysis and feedback

Some parts within this cycle are covered in the following chapters. A database work is conducted as influenced by this project and many added growth monitoring techniques and measurement techniques. Such data are collected from different project and aimed at across all reactors. It is worth to notice that the needs for measurement is for every time when the sample changes its bulk morphology. Chapter 4

Diamond Characterization

4.1 Overview of Diamond Characterization

Single crystal diamonds are being synthesized using multiple techniques including MPACD. The samples are called CVD diamond. To understand the features of single crystal CVD diamond and validate the applications of CVD diamonds, characterizations are required to illustrate as synthesized CVD diamonds' qualities for pushing this materials in an advanced progress pace[1], [3], [24], [107], [190], [191]. As progresses are made in growing single crystal diamond using MPACVD in this dissertation, the bulk morphologies and main crystal structures are key factors of these diamonds that need characterizations. The goal of many research effort throughout the semiconductor area including this research project and previous research projects at MSU is to achieve large area high quality single crystal CVD diamond[1], [10], [19], [24], [57], [64], [139], so that the following characterizations are needed:

- How physical morphology changes during the growth
- How crystal plane morphology changes during the growth
- How to characterize the relative geometry between diamond bulk surfaces and the crystal planes
- Crystal structure changes before and after growth
- Crystal structure difference between different locations within one diamond sample

• Evolution of defects distribution before and after growth

To replenish the characterization techniques used in CVD diamonds, and to fit the goal of the understandings of this dissertation research project, characterization techniques such as optical microscopy, X-ray diffraction (XRD), X-ray topography (XRT), and quantitative birefringence (QB), etc. are used as main characterizing techniques in this dissertation.

Optical microscopy technique is used mainly for accurately imaging diamond substrates and as grown diamonds in their morphology. Both Nikon microscopy and stereomicroscope are used for multiple purposes due to their different features and applications, so that dimensions of all samples can be obtained. Dimensions of the samples can also be obtained using a linear encoder for getting rough values. Cross polar birefringence (CPB) images of diamond samples are also taken under the Nikon microscope for visualizing defects in diamond samples.

Diamond crystal structural properties are mainly measured using XRD and multiple systematically established techniques based on XRD. Offcut measurement, X-ray rocking curve (XRC) mapping, and crystal plane morphologies are established for measuring single crystal diamond as a standard full set measurement under XRD. Data processing software are also built up based on theoretical calculations for processing batches of data since each measurement of the sample is a big data.

XRT is used for imaging some of the samples to visualize defects in both diamond substrates and as grown diamond samples. Certain geometries of the setup can help calculate and convert the defect features from images on the film back to the inside of the real sample. QB is set up as a relatively new technique to the group for characterizing the defects in diamond samples in a quantitative way. Changes between as grown samples and their substrates can reveal some of the information from how diamond grows in side of the MPACVD system.

All of the above characterizations and the results will provide feedbacks to either understanding the basic of diamond growth in MPCVD or can help improve the reactor design for getting better diamond growth performance.

4.2 Optical Microscopy



Figure 4.1 Linear encoder: a) spring actuation, b) digital readout[192]

Dimensions of the samples are measured before and after each process. Sample thickness is measured by a linear encoder Model Solatron DR600, as shown in **Figure 4.1**, with a resolution



Figure 4.2 Nikon Eclipse ME 600 optical microscope

of 0.05 um. The setup is consist of a spring actuation and a digital readout. When the sample is measured, it is placed at the horizontal flat stage. The level of the surface of the stage can be set to 0, so that the level of the top surface of the sample is read out as the thickness of the sample.

Sample dimensions are also measured by two optical microscopes. A low magnification (20x) Stereomicroscope is used for macro scope view of the sample and a Nikon Eclipse ME 600 optical is used, as shown in **Figure 4.2**. Several modes are used in the Nikon, including reflection mode, differential interface Contrast Microscopy (DICM) mode, and transmission mode. These modes can reveal the surface morphology features and internal features such as edge shapes and cracks.

Both microscopes have features of the extended depth of focus (EDF) technique, which assembles a series of images focusing on different areas of the sample. The assembled image shows the sample that is focused everywhere, while one normal image can only focuses on the certain area of the focused zone. As **Figure 4.3** shows, the EDF feature of a) in the Nikon is analyzed using Nikon's NIS-elements imaging software. The EDF image in b) the stereomicroscope is analyzed by its photographing software. The Nikon's imaging is better in assembling EDF image within micro scope, and the stereomicroscope's EDF is more useful in macro scope. Both EDF images clearly show the focuses are successful for the sample. The stereomicroscope doesn't show a scale mark, though the Nikon image shows.





Figure 4.3 Extended Depth of Focus images taken in a) Nikon, and b) stereomicroscope

For analyzing the growth morphology, the images taken under microscopes are analyzed by a data plot digitizer where coordinates relative to set origin and set length scale can be read out for any point in the image. The basic 2D XY plot mode is used for all samples in this dissertation, as **Figure 4.4** illustrates. Take the sample in the figure as a representative image, the origin point is set at a top corner, the x axis is set with $x_1 = -3.5$ mm (negative value of sample length), and $x_2=0$, and the y axis is set with $y_1 = -1$ mm (negative value of sample thickness), and $y_2=0$. After such coordinates are set, any point on the image can be expressed as (x,y). The lateral growth side points (colored in yellow) are manually picked for reading their quantitative positions. All

coordinates are saved for calculating the lateral gain versus the thickness gain, and thus, the lateral growth profile is achieved. The profile is achieved in the same manner for the left growth profile as the right hand side profile, when setting the origin point to the left top corner, and set positive x direction to the left.



Figure 4.4 Side profiling method from microscope images

The points of the lateral gain versus thickness gain profile are fitted in the following chapters just like the yellow curve presents. Different profiles of picked points and the fitted curves for different series of CVD diamond samples can be compared for further studies.

Cross polarized birefringence (CPB) under Nikon microscope is also used for imaging quality of diamond samples. When measured with the birefringence technique, the sample is placed

between two crossed polarizers that are aligned perpendicular to each other, and illustrated with transmitted white light. Rotating the diamond alters the observed image.



Figure 4.5 Mechanism of birefringence in a crystal[193]

Diamond normally doesn't show birefringence since ideally it has isotropic crystal structure, i.e. no light should be detected for perfect structured diamond. When diamond is stressed and with strain, crystal defects and plastic deformation can be formed which makes diamond exhibit birefringence. As **Figure 4.6** illustrates, the out of plane stress is detected to show a cauliflower shape typically due to its 100 oriented feature, and in plane features can be detected in its original shape.



Figure 4.6 CPB images for a substrate used in diamond growth

Typical cauliflower pattern doesn't rotate with the sample, as shown in **Figure 4.6**, which indicates the stresses are coming from the anisotropic defects at the center of internal of the sample.

4.3 X-ray Diffraction

4.3.1 XRD Hardware

The XRD characterization conducted at the engineering research complex uses a Rigaku SmartLab XRD, as shown in **Figure 4.7**. The X-ray generator system uses a 3.0 kW continuously rated output power with both computer-controlled and manual operation. The operating voltage sets at 40 kV and the operating current sets at 44 mA. The safety enclosure helps to keep the experimental and the user's safety while operating X-ray. A lead panel direct beam stop is integrated with the steel construction, and an electromagnetic shutter mechanism with interlocks protects the users from entire X-ray.



3 Switch Water Chiller

Figure 4.7 Front overview of the SmartLab XRD

Figure 4.8 illustrates the inside view of the XRD. The X-ray is generated and comes out from the source tube on the left hand side. A copper (Cu) X-ray tube is used in the system as the target source for generating X-ray. The tube is shielded and working at 2.2 kW with a Long-Fine Focus with a focal spot of 0.4 mm x 12.0 mm. After coming out from the source tube, the X-ray goes through incident beam optics called cross beam optics (CBO). The CBO technology allows user selectable parallel beam and focusing optical configurations for both symmetric and asymmetric scanning geometries. A permanently mounted, permanently aligned parabolic multilayer X-ray mirror is applied with all optical and goniometer configurations.



Figure 4.8 Inside hardware of SmartLab XRD

The parallel beam (PB) mode is selected using the multi-layer mirror as shown in **Figure 4.9**, for single crystal diamond measurements. The PB is also selected for XRD measurements for powders, thin films, and polycrystalline and nano crystalline and ultra nano crystalline samples. MA (0.5 mm) is one other option for PB mode with narrower width of the slit. The BB mode is usually selected for normal powder measurements.

In the high-resolution PB optics, the laterally graded multilayer mirror is automated control and aligned. Variable incident slit from 0.05 to 7.0 mm and height limiting slit of 0.5, 2.0, 5.0, and 10.0 mm are the options. The Bragg-Brentano (BB) option uses the same slit sizes and a soller slit with 5 degree axial divergence.



Figure 4.9 Selection slits between para-focusing optics and parallel beam optics

After going through the selection slit, the parallel beam X-ray goes through a Ge (220) 4-bounce incident beam monochromator, as shown in **Figure 4.10**. The 4 bounce Ge (220) channel cut crystals provide ultra-high resolution measurement for epitaxial materials with a resolution of 0.003°. The incident beam divergence is limited as low as 12 arcsec. The useful small area measurements are required for diamond XRD mapping which uses 0.5mm MA-Ge-0.5mm setup.

The goniometer system provides the highest resolution. Both optical and sample alignments are fully automated with independent source (θ s) and detector (θ d) axes. 2 θ measuring range is from -3° to 160° with scanning speed 0.01 °/min – 20.0 °/min, slewing speed max. 250 °/min. Step resolution of θ s and θ d is 0.0001°.



Figure 4.10 Technical sectional view pf XRD setups

The sample stage section contains SmartLab horizontal sample stage and Eulerian Cradle. The high resolution motor driven sample stage allows fully automated sample alignment. Z axis covers -4 to 1 mm with 0.0005 mm step. χ ranges from -5° to 95° with 0.001° step. Φ ranges from -720° to 720° with step 0.001°. For moving any sample on the stage, the XY sample stage allows 50 mm radius range with 0.0005 mm step.

On the right hand side, the detector is made with a high efficiency scintillation counter and measuring electronics provide high count rate linearity. Features of the detector, such as linearity, pulse height analyzer, high voltage and dead time correction, are all computer controlled and all automated. A SmartLab Guidance software is used for controlling the measurement and a SmartLab Studio II software is used for data analysis.



Figure 4.11 X-ray rocking curve mechanism on single crystal 100 oriented diamond sample

Figure 4.11 illustrates the mechanism of rocking curve measurement on 100 diamond. The 400 diamond crystal planes are measured using ω scans that keeps the 2 θ values fixed for diamond 400. The Rocking curve peak features stands for the orientation and quality of the measured crystal structures.



Figure 4.12 A micro camera used for locating the sample

An above sample camera is installed for viewing the sample location before actual XRD measurement, as shown in **Figure 4.12**. The lens is right above the center of the stage, and adjustable surrounding light is shined on the sample stage for better viewing any sample. The imaging technique provided from the camera helps locate the desired location at the cross origin, of which the coordinates can be read out by x and y. By moving the stage in either x or y direction, more locations of the sample can be read out and used for further study. It is worth to notice that the X-ray always measure the center cross origin when the stage doesn't move any more.

A full set of XRD parts options for the specific SmartLab is shown in Figure 4.13.



Figure 4.13 All options of the setup in the system

4.3.2 XRD Software

The SmartLab Guidance software is used for running and controlling the system and measuring the samples, as illustrated in **Figure 4.14**. In the software home interface as shown in the figure, the hardware monitoring zone is located at the bottom left, where the user can monitor real time values such as goniometer angles, axes locations, slit width, and tube voltage and current, etc.



Figure 4.14 Home interface of SmartLab guidance software

The top left zone includes the steps set for the measurements. The measurement may contain more than 1 steps and all steps can be planned well ahead by the users. Well established steps for mostly used measurements are either in the preinstalled region form the top right zone, or can be defined by the users and stored in the user defined region from the top right zone. The steps are working similar to recipes for DS4 in the CVD technique. The steps can be modified every time before the user runs the steps. The user can either execute the whole measurement steps from the top or execute each step one by one manually. Within each measurement step, the functions are varied from either moving axes, optical alignment, sample alignment, to the actual X-ray measurement. It is worth to notice that the measurement steps enables loop measurement in which certain type measurements can be applied many times repeatedly. This function is often used in the mapping technique where the same measurements are conducted on multiple locations of the same sample, typically m x n points of locations (values of m and n are integers depending the mapping parameters for the measurement). The mapping technique is well used in characterizing the uniformity of single crystal structure distribution in this dissertation. As the sample stage is capable of moving in x and y axes, and the software is capable of looping, the XRD system is also in favor of measuring multiple samples in one measurement. The latest measured XRD profile is always displayed in the middle main window of the home interface always colored in red. The profile data is also stored into .ras, .acs, and .raw documents for further use and analysis. Within the data files, .ras file is the typical file that can be opened in .txt file for .csv file and contains the most detailed information for the measurements.



Figure 4.15 Data visualization feature of data analysis in SmartLab Studio II software

Data files can be analyzed using the SmartLab Studio II analyzing software. **Figure 4.15** illustrates the home user interface of the software. The software is capable of several key features in working with different types of XRD data including powder XRD, phase identification,

texture, stress analysis, data visualization, and data manager etc. The analysis also contains databases of regular XRD pattern for different materials. The database can be used for identifying peak information and materials information. The full diffraction lines from Cu other than the main k α lines, including k $_{\alpha 1}$, k $_{\alpha 2}$, k $_{\beta}$, WL $_{\alpha 1}$, and WL $_{\alpha 2}$, are also featured in changing together for convenient of viewing the XRD raw data. It is necessary to notice that the using of normal soller monochromator will include such diffraction lines within the results and the k $_{\beta}$ line can be filtered out using the k $_{\beta}$ filter. The use of 4 bounce Ge (220) monochromator uses its symmetric optical alignment of the 4 bounces so that only k $_{\alpha 1}$ line exists in the results.

In the powder XRD feature, peak profile can be loaded and peaks can be analyzed using fitting method like Gaussian, and pseudo-Voight, etc. to find key peak parameters such as peak location, peak height, and peak width (FWHM), etc. Phase ID compares the measured XRD profile with the database for the user to get knowledge of what are the possible components in the measured materials. Mass ratio between each component is also possible in the analyzed results. The stress feature analyzes the difference and the trend among a series of the peaks, and calculates how much residual stress the measured material possess. The analysis method uses $\sin 2\psi$ calculations to provide the only non-contact unsurpassed spatial resolution and the ability to measure hardened materials. The texture feature provide the typical method called pole figure to determine the crystallographic texture, i.e. the preferred crystal structural orientation. In the data visualization feature, multiple XRD data can be displayed into one certain parameter map. The mapping technique collects one type of measurement data for many locations and the data of such mapping technique can be analyzed using the data visualization feature. One of the

parameters from the measurement can be plotted in a map of locations to understand the distribution of the value of such parameter. For example, regular theta 2theta measurement of a single peak can give FWHM value, and the data visualization feature allows to show the FWHM distribution of the certain sample over its surface area. Normally the FWHM stands for quality of the structure, so that the FWHM map, in the same way, represents the quality distribution of the sample. **Figure 4.15** is actually one mapping results of a single crystal diamond sample. In the map, the higher vale region is colored in red and lower value region is colored in blue. Statistical data ca be collected in the data analysis zone for certain types such as average values, max value, min value, standard deviation, etc. Maps are the results from the data visualization feature and together with all others, the results can be exported into figures or pure data for further processes.

4.3.3 XRD Theories

X-ray diffraction is defined as a phenomenon where the crystal structure, by virtue of its uniform spacing, causes an interference pattern of the wave present in an incident beam of X-rays[194]. The Bragg law, firsts formulated by an English physicist Lawrence Bragg, is the governing physics formula in XRD[195]. The Bragg law indicates that the relation between the spacing of atomic planes in crystals and the angles of incidence at which these planes produce the most intense reflections of electromagnetic radiations[196]. X-rays is one of those electromagnetic radiations, along with other rays and waves like gamma rays, particle waves, electrons and neutrons. **Figure 4.16** shows an illustration mechanism of how the reflected beams (diffracted beam in XRD) coherent to show interference. The two incident waves, wave 1 in green and wave

2 in red, are in phase with the same wavelength λ with each other and incident to the parallel atomic planes A and B with a spacing of d, at an angle θ .



Figure 4.16 Illustration of Bragg law[197]

It clears shows that the beam path of wave q is longer than that of wave 2 from the geometry provided in the figure. To geometrically keep both reflected waves of wave 1 and wave 2 in phase, the length of the difference between both wave paths should be mathematically a multiple of the wave length $n\lambda$ (where n is an integer, and λ is the wave length). Thus, considering the d spacing and the incident angle θ , the governing Bragg law is formulated as

$2dsin\theta = n\lambda$

Since the additional paths for wave 1 in green CB and BD each equals to one wavelength in the figure, n=2 for the specific circumstance in the figure. Experimentally, d spacing are small for

most crystal structures and n=1 dominates most XRD phenomenon on those crystals which are called 1st order of reflection (diffraction in XRD). For most XRD work in research and development, the wavelength of the XRD system is known and fixed, so that the 1st order diffraction gives a simple one to one bijection (injective and surjective) of incident angle θ , and d spacing.



Figure 4.17 Diamond sample aligned based on its orientation

The mechanism above simply shows a 1 dimensional ideal situation when the crystal planes are taken care of their alignment orientations so that other spatial parameters are ignored. In the actual measuring environment, the spatial reference is usually divided into two categories, the sample (crystal) coordinates, and the lab (system) coordinates. To better perform any measurement using XRD, aligning to coherent both coordinates is the key factor.



Figure 4.18 General setup of a diamond substrate with a corner mark at bottom left front (phi=45°)

As **Figure 4.17** shows, diamond samples used in this dissertation is mostly 100 oriented and with 010 and 001 side surfaces. The coherent alignment is to put the 100, 010, and 001 surfaces along the x, y and z directions respectively, such that and 90 degrees of rotation can be considered as the same condition meaning the setup is a 4-fold rotational symmetry. To identify the specific difference between the orientations of the sample, the corner mark of the diamond crystal substrate is one useful method, as shown in **Figure 4.18**. One corner is usually catted for referencing the orientation of the sample. The coordinates are then labeled in (a) for a general setup of a diamond substrate XRD measurement with a corner mark at bottom left front, i.e. bottom of phi=45°. Front view of a representative substrate is shown in (b).

In this setup, the X-ray incidents from phi=0 and the diffracted X-ray beam is collected using the detector at phi=180 direction. When phi rotates to phi=45°, the X-ray incidents from the corner marked direction and diffracted to the opposite direction, in which scenario, the X-ray doesn't rotates while the sample stage rotates clockwise. Thus, possible diffraction modes for diamond XRD peaks can be calculated as for Cu $k_{\alpha 1}$ X-ray with wavelength $\lambda = 1.54$ Å with Rigaku SmartLab XRD system, as listed in **Table 4.1**. The diffraction modes are only true when the above geometry alignment is used where 100, 010, and 001 surfaces are aligned to x, y, and z directions respectively for 100 oriented samples. For diamond samples with other orientations or other geometries, necessary rotations in either the sample itself or the axes would allow the diffraction modes again for the same analysis.

Peak Indices (hkl)	Phi φο (°)	Chi χ ₀ (°)	Omega ω₀ (°)	2theta 2θ₀ (°)	d spacing (Å)
400	0 - 360	0	59.75	119.5101	0.8913
113 low	45, 135, 225, 315	0	20.5049	91.4886	1.075
113 high	45, 135, 225, 315	0	70.9837	91.4886	1.075
111	45, 135, 225, 315	54.7356	21.965	43.93	2.0586
220	0, 90, 180, 270	45	37.6477	75.2955	1.2606

 Table 4.1 Regular diffraction modes of a 100 oriented diamond substrate

Scanning of XRD measures the intensity that the detector detects such that a certain combination of axes values in **Table 4.1** would provide a high intense while other combinations would provide zero intensity according to the Bragg law. Due to Bragg law, d spacing is a one to one of

20, so the XRD diffraction intensity is a four dimensional space with (ϕ , χ , ω , 2 θ), which can be expressed as

$$I = I (\varphi, \chi, \omega, 2\theta)$$

Using a delta function to understand the intensity distributed in this 4 dimensional space, the intensity *I* can be expressed as

$$I = \begin{cases} I_0, & \text{when } \varphi = \varphi_0, \chi = \chi_0, \omega = \omega_0, \text{ and } 2\theta = 2\theta_0 \\ 0, & \text{else} \end{cases}$$

The entire delta function can be expressed as a multiplication of each delta function of the 4 dimensional space.

$$I = I \ (\phi, \phi_0; \chi, \chi_0; \omega, \omega_0; 2\theta, 2\theta_0) = \prod_i I_i (i, i_0), \text{ where } i = \phi, \chi, \omega, 2\theta$$

$$Ii = \begin{cases} I_{i0}, & when i = i_0 \\ 0, & else \end{cases}$$

Ideally, since the intensity doesn't express a delta function but with Darwin width in each of the 4 dimensional space, the intensity would show the highest at a certain combination and each of its adjacent areas. Considering Darwin width, each of the space is given a half width notes with Δ . Thus, the expression is changed much more real:

$$I = \begin{cases} I_0, & \text{when } \varphi \in \varphi_0 \pm \Delta \varphi, \chi \in \chi_0 \pm \Delta \chi, \omega \in \omega_0 \pm \Delta \omega, \text{ and } 2\theta \in 2\theta_0 \pm \Delta 2\theta \\ 0, & \text{else} \end{cases}$$

And in the same way when degraded into each individual space, the intensity can be derived as

$$I = \prod_i I_i(i, i_0)$$
, where $i = \varphi, \chi, \omega, 2\theta$

$$Ii = \begin{cases} I_{i0}, & when \ i \in i_0 \pm \Delta i \\ 0, & else \end{cases}$$

The actual XRD scanning in Rigaku SmartLab system has to degrade the intensity space down to a 1 dimensional scanning with the other 3 dimensions fixed sue to the system operating manner. For example, the regular rocking curve scan has to fix 2θ , φ , and χ , and scan ω around ω_0 . The key point there is to try the best to fix 2θ , φ , and χ at $2\theta_0$, φ_0 , and χ_0 , respectively. The closest the axes are towards their zero position, the best conditions are able to create the most accurate measurement results. The actual zero positions of axes φ , χ , ω are not exactly the same as the values listed in the table due to several geometric reasons like the natural offcut angle in all 100, 010, and 001surfaces from the sample. 2θ might be away from its zero position of the peak due to lattice stress in the crystal structure such as compression and tensile strength, which causes the deformation of lattice and changes the corresponding d spacing. The influence of the difference from zero positions doesn't apply the same to the results scanning intensity. Take the diamond sample for an example, among the 4 dimensional spaces (φ , χ , ω , 2 θ), 2 θ values are mostly fixed due to their little changes before and after growth. Since 100 surfaces are aligned, and no matter which plane is to be measured, the plane is adjusted to be horizontal for the measurement, the
influence of change in φ on the peak intensity is little compared to the changes in χ or ω . Generally, a φ scan results in a wide peak with several degree of FWHM, a χ scan results in a peak with 0.3 - 1 degree FWHM, and ω scam results in a sharp peak with 0.003 - 0.02 degree of FWHM. Since ω is the first scan axis, or called the major scan axis, to better scan ω for accurate result, a second scan axis of χ is established for searching optimized ω scans. The scan step size and speed is fixed for ω scan but the same ω scans take places at a series of χ values around χ_0 . Thus, the scans using ω as the major scan axis and using χ as the second scan axis establishes a 2 dimensional scanning method. This 2D scan provides the optimized peak intensity.

4.3.4 XRC Technique

The 2D scan mentioned above is frequently used in this dissertation and within the 2D scan, the major scan axis is the incident angle, which is ω . So the measurement is called ω scan, as known as the rocking curve scan. The X-ray rocking curve (XRC) scan fixes the 2theta angle makes both the incident arm and the detector arm rocks at the same speed. A single rocking curve scan may not return in an optimized peak results, while the 2D scan includes XRC scans at a series of χ angles can enhance the optimized XRC peak. A typical 2D measurement of XRC scans mainly scans ω around ω_0 , with a scan range such as from $\omega_0 - n \cdot \Delta \omega$ to $\omega_0 + n \cdot \Delta \omega$, where n is an integer typically 10 – 50. Such scan range of ω makes sure the whole peak is taken care of within the range. The scan is repeated several times at a series of χ angles around χ_0 , and values of χ angles are also used from $\chi_0 - n \cdot \Delta \chi$ to $\chi_0 + n \cdot \Delta \chi$.

One of the features from X-ray rocking curve (XRC) is to determine the crystal orientation and its quality. The peak location results in information of the crystal structural orientation and the peak FWHM is corresponded to the quality. In this dissertation, single crystal diamond sample is measured by Rigaku SmartLab XRD with Cu $k_{\alpha 1}$ source and using optical settings with MA-Ge (220) x4-0.5mm.



Figure 4.19 Example of 400 XRC peaks



Figure 4.20 XRC on different crystal orientations

As shown in **Figure 4.19**, examples of XRC peaks for diamond 400 of a HPHT type Ib substrate illustrate the peak location and peak width (FWHM). The peak location is corresponded to the crystal orientation as shown in **Figure 4.20**. The smaller the peak location, i.e. the blue curve in XRC plot, is corresponding to the blue crystal region since the X-ray incidents from left to right. The bigger peak location, the red XRC curve, is corresponding to the red crystal region, and the green curve corresponds to the green crystal region. The FWHM of the peaks are about 0.008°, which is typical for HPHT type Ib diamond 400 crystal plane. The difference in XRC peak locations is also corresponding to the difference in crystal orientations. In this figure, for example, the difference of blue and green curve is about 1 degree, so that the difference between the green and blue crystals is also about 1 degree.

Table 4.2 Typical FWHM of diamond substrates of different diffraction modes

Peak Indices (hkl)	400	113 high	113 low	111	220
FWHM (°)	0.008	0.004	0.005	0.003	0.006
	-0.010	- 0.005	-0.006	-0.004	-0.008



Figure 4.21 Theoretical values of FWHM of multiple semiconductors and diamonds[198]

XRC peak FWHM of each diffraction modes illustrate different values since the corresponding crystal planes have different packing results due to their d spacing. The actual measurement results also have to consider the synthesis method for HPHT type Ib diamond, where for example, growth preference of 100 is not the same as that of 111 directions. Table 4.2 lists the typical XRC peak FWHM values measured with the HPHT type Ib diamond samples in this dissertation. Obviously, the 111 crystal plane has the smallest FWHM of its XRC peak since the 111 crystal plane is the closest packed crystal plane. 113 high incident has smaller FWHM than 113 low incident since the higher incident angle is, the smaller cross section of the beam size (spot size) is on the sample surface, and thus better spatial resolution provides the sharper XRC peak. 400 diamond XRC peak has the largest FWHM with typically 0.008° as the smallest value. This result in 400 peak width indicates the crystal structure is not in 100% perfect conditions and includes certain degree of defects. This result is also in agreement with typical seeds defect densities of $10^4 - 10^5$ /cm², which is considered high. In a comparison, the theoretical synthetic diamond FWHM values are shown in Figure 4.21, where the theoretical value of type IIa synthetic diamond is only 4 arcsec[199], and theoretical type Ib diamond has FWHM around 12 arcsec (around 0.003°)[198].



Figure 4.22 XRC peaks for different diffraction modes of diamond

The scanning speed is typically the slowest speed 0.48° /min with the smallest step size 0.0004° , or the 2.4°/min with the step size of 0.002° . The use of 2.4°/min with the step size of 0.002° is approved to show no difference from the use of 0.48° /min with the smallest step size 0.0004° . Actual example of XRC peaks of 400, 111, 113 high and 113 low are illustrated in **Figure 4.22** to show their typical FWHM and peak shapes.

The peak location difference discussed above may exist in the same diamond sample, or in different samples crystal structure orientations of which need to be compared. The actual crystal orientation may also not be exactly parallel to the samples bulk surfaces, which creates an offcut angle between the crystal plane and the surface plane. These scenarios are discussed in this

section where the angle between crystal plane and surface plane is defined as offcut angle, and the angle between crystal planes in either different locations of the same sample or different sample is defined as misorientation.



Figure 4.23 Example illustration of offcut in 400 plane



Figure 4.24 72 Peak locations at multiple phi for every 5 degrees

Figure 4.23 shows the example of offcut angle. In this example, XRC of the 400 diamond plane is directed measured. **Figure 4.24** illustrates the plotted 72 XRC peaks where the max omega value (ω_{max}) is at phi = 315°, and the min omega value (ω_{min}) is at phi=135°. The offcut angle is calculated by the half of the difference between ω_{max} and ω_{min} . The offcut angle θ is thus calculated as:

$$\theta = (\omega_{\rm max} - \omega_{\rm min})/2$$

It is worth to notice, the phi angle corresponding to max omega value and the phi angle corresponding to min omega value are always separated by 180°. The offcut angle calculated in

this way for phi angles from 0° to 360° is the true offcut angle, and since two planes always have one intersected line, thus the true offcut angle is always perpendicular to the intersected line and the offcut angle parallel to the intersected line is always zero. In a summary, the offcut angle can be seen as a vector that has a magnitude θ and a direction phi@ ω_{max} . The offcut can be written as (θ , phi@ ω_{max}), and in the example the offcut is written as (0.363°, 315°).

The true offcut angle is a 2D feature and when degraded to 1 dimensional, the offcut always varies from θ to 0. The peak locations of 72 XRC peaks are extracted and plotted in **Figure 4.25**.



Figure 4.25 Peak positions vs phi angles of offcut angle

The peak position of XRC peaks at multiple phi angles can be expressed as a function of phi:

$$\omega = \theta \cdot \cos(\varphi \cdot \phi_0) + \omega_0$$

where ω is the peak position, θ is the true magnitude of offcut angle, ϕ is the rotational angle, ϕ_0 is the rotational angle corresponding to the largest peak position value ω_{max} , and ω_0 is the average peak positions with zero offcut. The plot also returns to the offcut angle written as (0.363°, 315°).

When the offcut angle is too large, the XRC scan may not collect all peaks at 72 phi angles, but will only collect peaks at the adjacent areas of the max and min values due to the limitations of XRD system settings (the detector only scans in XZ plane so that the large offcut angle will bounce off the diffracted X-ray far off the center plane), as **Figure 4.26** shows. However, the maximum and minimum peak location values and their corresponding phi angles are enough for calculating the offcut vector (θ , phi@ ω_{max}). In the large offcut example, the plotted 72 peaks only show several peaks, however, the largest peak position is read to be 63.084° and the minimum peak location is read to be 56.826°, so that the offcut is (63.084-56.826)/2=3.129°.



Figure 4.26 72 XRC peak locations with large offcut angle

The difference between crystal structure orientations is called misorientation. The misorientation may exist in the same sample for multiple reasons of defects. **Figure 4.27** shows the misorientation in the same diamond sample. The sample SBLB00 has a cracked corner on the bottom left, where is shows color deflection. The same XRC measurement on at the interface between the two regions always detects two XRC peaks that has a certain difference between the peak locations. The difference is the misorientation and the misorientation varies when phi changes from 0° to 360°, just as the behavior of offcut angle. It is obvious the interface is the intersected line between the two crystal regions and the 45°/225° direction is the misorientation direction. According to the measurement data, the misorientation can also be regarded as a vector (θ , phi@ ω_{max}), and for this specific sample, the misorientation is written as (0.154°, 45°).



Figure 4.27 Misorientation angle within one diamond sample

The misorientation plotted with phi angles in the polar coordinates shows the plot is in two circles shape and the only connected point is on the interface with the diameter of the two circles perpendicular to the interface.

Another type of misorientation is seen in mosaic growth samples where two diamond substrates have crystal orientation difference before and after growth. The diamond 400 crystal plane misorientation is measured for mosaic sample S03, and illustrated in **Figure 4.28**.



Figure 4.28 Misorientation angles evolution over growth time for mosaic sample S03

The mosaic sample S03 shows an arbitrary offcut angle and direction for two diamond substrates before growth. The mosaic growth carries out for several times and in total 72 hours. The CVD plates are cut into j, m, and n after each 24 hour growth. XRC peaks from phi angle from 0° – 360° are measured for j back, j, m, and n. Two circles shape of peak locations versus phi angles are plotted for j back, j, m, and n. Clearly, the two circles shape rotates and shrink over time. Offcut in phi=0° direction decreases to zero and only offcut angle exists in phi= 90°/270° direction, i.e. parallel to the interface. The misorientation angle in perpendicular to interface direction decreases a little from 0.14° to 0.12°. This result is in agreement with recent MSU's mosaic growth work[86]. Such results indicate lateral step flow growth in perpendicular to the interface direction decreases the misorientation and is able to zero the misorientation in a short time duration (less than 72

hours). The step flow is normal to the interface is that the merging of two crystal region in parallel to interface direction doesn't decrease the misorientation easily.



Figure 4.29 Typical XRC mapping points on as grown CVD diamond sample

XRC mapping technique uses MA-Ge(220)x4-0.5 mm optics for optimized resolution and covers the whole sample top surface with 0.3 mm separation between point sin both x and y directions. For substrates with dimensions 3.5 mm x 3.5 mm, typical mapping data are 13 x 13 points. For as grown CVD sample that may have a larger area, more data points are applied to the sample.



Figure 4.30 Optimizing XRC scans around χ_0

For each location, the XRC measurement may include diffraction modes of 400 for phi=0°, 90°, 180°, 270°, and 113 for phi= 45°, 111 for phi=45°, and 220 for phi=0°. For each mode, the measurement needs a rough scan at first and a fine scan before the actual mapping process. The 2D scan is used for each diffraction mode and ω_0 value and χ_0 value can be determined, as shown in **Figure 4.30**. The XRC peak of the representative sample SB20L05a optimizes at χ_0 and the peak location of optimized XRC peak is ω_0 .

Once ω_0 and χ_0 are determined, together with ϕ_0 and $2\theta_0$, XRC scan of each diffraction mode can be started. The same scan over all mapping points allow the sample to be measured using the XRC mapping technique. The XRC peak location and XRC peak FWHM can be plotted as a map from the results of XRC mapping technique. Both SmartLab Studio II software and the selfmade matlab based XRC data analysis software can plot peak location maps and FWHM maps for visualization.



Figure 4.31 Example 400 phi=0° Peak location map and FWHM map exported from the SmartLab Studio II software



Figure 4.32 Example 400 phi=0° Peak location map and FWHM map exported from the selfmade Matlab XRC analysis software

Figure 4.31 shows the peak location map and a FWHM map generated from the SmartLab Studio II software, in the maps, blue colors denote smaller values, and red colors denote larger values. **Figure 4.32** shows the peak location map and a FWHM map generated from the selfmade matlab XRC data analysis software, in the maps, the data also ranges from smaller to larger labeled with different colors.

Crystal morphology is plotted by self-made software that calculates the Z values for each of the points from XRC mapping measurements. The crystal plane orientation of each measurement point can be calculated based on the XRC peak locations. For example, the 400 crystal planes are measured for each point at phi = 0°, 90°, 180°, 270° on a 100 oriented diamond sample. The peak position for a certain point can be extracted as: $\omega_0, \omega_{90}, \omega_{180}, \omega_{270}$.



Figure 4.33 Crystal plane morphology created from orientation of each point

The angle between the measured crystal plane and the horizontal plane can be calculated in both x and y directions, as shown in **Figure 4.33**, just like the calculation of offcut angle:

$$\theta x = (\omega_{180} - \omega_0)/2$$

 $\theta y = (\omega_{270} - \omega_{90})/2$

The crystal plane orientation can thus be visualized for the measured point based on its θx and θy value, and after connecting the crystal plane for all measured points, a crystal morphology for diamond 400 crystal plane can be formed. The method in connecting all measured points is to set one measured point as the zero position in Z direction, and the Z values for its adjacent points can be calculated based on their θx and θy values and the separation distance (0.3 mm in this dissertation). After Z values are calculated for all points, the morphology software can be plotted in X-Y-Z coordinates to visualize the crystal plane morphology (diamond 400 in this dissertation). It is worth to notice that this morphology is measured directly on the same crystal plane at phi= 0°, 90°, 180°, 270°. Any crystal orientations other than 400 diamond may not be

easy to focus on the same plane. However, this method is also applicable to other single crystal materials and other crystal orientations.



Figure 4.34 Flattened crystal plane morphology

The crystal plane plotted always seem to be flat. However, in later research, the as grown CVD diamond may exhibit a curved crystal plane morphology. So to study the phenomenon, the crystal plane is flattened to better visualize its detailed feature, as **Figure 4.34** shows. To flatten the curved plane, three points from three corners are selected for making a virtual flat plane (x', y'), and the perpendicular distance Z' from the curved plane to the flat plane can be calculated and the new flattened morphology can be plotted in a much finer Z axis.



Figure 4.35 Curvatures calculated from example 400 diamond morphology

Z values of each measured point connect with each other to visualize the crystal plane morphology, and the curvatures such as x-curvature, y curvature, Gaussian curvature, and mean curvature and the error can be calculated and also can be plotted as shown in **Figure 4.35**.

4.3.5 XRD Work Steps

The XRD working steps are summarized as the following:

1. Start Up

- Check if chiller is on, check if X-ray is on
- Turn on water chiller
 - 3 buttons (1 for Haskris, 2 for homemade panel)
- Unlock computer
 - o Rigaku
- Start SmartLab guidance software
 - username: administrator
- Make sure Rigaku door is locked
 - yellow button on the front door is not flashing
 - if flashing, close the door and click the button
- Click "Start Up" in the guidance software
- Select "Everyday use" and click "execute"
- Wait for x-ray aging, about 13min

2. Alignments

- Choose measurement package
- Optical alignment

- PB/PSA (medium resolution): CBO-PB-Soller-10mm-center slit-PSA open/PSA
 0.5
- Ultrahigh resolution: CBO-PB/MA-Ge(220)x4-10mm/0.5mm-center slit-PSA open
- Follow instruction from guidance
- Mount sample
- Camera use (if necessary)
- Sample alignment

3. Start measurements

- Create data file in the user's folder
- Rough measurement
 - Use SmartLab studio II to analyze data (if necessary)
- Fine measurement (if necessary)
- Final measurements
- Wait for measurements to finish
- Reset settings after measurements finish

4. Shut down

- Open door
- Take away sample
- Close door
- Turn off x-ray: click "Shut down" in guidance, and wait for 1 min, then click "ok"

- Log use on log book/calendars/system
- Close guidance software
 - Never shut down the computer
- Turn off chiller
 - 3 buttons (1 for Haskris, 2 for homemade panel)

4.4 X-ray Topography

X-ray Topography (XRT) technique is also used for characterizing diamond samples. All XRT experiments are conducted at beamline 1-BM, X-ray Science Division (XSD) beamlines, Advanced Photon Source (APS), Argonne National Lab (ANL).

XRT is a very powerful technique for evaluating crystals for characterizing single crystals. It is a technique capable of providing information on the nature and distribution of structural defects such as dislocations, inclusions/precipitates, stacking faults, growth sector boundaries, twins and low-angle grain boundaries in single crystal materials[200]. In particular, synchrotron white beam x-ray topography is a fast and non-destructive characterization method for defects and of strain in bulk crystals, epitaxial layers, and electronic device structures. Synchrotron white beam x-ray topography is based on a Laue technique as shown in **Figure 4.36**, that is, the diffraction Laue pattern consists of a number of large area diffraction spots, and each spot is a high resolution x-ray topographical image for a specific diffraction crystal plane. Beamline 1-BM at the APS delivers a white beam from a bending magnet with very intense x-ray photon flux[97],

[160], [161], [163], [165], [200]. As mechanical fast shutter that is vacuum compatible to $\sim 10^{-8}$ Torr is used to control the exposure time of the imaging process accurately down to the millisecond level to avoid over exposure. Both transmission mode and reflection mode of the XRT are capable for XRT at the APS. All diamond samples taken images using XRT technique are for the goal of visualizing inner defects and misorientation angles between mosaic regions.



Figure 4.36 White beam XRT experimental setup at APS



Figure 4.37 Sample setup with sample SBLB00

Figure 4.37 presents the setup of a transmission mode diamond XRT imaging on sample SBLB00, The sample is placed and mounted in the center of a self-made 3D printed sample holder with only four corners are fixed and touching the sample holder. The sample holder allows the sample to rotate in all axes for its optimized orientation for which the sample can be parallel with the film at its best. The sample stage can move in x, y and Z axes for its optimized position. The exposure film is placed at a 6 inch distance behind the sample. The GE Inspection Technologies Structurix D3-SC industrial X-ray films by Agfa-Gevaert N.V. with 100 NIF size 8 x 10 inch are used for XRT imaging processes. The beam size is up to 70 mm horizontally by 5 mm vertically. A Be filter blocks the center for over exposure from the high energy direct beam. A camera is set for monitoring the exposing process since the user need to stay outside of the room during the exposure time.



Figure 4.38 XRT film and diffracted images on the film



Figure 4.39 XRT image compared with Birefringence and DICM pictures

The Laue pattern achieved on the film contains multiple diffraction images including corresponding hkl indices but not limited to 311, 151, or 220 planes. As shown in **Figure 4.38**, each images is corresponding to one diffraction plane. Since each diffraction has its specific angle due to the Bragg law, the image shows different projection angle. The Laue pattern can be

matched using SingleCrystal software, and the diffraction indices of each image on the film can be labeled. The images on the film are digitally stored into individual pictures using a film scanner Pro in MSU main library. These images have white background with good contrast in color but without a scale. According to the comparison of images under birefringence, DICM and XRT under the same sample, as shown in **Figure 4.39**, it is clear that the cracked corner of sample SBLB00 shows dark color due to worse light deflection under the birefringence and DICM, but shows certain separation distance from the major part in one of its XRT images.



Figure 4.40 Dimensional comparison of XRT images

The XRT image is placed under a Nikon Microscope in a transmission mode to measure the accurate distance from the separated two parts. **Figure 4.40** presents the comparison between the same image from the film scanner, birefringence, and the microscope. The distance of length of certain defect, dimensions, and distances between two separations are capable to be measured

accurately. In the photos, the center stress is shown as a point bright dot in the birefringence image, which is corresponded to the dark line at the center in the XRT image. The center stress in dark color is parallel to the edge meaning its exact perpendicular direction to the top surface. The dimensions have the same magnitude with the actual dimensions directly measured from the sample due to the collimated incident white beam also diffracts into collimated diffracted beam and projects onto the film. The separation distance measured from the microscope can be used to calculate the misorientation between the two crystal parts and the results is in agreement with the 0.154° directly measured from the XRC technique.



Figure 4.41 XRT film and images of mosaic sample S03j

Other than the main stress and mosaic separation from the XRT image, threading dislocation bundles and stacking faults are also visualized in the pictures. Though the dislocations can be clearly displayed, the defect densities of the used HPHT type Ib substrates are still high compared to the XRT images of other diamond substrates.

As grown mosaic sample S03j is also imaged using XRT, as shown in **Figure 4.41**. The Laue pattern is also compared and matched using the LauePt program. Parameters such as imaging distance, rotation angles around x, y, and z axes, film tilting angles, and sample shifting distances are taken for considerations. The distance between the two separated parts can be measured and the resulting parameters can be sued for calculating the misorientation between the two mosaic crystals. The misorientation angle achieved from the XRT images are in agreement with the misorientation angles using XRC technique. The crystal qualities can also be viewed from the XRT image. The dislocations are clearly very dense and are in the same direction as the growth direction.

4.5 Quantitative Birefringence

A quantitative birefringence (QB) system is made at MSU for measuring how a diamond sample alters the polarization of light traveling through it. As shown in the layout in **Figure 4.42**, a laser diode generates a 633 nm light which is depolarized using a rotating ground glass diffuser to reduce diffraction fringing. A pinhole cleans up the light and allows it to be collimated before going into the polarimeter. The polarimeter itself consists of two stationary polarizers and two motorized quarter-waveplates, as shown in **Figure 4.43**. A Glan-Taylor prism serves as the second polarizer. By rotating the waveplates, the polarization of light entering and exiting the diamond can be controlled. A 9.1 megapixel monochromatic CCD camera at the end records a

large dataset of the images, which are processed to different optical parameters across the diamond as a map.



Figure 4.42 Light source layout



Figure 4.43 Polarimeter layout

The working steps of QB includes system power on, system calibration, light path alignment, data collection, and data analysis, and power off. The phase delay δ between the ordinary and the extraordinary rays caused by the difference in refractive indices Δn describes the quantitative birefringence phenomenon of diamond, given by

$$\delta = \frac{2\pi(\Delta n)L}{\lambda}$$



Figure 4.44 Comparison of QB $|\delta|$ image and birefringence images of sample SB20L10a

where L is the thickness of diamond, and λ is the wavelength, 633 nm, and for ultra-low birefringence, $\Delta n < 1 \times 10^{-5}$. In the QB setup, the $|\sin \delta|$ is calculated which is independent of the orientation of the diamond. As shown in **Figure 4.44**, therefore, $|\delta|$ is then calculated and plotted as a quantitative result for visualizing the birefringence phenomenon of the diamond samples. Polarized light images for SB20L10a have polarizers are aligned along the diamond edges (left) and diagonals (right).

Chapter 5

Epitaxial Lateral Outgrowth in Traditional Sample Holder – Exponential Decay Growth Mode

5.1 Kinetics of Phase Change in Diamond Growth

The kinetics of phase change is presented in many complicated mathematical expressions by M. Avrami more than 80 years ago[201]–[204]. The entire theory was presented in three parts: I. General theory, II. Transformation -time relation for random distribution of nuclei, and III. Granulation, phase change and microstructure. The kinetic model has been used for describing the general behavior of phase change over years. The nucleation and growth of new phases in crystal studies are the appropriate environment to use the Avrami's model. The traditional Avrami's model assumes the phase change is composed by germs that are transitory molecules arranging averagely distributed. The growth of the new phase suffers an expansion process where germs transfer to grain and growing grain swallows the existent germs. The Avrami's kinetic model considers a function between the amount of total germs and the volume of new forming growing phase over time[205]. The model is further regarded as Avrami's equation and expanded to describe how crystal is transformed from one phase to another at a constant temperature. The Avrami's equation can specifically describe the kinetics of crystallization and can be applied generally to many types of phase change in materials. The initial Avrami's model describing the germs transforming into grains is expressed mathematically where N=N(t) is the number of germs for the new phase per unit volume at the instant time t. At the initial time t = 0, the number is N(t=0) = N₀. The grains of the new phase at time t per unit volume is expressed asN' = N'(t). Therefore, the variation of the number of germs that transforms into grain per unit volume at a time period Δt is expressed as:

$$\Delta N' = nN\Delta t$$

Due to the compensate relationship between N and N', the relationship between N and time t can be expressed as:

$$\frac{dN}{dt} = -\frac{dN'}{dt} = -nN$$

To solve the differential equation, the separation of variable gives:

$$\frac{dN}{N} = -n \, dt$$

So,

$$\ln N(t) - \ln N(0) = -nt$$

Apply the initial condition N (t=0) = N_0

So the number N(t) as a function of time t can be calculated as:

$$N(t) = N_0 e^{-nt}$$

Thus,

$$N'(t) = N_0 - N(t)$$

 $N'(t) = N_0 (1 - e^{-nt})$

Figure 5.1 shows the curves for N'(t) with n = 1,2 and 5, and $N_0 = 1$.



Figure 5.1. Curves for N'(t) where the solid line is for n=5, the dashed line is for n=2, the dptted line is for n=1.[204]

After further expanded understanding of the Avrami's equation in phase transformation from phase A to phase B, N_0 is the initial amount of phase A, and N(t) is the amount of phase A at time t, and N'(t) is the amount of phase B at time t. In a conclusion, the amount of phase A increases in an exponential decay fashion over time.

Transferred to diamond crystal growth environment in a CVD reactor, the Avrami's model is considered as a theory describing the transformation from hydrocarbon plasma phase (phase A) to diamond single crystal phase (phase B)[205]. The growth behavior of a CVD diamond growth can be considered in a 3 dimensional process with one vertical direction and two horizontal (lateral) directions. The vertical direction growth of diamond doesn't have any limitation for vertical growth so that the initial amount N₀ for the vertical direction can be regarded as infinity and the vertical growth rate is a constant learned from previous researches, meaning the vertical size changes linearly of time t. The horizontal (lateral) directions are limited by the sample holder which are introduced in the previous chapter. The Avrami's model can be applied to the one dimensional single crystal diamond lateral growth as shown in Figure 5.2. In one dimensional space, the initial amount of plasma phase (phase A), N₀, is corresponding to the space between the substrate and the sample holder in the lateral direction, which is also the total space. The space for single crystal diamond phase (phase B) is N'(t) and the remaining space of plasma phase (phase A) is N(t). The total space for diamond growth is corresponding to N_0 , so $N'(t)+N(t)=N_0$. And in the lateral direction, the single crystal diamond is growing as the Avrami's model describes and follows the Avrami's equation. Figure 5.2 illustrates a right half side look of the illustration of phase change at time t in a CVD diamond growth within a pocket holder. The vertical axis in **Figure 5.1**, N'(t) has the origin on the edge of the substrate and extends horizontally in the actual experimental environment, as shown in **Figure 5.2**. The horizontal axis in **Figure 5.1**, time t, has the origin at the top surface of the substrate and extends vertically in the actual growth environment as shown in Figure 5.2. N'(t) is considered as lateral growth gain and can be considered as a function of time t, as described by the Avrami's equation. Vertical growth gain can be considered as a linear change of time t based on previous
experiments. In this way, the vertical gain can be seen as equivalent to time t, so that the lateral growth profile that extracts the data points introduced in the previous chapter can describe the lateral growth gain over time t by some simple mathematical treatment.



Figure 5.2 Phase change at time t in CVD diamond growth within a pocket holder

5.2 Exponential Decay Growth Mode

The lateral growth of CVD single crystal diamond in a straight walled pocket holder is considered as a 1^{st} order exponential decay growth fashion. The lateral gain for a single side is described as the distance between the current edge and the substrate edge, and denoted as L(t), which is a function of time t. L(t) is described as

$$L(t) = A (1 - e^{-t/\tau})$$

where A is the upper limit of the size of lateral gain, with unit usually in mm, similar to N₀ from the above section, and τ is defined as characterize time which describes the changing speed of the curve, with unit usually in hr, similar to n from the above section. All lateral growth profiles are extracted, calculated, and plotted to fit this equation for further understanding in diamond epitaxial lateral outgrowth (ELO). Parameters A and τ are key basic parameters for all growth.

The lateral growth sizes of sample SBLA is analyzed after 3, 6, and 9 hours using sample holder ACHH02b (width = 6.00 mm, depth = 2.60 mm), at 240 Torr 980 °C. The top views and side views of sample SBLA overlay as shown in **Figure 5.3** and close up views clearly illustrates the morphology changes after CVD growth every 3 hours. (a) illustrates the growth mechanism and (b) presents the overlay of 4 side view photos of the sample SBLA. (c) presents the overlay of 4 top view photos and (d) shows the close up views that clearly shows the specific sample edges for each growth. The length and the thickness of the sample are measured after each growth, and



Figure 5.3 Lateral growth pictures overlay of diamond sample SBLA



Figure 5.4 Evolution of (a) gap distance and (b) lateral gain of sample SBLA after 3, 6, and 9 hours

plotted in **Figure 5.4** for understanding the change of morphologies over time. (c) also shows the island growth of top surfaces for short duration growth.

The lateral gain increases after each growth for sample SBLA so that the distance between the sample and the pocket wall decreases after each growth. The distance between the sample and the pocket wall is defined as gap distance. Vertical growth has a constant growth rate so that the growth profile can be plotted equally over thickness gain or time. The gap distance in (a) decreases in a fit of exponential decay function with the tangent line shown in a black line with the tangent value $\Delta gap/\Delta th=1.369$. The exponential decay fitted curve also has an asymptote shown as the blue dashed line which stands for the lower limit for the gap distance. The R-square value of the fitted curve is 0.999 meaning a great fitting quality. The tangent value is the biggest at the starting point, i.e. t = 0, meaning it has the fastest changes in the morphology. The changes which is the rate decreases during the growth. The lateral length is also plotted over time in (b), which is also fitted using the exponential decay function. As shown in (b), the lateral length increasing rate is slower over time, which is equivalent to the changing rate of gap distance slows down during the growth. The fitting parameter A is 0.436 mm, and the characterize time τ is 8.79 hr. The final length of the prediction using the fitted function is 3.992 mm, meaning within this experimental situation of the sample and the sample holder geometry, the upper limit length size is 3.992 mm from a 3.55 mm substrate. The average total lateral growth rate is calculated as $(3.83 \text{ mm} - 3.55 \text{ mm})/9 \text{ hr} = 31.11 \mu\text{m/hr}$. The single side lateral growth rate is the half of the total rate: 31.11 μ m/hr /2= 15.55 μ m/hr. The exponential decay growth of diamond is firstly discovered in a mathematical situation.



Figure 5.5 Sample sizes and growth conditions over time

The dimensions of sample SBLA and the growth conditions of temperature and the microwave power are plotted over the growth time shown in **Figure 5.5**. The weight and the thickness are both increasing with the growth time as the length increases exponentially decay way. The microwave power is set between around 2200 W and 2900 W for each of all three growth. It is clear that the temperature fluctuation decreases and is not obvious after hours. The microwave power decreasing rate also slows down until the power maintains flat after hours. The lateral growth rate decreases is the main reason that temperature changes also slows down.

5.3 Pocket Holder Use in ACH Samples

Data from Figure 6.5 and 6.6 on page 226 and 227 from Charris thesis[64] are reproduced by taking the square root of the normalized area gain to achieve the normalized total length/lateral size gain. This way, when plotted the normalized lateral size gain over the growth time, the mathematical growth model introduced in the previous section can be used to fit the data to show the validity of the mathematical growth model.

All data used in this figure are collected by A. Charris SCD growth at 240 Torr, microwave plasma density approximately 500 W/cm³. With 400 sccm H₂ and a methane concentration of 5%. The substrate temperature was controlled around 1020 °C. In **Figure 5.6**, square root of Area Gain means the normalized lateral size gain. 4 types of pocket holders (width=6 mm/depth=2.6 mm, width=6.6 mm/depth=2.6 mm, width=7 mm/depth=2.6 mm, width=7 mm/depth=2.9 mm,) are used, and each type holder is used for multiple growth durations from

12 hr to 50 hr. Growth time longer than 50 hr is not discussed here since the sample will be grown over the pocket condition and form into an open holder condition. All 4 type holders using the mathematical growth model are well fitted with R-square ~ 99%.



Figure 5.6 ACH samples lateral size evolution

From the aspect of the mathematical growth model, larger A means more lateral size gain and longer time t means the growth takes longer time to decay, which further means more lateral gain. Based on the fitting results of the 4 type holders, the conclusion is made: wider and deeper pocket tends to achieve more lateral gain and slower growth decay, which is tested solid experimentally and mathematically in theory, and scientifically.

Based on the previous introduction about the mathematical growth model, variable A means the potential lateral gain available. To discuss the relationship between the available potential lateral gain and the 4 type holders, such information is plotted in the below **Figure 5.7**.



Figure 5.7 ACH samples lateral growth profiles fitting parameter A vs pocket holder geometries

Clearly, an increasing trend is shown for the potential lateral size gain when using wider and deeper pocket. This means to increase the probability of more lateral growth of CVD diamond, both wider and deeper pocket will help. However, single use of wide pocket will perform PCD growth on the rim, so to avoid PCD growth but keep more lateral size gain, a pocket with

multiple level from small to large, from center to outside, and from shallow to deep is promising, such that the angled holder with a correct angle will keep the CVD diamond growth fast and lateral.



Figure 5.8 XRC maps of ACH3 and ACH4

Sample ACH3 (original ACH 78) and ACH4 (original ACH67) are measured under XRD using XRC mapping technique for understanding their crystal structural qualities. XRC mapping results for ACH 3 and ACH 4 are shown in **Figure 5.8**. To examine the effects of varying growth rates on lattice structure x-ray rocking curve scans of the (400) reflection was performed across all data sets and the variation in FWHM, and orientation was examined between the center and

outgrown regions and between datasets. Data was analyzed (parsed, modeled, and aggregated) using in-house MATLAB apps to produce visualizations of FWHM and planar orientation distributions across each sample.

ACH samples were grown in reactor C. The lateral growth rate can be derived by the 1st derivative of (*t*) over *t*, described as $R_L(t) = (t)/dt = A/\tau * \exp(-t/\tau)$. The average lateral growth rate R_{AL} is calculated by total lateral gain over total growth time. However, for pockets which are too wide the effect of the pocket to suppress PCD growth will be lost so the validity of this model is limited to growth conditions where diamond growth leads to a smooth top surface morphology. Average vertical growth rates R_V for ACH 1, 2, 3, and 4 were kept at 26.5 µm/hour, and average lateral growth rates R_{AL} are respectively: 2.5, 6.6, 9.78, and 10.2 µm/hour. Further examination of lateral growth rate for ACH samples, all grown in reactor C, show the same pattern of changing lateral rate as a function of time. Fitted curves to ACH growth data, which measured the lateral dimensions of diamond after continuous growth for 12, 23, 30, and up to 50 hours (and in-between) show initial rates vary as a function of holder dimension. Smallest holders at 6 x 6 x 2.6 mm show the smallest initial growth rate and lowest overall lateral growth rate and largest overall gain.



Figure 5.9 400 crystal plane morphology of ACH 3 and ACH 4

The crystal plane morphology of sample ACH 3 and ACH 4 are plotted in **Figure 5.9**. The normal look of the crystal plane shows a relative flat plane but when zoom in z axis, ACH 3 400 crystal plane presents a typical curved morphology with curvature ranges from 0 to 0.15/m. The curvature is close to 0 at the center and increases for the locations closer to the edges. The corresponding radius ranges from 6 m – 40 m and above. The x-curvature, y-curvature Gaussian curvature and the error are also calculated and plotted. The same type of data are also analyzed and plotted for ACH 4.

5.4 Pocket Holder Use in SB Samples

Other than SB A sample presenting first three times 3 hour growth which only representing short hour CVD diamond growth, two other growth SB C and SB F are conducted as representatives for long hour growth. The SB A sample and other previous ACH samples have clearly shown the lateral outgrowth dimensions are influenced by the pocket holder geometry and dimensions. The SB samples are carried out in two categories: asymmetric growth (SB C) and symmetric growth (SB F). As shown in **Figure 5.10**, the symmetric growth provides the pocket environment with symmetric boundary conditions that initial gap distance are average for both sides: $G_{SL} = G_{SR}$, and the asymmetric growth environment places sample SB C towards the left edge of the inner pocket which creates asymmetric boundary conditions: $G_{AL} < G_{AR}$. Average vertical growth rates R_V for SB A, F, and C are respectively: 18.89, 27.5, and 25.0 μ m/hour. Average lateral growth rates R_{AL} for SB A, F, C_left and C_right are respectively: 31.1, 7.33, 6.67, and 14.4 μ m/hour.



Figure 5.10 Sample SBF symmetric and SBC asymmetric growth layout

Results from growth show a similar pattern of change in the lateral growth rate as a function of time for all reactor C samples. SB C is grown for 48 hours in asymmetric boundary conditions and SB F is grown for 60 hours in a symmetric boundary conditions. As **Figure 5.11** shows, the initial lateral gain within the first 5 hours of growth is high for the two holder types illustrated (6 x 6 x 2.6 mm and 6.6 x 6.6 x 2.6 mm in length, width, and depth), with gain slowly decreasing from 5 to 20 hours into growth. After 20 hours until the conclusion of growth for samples SB F and the left side of sample SB C, there is almost zero lateral gain.

Contrasting this result, we see for the right side of sample SB C, the lateral gain continues in an almost linear fashion for the entire duration of growth. This distinct difference between SB C right side and the left is due to the asymmetric seating of the substrate in the pocket. Since the gap on the left side of the substrate was closer to the holder wall there was less available space for the diamond to grow into, resulting in an early termination of lateral gain. Nevertheless, the total lateral gain seen for SB C, which has a smaller holder dimension than that grown in SB F, indicates there is a strong connection between optimum growth conditions and holder dimension. From the perspective of high-quality growth, changing the rate of lateral gain, or changing growth rate, belies a change in the growth surface conditions of temperature and or gas precursor concentration. These can lead to unwanted effects like defect formation which need to be suppressed in the growth of high-quality substrates.



Figure 5.11 ELO growth profiles for SB samples compared to ACH samples

To examine the effects of varying growth rates on lattice structure x-ray rocking curve scans of the (400) reflection was performed across all data sets and the variation in FWHM, and orientation was examined between the center and outgrown regions and between datasets. Data was analyzed (parsed, modeled, and aggregated) using in-house MATLAB apps to produce visualizations of FWHM and planar orientation distributions across each sample.



Figure 5.12 XRC mapping results for sample SBC and SBF

Figure 5.12 shows XRC mapping results for samples from SB C, and SB F. The quality of CVD growth is measured approximately as the FWHM of the (400) for each peak. Diamond substrates for all samples varies between 25 and 30 arcseconds (written with a single quotation mark, "). The FWHM for all samples vary as a function of location, with the ELO region increasing in FWHM (decreasing in quality) compared to the center. SB C sample shows an average FWHM of 176" and ELO region of 241", while ACH 3 has the poorest quality of samples with an average FWHM of 204", and ELO FWHM of 274".



Figure 5.13 400 crystal plane morphology of sample SBC and SBF

Both phi=0 XRC mapping results for SB samples and ACH samples show low FWHM center and wide FWHM at the ELO edges. In the peak location maps, the phi=0 maps also show a continuous change of peak position from low to high from left to right for both SB and ACH samples. The peak position ranges are typically around $0.14^{\circ} - 0.36^{\circ}$ while SB F has a range of 0.93° since a crack emerges during the growth and the crack increases the peak location range.

The crystal plane morphology of sample SB C and SB F are plotted in **Figure 5.13**. The normal look of the crystal plane shows a relative flat plane but when zoom in z axis, SB C 400 crystal plane presents a typical curved morphology with curvature ranges from 0 to 0.1/m. The curvature is close to 0 at the center and increases for the locations closer to the edges. The corresponding radius ranges from 10 m - 50 m and above. The wider range the peak location spans, the more curved the crystal morphology is. The x-curvature, y-curvature Gaussian curvature and the error are also calculated and plotted. The same type of data are also analyzed and plotted for SB F. Sample F has an obvious crack at the lower part of the sample and it is clear to see the crystal plane turning in the 400 morphology. The turning is corresponding to a very sharp curvature as shown in the curvature maps including the mean curvature, x-curvature, y-curvature and the Gaussian curvature.

5.5 Pocket Holder Use in AI Samples

CVD diamond growth are also carried out in reactor B (DS II) for an AI project. Some selected AI samples that have similar growth conditions (temperature, growth time, power, etc.) are

selected for analyzing the ELO growth profiles and XRD characterization like XRC mapping technique is also used for AI samples.

Deposition runs in reactor B are on substrates AI 03, 05, 06, 07, 17 and 18 resulted in average vertical growth rates R_V of respectively: 26.8, 17.4. 24, 24.68, 12.67 and 18.5 µm/hour. Average lateral growth rates R_{AL} are respectively: 15.5, 7.0, 16.8, 19.8, 7.83, and 14.3 µm/hour, with AI 07 and AI 17 shown in **Figure 5.14** as a representative. All samples are grown using the same pocket hodler with 7 x 7 mm dimensions and the depth distance between sample hoder top surface and sample's top suface, Δd , is 1.5 mm.



Figure 5.14 Top view and side view of AI 07 and AI 17 samples



Figure 5.15 ELO growth profile for AI samples compared to SB and ACH samples

AI samples, grown in reactor B, were grown for less time overall, this condition was chosen to restrict overall growth to within the pocket (at 7 x 7 x 2 mm), which is shallower than those used in reactor C (at 7 x 7 x 2.6 mm). As shown in **Figure 5.15**, the pattern of growth for reactor B to follow a more linear fashion than that for reactor C, where growth rates start initially fast and decay over time. In contrast, growth rates in reactor B are nearly linear, only dropping off towards the end of the run. Reactor B samples grew overall faster initially, with a range of between 19 and 91 μ m/hr, and final growth rates slowed to between 7 and 19 μ m/hr. Substrate temperature control are manually performed in reactor B, which resulted in variable growth temperatures per run.

As shown in **Figure 5.16**, 400 crystal plane XRC mapping results are plotted for AI 07 and AI 17 as representative AI samples. The FWHM for all samples vary as a function of location, with the ELO region increasing in FWHM (decreasing in quality) compared to the center. AI 17, despite having the fastest overall lateral growth times shows the lowest overall FWHM, which is reflected in the widespread distribution of regions between 30" and 124". This may be reflected by different lateral profiles of AI samples compared to SB and ACH samples. AI samples grown in reactor B show a nearly linear gain over time and therefore flat lateral growth rate, compared with SB and ACH samples which display an exponentially decaying lateral gain and therefore a constantly changing growth rate. The average FWHM value for AI 17 also reflects this quality, at 102", with the ELO region decreasing in quality to 167". Other than AI 17, AI 07 also shows a low FWHM center after growth. The peak location of phi=0 spans in a range around 0.23°, and distributed from low to high from left to right.



Figure 5.16 XRC mapping results for AI 07 and AI 17

The crystal plane morphology of sample AI 07 and AI 17 are plotted in **Figure 5.17**. The normal look of the crystal plane shows a relative flat plane when plotted in a x:y:z=1:1:1 coordinate system, but when zoom in z axis, both AI 07 and AI 17 400 crystal planes present rough morphologies. The curvature is close to 0 at the center and increases for the locations closer to the edges. The corresponding radius for some locations are less than 1 m. The wider range the peak location spans, the more curved the crystal morphology is. The x-curvature, y-curvature Gaussian curvature and the error are also calculated and plotted for the AI samples. The rough



Figure 5.17 400 morphologies of AI 07 and AI17

growth morphologies in ELO regions of AI samples are considered to be the results of the rough temperature controlling.

5.6 Traditional Pocket Holder Summary

In the CVD diamond growth using traditional pocket holders, the results demonstrate examine the relationship between diamond lateral outgrowth behavior, pocket dimension, and reactor type. Pockets of increasing dimension in width and length, as well as depth, are studied for their effectiveness in producing high quality lateral outgrowth. Changes in growth rate as a function of proximity to the holder wall are modeled for one reactor type, and the differences between growth behaviors between reactors is analyzed.

Sample ID	H₂/CH₄ (sccm)	Temperature (°C)	Pressure (Torr)	Time ∆t (hr.)	Vertical Growth Rate R_V (µm/hr)
SB A	400/20	980 ± 10	240	9	18.89
SB C	400/20	980 ± 10	240	48	27.5
SB F	400/20	980 ± 10	240	60	25.0
ACH 1	400/20	1020 ± 20	240	50	26.5
ACH 2	400/20	1020 ± 20	240	50	26.5
ACH 3	400/20	1020 ± 20	240	48	26.5
ACH 4	400/20	1020 ± 20	240	50	26.5
AI 03	400/20	800 ± 5	240	25	26.8
AI 05	400/20	763 ± 10	240	25	17.4
AI 06	400/20	790 ± 15	240	25	24
AI 07	400/20	760 ± 10	240	25	24.68
AI 17	400/20	800 ± 10	240	30	12.67
AI 18	400/24	775 ± 15	240	30	18.5

Table 5.1 Nominal growth conditions for samples grown in reactor B and C

			Total							As	
Sample ID	Widt h (mm)	Depth (mm)	Pocket Volume (mm ³)	∆d (mm)	G (mm)	A (mm)	τ (hr)	<i>R_L</i> at t=0 (μm/hr)	<i>R_L</i> at t=τ (μm/hr)	grown Average <i>R_{AL}</i> (μm/hr)	Ratio of R_{AL}/R_V
SB A	6	2.6	93.6	1.21	1.25	0.43 6	8.79	49.601	18.247	31.1	1.65
SB C	6	2.6	93.6	1.65	0.85, 1.65	0.32, 0.97	9.79 <i>,</i> 51.66	32.686 18.776	12.024 6.907	6.67 14.4	0.24 0.52
SB F	6.6	2.6	113.3	1.2	1.55	0.56	44.94	12.461	4.584	7.33	0.29
ACH 1	6	2.6	93.6	1.2	1.25	0.24	10.34 7	23.388	8.604	2.5	0.09
ACH 2	6.6	2.6	113.3	1.2	1.55	0.60 4	6.852	88.149	32.428	6.6	0.25
ACH 3	7	2.6	127.4	1.2	1.75	0.79 5	10.80 6	73.570	27.065	9.78	0.37
ACH 4	7	2.9	142.1	1.5	1.75	0.90 5	12.46 8	72.585	26.703	10.2	0.39
AI 03	7	2.0	98	1.5	1.75	0.77 2	8.42	91.686	33.733	15.5	0.58
AI 05	7	2.0	98	1.5	1.75	0.42 6	18.14	23.484	8.639	7.0	0.40
AI 06	7	2.0	98	1.5	1.75	0.58 4	7.516	77.70	35.642	16.8	0.70
AI 07	7	2.0	98	1.5	1.75	0.71 8	20.17 5	35.588	13.092	19.8	0.80
AI 17	7	2.0	98	1.5	1.71 5	0.55 4	28.48 9	19.446	7.153	7.83	0.62
AI 18	7	2.0	98	1.5	1.77	1.19	59.83	19.889	7.317	14.3	0.77

Table 5.2 Dimensions of pocket holders for samples grown in Reactor B and C

CVD diamond growth conditions are listed in **Table 5.1**. Diamond growths under sample ID prefixes AI used reactor type B configuration while SB and ACH prefixes used type C configurations. Samples AI were grown using a hybrid TM_{013}/TEM_{001} electromagnetic mode with a short distance $L_s=21.3$ cm and a probe distance $L_p=3.8$ cm. This electromagnetic cavity configuration resulted in nominally no reflected power. In reactor B, depositions are carried out at substrate temperatures of around 800°C with an emission coefficient of 0.6, measured using the optical pyrometer technique which makes the temperature shows similar level of temperature of depositions from reactor C, and using input microwave power levels between 2 and 3 kW.

Samples SB were grown using a hybrid TM_{001}/TM_{01n} electromagnetic mode with short distance L_s =16.25 cm and probe distance L_p =3 cm to reduce the reflected power to a minimum value and to achieve the desired deposition results including growth uniformity. All samples were grown under 240 Torr with 400 sccm H₂ and 20 sccm CH₄. While in reactor C, depositions are carried out at substrate temperatures of 980°C with an emission coefficient of 0.1, measured using the optical pyrometer technique described by Nad, and using input microwave power levels between 2 and 3 kW. As such, growth rates for SB diamond depositions are controlled to approximately 25 µm/hour in the vertical direction. ACH samples were also grown in reactor C geometry with substrate temperatures of 1020°C.

Diamond seeds (type Ib high pressure high temperature (HPHT)) are cleaned by using a sequence of acids and solvent including Sulfuric, Nitric, Hydrochloric Acid, and Acetone, Methanol, Isopropyl Alcohol, to remove contaminants and impurities before loading into CVD chamber. Seeds are then carefully positioned in the designated conditioned pocket holder and loaded to the CVD chamber. The CVD chamber is held under constant vacuum at base pressure ($\sim 10^{-5}$ Torr) for at least 12 hours before deposition. An initial etch is performed at the start of growth using 2800 W microwave plasma at 400 sccm H₂ flow, 950°C substrate temperature for 10 min to 1 hour to obtain a clean and fresh surface of the substrates. Growths were performed over a range of times from 3 hours to 60 hours according to pocket holder size, under a 5% CH₄/H₂ flow ratio and 980°C substrate temperature, only AI18 was grown under a 6% methane environment. A water-cooling system is used to in part cool the substrate holder, which together with the adjustment of input power, is designed to regulate the substrate temperature during growth.

The lateral growth rate can be derived by the 1st derivative of L(t) over t, described as $R_L(t) = \frac{dL(t)}{dt} = A/\tau * \exp(-t/\tau)$. The average lateral growth rate R_{AL} is calculated by total lateral gain over total growth time. However, for pockets which are too wide the effect of the pocket to suppress PCD growth will be lost[52], [58], [64] so the validity of this model is limited to growth conditions where diamond growth leads to a smooth top surface morphology. All pocket dimensions used for the three type samples as well as the fitting parameters especially A and τ are listed in **Table 5.2**.



Figure 5.18 ELO growth coefficients and relationship between holder dimensions and growth rates

Results indicate increasing width dimensions in a pocket mode will lead to better outgrowth performance, measured as lateral gain per hour. However, if lateral dimension is increased too much the conditions under which PCD grows will return. Based on this hypothesis, increasing the *G* parameter will lead to higher values of *A* and τ , as listed in **Table 5.2** and plotted in **Figure 5.18**. Results indicate from both AI, SB and historical ACH data this is the case – an analysis of *G* with *A* shows a strong positive correlation (0.983 Pearson's correlation test). However, τ

shows only a weak positive relation (0.309). Contrasting these results with a test of Δd shows strong positive correlations with both A and τ (0.628 and 0.684, respectively). This indicates the best performance of the lateral outgrowth (measured as lateral gain per hour), based on experimental fitting of data, is a combination of Δd and G with Δd mediating the value of τ to extend the asymptote of the curve, increasing lateral gain over the duration of growth in a single run.

Examining the relationship between Δd and G further, results show the lateral growth performance does not scale linearly with increasing G. Lateral growth performance is weakest when the ratio between G and Δd is 1.24 (samples SB F and ACH 3), despite these configurations having a greater width than ACH 1. This is because the τ value is the lowest for these samples. At a ratio of 1.45 (ACH 3 and SB F) the lateral performance leads to ~0.4 mm of outgrowth. The best lateral growth performance is observed for ACH 4, where the ratio of G over Δd is 1.16, and the ultimate lateral gain is ~0.54 mm. Based on these results, maintaining a ratio of G to Δd of 1 and 1.16 (τ >10 hr) leads to the best lateral growth performance possible.

In reactor B, the holder dimensions are held fixed with AI samples grown as **Table 5.2** lists. Growth time are fixed at 25 and 30 hours due to considerations with the vertical growth rate and the depth of holder. However, the average lateral growth rates ranges from 7 to 19.8 μ m/hr since the growth conditions are at different temperatures. Vertical growth rates also ranges from 12.67 to 24.68 μ m/hr. A clear positive correlation is achieved between the lateral and vertical growth rates at different temperatures, with the ratio of R_{AL}/R_V locating between 0.4 and 0.8. In reactor C, the relationship is analyzed using SB and ACH samples separately grown as listed. SB samples focuses difference between long growth SBC and SBF, and short growth SBA. Growth time are set longer than growth in reactor B since holders are deeper. Since lateral growth behavior is in a good fit with the exponential decay fashion, lateral growth rate over time then is the first derivative of the lateral growth, and is also in the exponential decay fashion. This result clearly indicates in the early stage of a growth, lateral growth rate is faster and when time goes longer lateral growth rates drops in the exponential decay way. The ratio of R_{AL}/R_V for SB A has the greatest value 1.65 since it has only 9 hours growth, which is short compare to other growth always have longer than 48 hours. This further indicates the longer the growth is, the slower the average lateral growth rate R_{AL} is. Since the vertical rate is considered as a constant, then the ratio of R_{AL}/R_V also drops over time.

In ACH samples, the holder dimensions is set with wider and/or deeper pocket. From the data, it shows another clear positive correlation between the holder dimensions (width and depth) and lateral growth rates. From ACH 1 to ACH 4, the wider the holder is, the faster the average lateral growth rate R_{AL} is, and the larger ratio of R_{AL}/R_V can be. As width increased from 6 mm to 7 mm, the average lateral growth rate increases clearly and so as the ratio of R_{AL}/R_V . While when holder is made deeper from 2.6 mm to 2.9 mm, R_{AL} and the ratio of R_{AL}/R_V increase slightly.

In a conclusion, results of ELO growth profiles of AI, SB, and ACH samples from reactor B and C configurations show that traditional pocket holders will constrain ELO of CVD diamond in 1st order exponential decay fashion, and appropriately wider pocket allows wider as grown CVD diamond lateral size (corresponding to A) and longer decaying time (corresponding to τ).

Generally, a set up with gap distance of 1.5-1.75 mm can allow CVD diamond have up to over 0.9 mm on a single 100 edge after 48 hour growth at vertical growth rate around 25-28 μ m/hr.



Figure 5.19 Cross section view of XRC FWHM and peak location results for three types of samples

To directly view FWHM and Peak Location distribution, a cross section view of data is plotted in **Figure 5.19** for the three type samples. FWHM and peak location values extracted from XRC scans over the surface of 3 representative samples are brought down into 1 dimensional data in a) to show better understanding. The cross section view shows broadening of the FWHM (up to 1300 arcsec) corresponding to changes in crystallographic errors especially at edges (x<1, x>5 mm). Detailed information can be drawn here: FWHM of SBC, ACH3 and AI17 at center keeps original <100 arcsec level FWHM (1.5 <x<4.5 mm). Peak location values increases as x increases across the sample for all. Peak location values of SB C, ACH 3 and AI 17 increases steadily due to the constrained growth environment. This phenomenon enhances that both the constraining of the growth and the structural deformation may happening for the grown samples. SB C, SB F, ACH 3 and ACH 4, and AI 17 are shown as plotted data in b) represent for FWHM, it shows for 4 samples, the center region keeps the crystal quality (low FWHM) as discussed, and raises up to 1200 arcsec when it is measured on the edges. Both long grown sample SB F and ACH 4 show FWHM higher than 1200 arcsec on the edges. SBF shows slight worse quality (higher FWHM) because of the clear crack on the top surface. This also influence the peak location distribution for SBF, where it shows abrupt rising from 4.5 m to 5 mm range meaning the crystal orientation changes abruptly because of the cracking. However, the changing rate on both left and right side of the crack (4.5 mm -5 mm) keeps the same and low. This low changing rate of peak locations also applies to the other samples, meaning crystal orientation changes slightly over locations after growth. The range of the peak location varies from 0.1° to 0.2° and the range is large when the growth is longer. Generally, FWHM increases to above 1000 arcsec on the lateral edges in contrast to the center maintains around 30-40 arcsec. The peak location varies indicates the crystal orientation with respect to the center changes from -0.06° to $+0.06^{\circ}$ typically from edge to edge with clear changes on the lateral edges but nearly no change in diamond center.

Despite these disparities between the two samples, increases in mosaicity in the ELO regions follow similar patterns, with the ELO regions having the highest FWHM values (and therefore highest mosaicity). As Sample C indicates, the nucleation rate/growth rate can be regulated through choice of gap distance of the holder itself, which regulates the transport of gas radicals and distribution of temperature as function of the gap distance. This further implies regulation of the reactor conditions (adjustment of parameters in-situ) as both a function of the holder geometry and the evolving conditions at the surface and ELO growth fronts will enable

regulation of mass transport and temperature distribution on the growth surface. By controlling these conditions, it will be possible to regulate nucleation rates and their density, leading to a uniform expansion of ELO fronts and uniform condition of crystal quality.



Figure 5.20 FWHM overview distribution of all three type of samples

Figure 5.20 presents a comprehensive statistical total distribution of XRC FWHM of diamond (400) peaks for representative samples. Individual and overall statistical FWHM values collected

from XRC scans over all 3 representative sample AI 17, SB C, and ACH 3 surfaces show a decaying distribution corresponding to changes in crystallographic errors from center to edge. FWHM value of most measured points in the center keep low level (<100 arcsec) and as the point moves to the edge FWHM value increases up to 1400 arcsec. In general, such results suggest that around 50% of the overall points would have low FWHM (<100 arcsec), while the points that have FWHM larger than 100 arcsec make up the rest of 50%. The counts of points should be decreased as FWHM increases up to 1400 arcsec, following a decaying distribution. More data are collected for other SB samples and ACH samples as (c) and (d) show.

From these results of CVD diamond growth in traditional straight walled pocket holders, it can be concluded that the effect of holder geometry (dimensions) on lateral growth rate are affected not only by the width of the pocket but also the depth. Shallow holders appear to perform better than deep holders by producing near-linear growth rate. The decay in lateral growth rate for deep pocket holders can be modeled by a 1st order exponential decay function, which produces a constant change in lateral rate over the course of the growth run. Results indicate this changing rate is directly responsible for the degrading quality of the grown material, as it indicates the chemical reaction rates at the growing surface are non-uniform and lead to degrading lattice quality. This phenomenon can be described as a change in driving force conditions, or an imbalance of the temperature of the growth surface with the chemical potential difference between carbon-hydrogen molecules or carbon atoms at the surface and growth species in the gas phase. In general, this tells us that deep pocket designs suffer from dynamically changing rates over time, and the design of the pocket holders may require shapes other than vertical walls to promote stable growth conditions over time for each growth run. The experiments and analysis of SCD growth in a pocket holder show the outward lateral growth is constrained by the dimensions of the pocket, resulting in a slowing of diamond ELO following a 1st order exponential decay function. Additionally, a rough fractal morphology is produced in the ELO regions, increasing the FWHM of the (400) crystal lattice places 1 - 2 orders of magnitude. The fractal morphology produced indicates the driving force, a ratio describing the balance between supersaturation and temperature conditions, is high. This result is supported by observations of the fastest growth rates occurring at the outset of growth. Evidence from previous studies leads us to consider two possible mechanisms: (1) the initial driving force conditions are constant, therefore a possible mechanism driving fast initial growth rates and fractal morphology are roughened edges and corners of the diamond sample, and/or (2) the formation of localized electric fields observed and modeled in open and pocket holder configurations enhance nucleation behavior/rates due to increased temperature. Rough initial morphologies may lead to enhanced nucleation, and mergers between expanding nucleated islands are statistically more likely to be misaligned on an initial rough surface compared to smooth faceted surfaces. Further, rough nucleating surfaces combined with locally enhanced electric fields may work synergistically to create the rough fractal morphologies observed, including the formation of rivulets in the laterally outgrown regions. XRC maps support the assertion of changing nucleation behavior, and therefore changing growth rates, are present during growth due to the location-dependent changes in FWHM, from lowest values of CVDgrown lattice to highest from center to edge. Overall, this study points towards a need for models, such as phase-field models, and experimentation which can account for non-uniformities in driving force conditions due to elevated temperature and plasma interaction with growing diamond. Understanding in more detail the effects diamond substrate and plasma interaction

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have on the conditions of supersaturation and temperature will lead to future advancements in shaping crystals and driving crystal growth using plasma-based deposition.

In continuing studies, this research project is going to plan to investigate these process-structure relationships towards achieving optimized crystal quality while expanding diamond size based on the designing of future holders.

Epitaxial Lateral Outgrowth in Novel Designed Angled Sample Holder – Steady State Lateral Outgrowth Mode

6.1 Concept Derivation of Angled pocket Holder with Kinetics of Phase Change Applied

In past decades, single crystal diamond serves as a promising material in its optical properties, its outstanding physical properties like hardness, and rich in minerals all over the world. Diamond is also outstanding for its promising electronic properties where diamond surpasses other wide band gap semiconductor materials such as SiC and GaN, etc. Thus, diamond tops the promising ultimate materials for power electronics in high voltage, high temperature and high frequency applications, and as detectors for high energy physics[1], [6], [21], [166], [206].

6.1.1 Background in CVD Diamond Growth in Pocket Holder

As technology is developing rapidly, 6G is already starting to form as a platform to network the world's most advanced technologies so far, such as VR/AR, IoT, quantum computing, and AI/ML, etc., even though 5G has dominated only a few years. Later technologies and applications are also found possible via diamond for near future applications since diamond can host color centers for quantum devices[5], [19], [114].
To realize such applications, the followings are required for diamond: 1) scalable single crystal wafer, 2) excellent crystalline quality, and 3) accurate control of diamond doping. As reported by Frost & Sullivan, synthetic diamond is starting to dominate over mined diamond in diamond market recently, and synthetic diamond is forecasted to dominate more global market supply in the next decades. Pathways to fulfill the requirements are proposed with synthetic diamond, containing both high pressure high temperature (HPHT) and chemical vapor deposition (CVD) growth of large area diamond and doped diamond, ways of measurements to characterize crystal structure and electronic properties of as grown diamond. A market research report shows CVD diamond is starting to dominate the synthetic diamond market in the current decade, and it is obvious that CVD diamond is increasing in demand and supply. Since more diamond is synthesized in labs rather than mined naturally, and CVD is dominating the lab grown diamond, growing CVD diamond is in a great demand to realize the 3 requirements mentioned above. MPACVD has been showing it promising unique kinds in growing large size high quality single crystal diamond over the past decade. CVD diamond is approved to show lateral growth behavior in pocket holders and are promising to grow both in larger area and ticker. This will make a major breakthrough for CVD diamond that is earlier thought only grow in 1 dimensional (thicker). Such effort needs to be put in to grow bigger CVD diamond with larger area and high qualities. Traditional straight walled pocket holders are proved to be promising in growing larger area SCD but constrain the lateral growth size to have an upper limit. The angled pocket holders are recently discovered with our previous experiments to show constant lateral growth rates for SCD large area growth.

For better understanding SCD growth quality, crystal structural characterization is necessary. Structural defect is also required to shoe quality of CVD SCD. Traditional pocket holders are shown to constrain epitaxial lateral outgrowth (ELO) in a 1st order exponential decay fashion in previous work and the lateral size of as grown diamond has an upper limit subject to its holder configurations. As an upgraded research project, this research will include the single crystal diamond (SCD) grown by microwave plasma assisted chemical vapor deposition (MPACVD) in a series of angled holders designed to achieve better ELO and to maintain a good lateral growth rate. The growth using angled holders from wider pocket to narrower pocket, respectively results in larger size ELO with polycrystalline diamond (PCD) growth, appropriate smooth ELO growth at constant lateral growth rate, and inward lateral growth. Constant lateral growth rate method is selected for iterative regrowth using regrowth angled holder. Larger area SCD are thus grown by MPACVD with constant vertical rate about 25 um/hr, 100 lateral rate about 18 um/hr, and 110 lateral rate about 12 um/hr.

All as grown samples are measured with x-ray rocking curve (XRC) mapping technique to reveal the crystallographic structural properties, and compared to the original substrates. Diamond 400 crystal plane curvature/flatness and morphology, XRC FWHM of 400/113/111 diamond peaks are plotted using self-made analytical software to compare the quality revolution before and after the growth. Quantitative birefringence (QB) maps and cross polar birefringence (CPB) photos are also taken to present the internal crystal structural defect within the CVD diamond. XRC mapping results show that growth using wider angled pocket, though with PCD rims, has better flatness (small curvature) and higher average structural quality (small FWHM); growth with intermediate pocket, with pure SCD growth, also has a good lateral growth behavior, with

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intermediate crystal morphology and intermediate structural quality; growth using smaller pocket results area shrink, but with larger crystal plane curvature, indicating the SCD is compressed due to the smaller size of the pocket. Thus, an intermediate choice would be the best way for iterative SCD growth to maintain the lateral growth rate and the crystal quality at the same time.

6.1.2 Constant ELO Growth Derivation Based on Kinetics of Phase Change

It has been approved in Chapter 5 that CVD diamond growth lateral outgrowth profile is governed by a first order exponential decay function. This is because the growth behaviors is governed by kinetics of phase change in a fixed size due to the straight walled pocket which makes the governing equation a first-order autonomous ordinary differential equation (ODE). The governing equations are copied as the followings:

$$\frac{dN}{dt} = -\frac{dN'}{dt} = -nN$$
$$N(t) = N_0 e^{-nt}$$
$$N'(t) = N_0 (1 - e^{-nt})$$

As mentioned in Chapter 5, N' stands for the amount of single crystal phase, and N stands for the rest plasma gases phase. The limitation of the ELO growth is exponentially decay that can be seen from the equation, and the source reason for the behavior can be seen mathematically from the original first order autonomous ODE. Thus, to expand the ELO growth and make a

breakthrough in this limitation, the mathematical change of the ODE equation needs to be made. Experimentally, the new pocket holder design is required for certain change in the equation.

To start with the change, scientific understandings are considered for the whole CVD diamond growth process. The physics value $\frac{dN'}{dt}$ also stands for the lateral growth rate during the CVD diamond growth. The optimal way to keep CVD diamond growing without the above mentioned limitation is to have it grow constantly which means the value $\frac{dN'}{dt}$ is set to be a constant. Thus, the simplified way for the governing equation is to change to:

$$\frac{dN'}{dt} = -\frac{dN}{dt} = C$$

Here C stands simply for the lateral growth rate which is also a constant. The results of N' and N are both having a linear change with time t. Considering the vertical growth rate is also a constant and the thickness gain is also linear with time t, the lateral gain as a result is linear with thickness gain. And another important results from this change is the pocket dimensions are also having a linear change with the thickness gain, meaning the pocket holder needs to be designed so that the pocket wall has a specific angle with the horizontal plane. The concept of the holder design is described in **Figure 6.1**.



Figure 6.1 Concept design of the new angled pocket holder

This new concept sample holder is called angled pocket holder since it has a fixed angle α for the pocket wall. The value of angle α is considered to be 90° for the previous traditional straight walled pocket holders. Considering the actual experimental situation in the chamber, PCD or graphite will get deposited to the pocket slope as it creates another part of the pocket. However, the deposition of PCD or graphite should not influence the growth behavior of the CVD diamond so that the governing equation still hold true. Thus, the CVD diamond should show a linear ELO profile other than previous 1st order exponential decay profile as the growth behaves with both vertical growth rates and lateral growth rates are constant.

6.2 Designing of a Series of Angled Holders

To design a new angled holder, some existent factors and new created factors are required to bring into the consideration based on the previous design of the traditional pocket holders. The existent factors are the factors that are typical in the previous straight walled traditional pocket. These factors are: inner pocket width, outer pocket width, step length, inner pocket depth, and total pocket depth. The new created factors are the factors that are new due to the design of the angle feature. These factors are: with a step or without a step, inner width between the starting ends of the slope, outer width between the finishing ends of the slope, and the angle α .



Figure 6.2 Right side half look of angled holder geometry with new created factors

As shown in **Figure 6.2**, the factors are illustrated as the key components are labeled in the figure. The existent factors are shown: the inner pocket depth is fixed at 1 mm to expose the certain top $200 - 400 \mu$ m of the substrate; the inner pocket width is fixed at around 4 mm to keep

the substrate at the center; the step length is also 1 mm if the holder design contains one. The new created factors are also labeled: example type of holder A has a larger angle α_A without a step, and the other example type of holder B has a smaller angle α_B with a step, so that 90° > $\alpha_A > \alpha_B$. The right hand side inner ends of the slopes and the right hand side outer ends of the slopes are also labeled. For the examples shown in the figure, the width between the inner ends of the slopes for the holders without step are always 4 mm, and the width between the inner ends of the slopes for the holders with a step are always 6 mm. The width between the outer ends of the slopes for the holders without step varies and is wider when the angle α get smaller or the total depth gets deeper.

The specific angle α is set to be around 37° as previous chapter and **Figure 5.4** mentioned. The starting stage of the ELO growth has a tangent value of $\Delta x/\Delta y=1.369$. This tangent line corresponds to an angle of 37° which provides a fastest ELO lateral growth. Such angle is promising then, to enable a fast and steady lateral out growth. The new series of angled holders are designed with the 37° as the major and expanded into more types of the holders to fulfill a completed series of angled holders for understanding the ELO growth in angled holders at an optimized experimental set. The new series of angled holders are considered to have different angles, with or without step, so that the space between the substrate and the pocket can range from narrow to wide, as **Table 6.1** lists.

Holder #	Holder	Angle		Width	Width	Initial Gap
in	Туре	(°)	Step	(inner)	(outer)	Distance
Figure 6.3				(mm)	(mm)	(mm)
0	Traditional	90	У	6	6	1.2
1	Angled	37	У	6	10	1.465
2	Angled	37	n	4	8	0.465
3	Angled	60	n	4	6	0.315
4	Angled	60	У	6	8	1.315

 Table 6.1 Initial angled holder design

The angle pocket holders are designed with different angles (37° and 60°) and categorized to with a step and without a step. Each of the two factors provides two options, which makes the new series providing 4 types of angled holders. Including the one of the traditional pocket holder, in total there are 5 types of holders that are brought into discussion for understanding the ELO growth to show constant lateral growth rates.

All 5 types of holders are listed in **Table 6.1** and are drawn together in **Figure 6.3** as a comparison to reveal details of geometry differences between the types:

- The traditional holder used in the previous experiments is labeled as holder 0, with straight pocket wall meaning the holder has an angle of 90°. The traditional holder 0 has a 1 mm step and the holder width is 6 mm.
- 2. The first angle holder is labeled as holder 1. It has 37° angle and with a 1 mm step. This makes holder 1 the widest holder. This makes holder 1 has distance between the inner

ends of the slopes is 6 mm and the distance between the outer ends of the slopes is 10 mm.

- 3. Holder 2 is an angled holder with 37° angle but without a step. This makes holder 2 has distance between the inner ends of the slopes is 4 mm and the distance between the outer ends of the slopes is 8 mm.
- 4. Holder 3 is an angled holder with 60° angle but without a step. This makes holder 3 the narrowest holder. This makes holder 3 has distance between the inner ends of the slopes is 4 mm and the distance between the outer ends of the slopes is 6 mm. This makes holder 3 narrower than holder 2.
- 5. Holder 4 is an angled holder with 60° angle and with a 1 mm step. This makes holder 4 has distance between the inner ends of the slopes is 6 mm and the distance between the outer ends of the slopes is 8 mm.



Figure 6.3 Angle holder geometries illustration based on the dimensions listed in Table 6.1

All 5 types of holders are set to have 1 mm inner depth and 2.6 mm total depth. The top surface of the substrate is always set at the 1.2 mm level. For recycled seeds thinner than 1 mm, Si inserts with 0.4 mm thickness are used to increase the top surface level to around 1.2 mm. Normally, the recycled seeds or the CVD plates are laser cut and polished to 400 µm thickness and two 0.4 mm Si inserts or PCD inserts are used underneath the sample to lift the sample up to the proper level in the pocket. The sample is lifted up so that the top part is above the inner pocket and the bottom part is below the inner pocket in order to keep the sample centered.

As discussed in Chapter 5 and based on the kinetics of phase change, the distance between the starting edge and the pocket wall (slope) is defined as the initial gap distance which plays an important role in the ELO growth especially in the lateral direction. Such 5 type of holders can provide the initial gap distance from narrow to wide: holder 3 (0.315 mm), holder 2 (0.465 mm),

holder 0 (1.2 mm), holder 4 (1.315 mm), and holder 1 (1.465 mm). The constraining ability can be seen from the space between the sample and the pocket wall. The constraining is considered as high when the space is little. Clearly, in a 2D drawing, the space between ranges as: holder 1 > holder 4 > holder 2 = holder 0 > holder 3. The space provided by holder 0 is considered as a square shape with area of 1 mm x 1.6 mm = 1.6 mm². The space provided by holder 2 is considered as a triangle with area of 2 mm x 1.6 mm /2 = 1.6 mm². The bottom half triangle of the square is considered to have little influence for the constraining of growth, so holder 2 is considered as less constraining than holder 0. This also applies to holder 4 which has a large bottom part of the space that provide little constraining to the growth. And since holder 2 and holder 4 both have around 8 mm outer width of the pocket, the constraining can only be compared with their angles and if they have the step. In this way, holder 4 has similar constraining to holder 2. As a conclusion, the space provided doesn't stand for the constraining ability provided by the holders. The constraining of the holders are considered as: holder 3 > holder 0 > holder 4 \approx holder 2 > holder 1.

6.3 Diamond Growth Using a Series of Angled Holders

CVD diamond growth using the above planned angled holders and the traditional pocket holders are carried out using the 2.45 GHz MPACVD reactor C (DS IV). All growth follows the steps described in Chapter 4 and includes pre-growth sample cleaning, sample holder conditioning, 10 min pre-deposition H_2 plasma etching and deposition. All depositions are conducted at 980 °C at 240 Torr for different growth time. Diamond sample IDs are listed with corresponding holders and growth times in **Table 6.2**.

Holder #	Holder ID	Substrate ID	As Grown ID	Position In Figure 6.4	Separated CVD	Growth Time (h)
0	ACHH	C00	C01	Up left	C02	48
1	SBH01	S33a	S33b	Up right	S33c	24
1	SBH01	04a	04b	Mid right	N/A	24
2	SBH03	05a	05b	Mid left	05c	52.25
3	SBH15	К00	K01	Bottom	N/A	60
				right		
3	SBH15	S33c	S33d	Figure 6.5	N/A	24
4	SBH16	06a	06b	Bottom left	06c	54

 Table 6.2 Diamond growth using angled holders

The samples are named and the suffix changes when the sample changes its shape, such as after growth, laser cut CVD plate, etc. The samples are grown using the MPACVD reactor C (DS4) from 24 hours to 60 hours depending on the growth results. The upper pocket depth is around 1.6 mm, and the vertical growth rate is typical around 25 μ m/hr which makes the longest growth time is around 1.6 mm/ 25 μ m/hr = 64 hours. The CVD plates are typically cut and polished with the top 400 μ m thickness. The side views of the samples grown in the 5 types holders are shown in **Figure 6.4** with the corresponding holder # labeled.



Figure 6.4 Side view pictures of diamond grown in angled holders



Figure 6.5 Top view of S33d and close up views showing inward growth

Other than the side view pictures, the top view of S33d and its close up look at the interface between the PCD growth and the SCD growth are shown in **Figure 6.5**. The S33d is a 24 hr growth using holder 3 which has the narrowest pocket so provides the most constraining environment. Another sample K01 using holder 3 is a 60 hour growth and clearly shows the 3D growth (inward growth and vertical growth) that the surface area shrinks all the time during the growth. The top view of S33d also shows the many growth fronts formed a virtual 45° rotation square though decreasing the surface area. The 100 side directions are shrunk less than the 110 corner directions. The virtual 45° rotation square can be explained in the crystal growth point of view that the crystal starts growing from the center with faster growth rate in the 100 sides and slower growth rates in the 110 corners. To have the virtually square shape, the growth rates of 100 sides R_{100} are required to be $\sqrt{2}$ times of the growth rates of 110 corners R_{110} , which can be expressed as:

$$\frac{R_{100}}{R_{110}} = \sqrt{2}$$

From the top view of S33d, it is clear to tell even the center part of the sample shows the virtual 45° rotation square, but it doesn't always form a square when other growth fronts are observed. This indicates the growth rates ratio between 100 sides and 110 corners may not always be $\sqrt{2}$ in a pocket holder condition, especially when the growth front gets closer to the sample edges and close to the pocket wall. This means the constraining of the pocket holder 3 influences the growth rates from time to time and the shrink in area is because the actual growth rates are decreased due to the constraining.

The side view profiles of the ELO growth are extracted using the side view pictures from **Figure 6.4** using the technique described in Chapter 4, and plotted in **Figure 6.6** for the samples grown using the 5 types of the holders. All nonlinear type of growth are constrained by the pocket holders more or less. Combining the plotted figure and the microscope figures, the ELO growth results can be classified into these situations by the holders:

- Traditional straight wall holder 0 provides smooth growth but with constrain as seen on sample C01.
- Angled holder 1 is too wide that forms PCD growth and barely with no constrain, as seen in sample S33b and 04b.
- Angled holder 2 is an intermediate holder to form smooth growth and provides a linear lateral growth, as seen in sample 05b.
- Angled holder 3 is too narrow that forms inward growth with shrink in area and provides a heavy constrain, as seen in sample K01 and S33d.
- Angled holder 4 is another intermediate holder to form smooth lateral growth with only little constrain during the growth.



Overlay of Lateral growth profiles



Figure 6.6 Growth profiles of CVD diamond using angled holders



Figure 6.7 400 morphology of K01

The most constrained sample K01 is grown for 60 hours with the heavily constrained holder 3. As discussed, the sample has shrunk area after growth and the morphology is constrained to an arched up shaped top surface. Due to the shrink in area, the 400 morphology of samples K01 is plotted only with its small top surface area in **Figure 6.7**, which shows the 400 crystal plane is obviously curved. The mean curvature of the plane is about 2/m, which transferring into around a radius of 0.5 m. The result curvature is considered as very high for a CVD diamond and the reason behind it is considered to be the heavily constraining from the angled pocket holder. The representative 400 XRC peak location map is also shown in **Figure 6.8**, where the 400 crystal plane changes fast in phi=0 direction. The crystal orientation changes in a rate of 0.04 °/mm, also considered high. This corresponds to a radius of $180/\pi/1000/0.04 = 1.43$ m.



Figure 6.8 400 XRC peak location map of K01 in phi=0

The least constrained angled holder is holder 1. Typical growth using holder 1 results in PCD growth on the rims. However, the 400 crystal plane morphology of sample S33b, one of the as grown samples using holder 1, doesn't show obvious curved crystal plane as **Figure 6.9** shows. This means the growth is less constrained and has barely no constraining from the pocket. The 400 crystal plane doesn't show an arched up geometry but still shows a random curvature distribution within the plane.



Figure 6.9 400 morphology of S33b

The crystal plane is less constrained due to the wide angled pocket and the formation of the PCD on the rims. The crystal defects are transferred into those grain boundaries between the PCD grains. Thus the center CVD part of sample S33b maintains good quality and are laser cut into a CVD plate S33c for another regrowth. The XRC peak location map is plotted using the Matlab software in **Figure 6.10**, where it shows the span of peak location is only from 58.11° to 58.145°, which is extremely narrow range for a CVD diamond.



Figure 6.10 400 XRC peak location map for S33b in phi=0

The most and the least constrained growth are discussed above to show the widest holder and the narrowest holder correctly set the two extreme holder geometry conditions so that the intermediate holders are more favored for linear lateral growth. The growth results also indicate the wide pocket makes the CVD diamond forms PCD rims with good quality on the center tile. And it, in the same way, indicates that to grow smooth edges without PCD rims, the as grown ELO CVD diamond will contain certain level of crystal orientation changes and XRC FWHM are increased to make tolerance for growth defects.

Results of the as grown samples from the angled holders showed the growth profiles are either inward, smoothly outward or with PCD according to their morphologies. And they are also either heavily constrained, intermediate constrained, linearly growth, or without constrained. Extraction of the ELO growth profiles and the side view pictures helped in identifying the growth results and it indicates the smooth linear lateral growth is the optimized ELO growth from such series of angled holders. To achieve smooth linear lateral growth, holder 2 and holder 4 are two optimized angled holders. As a comparison between holder 2 and holder 4, holder 2 results in better linear growth as seen in 05b while holder 4 results in a second optimized smooth lateral growth as seen in 06b. Both intermediate growth are discussed in the next chapter.

6.4 Discovery of Constant ELO in Angled Holder

The linear lateral growth using angle holder 2 and the semi-linear lateral growth using angled holder 4 are discussed here. The corresponding samples are 05b in holder 2 and 06b in holder 4. Both samples are considered as smooth linear lateral growth with sample 05b in holder 2 shows better constant lateral growth. The ELO growth profiles are extracted and plotted in **Figure 6.11**, where the lateral gain increases with the thickness gain are plotted.



Figure 6.11 Growth profiles of sample 05b and 06b

Clearly, the ELO growth profile of sample 05b shows a linear profile with a slope of 0.7 at thickness from 0 to 1.2 mm. The profile of sample 06b doesn't show a linear change at all time but presents the largest slope at around 1 at the first half growth duration for thickness from 0 to 0.6 mm. The slope of 06b profile decreases at the second half and both profiles are decreasing after 1.1 mm thick. The larger slope of sample 06b is because the holder 4 has a step so that the sample 06b has a wider lateral growth potential. However, the lateral growth cannot be kept at a high lateral growth rate because it is constrained by the 60° angle pocket. As a comparison, sample 05b is grown in holder 2 without a step at a 37° angle pocket, which makes the sample has a better linear lateral growth. As for the growth rates, the slope value of 1 is corresponded to a round 25 μ m/hr lateral growth rate which equals to the vertical growth rates. The slope value of 0.7 then corresponds to around 17.5 μ m/hr lateral growth rate.



Figure 6.12 Top views and side views of linear ELO samples 05b and 06b

Both top and side views of as grown sample 05b and 06b are shown in **Figure 6.12**. The sample 05b is grown for 52.25 hr and 06b is grown for 54 hr. The clear transparent sample 05b is acid cleaned after growth while 06b shows dark top surface as 06b is not acid cleaned when the picture is taken. Both samples show clear larger area on their top surfaces, however, 05b shows smoother edges but 06b shows more zigzag edges. The zigzag edges are formed due to a little constraining from holder 4, and the zigzag edges always form with a 90° turning which has the same reason with the virtual 45° rotational growth.



Figure 6.13 Representative 400 FWHM and peak location maps of sample 05b



Figure 6.14 400 morphology of sample 05b

The representative 400 XRC peak location map and FWHM map for as grown 05b are plotted in **Figure 6.13**. The most of the as grown diamond center kept the FWHM at a low level under 40". The FWHM of the ELO edges of sample 05b are up to over 200". As a typical CVD diamond,

sample 05b shows 400 XRC peak location from low to high with a range of 0.18° over a distance of 5.1 mm in phi=0 direction from left to right. From this view, the average x-radius is corresponded to about $5.1/1000*180/\pi/0.18 = 1.62$ m. The detailed morphology of 400 crystal plane is show in **Figure 6.14**, where the crystal plane shows an arched up morphology like a typical CVD diamond with a curvature ranges around 0.04 - 0.06 /m. The corresponding radius is actually 16 -25 m. The sample may include irregular crystal plane shapes from location to location.



Figure 6.15 Representative 400 FWHM and peak location maps of sample 06b

The representative 400 XRC peak location map and FWHM map for as grown 06b are plotted in **Figure 6.15**. The most of the as grown diamond center kept the FWHM at a low level under 40". The FWHM of the ELO edges of sample 06b are up to over 200". As a typical CVD diamond, sample 06b shows 400 XRC peak location from low to high with a range of 0.16° over a distance

of 4.8 mm in phi=0 direction from left to right. From this view, the average x-radius is corresponded to about $4.8/1000*180/\pi/0.16 = 1.71$ m. The detailed morphology of 400 crystal plane is show in **Figure 6.16**, where the crystal plane shows an arched up morphology like a typical CVD diamond with a curvature ranges around 0.02 - 0.04 /m. The corresponding radius is actually 25 -50 m. The sample may include irregular crystal plane shapes from location to location.



Figure 6.16 400 morphology of sample 06b

The other 400 XRC peak maps at phi=90°, 180°, and 270° and 113, 111, 220 XRC peak maps are also measured for both samples 05b and 06b.

6.5 Iterative Growth Using Angled Holder



Figure 6.17 Laser cut plan for CVD plates 05c and 06c from sample 05b and 06b

Both samples 05b and 06b are considered as good linear lateral growth using angled holder. The samples are good sources for considering to be laser cut into CVD plates for iterative regrowth using a regrowth angled pocket holder. The laser cut plan for both samples are shown in **Figure 6.17** with the top 400 um thick CVD plates are cut and polished on both their top and back surfaces.



Figure 6.18 Top views and side views of as polished CVD 05c and 06c

The edges of both samples 05b and 06b are grown lateral linearly. To achieve a good shape of CVD plate, the top edges around 100 - 200 um thick part are laser cut into regular sides for both sample 05b and 06b as seen in **Figure 6.18** in order to provide good growth qualities. The lower part of the edges remain lateral linear morphology. The laser cut and both sides polished samples are named as 05c and 06c with 8 sides as an octagonal shape with the diagonal distance are set to be around 4.0 - 4.4 mm. As the octagonal shape is cut for both samples, the 110 edges are cut to emerge with about 1.2 - 1.8 mm length whereas the 100 edges are 1.8 - 2.5 mm length.



Figure 6.19 Octagonal shape angled holder for iterative growth

The regrowth angled pocket holder is designed as **Figure 6.19** illustrates to carry out he iterative regrowth using CVD plates 05c and 06c. The design of the regrowth sample holder follows the principle used for designing holder 2. The initial gap distance are key values to consider, and holder 2 provides a 0.465 mm initial gap distance with inner pocket width of 4.0 mm at an angle of 37°. Using the same principle, the regrowth sample holder uses the inner pocket width of 4.9 mm with the regular octagonal shape 37° angled holder. The total depth is also set at 2.6 mm which means other conditions are kept the same with holder 2. This way, the outer width of the pocket is up to 9.2 mm. The same iterative regrowth angled holder is used for the growth on both 05c and 06c.



Figure 6.20 Example growth conditions and real time images for growth of 05c.

Sample 05c is grown for 60 hr into sample 05d. The temperature changes and the microwave power changes over time are recorded in **Figure 6.20** along with two real time growth pictures at the starting stage and the finishing stage during the growth. The temperature illustrates a typical behavior fluctuating up and down and the change over time is more linearly since the sample is grown using an angled holder. The temperature raises over time while the power is set 10 W lower when the temperature hits the upper limit 990°C and drops 6 °C at the starting point and develops to drop 16°C at the finishing stage. The reason is described in the previous chapters that the lower the power is, the bigger the influence in temperature is. On the other hand, the power also drops more linearly but not exponentially since the angled pocket is used. The conclusion is

drawn here that the geometry of the pocket holder influences the growth behavior and further influences the temperature changes and the power changes. It is also drawn that the increasing of the temperature indicates the synthesizing of single crystal diamond. The temperature increases linearly at the finishing stage also indicates that it keeps growing single crystalline from the start to the end. The linear lateral growth caused by the proper pocket boundary conditions provided by the angle pocket holder causes the linear change in both temperature and power over time.

In addition to the temperature and power, the real time growth photos show the 100 direction is growing laterally obviously faster than the 110 directions. This is the reason causing the virtual 45° rotational growth and as the growth continues the 100 edges is shorter but the 110 edges are longer.

The regrowth of sample 05c is carried out for 60 hr to 05d, which makes the total growth time for the sample is up to 112.25 hr. The regrowth of sample 06c is also carried out for 60 hr to 06d, which makes the total growth time for the sample is up to 114 hr. The top and bottom views of both 05d and 06d are shown in **Figure 6.21** and **Figure 6.22**. Just as the real time photos showed, the single crystal diamond grows at a faster lateral rate in 100 direction up to around 20.4 μ m/hr for 05d, and the 110 lateral growth rate is also up to 13.3 μ m/hr. The 100 direction is



Figure 6.21 As grown sample 05d



Figure 6.22 As grown sample 06d

grown to a final 6.55 mm size which makes it becomes the diagonal of the final grown shape. The 110 direction is grown to a final 5.7 mm or so size, which makes it becomes the regular side of the as grow sample 05d. The growth of sample 06c to 06d experienced the same scenario where it approves the iterative angled holder's validity. The upside down view images of 06d shows the 100 direction lateral growth rate is up to 18 μ m/hr and the 110 direction lateral growth rate is up to 12 μ m/hr. The final size of 06d is around 6.45 mm in 100 direction which is its diagonal and 5.65 mm in 110 direction which is its side for the final morphology. The growth rate ratios for the above mentioned values are 1.53 and 1.5, respectively. The values are a little bigger than $\sqrt{2}$, which makes the sample starting to show a regular square shape with a 45° rotation from the original seeds.

The XRC mapping results for sample 05d as a representative result is shown in **Figure 6.23**. The results show the phi=0 400 FWHM and 111, 220, and 113 FWHM maps for 05d. The measured surface is grown using MPACVD reactor C for 112.25 hr. The center region keeps low in FWHM with 0.01° from 400, 0.015° for 111, 0.01° for 220 and 0.005° for 113. Compared to original FWHM values measured on the HPHT seeds, the center region is considered to keep the good qualities while the 111 qualities are a little worse because the most close pack direction is also the direction to contain defects. The highest FWHM values are often at the edges where the crystal has the most defects. 400 FWHM is up to 0.632°, 220 FWHM is up to 0.786°, 111 and 113 FWHM are even up to 1°. It can be seen that although the 400 crystal plane may have wide FWHM at the original HPHT seed, the as grown surface quality is maintained better in 400 direction. In all XRC FWHM maps, it is obvious that the ELO grown region typically has wider

XRC peaks which make up around half of the measured points, and also meaning half of the as grown area.



Figure 6.23 FWHM maps of diamond 400, 111, 220, and 113 XRC peaks of sample 05d

Both 400 morphology for 05d and 06d are plotted in **Figure 6.24** and **Figure 6.25**. The curvatures of the samples 05d and 06d are range typically between 1 - 4 /m which corresponds to 0.25 - 1 m radius. Such curved plane are quite curved for CVD diamond. This can see the CVD diamond are constrained to be more curved over time. Both morphologies are arched up shapes.



Figure 6.24 400 morphology of 05d



Figure 6.25 400 morphology of 06d



06e



Figure 6.26 CVD plates 05e and 06e

The CVD plates are laser cut and polished from 05d and 06d into 05e and 06e as shown in **Figure 6.26**. The thicknesses are cut to be 400 um and the shapes are clearly 45° rotational square compared to their original HPHT seeds. The 110 sides are obviously longer and dominate
the sides which will end up to be the side of the square shape. The 100 sides are shorter and will end up being the corner of the square shape.

6.6 Angled Holder Summary

Holder #	Angle (°)	Step	Width (mm)	Lateral Growth
0	90	у	6	Smooth + constrain
1	37	у	6;10	PCD + no constrain
2	37	n	4;8	Smooth + linear lateral growth
3	60	n	4;6	Shrink + heavy constrain
4	60	у	6;8	Smooth + less constrain
Regrowth	37	n	4.9:9.2	Smooth + linear lateral growth

Table 6.3 Categories of as grown CVD diamond morphology using angled holders



Figure 6.27 Linear lateral growth can be achieved by using properly angled holder

In a summary, the angled holders listed in **Table 6.3** are designed to range from narrow to wide as for realizing linear lateral growth. The linear grown samples are cut into CVD plates for regrowth in further approving linear lateral growth to achieve constant lateral growth rates.

The lateral growth are categorized into several types: smooth with constraining, PCD without constraining, smooth with linear lateral growth, shrink in area with heavy constraining, and smooth with less constraining. The smooth growth with linear lateral growth samples, as shown in **Figure 6.27**, are cut into CVD plates for iterative linear lateral regrowth of larger area single crystal diamond samples.



Figure 6.28 Selected lateral growth profiles of linear ELO compared with exponential ELO

The initial lateral gain over time as plotted in **Figure 6.28** indicates the lateral growth rates tend to be constant during the growth which differentiate to the exponential decay growth from the traditional sample holders. The linear shape of lateral growth are also influenced by the holder geometries which further influence the temperature and microwave power setting during the growth. The temperature and the power, just like the ELO growth profile, changes tending to linear over time, but is not exponentially seen from the ones in traditional sample holders. The 100 direction growth rates are around 18 -20 um/hr and the 110 direction lateral growth rates are around 12 - 13 um/hr. The fast 100 direction rates make the final sample showing a square that has virtual 45 rotational growth with 100 directions in the corner ad 110 directions in the sides.

The final size of the project provides the 100 length (diagonal of final shape) to be around 6.7 mm, and the 110 length (side of the final shape) to be around 5.75 mm. CVD plates are cut from the as grown large area single crystal samples.



Figure 6.29 XRC measurement illustration on different locations on the same sample

Sample ID	Average 400 curvature 1/m	Corresponding Holder Type
HPHT 05a	-0.0160	Representative Substrate
S33b	-0.1083	Angled
S33d	0.0867	Angled
K01	1.1838	Angled
04b	0.0290	Angled
C01	0.4996	Traditional
05b	0.0207	Angled
06b	0.0209	Angled
ACH3	0.0812	Traditional
05d	0.4551	Angled
06d	0.7984	Angled

Table 6.4 Diamond 400 crystal plane single value mean curvature

Diamond XRC mapping techniques are used to show the crystal planes properties including peak location maps and FWHM maps for 400, 111, 113, and 220 peaks. The peaks are measured for 14 by 14 points to 23 by 23 points depending on the size of the samples. The peak location varies from point to point as well as the FWHM, as shown in **Figure 6.29**. Data are analyzed by Matlab software and Python software for massive data processing and visualizations, along with the use of Rigaku SmartLab Studio II software. The FWHM are increased especially in the ELO growth region over time to up to almost 1° but still present the center region with low FWHM around 0.01° . Typical CVD diamond shows arched up 400 crystal plane morphology with around 1 - 50m as the radius as selected curvatures are listed in **Table 6.4**. The 400 crystal plane is more curved as the sample is grown longer time. Optical images and quantitative birefringence pictures are taken to show the internal structural defects before and after the growth. The laser cut CVD plates are used as iterative regrowth CVD substrates and results approved the iterative growth method is promising in achieving constant lateral growth rates in the 2D (both 100 and 110 directions) for the top surfaces, meaning the area is enlarged iteratively by using angled holders. Combined with the constant vertical growth model, such designated angled holders are used in keep growing large area single crystal diamond as constant growth rates in 3D. The proposed angled holders have such breakthrough over the limitation observed from historical exponential decay growth mode. The background of the single crystal growth in the pocket is under support with the kinetics of phase change.

Chapter 7

Diamond Growth Results Analysis and Conclusions

7.1 Kinetics of Phase Change in Sample Holder Designs

The CVD diamonds are grown using MPACVD reactor B and C at MSU with pocket holders. The pocket holders are firstly used years ago while the CVD growth morphologies are less analyzed. A historic set of ACH samples that are grown with traditional straight walled sample holders at reactor C a decade ago, are firstly analyzed in their growth profiles over time in this project. The ELO growth results of the ACH samples are extracted from their top surface area evolution and the results indicated the ELO growth follows 1st order exponential decay growth function with traditional pocket holders. The exponential decay growth models are applied based on the theory of kinetics of phase change proposed by Avrami 80 years ago. The 1st order exponential decay growth model is derived to describe the ELO growth within traditional pocket holders. The new sample holders called angled sample holders are designed to weaken the limitation form the traditional pocket, as shown in **Figure 7.1**, and provide better optimized space within the pocket for CVD diamond to grow laterally larger. Based on the application of kinetics of phase change, the new designed angled holders are distributed from narrow to wide and the intermediate appropriate angled holder with 37° angled pocket resulted in smooth linear lateral outgrowth with constant lateral growth rates. The series of the samples grown in MAPCVD also proved the results by regrowth using the sample angle.

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Figure 7.1 Holder designs and corresponding CVD diamonds based on kinetics of phase change

7.2 Diamond Growth Using Traditional and Angled Pocket Holders

Angled pocket holders are designed in this dissertation to maintain constant lateral growth rates for ELO CVD diamond growth. The growth profiles are discussed based on the holder geometries designed based on the theory of kinetics of phase change. Other than as grown CVD diamond morphologies, the CVD reactor growth conditions are also discussed, as **Figure 7.2**



Figure 7.2 Temperatures and power changes over time

illustrates the difference between temperatures and microwave power in traditional holders and angled pocket holders. Results indicated temperature increases in a slower exponentially mode and the power decreases in the same mode to maintain the temperature in a set range. The CVD diamond growth in traditional pocket holder is suppressed in its morphology by the holder and it suggested the increasing in temperature stands for the growth of CVD diamond.

Based on the above suggestion, the constant increasing of temperature and its power decreasing to maintain the temperature is also constantly for angled pocket holders. The correspondence here shows the constant lateral growth rates are caused by the angle holders which are corresponding to the constant change in temperature and the microwave power. The results also indicate the growth of single crystalline sample corresponds to the increasing of temperature, and the growth of partial single crystal and partial polycrystalline sample corresponds to rough flat or fluctuation change temperatures. The scientific reason behind the findings are considered to be that the forming of diamond bonds between carbon atoms are releasing energies so that the temperature changes are linked to the formation of single crystal CVD diamonds. In such a conclusion, the constant forming of diamond corresponds to the constant change in temperature, which explains the linear diamond growth in angled pocket holders have constant lateral growth rates and corresponds to constant temperature changes.

7.3 Characterization on CVD Diamonds

Other than as grown CVD diamond morphology and growth conditions analysis, the top surfaces of as grown samples are measured using XRC mapping technique for revealing the crystal structural properties.



Figure 7.3 Overview of XRC 400 morphology of CVD diamonds

Table 7.1 Average and Standard Deviation FWHM (°) of CVD diamonds grown using pocket
holders	

Holder	Sample ID	400	400	113	113	111	111	220	220
#		Avg	StD	Avg	StD	Avg	StD	Avg	StD
-	HPHT	0.008544	0.00112	0.006544	0.00112	0.006819	0.001717	-	-
	05a								
0	C01	0.048941	0.045121	-	-	-	-	-	-
0'	ACH3	0.05668	0.042403	-	-	-	-	-	-
1	S33b								
1	04b	0.02663	0.014424	0.030102	0.014405	0.04225	0.025572	0.033232	0.020091
2	05b	0.057161	0.059521	0.050252	0.035853	0.107868	0.092188	0.089056	0.088549
3	K01	0.097196	0.084575	-	-	-	-	-	-
3	S33d	0.039705	0.040344	-	-	-	-	-	-
4	06b	0.055429	0.05046	0.057474	0.040674	0.146718	0.155236	0.103124	0.124667
Re	05d	0.064494	0.070527	0.096654	0.168942	0.22533	0.234299	0.141051	0.150907
Re	06d	0.10251	0.081608	0.104425	0.091134	0.310603	0.269911	0.238334	0.228557

Out of the results, the peak location maps and FWHM maps are achieved. The 400 crystal plane morphologies are also achieved based on the peak location maps, as shown in **Figure 7.3**. Selected 400 morphologies are compared together in the same coordinate axes. The morphologies of 400 crystal planes of as grown samples selected from pure HPHT substrates to iterative regrown as grown CVD diamonds have shown the change over time in their curvature distributions. As HPHT samples show pure flat 400 crystal planes but as the growth duration increases, the morphologies of 400 crystal plane is more curved.

The average XRC peak FWHM for 400, 113, 111, and 220 are listed in **Table 7.1** with their standard deviation values as a comprehensive overview of the as grown CVD diamond qualities. The selected samples are between HPHT substrates and over 110+ hr grown CVD samples.



Figure 7.4 Average FWHM of XRC peaks over time

The FWHM values are plotted over corresponded as grown durations as shown in **Figure 7.4**, with the location being the average values and the size being the standard deviation values. The FWHM values are increased over time since more structural imperfections are formed. The standard deviation values are also increased over time as the areas are larger for as grown samples. The 111 peaks are increased the most in FWHM since the 111 planes are the most packed planes which are influenced the most by the formed defects in the crystal structures. The

220 planes FWHM are increased faster than 113 planes. The 400 planes are increased slowly in FWHM over time which corresponds to the vertical growing directions.

7.4 Research Conclusions

The major scientific findings and conclusions of this dissertation project of lateral outgrowth towards large area single crystal CVD diamond using pocket holders are briefly stated in this section. The research activities for this dissertation mainly includes but not limited to: **1**. Scientific derivation of diamond growth morphologies using pocket holders, **2**. Designing pocket holders and carrying out diamond growth, **3**. Diamond characterizations including microscopy imaging, XRC measurements, birefringence imaging, **4**. Data acquisition using specified software and data analysis, and **5**. Feedbacks to CVD diamond growth.

Core findings are discussed briefly as follows. The theory of kinetics of phase change is used in describing how CVD diamond is grown in a pocket holder, and the 1st order exponential decay growth is illustrated using traditional straight walled pocket holders. The angled holders are thus developed and designed in series to find intermediate appropriate angled holders allow constant lateral growth which resulted in linear ELO growth. ELO growth profiles are imaged using side view pictures under microscopes which are used to collect growth data and fit the ELO growth model. Many types of measurements are conducted to understand the growth quality. The optical cross polar birefringence images and quantitative birefringence pictures are taken to reveal the internal imperfections of the diamond structures. The XRC mapping measurements resulted 400, 111, 113, and 220 peak location maps and FWHM maps which can bring crystal structure

qualities and misalignments. The software made based on Matlab and Python worked for collecting data and processing peak location and FWHM maps, and 400 crystal plane morphologies. Curvature values and curvature maps are also acquired to show crystal plane morphology changes over the space. FWHM and curvature values are found larger over longer duration of diamond growth. All results discussed helped the iterative regrowth of CVD diamond using angled pocket holders to achieve larger CVD diamond plates at constant lateral and vertical growth rates.

In a conclusion, the dissertation project made an effort in searching for an optimized way to grow larger size single crystal CVD diamond using angled pocket holders and proposed to keep the growth activity optimized over time.

Chapter 8

Summary, Accomplishments and Future Scope

8.1 Summary

This dissertation project uses many of the previous CVD diamond growth findings as the background to establish certain fundamental basics and complete the CVD diamond growth strategies especially in growing larger area single crystal diamond using the traditional pocket holders and angled pocket holders geometries via MPACVD technique. The CVD diamond growth processes are enhanced in a semi-automatically method for more steady long duration growth with more user friendly controlling and monitoring. Many specific growth conditions and sample holder dimensions are made optimal for growing diamonds. The progresses made through this dissertation work is described in a roadmap shown in **Figure 8.1**. The previous observed and made progresses are illustrated as initial growth temperatures and pressures at the bottom middle position describing the research progresses made by Lu, Gu, Nad, and A. Charris, etc. The initial effort in building up the advanced CVD, working towards the optimal growth conditions of temperature, power and electromagnetic types, and using of traditional pocket holders are the base of this dissertation work. This dissertation made certain progress in optimizing pocket holder geometries and used angled sample holders for growing larger area single crystal diamonds, as shown at the middle level position in the roadmap. The other conditions maybe remain unknown or unclear so far for scientists and engineers to develop further advanced research topics in realizing the ultimate goal of keep growing large size and

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high quality single crystal diamonds. Thus, the diamond growth roadmap can direct the researchers in conducting the related research activities.



Figure 8.1 CVD diamond growth roadmap

8.2 Accomplishments

CVD diamond growth using pocket holders have progressed in many specific areas such that larger area single crystal CVD diamond plates are finally achieved after optimized epitaxial lateral outgrowth using updated angled pocket holders. Scientific understanding and mathematical derivations are firstly involved when designing for making progresses in growing diamond in both traditional and advanced pocket holders. The measurements techniques are established for standardizing the explanations of diamond crystal structural data. XRD, offcut measurements and the XRC mapping techniques are built for understanding the diamond crystal properties, quantitatively. The crystal morphologies are also established, and also analyzed quantitatively, especially in their 400 crystal plane morphologies. The internal structure are also imaged using optical microscopes and quantitative birefringence to collect quantitative data.



Figure 8.2 Research cycle

Beyond the above single research activities, the completed research conducting cycle is established in scientific understanding and derivation, diamond growth reactor design, diamond characterization, data collection in database and analysis, and feedbacks for level up, as shown in **Figure 8.2**. As more projects are emerged using more reactors or other techniques, the research conducting cycle can be enlarged and updated for optimal level up.

8.3 Future Scope

The following recommendations are potential projects based on the current results presented in this dissertation:

- An overall goal to find the limitation size of CVD diamond sample in a specific reactor (DS4 for example) and work beyond that.
- Keep tracking the crystal qualities and internal structure over time for iterative regrown diamond samples using angled holders no matter if the sample is grown from HPHT substrates or CVD plates.
- 3. Expand the using of angled holders, such as in other reactors, indifferent angled geometries, etc.
- Keep tracking the crystal plane morphologies over time as crystal planes differ from physical bulk surfaces
- 5. Find a way to minimize the curved top plane after growth, for example, flip over the as grown sample and grow from the bottom when the crystal plane shows an opposite curvature.

The suggested potential work are listed but not limited to the above bullet points.

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