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LOW-TEMPERATURE DEPOSITION OF
TRANSPARENT DIAMOND FILMS WITH A
MICROWAVE CAVITY PLASMA REACTOR

presented by

Michael J. Ulczynski

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Electrical Eng

D. K. Richardson
Major professor

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**LOW-TEMPERATURE DEPOSITION OF
TRANSPARENT DIAMOND FILMS WITH A
MICROWAVE CAVITY PLASMA REACTOR**

VOLUME I

By

Michael J. Ulczynski

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

DOCTOR OF PHILOSOPHY

Department of Electrical Engineering

1998

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ABSTRACT
LOW-TEMPERATURE DEPOSITION OF
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By

Michael J. Ulczynski

Low-temperature diamond deposition with Microwave Cavity Plasma Reactor (MCPR) technology was investigated for application to temperature sensitive substrates. The substrate temperature during most CVD diamond deposition processes is typically greater than 600 C; however, there are some applications where temperature sensitive materials are used and the deposition temperature must be maintained below 550 C. These applications include materials like boro-silicate glass, which has a relatively low strain-point temperature, and integrated circuits that contain low melting point components. Experiments were conducted in three areas. The first area was MCPR development, the second was benchmark deposition and characterization of diamond films on silicon substrates and the third was deposition and characterization of diamond films on boro-silicate glass substrates.

MCPR development included an investigation of various MCPR configurations that were designed and adapted for uniform, low-temperature diamond deposition over areas as large as 80-cm². Reactors were investigated with end-feed microwave excitation and side-feed microwave excitation for maximum deposition area and uniformity. Various substrate receptor configurations were also investigated including a substrate heater and cooler. From these investigations, deposition parameters such as substrate temperature,

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deposition rate, deposition area and deposition uniformity were characterized.

The benchmark silicon diamond deposition experiments were conducted for comparison to previous high temperature, >550 C, MCPR research and growth models. Here deposition results such as deposition rate and film quality were compared with applications of diamond growth models by Harris-Goodwin and Bachmann. Additionally, characterization experiments were conducted to investigate film attributes that are critical to optical applications, such as film surface roughness and deposition uniformity. Included as variables in these benchmark experiments were various mixtures of H₂, CO₂ and CH₄ gases and two substrate pre-treatment methods, which were photo-resist seeding and diamond powder scratch seeding. The typical operating range of the MCPR were gas pressures in the range of 5 to 15 torr and incident microwave power levels in the range of 300 Watts to 1.2 KW. Typical deposition rates at approximately 470 C were in the range of 20 nm/hr to 100 nm/hr. Uniform deposition on the order of $\pm 10\%$ was achieved over areas as large as approximately 45 cm⁻²

The focus of diamond deposition on boro-silicate glass substrates was to investigate deposition parameters that influence optical diamond film characteristics such as transmission and adhesion. Two loss mechanisms for optical transmission through poly-crystalline diamond films are bulk absorption and surface scattering, which both tend to have inverse λ dependencies. Measured optical transmission and fitted rms surface roughness data indicate that diamond films that have a thickness on the order of 1 to 2- μ m can be deposited with transmission as high as 70% at 400-nm. Adhesion was somewhat problematic for films with a thickness of > 2 μ m, many of them had a tendency to peel. Many films with a thickness under 2 μ m have exhibited long term adhesion over several years.

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INTRODUCTION

1.1 Motivation

Since the early 1980's researchers throughout the world have been pursuing applications and deposition processes for thin polycrystalline diamond films. The motivation for this research effort is driven by diamond's unique physical properties of extreme hardness, chemical resistance, high thermal conductivity, and wide spectral optical transmission range. Predictions for applications include (1) mechanical functions such as wear resistant coatings for cutting tools, and thermal sinks, (2) electronic devices such as diodes, transistors and electron emitters, and (3) optically transparent coatings that protect components exposed to chemically harsh environments, or provide transmission for wavelengths varying between ultraviolet and infrared.

Over the past two decades, a variety of chemical vapor deposition processes have been developed that produce polycrystalline diamond from a low concentration mixture of methane in hydrogen. Other gases such as oxygen, carbon dioxide, and some halogens are sometimes added to enhance the growth rate and the properties of the deposited films, but a simple 1% methane in hydrogen mixture produces high quality diamond in most processes. Although CVD processes do not produce single crystal diamond films on non-diamond substrate yet, the properties of deposited polycrystalline films are quite good. In

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Some diamond film applications have little constraints on the deposition process; however, others require uniform, low-temperature and large area deposition. For example an optical coating that protects an optical component from a harsh environment must be deposited uniformly, have minimal surface roughness and low impurity content. These characteristics are necessary for the product to have high transmission in the spectrum from ultra-violet light to long wavelength infrared. Deposition temperature is also a critical parameter when coating optical components. The softening point temperature of most optical materials is well below the typical 1000 C deposition temperature of high deposition rate processes. Furthermore, the thermal expansion of optical materials is not well matched with that of diamond. Together these properties create internal stresses in deposited diamond films which lead to cracking and adhesion problems. To reduce the probability of delamination of the deposited film, it is necessary to reduce the deposition temperature as low as possible without sacrificing the quality of the film. Unfortunately, the rate of film deposition is often times strongly proportional to the substrate temperature. As a result, lower deposition temperatures yield lower diamond deposition rates. Since the various CVD processes are so different, it follows that several different approaches to low temperature deposition might be employed. Cooling the substrate with a chilled liquid is a technique that can be applied to almost any CVD process. Lowering the process gas pressure is another universal technique for lowering the substrate temperature. Both of these techniques reduce the deposition rate of diamond and usually change the properties of the film such as morphology. For processes that use microwave energy to activate the gas-

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1.2 Research Objectives

The primary objective of this investigation was to advance the current MCPR diamond deposition apparatus and methods toward the goal of achieving diamond deposition under low pressure and low temperature conditions. A practical importance of this goal lies in the fact that deposition of diamond on temperature-sensitive substrates offers the possibility of considerably expanding the applications of diamond coatings. The investigation is also expected to provide new information on the operating properties of the MCPR over an expanded range of parameter space and to provide insight on key limitations associated with low temperature and low pressure diamond growth. The primary goal had several related sub-objectives including (1) an experimental investigation at low pressures of performance limitations of MCPR designs which existed prior to the beginning of this research, (2) development of an apparatus to provide improved diamond deposition under these conditions, (3) an experimental investigation of diamond film quality grown under various low pressure and low temperature conditions, (4) comparison of growth results with established models, (5) application of the low-temperature diamond deposition processes to temperature sensitive substrates, including boro-silicate glass materials and (6) and optical characterization of the coatings on the glass substrates.

In order to perform these experiments, the design and assembly of a deposition system was required. Consequently, as a first step a semi-automated MCPR diamond deposition system was constructed. The machine is controllable by a Visual C++ program.

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The notable requirements of the apparatus are (1) adapt to both 4" and 5" MCPR's, (2) provide a substrate bias, a cooling stage and a heating stage, (3) be able to supply and control up to 4 process gases simultaneously, (4) operate in a gas pressure range of 1 torr to 50 torr, and (5) provide microwave energy up to 1 KW. Using this system, existing Microwave Cavity Plasma Reactors were operated at low pressures and low substrate temperatures, which were generally less than 15 torr and 550 C. Various MCPR designs were investigated for plasma stability and deposition uniformity, and design modifications were developed as were necessary. Deposition enhancing techniques such as substrate temperature control and bias were employed to determine their contribution towards achieving adherent, uniform films. The effect of a dc bias was explored in both MCPR's; however, the substrate temperature control was limited to the 5" reactor because of size constraints.

A variety of operating conditions including power, pressure, gas mixtures and substrate temperatures were investigated and mapped to the attributes of film growth rate, film uniformity and film quality. The film growth rate was measured by two methods (1) direct weight gain and (2) minimum and maximum in optical transmission. The film uniformity was measured by color fringes. The deposition rates were compared to applications of growth models including a model by Harris and Goodwin, and one by Bachmann. These comparisons were focused on investigating the chief limitations to growth rate at low pressure and temperature. Finally, film quality was measured by Raman analysis on selected samples.

It is helpful to have goals which are application driven. The primary application specific goal of this research was to deposit intact, adhesive and transparent diamond films on borosilicate glass substrates with a high degree of uniformity over diameters between 2

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inches and 4 inches. A secondary application specific goal was to deposit diamond films on metallized silicon IC devices. In terms of glass substrates, the deposition processes were optimized to minimize the surface roughness of the deposited films.

The surface roughness of diamond films on glass was measured and the contribution of the surface roughness to transmission, in terms of scattering, was quantized. Hence the optical transmission of the diamond films deposited on glass was maximized. In terms of the IC substrates, the objective was to deposit diamond films on silicon substrates that were processed to contain simple devices and coated with aluminum metallization. Here, the deposition process must not harm the aluminum or the underlying devices. The above mentioned processes were utilized with both photo-resist and abrasion seeding to identify which methods are best for depositing diamond on processed IC substrates.

1.3 Dissertation Outline

Beyond this introductory chapter, this dissertation is separated into three areas, which are (1) a review of relevant literature, (2) a description of experimental methods, and (3) the results of low temperature diamond deposition experiments. The first section, a review of relevant literature, is contained within chapter 2. It includes literature pertaining to CVD processes, techniques for controlling the substrate temperature in a CVD process, analysis and models of gas-phase chemistry, and methods of substrate pre-treatment. There is also an overview of the MCPR concept, which is the method of diamond deposition apparatus used for this work. The second topic, a description of experimental methods, is mostly detailed in chapter 3. The subsections of this chapter include a description of the experimental apparatus used for this research, the methods of depositing diamond

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films with the apparatus, and how the characteristics of the deposited films were measured. The last section of this dissertation, the results of diamond deposition experiments, is divided between chapters 4, 5 and 6. Chapter 4 summarizes 9 different MCPR configurations that were investigated during this dissertation. They include side-feed and end-feed configurations, as well as numerous substrate receptors including a heated receptor, a cooled receptor and a dc biased receptor among others. Chapter 5 summarizes benchmark diamond deposition experiments that were conducted with silicon substrates. These discussions include comparisons of growth rates and film quality to growth models, deposition results with a liquid cooled substrate receptor, deposition results with a dc biased substrate receptor, and observations of film surface roughness, uniformity and surface area. Chapter 6 summarizes the deposition, optical characterization and observations of adhesion of diamond films that were deposited on boro-silicate glass substrates.

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Chapter 2

A Review of Diamond Deposition Processes and Models

2.1 The MCPR Concept

The Microwave Cavity Plasma Reactor (MCPR) is a machine that was developed at Michigan State University by Asmussen, et al., for plasma, materials processing. In the MCPR, a weakly ionized plasma that contains electrons, ions, and radicals is created by combining input gases and electromagnetic energy. The MCPR plasma is created inside a discharge processing chamber at sub-atmospheric pressures. Like other plasma processing machines, the discharge chemistry of the MCPR provides a means of processing materials that conventional non-plasma processes can not achieve.

A notable feature of the MCPR family of plasma sources is that they generate uniform, large area, high density plasmas over a wide range of pressures. Charge densities between 10^{11} and 10^{13} cm^{-3} are sustained over a gas pressure range from a few milli-torr to greater than 100 torr^[1]. Furthermore, the MCPR plasma sources typically generate low energy ions, thus reducing surface damage to substrates. These high density plasma sources also produce copious radical flux densities from a variety of input gases. The large area, uniform generation of radicals from feed gases such as H_2 , CH_4 , CO_2 , and others make the MCPR an ideal machine for a variety of industrial applications. Research indicates that the MCPR can be a competitive machine for applications such as anisotropic

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etching of silicon^{[2][3]} and silicon dioxide^[4], uniform deposition of oxides on silicon^{[5][6]} and uniform deposition of polycrystalline diamond films on a variety of substrates^{[7][8]}. Currently, the MCPR is in use as a commercial diamond coating machine at Norton Diamond Films Inc. in Northboro, MA.

Plasma processes in a MCPR can be divided into three groups (1) low pressure, (2) moderate pressure, and (3) high pressure. In the low pressure MCPR, materials are processed down stream from the plasma. Such a configuration is necessary for the formation of a large area uniform process. The gas pressure in these processes is typically in the range of a few milli-torr to 1 torr. Hence, the diffusion lengths are long enough to reach the down stream material substrate. The pressure range of the moderate pressure MCPR ranges from 1 torr to 150 torr. In these processes, the diffusion length of necessary radicals is on the order of a cm. To avoid concerns with diffusion losses in the moderate pressure MCPR, the material substrate is located in direct contact with the plasma discharge. This ensures that processing takes place where the generated ion and radical densities are at a maximum.

Diamond deposition for this dissertation was performed with versions of the moderate pressure MCPR. Hence further details summarizing the operation of this type of MCPR is provided in the next few sections.

2.1.1 Theory of the Moderate Pressure MCPR

Substrate processing in the moderate pressure MCPR takes place with the substrate in direct contact with the plasma. The primary components of the moderate pressure MCPR are (1) a microwave power supply, (2) an internally tuned microwave cavity appli-

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cator, and (3) a discharge processing chamber. The plasma source is made up of the cavity applicator and the discharge processing chamber (figure 2.1). The MCPR combines input gases and electromagnetic energy to produce electrons, ions and radicals inside the discharge processing chamber.

The power supply circuit is summarized of a microwave power supply and a transmission line. The microwave power supply is typically a commercial unit with an operating frequency of either 915 MHz or 2.45 GHz. The transmission line transports microwave energy from the microwave power supply to the cavity applicator. It can be any one of various waveguides or coaxial cables.

The cavity applicator is a circular cylindrical microwave resonator that is simply described as a metallic (typically brass) tube that is terminated at both ends to form a resonating electromagnetic cavity. Inside the brass cavity is a discharge chamber where the plasma is generated and materials processing takes place. The discharge chamber is an evacuated volume region that is located inside of a quartz dome bell jar. The quartz dome bell jar is located in the centered of the bottom of the cavity. The cavity assembly is designed such that process gases can be flowed into the quartz bell jar by a precision flow system and then pumped away by a mechanical vacuum pump.

Microwave energy is coupled into the brass cavity from the transmission line via a coupling probe. The coupling probe projects into the cavity at the top end. It is located in the center of the top end of the cavity, opposite to the discharge chamber and longitudinal to the axis of the brass tube. The length that the coupling probe projects into the cavity is an adjustable parameter of the cavity applicator. The location of the end plate of the cavity that the coupling probe projects through is also an adjustable variable of the cavity



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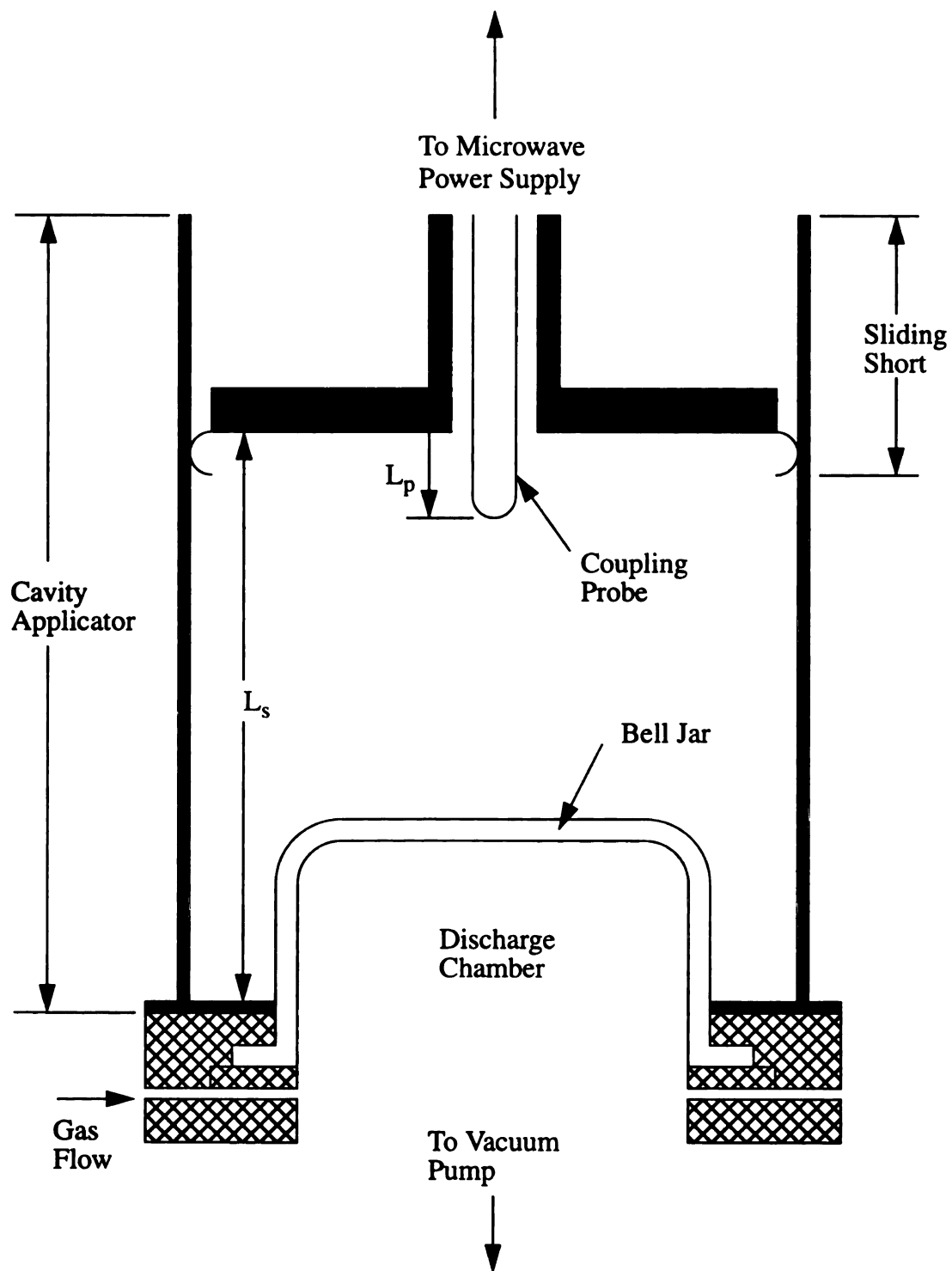


Figure 2.1 Cross-section of the Moderate Pressure MCPR.

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applicator. The movable end plate is named the sliding short. The sliding short serves to vary the overall length of the brass cavity.

During operation, a plasma is induced in the discharge chamber by electromagnetic energy that is coupled into the cavity. This energy is focused into a specific electromagnetic cavity resonating mode. The mode is excited inside the cavity by adjusting the length of the coupling probe and the location of the sliding short. Together these two parameters make up the internal tuning features of the MCPR cavity applicator. Besides focusing the microwave energy into a specific electromagnetic resonance mode, the sliding short and coupling probe also serve to match the load of the induced plasmas to that of the transmission line between the coupling probe and the power supply. For diamond film deposition in the moderate pressure MCPR, the cavity resonator is typically tuned to a TM_{01n} resonant mode. These modes have an axial symmetry that is conducive for creating a uniform plasma throughout the discharge chamber.

2.1.2 TM_{01n} Modes of the MCPR

In the moderate pressure MCPR, the resonating electromagnetic fields are generally tuned to a single TM_{01n} mode. For analysis of the electromagnetic fields that are present in the MCPR, the discharge loaded cavity applicator can be viewed as a loaded microwave cavity. To further simplify the analysis, the fields of an ideal lossless unloaded cavity are compared to those of the MCPR without loss of generality.

In an ideal lossless circular cavity with a cross section such as that in figure 2.2 there is an infinite set of resonant frequencies at which a particular standing wave pattern of electric and magnetic fields can be induced. In this empty lossless circular cavity of

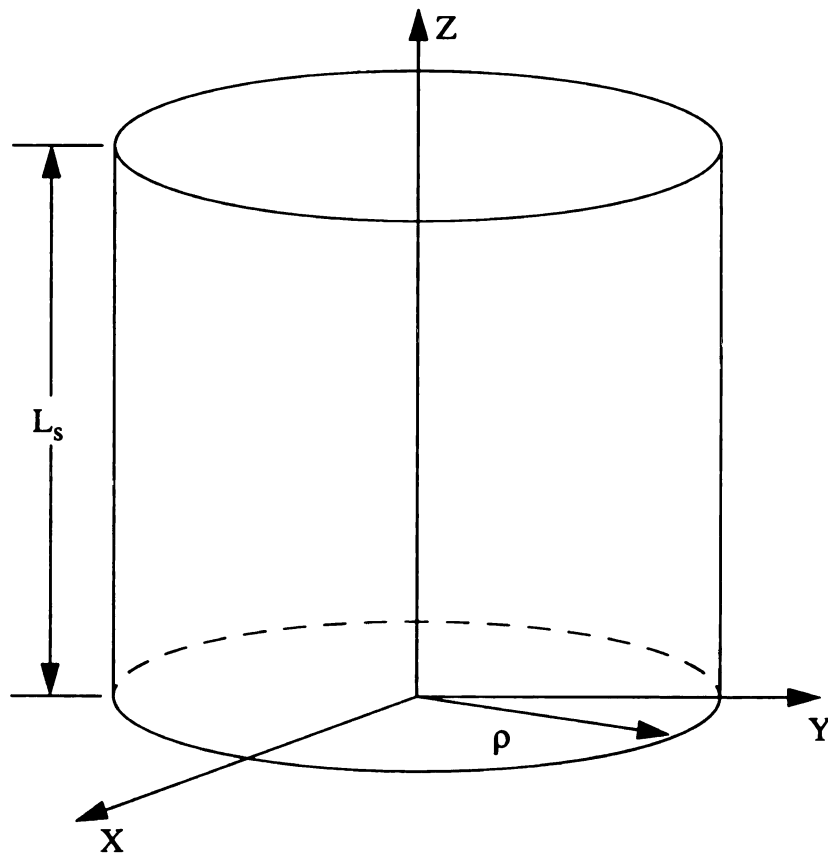


Figure 2.2 The circular cylindrical cavity

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length L_s and radius ρ both TE_{npq} (H mode) and TM_{npq} (E mode) standing waves can be generated. For the TM_{npq} modes and the TE_{npq} modes the corresponding wave functions for a cavity with radius ρ and length d are specified by equation [2.1] and equation [2.2]^[9].

$$\psi_{npq}^{TM} = J_n\left(\frac{x_{np}\rho}{a}\right) \left\{ \frac{\sin n\phi}{\cos n\phi} \right\} \cos\left(\frac{q\pi}{d}z\right) \quad \text{eq (2.1)}$$

where $n=0,2,3,\dots$; $p=1,2,3,\dots$; and $q=0,1,2,\dots$.

$$\psi_{npq}^{TE} = J_n\left(\frac{x'_{np}\rho}{a}\right) \left\{ \frac{\sin n\phi}{\cos n\phi} \right\} \cos\left(\frac{q\pi}{d}z\right) \quad \text{eq (2.2)}$$

where $n=0,2,3,\dots$; $p=1,2,3,\dots$; and $q=1,2,3,\dots$.

X_{np} = zeros of $J_n(X)$.

X'_{np} = zeros of $J'_n(X)$.

The terms $J_n(X)$ and $J'_n(X)$ in equation [2.1] and equation [2.2] are the first order Bessel function and the derivative of the first order Bessel function respectively.

The corresponding resonant frequencies for the TM and TE modes are described by equation [2.3] and equation [2.4].

$$(f_r)_{npq}^{TM} = \frac{1}{2\pi a \sqrt{\epsilon\mu}} \sqrt{x_{np}^2 + \left(\frac{q\pi a}{d}\right)^2} \quad \text{eq (2.3)}$$

$$(f_r)_{npq}^{TE} = \frac{1}{2\pi a \sqrt{\epsilon\mu}} \sqrt{x'_{np}^2 + \left(\frac{q\pi a}{d}\right)^2} \quad \text{eq (2.4)}$$

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filling the cavity. Each of the above mentioned frequencies relates to a specific TM_{npq} or TE_{npq} resonant mode. Figure 2.3 and figure 2.4 show the field patterns for the TM_{011} and TM_{012} modes in an empty lossless circular cavity. The thin solid lines represent the direction of the electric fields and the thin dashed lines represent the direction of the magnetic field lines. The electric field lines in both plots show that the intensity of the electric field is largest at the center of the side walls and the center of the top and bottom of the cavity. Also, the tangential component of the electric field vanishes at the side walls of the reactor. The magnetic field in the TM_{01n} mode has only a ϕ component. Its intensity is greatest in the center of the top and bottom of the cavity. The intensity of H decreases towards the center of the cavity and with increasing radius ρ .

For each resonant frequency in equations [2.3] and [2.4] there is an infinite number of electromagnetic modes that can be generated. In these equations, the excitation of a specific resonant mode field pattern at a particular frequency is determined by the dimensions of the cavity. For example, if the frequency and diameter of the cavity are held constant one can excite TM and TE modes by adjusting the length of the cavity to specific dimensions. Figure 2.5 shows the relationship between frequency and length for a cavity of a fixed diameter of 17.89 cm. The curves labeled with TM and TE modes indicate how the resonant frequency of a particular mode varies with cavity length. The solid horizontal line drawn at 2.45 GHz shows how different resonant modes are excited at different cavity lengths. It is also shown in figure 2.5 that the lowest resonant mode in a 17.78 cm diameter cavity is TE_{111} if the resonant frequency is near 2.45 GHz. Since the resonant frequency of a particular mode is a function of both the radius and the length, the effects of the radius must also be considered. At first glance it might appear that increasing the radius of the

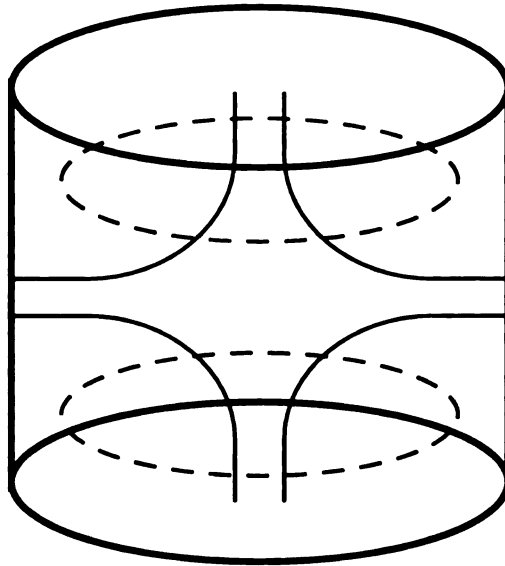


Figure 2.3 The TM₀₁₁ mode.

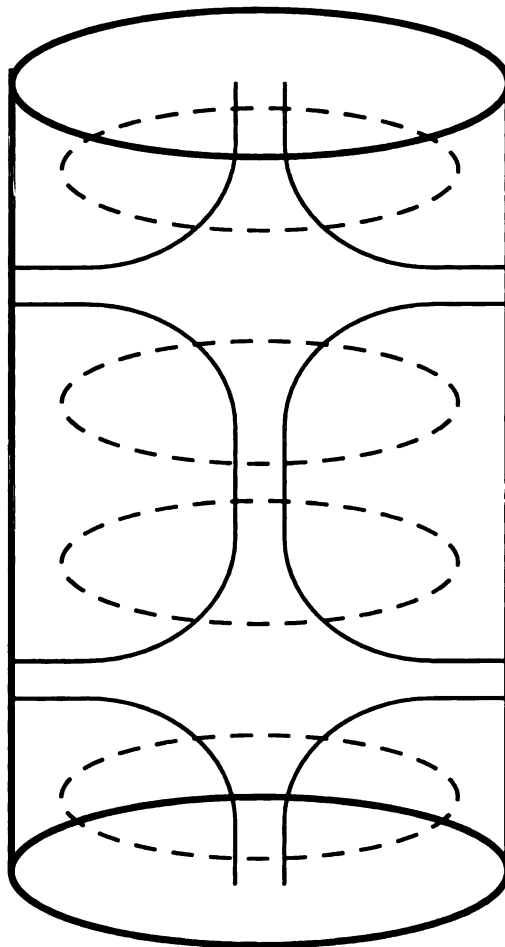
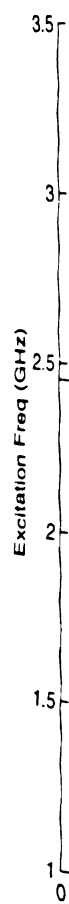


Figure 2.4 The TM₀₁₂ mode.



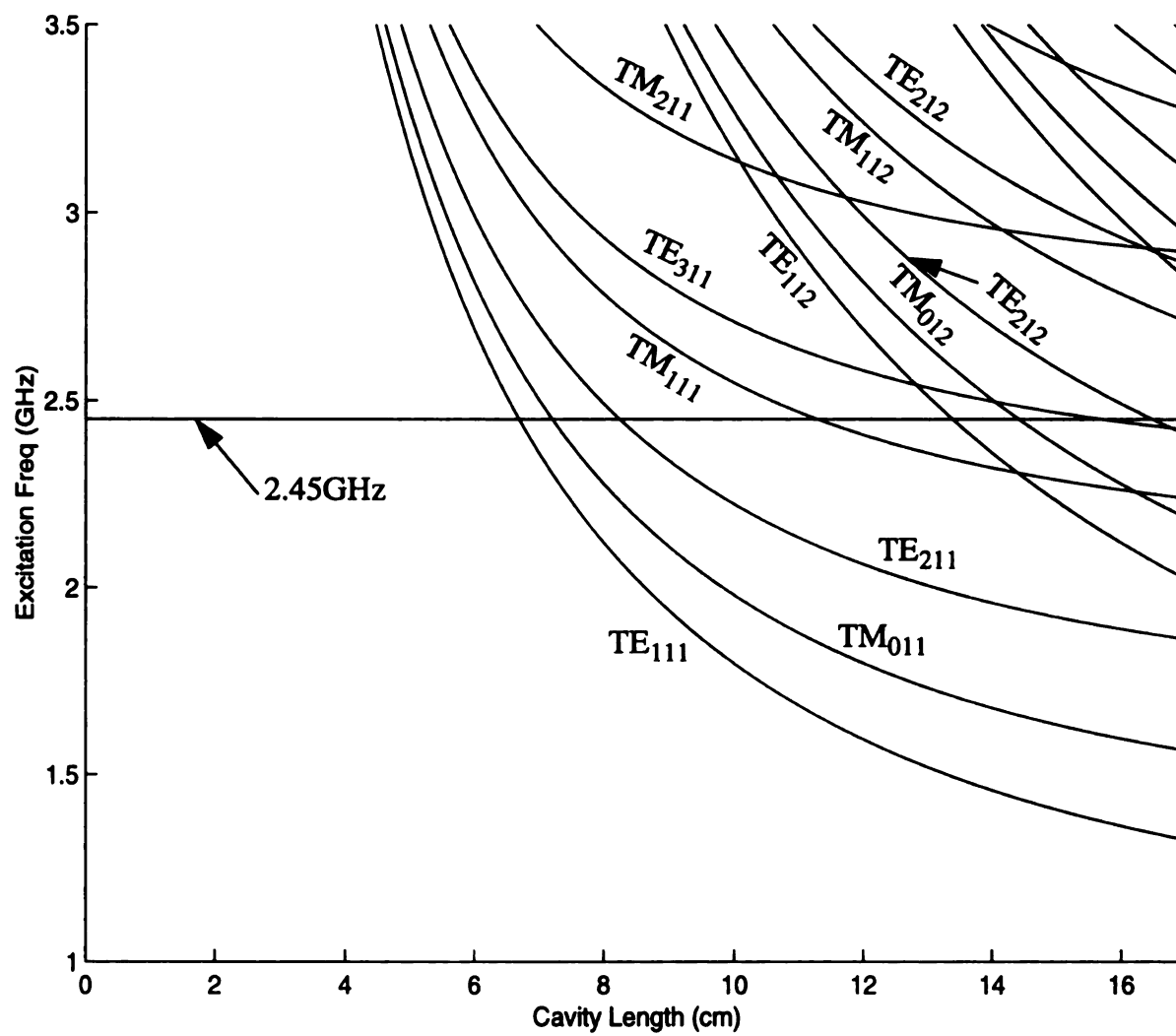


Figure 2.5 The resonant modes of a 17.78 cm diameter circular cavity.

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cavity only affects the length of the cavity for a mode excited at a particular frequency. However, increasing the radius of the cavity also moves the modes of a particular frequency closer together. This is illustrated for a cavity with a radius of 19 cm in figure 2.6.

It is implied by equations [2.3] and [2.4], and figures [2.5] and [2.6] that if one were attempting to excite a particular resonance mode, no fields of that mode will be present unless the exciting frequency is exactly equal to the resonant frequency. In real resonating cavities there is not a delta function singularity, but rather a narrow band of frequencies around the resonant frequency over which appreciable mode excitation can occur^[10]. One source of this smearing out of the sharp frequency of oscillation is the dissipation of energy in the cavity walls and in the material filling the cavity. A measure of the sharpness of the width of this band of frequencies is the Q of the cavity. For a resonant cavity, the Q is defined as 2π times the ratio of the time-averaged energy stored in the cavity to the energy loss per cycle.

$$Q = \omega_o \frac{\text{Stored Energy}}{\text{Power Loss}} \quad \text{eq (2.5)}$$

The Q of an empty MCPR cavity resonator is typically around 5000; however, the Q of a plasma loaded cavity is around 100. This lowering of the cavity Q when the plasma is present causes significant smearing of the curves shown in figures 4 and 5. The positive aspect of the lower Q value is that it becomes easier to tune the length of the cavity resonator to a match point. A drawback of the low Q is that if the modes smear too much they excitation frequencies begin to overlap. This means that multiple modes can be excited at

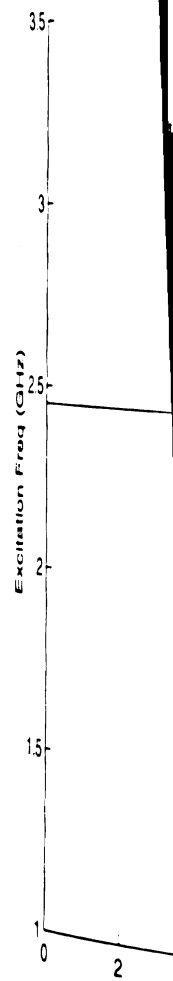


Figure 2.6

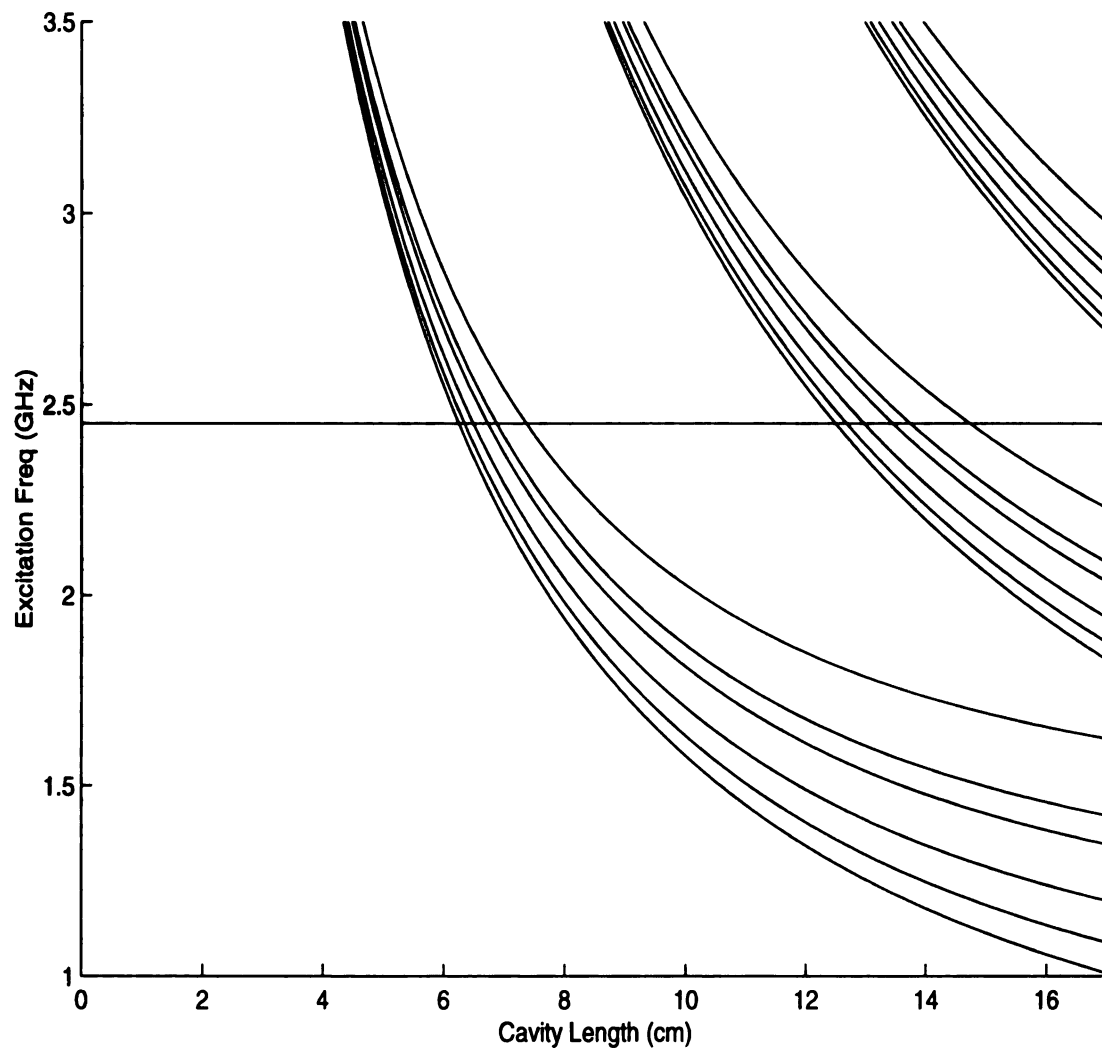


Figure 2.6 The resonant modes of a 38 cm diameter circular cavity.

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This review sect

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22.1 Thermal Decom

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the same time. As was indicated by the curves in figure 2.6, mode smearing can become a significant concern for larger radius cavities where the modes are already close together.

2.2 CVD Processes for Diamond Synthesis from the Gas Phase

Chemical Vapor Deposition (CVD) is a process that causes deposition on a solid surface from a gas-phase chemical reaction. CVD techniques that deposit diamond require a means of activating gas-phase carbon-containing molecules. This usually involves thermal or plasma activation. Diamond deposition from a CVD process also requires that the substrate be maintained in a range below 1300 C, and that the precursor gas be diluted in an excess of hydrogen. The significance of the 1300 C threshold is that at temperatures above this diamond spontaneously transforms into graphite. The resulting measurables such as growth rate, film uniformity, film quality, and the physical properties of the film vary widely. This is a result of the various methods of gas-phase activation as well as system input parameters. Input parameters include substrate temperature control techniques, substrate pre-treatments and many different input gas mixtures.

This review section is split into two parts the first presents an overview of thermal decomposition CVD processes and the latter looks at various plasma CVD processes. Furthermore, the plasma section is divided in dc plasmas and microwave processes.

2.2.1 Thermal Decomposition Processes

The first successful diamond synthesis processes were thermal decomposition processes. They are very simple inexpensive techniques that activate the gas-phase chemistry via a convective heating method such as a heated wire filament. The next few sections give

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22.1.1 Diamond

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a brief overview of the historical progression of thermal decomposition methods leading up to the economically appealing hot filament CVD process.

2.2.1.1 Diamond Synthesis on a Diamond Seed in a Furnace

Attempts to deposit diamond on diamond substrates from the gas phase can be traced back to the late 1950's and early 1960's. Eversole investigated growing diamond on diamond seeds in a furnace at sub atmospheric pressures and with a temperature between 900 C and 1100 C. He successfully developed a two step process where diamond and graphite could be deposited from CO or CH₄^[11]. Afterwards the graphite would be etched in a pure hydrogen environment. Separately, Angus also pursued thermal decomposition of CH₄ as a means of growing diamond, only it was mixed with H₂.

In 1968 J. Angus et. al. published the results of research using CH₄ as a carbon source for growing diamond onto diamond substrates^[12]. Like Eversole, he develop a multi cycle diamond synthesis process. Each cycle has a deposition step and a cleaning step. For deposition, a gas phase supersaturated with carbon was created by thermal decomposition of methane gas in a furnace (figure 2.7) at temperatures between 1253 K and 1338 K. The gas pressure range was 0.15 to 458 torr. Various mixtures of methane in hydrogen and methane in helium were used, but the helium mixtures did not yield any new diamond. The substrate temperature was held to 1049 C. After each deposition step graphite was removed by reaction with hydrogen gas at 1033 C and 50 atm for 7 hours. From separate studies of pyrolytically deposited graphite and 1 µm diamond dust, Angus concluded that this process etches 99.90% of graphite and 0.22% of diamond. The activation energy and the pressure dependence for the diamond reaction are much higher than for the

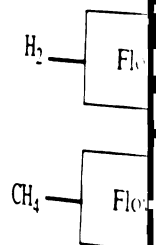


Figure 2.7
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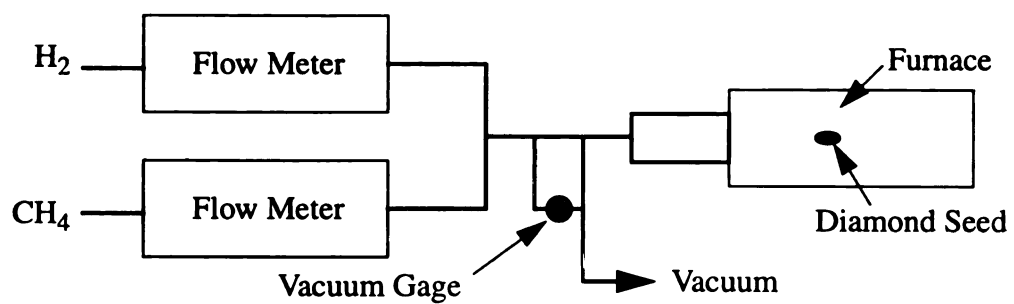


Figure 2.7 Experimental set up for diamond deposition on a diamond seed.

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22.12 Chemical

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graphite reaction. Longer reaction times at lower temperatures and pressures will reduce the diamond loss, but this requires a longer process time. Hence, Angus chose the reaction at 1033 C and 50 atm as the best compromise.

The deposition and cleaning cycle was repeated on the substrate until the desired mass increase was obtained. The resulting growth rate was less than $0.01 \mu\text{m h}^{-1}$. The quality of the films was poor because they were contaminated with non-diamond carbon.

2.2.1.2 Chemical Transport Reaction (CTR) growth of Diamond

Development of CVD processes for deposition of high quality diamond films was delayed until substrate temperature and gas phase temperature were decoupled. The temperatures required to effectively decompose the carbon carrier and simultaneously create a sufficient amount of atomic hydrogen are higher than the 1300 C limit for diamond growth on a substrate.

Chemical Transport Reaction (CTR) is a process developed by Spitzyn (1981) that uses a heated graphite disk in a hydrogen atmosphere to grow diamond on a cooled substrate (figure 2.8)^[13]. In CTR the graphite source is heated to around 2000 C while the substrate temperature is maintained at 1000 C. With CTR, high quality diamond deposition takes place at substrate temperatures as low as 750 C, with the gas pressure ranging from 7 - 300 torr. It's reported that higher gas pressures yield higher growth rates. This process eliminates the need for a separate substrate graphite cleaning step like that used by Angus because it produces enough atomic hydrogen to etch any graphite nucleation that might appear on the substrate surface. Spitzyn reports that the growth rate of this process

$T_2 = 1000\text{ C}$ ---

$T_1 = 2000\text{ C}$ ---

Figure 2.8

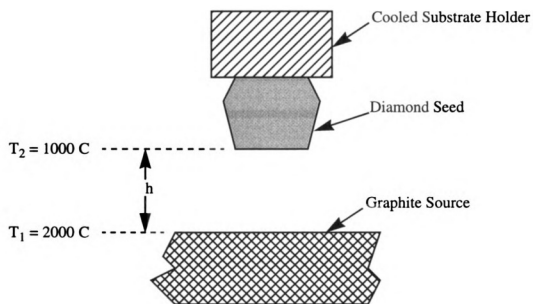


Figure 2.8 Chemical Transport Reaction configuration.

is about $1 \mu\text{m/hr}^{(14)}$.

is about 1 KW/cm^2 .

22.1.3 Hot Filament

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Process data for Hot Fil

22.2 Plasma CVD Pro

Plasma CVD pro

discharge. Typically, the

is about $1 \mu\text{m/hr}^{[14]}$. The major short fall of CTR is that the calculated power requirement is about 1 KW/cm^2 .

2.2.1.3 Hot Filament CVD Diamond

The Hot Filament CVD technique described by Matsumoto (1982) is a very easy method of growing diamond^[15]. It's a thermal decomposition process where a mixture of methane and hydrogen is passed through a vacuum chamber in which a tungsten filament is mounted near a substrate (figure 2.9).

This process is appealing because it can in principle be designed to deposit diamond on large area substrates and its components require a low capital investment. The filament can also be shaped to coat 3-dimensional substrates uniformly. Various substrates including silicon and molybdenum have been coated by this method.

The drawbacks of these systems are contamination from feed gas reaction with the filament, limited filament life and filament sag. Furthermore, large area hot filament systems are reported to involve multiple filaments. Hence multiple filaments with varying amounts of sag result in uniform coverage becoming a non-trivial issue. For large area deposition moving substrate stages are sometimes used to increase deposition uniformity. Process data for Hot Filament CVD diamond deposition is listed in table 2.1

2.2.2 Plasma CVD Processes for Diamond Synthesis

Plasma CVD processes activate the gas-phase chemistry by creating an electrical discharge. Typically, they can produce deposition rates far greater than thermal decompo-

Input Gas
Mixture

Figure 2.9

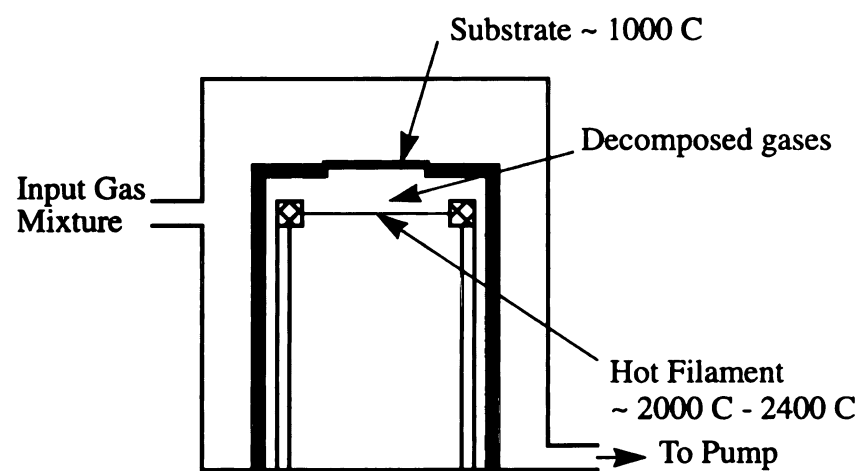


Figure 2.9 Diagram of a Hot Filament System.

substrate temperature
typical gas mixture
typical total gas flow
tempera- ture of fila- ment
deposition area
linear growth rate

Table

substrate temperature	300 - 1000 C
typical gas mixture	1% CH ₄ in H ₂ , small quantities of oxygen tolerable
typical total gas flow	500 sccm - 1000 sccm
temperature of filament	2000 C - 2400 C
deposition area	900 cm ² demonstrated
linear growth rate	0.3 μm/hr - 8μm/hr

Table 2.1: Performance of the Hot-Filament System.

sition methods; how

costs much more than

22.2.1 dc Plasma

22.2.1.1 Parallel Plate

An alternative

One of the simplest

source forms a discharge

electric fields are created

separated by a small gap

attached to a water cooled

cathode (figure 2.10)

plasma and cooling pipes

K. Suzuki et al.

source^{[16][17]}. Diamond

temperatures between

The large growth

amounts of neutral atoms

A/cm^2 the average growth

6000 K. Measurement

of carbon radicals is

sition methods; however, the capital equipment required to assemble a plasma system costs much more than that of a hot filament system.

2.2.2.1 dc Plasma

2.2.2.1.1 Parallel Plate dc Plasma

An alternative method for diamond synthesis is CVD from an electrical discharge. One of the simplest methods of forming a plasma is the dc plasma source. A dc plasma source forms a discharge by ionizing a low pressure gas in high dc electric fields. The electric fields are created when a dc voltage is applied between two metallic plates that are separated by a small distance. To synthesize diamond with this method the substrate is attached to a water cooled anode, and the feed gases are supplied through holes in the cathode (figure 2.10). The substrate temperature is controlled by heat supplied from the plasma and cooling provided by water flowing through the anode.

K. Suzuki et. al. used 2% methane in hydrogen for diamond synthesis with this source^{[16][17]}. Diamond films have been grown on silicon and molybdenum substrates at temperatures between 600 C and 850 C. Their growth conditions are listed in table 2.2

The large growth rates at current densities above 4 A/cm² are attributed to the large amounts of neutral atomic hydrogen and atomic carbon created at these conditions. At 5 A/cm² the average gas temperature is 4000 K. At 10 A/cm² the temperature increases to 6000 K. Measurement of gas species at these temperatures show that the partial pressure of carbon radicals is < 0.1% at temperatures above 5300 K. Hence, at 200 torr and a gas

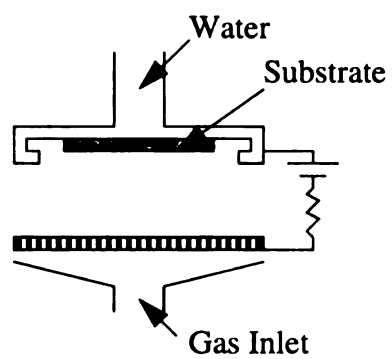


Figure 2.10 Diagram of a dc Plasma CVD source.

Gas
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Table

Gas Pressure	20 torr - 200 torr
Flow Rate (2% CH ₄ in H ₂)	10 sccm - 100 sccm
Substrate Temperatures	600 C - 850 C
DC Discharge Current Density	4 A/cm ² - >10 A/cm ²
Gas Temperature	5300 K - 6000 K
Growth Rate	20 μm/hr - 250 μm/hr

Table 2.2: Performance of the DC Parallel Plate system.

pressure above 500 μ

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222.1.2 DC Plas

A Plasma Jet

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pressure above 5000 K, H_2 and CH_4 are decomposed into neutral atomic hydrogen and atomic carbon.

The major short fall of this process is the small deposition area. In the Suzuki set-up the cathode has a diameter of 2 cm and the anode a diameter of 1 cm. Also, at lower pressures the growth rate and film quality decrease dramatically.

2.2.2.1.2 DC Plasma Jets

A Plasma Jet is a high pressure apparatus that produces a flame shaped plasma (figure 2.11). The idea was first developed by Matsumoto et. al. in 1987^[18]. This type of plasma device has produced the highest diamond deposition rate to date. Othake reported that a growth rate as high as 930 $\mu\text{m/hr}$ has been achieved^[19]. The major drawbacks of the basic Plasma Jet are that it has a very small deposition area ($1\text{ cm}^2 - 2\text{ cm}^2$), very poor deposition uniformity, deposited films usually contain non-diamond carbon around the periphery and they are very expensive to produce.

Norton Company has overcome the limited deposition area of the basic Plasma Jet with a Magnetically Mixed and Spread Arc Jet (MMSARC) as reported by Woodin and Bigelow^[20]. This system uses a solenoid magnetic field to alter the arc properties and control the electrons and ions. The shape of the plasma arc is modified into a helix, which helps to reduce the current in the arc and spread out the deposition area. This allows uniform deposition over substrates as large as 6" in diameter at a deposition rate of 25 $\mu\text{m/hr}$.

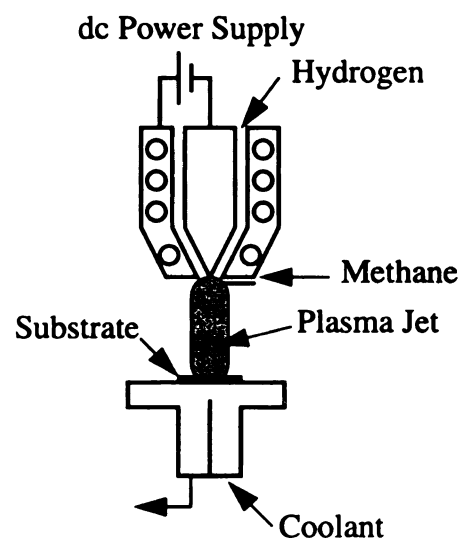


Figure 2.11 Diagram of a dc Arc Jet Plasma CVD source.

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2.2.2.2 Microwave Plasma CVD

2.2.2.2.1 Tubular Microwave Plasma System

Another CVD method that was adopted for diamond deposition in the early 1980's was the 2.45 GHz microwave plasma. It was first reported by NIRIM's Kamo that diamond could be grown from the gas phase with a microwave plasma on non-diamond substrates in 1983^[21]. Kamo created a discharge in a silica tube 40mm in diameter that was passed through a sleeve in a rectangular waveguide (figure 2.12). Deposition was performed by flowing methane and hydrogen through the tube and applying microwave energy to induce the plasma. Diamond was deposited on silicon substrates with a 1% - 3% methane in hydrogen mixture at 7 torr to 60 torr. The applied microwave power ranged from 300 W - 700 W. The plasma was placed over the substrate by adjusting a tuning stub at the terminating end of the waveguide.

Diamond synthesis was later achieved on silica substrates at Pennsylvania State University by Yarbough et. al. (1990)^[22]. In their experiments the temperature sensitive substrate was positioned below the plasma and heated to 860 C with a heater. The mixture of CH₄ in H₂ was 0.5%. The flow rate was 100 sccm, and the pressure was 90 torr.

Although this technique does yield high quality diamond on non-diamond substrates it has problems with limited deposition area and plasma contamination. The limited dimensions of the quartz tube and substrate diameters can not exceed 7 cm since the wide side of a single mode 2.45 GHz rectangular waveguide can be no bigger than 7.2 cm. Films deposited with the microwave tube system contain contaminants as a result of plasma interaction with the walls of the silica tube.

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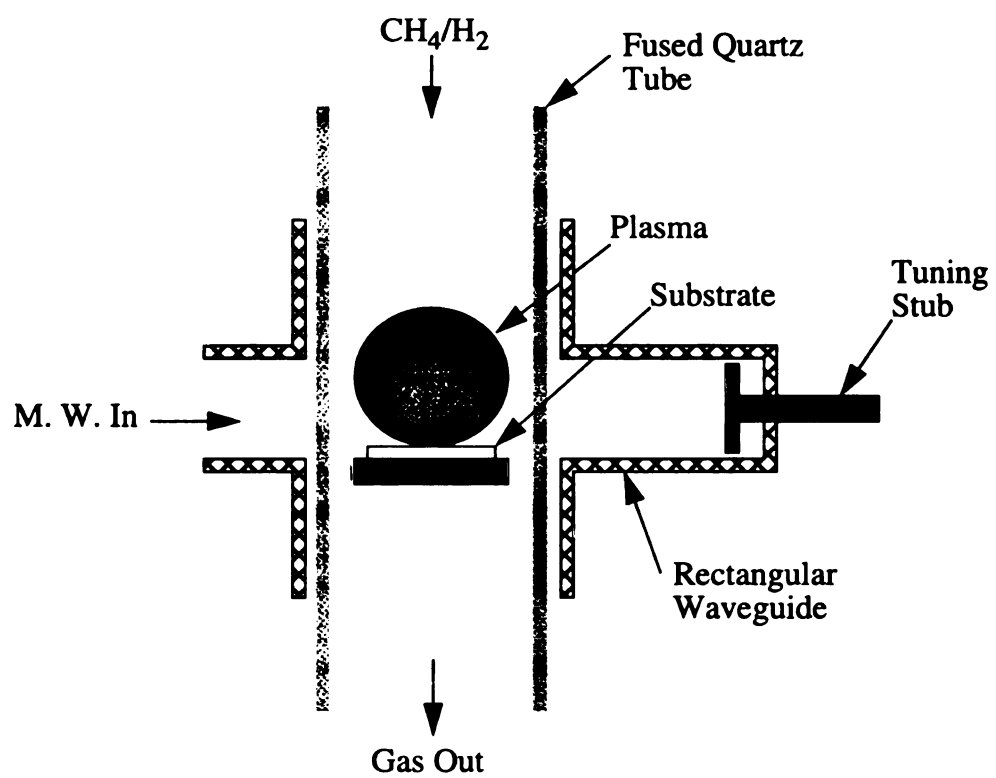


Figure 2.12 Cross section of the 2.45 MHz tubular microwave plasma.

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2.2.2.2.2 Bell Jar Microwave Plasma System

The “Bell Jar” microwave plasma system, which was developed by ASTeX, uses a tuned microwave cavity to create a plasma discharge, as reported by Bachmann^[23]. This system has advantages over the tubular design described by Kamo including a larger deposition area and a reduction in contamination from plasma interactions with the walls of the silica vacuum chamber. In this system a ball shaped plasma is formed directly over the substrate which can be up to 4” in diameter (figure 2.13). Microwave energy is coupled from a rectangular waveguide into the cavity via a tunable probe. The substrate may be heated or cooled to achieve desired substrate temperatures independent of microwave heating of the glow discharge. A bias has been used by Jiang and Klages to control the potential of the substrate with respect to the plasma^[24]. This system can be operated in the low and medium pressure regimes. Growth rates up to 3 $\mu\text{m/hr}$ have been reported at medium pressures using microwave power up to 1.5 KW.

2.2.2.2.3 Magneto-Microwave Plasma System

The MMPA CVD system is a low pressure microwave ECR plasma source that operates in the 0.1 - 10 torr range. The system consists of an evacuated cylindrical waveguide chamber with a 16cm diameter (figure 2.14). Outside the chamber are two electric coils that can produce magnetic fields as strong as 2.2 kG. Inside the chamber a low pressure ECR plasma is created with 2.45 GHz microwave energy. The substrate is positioned at the 875 G ECR location. A positive bias is required for diamond deposition at low pressures. The substrate is heated by the plasma and a tungsten heater. The input microwave power is between 800 W - 1300 W. Another important parameter for diamond

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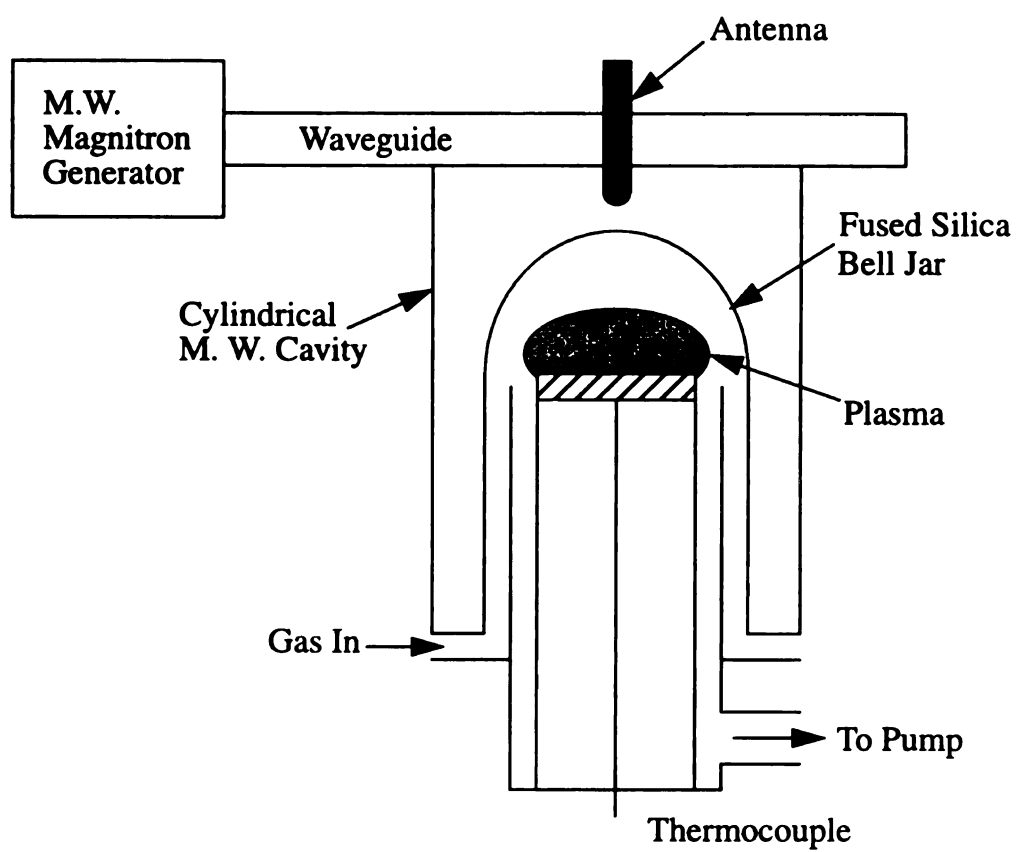


Figure 2.13 Belljar Microwave System.

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Figure

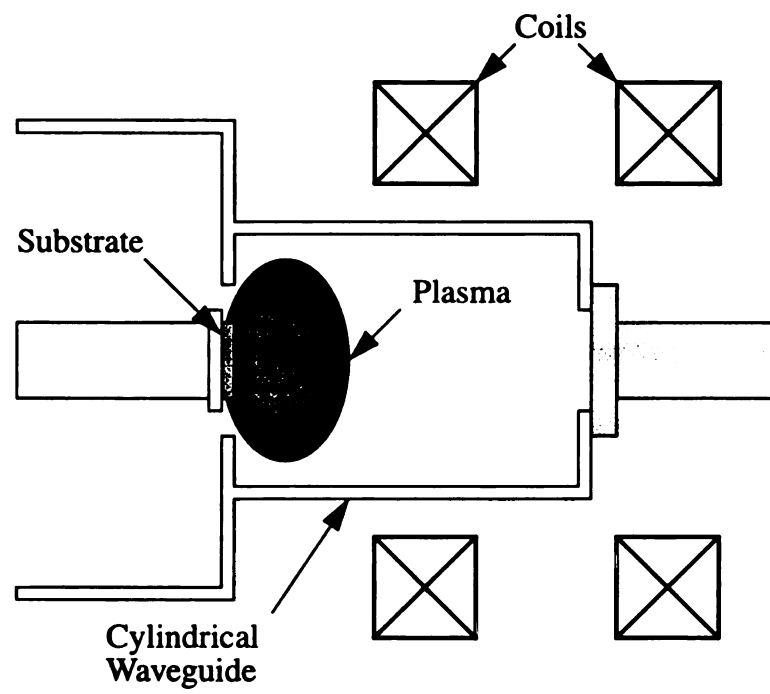


Figure 2.14 Magneto-Microwave Plasma System.

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growth in this system is the plasma density. The lower limit for diamond deposition at 0.1 torr is reported to be $1 \times 10^{11} \text{ cm}^{-3}$ for high quality diamond growth.

Magneto-Microwave Plasma Assisted (MMPA) CVD systems have produced high quality diamond with plasma pressures in the range of 0.1 torr - 10.0 torr. The advantage of MMPA CVD over higher pressure microwave plasma systems for diamond growth is that it can deposit diamond uniformly over larger areas. This is due to the fact that at 0.1 torr the plasma in the MMPA CVD system extends over an area with a 16cm diameter.

Suzuki et. al.^[25] and Wei et. al.^{[26][27]} have achieved high quality diamond deposition on silicon substrates with this system using mixtures of CH_4/H_2 , CO/H_2 and $\text{CH}_4 + \text{CO}_2/\text{H}_2$. Both groups report that diamond can be deposited on pre-treated silicon substrates at 0.1 torr when a positive bias is applied to the substrate; however, neither reports the resulting growth rate. If negative bias is applied to the substrate with the same process conditions, either SiC is deposited or the Si substrate is etched.

Suzuki used 5% CO in H_2 at 0.1 torr with a positive substrate bias, and achieved high quality diamond when the substrate temperature was between 600 C and 750 C. At higher pressures in the range 10 - 50 torr with a CO/H_2 mixture between 3-20% and a temperature between 800 C-900 C diamond was deposited without a bias.

Wei's process is the similar to Suzuki's except that the substrate temperature is set to between 500 C and 600 C. This lower temperature allows deposition on temperature sensitive substrates such as aluminum. At the lower substrate temperatures, Wei reported that diamond no longer grows with mixtures of CO/H_2 or CH_4/H_2 ; however, $\text{CH}_4 + \text{CO}_2/\text{H}_2$ does produce high quality diamond on silicon and aluminum substrates. Here to, it is believed that the formation of OH plays a critical role in diamond growth on the surface.

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The optimum ratio of CH_4 to CO_2 is 1:2 for deposition of high quality diamond. Furthermore, the concentration of CH_4 is limited to between 3% and 5%.

2.2.2.2.4 Magneto-Active Plasma System

Magneto-Active Plasma (MAP) CVD is another microwave-plasma-assisted system that is used for diamond deposition. Similar to the MPPA CVD technique mentioned in the previous section, MAP forms an ECR plasma with an externally applied magnetic field (figure 2.15); however, in this instance an Nd-Fe-B permanent magnet replaces the electric coils. The operating pressures for MAP are 2.0 torr - 20.0 torr.

Mantei et. al. have successfully deposited diamond on pre-treated silicon substrates with MAP at backside temperatures between 550 C - 650 C and input power levels 400 W - 1000 W [28][29][30]. Mixtures of CH_4 , H_2 and O_2 are used, but 2% O_2 in H_2 yields the highest quality films in this temperature range. In these experiments, the substrate is heated by a tungsten filament located above the substrate that is maintained at 2040 C.

Microwave power is coupled into the evacuated process chamber through a quartz window at the top of the chamber. The magnitude of the Nd-Fe-B magnet is 3250 G at its surface an ECR zone where the applied dc magnetic field equals 875 G is at about 8cm below the magnet. The substrate is placed about 6cm below this point.

Another important feature in this system is the dc bias that is applied to the substrate. Without it no diamond material is deposited. When either a positive or negative bias is applied, diamond is grown, although the quality of the diamond formed with a positive bias better. When a -100 V bias is applied, (100) faceted diamond is deposited.

For negative voltages above and below -100 V, non-diamond carbon is deposited. When a

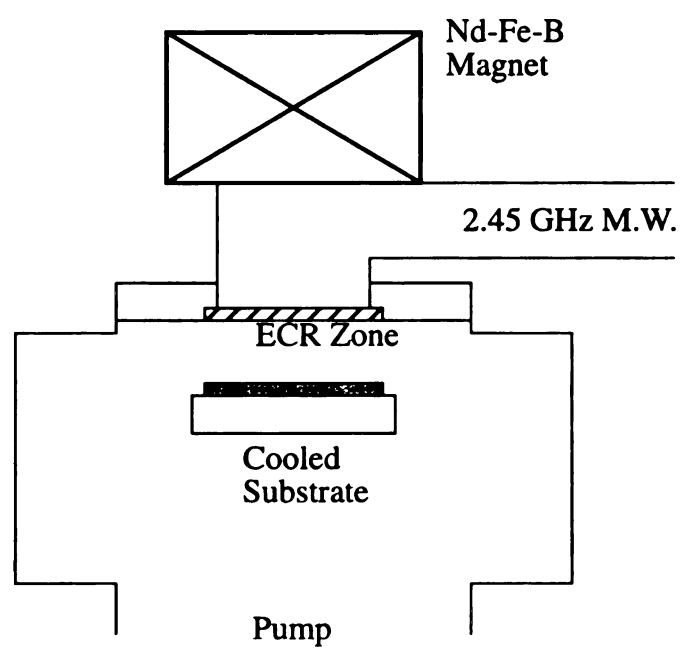


Figure 2.15 The 2.45 GHz Magneto-Active Plasma System.

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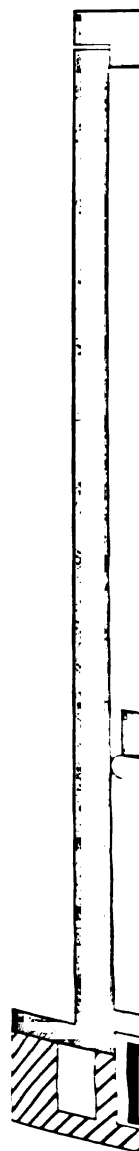
positive bias is applied, the diamond quality improves as the magnitude of the bias is increased from +50 V to +180 V. At +100 V the morphology of the deposited diamond is (100), at +180 V it changes to (111). The measured current at 100 V is 0.15 mA.

2.2.2.2.5 4" Microwave Cavity Plasma Reactor (4" MCPR)

The Microwave Cavity Plasma Reactor described generally in section 2.1 is a microwave generated plasma sources that was developed at Michigan State University^{[31][32][33][34]}. It differs from other microwave plasma CVD systems in that it uses a resonant cavity that is internally tuned, hence external tuning stubs are not required. The microwave energy can be focused into various of several resonant modes, depending on the details of the cavity geometry.

The primary components of the MCPR design are the vacuum sealed base plate, the tubular cross section microwave cavity, an adjustable height tuning short and the microwave power input probe. The 4" MCPR gets its name from another essential component, the microwave transparent quartz bell jar. The bell jar has an outer diameter of 4" and is located in the base plate. Its purpose is to provide a medium for microwave energy to couple from the atmospheric cavity into the evacuated base plate.

A MCPR forms a plasma discharge inside the quartz bell jar via microwave energy which is tuned to a specific cylindrical microwave cavity resonating mode. Microwave energy is generated by a magnetron supply at a frequency of 2.45 GHz and transported to the cavity through rectangular or coaxial waveguide. In the reactor cross section shown in figure 2.16 microwave energy is coupled from the wave guide into the cavity by the side mounted probe. The location of the side mounted probe allows excitation of either a TE_{nml}



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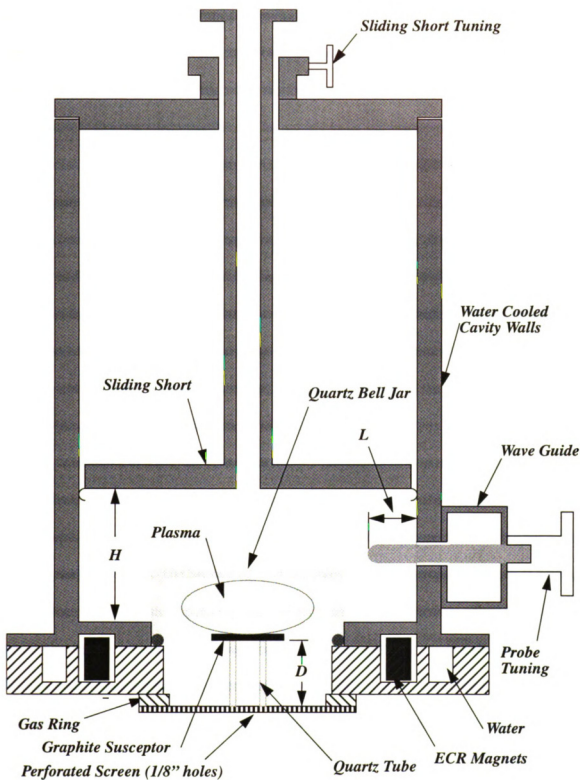


Figure 2.16 Side Feed Configuration of the 4" MCP.

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or a TM_{nml} microwave mode inside the cylindrical cavity. The specific resonant mode used for plasma generation is excited by adjusting the height of the cavity and the distance the probe projects into the cavity. The theoretical dimensions of cavity length and probe insertion length for a particular TE or TM mode can be obtained by simple calculation or from a plot such as that shown in figure 2.5 for an empty cavity. However; when a substrate assembly such as that shown in figure 2.16 is inserted into the bottom of the cavity and the pressure of the deposition gases is raised above vacuum, the tuning parameters vary from the empty cavity values. For each desired plasma processing gas pressure, or substrate assembly, tuning conditions for a particular resonant mode must be determined. Other variables that affect cavity tuning, and the shape and location of the plasma include, materials used in the substrate susceptor assembly, the height of the substrate susceptor assembly, and the height of the quartz bell jar.

Diamond films have been deposited on 1" diameter silicon and boron nitride substrates using the 4" MCPR configuration diagramed in figure 2.16 by B. Huang^[35] and J. Zhang^[36] at pressures between 50 torr - 80 torr. A mixture of methane in hydrogen was used as the process gas. The percent of methane to hydrogen was varied between 0.5% and 1.5%. The total flow rate had a range of 100 sccm to 250 sccm. It was determined experimentally that the highest quality diamond is deposited when the cavity is tuned to the TM_{011} mode, and the substrate is positioned in a location where its surface is in direct contact with the plasma. Huang and Zhang positioned the substrate in the cavity by placing it in a graphite substrate holder which is centered in the cavity on top of a quartz tube. The height of the quartz tube effects the electromagnetic field patterns in the cavity, and in turn the shape of the plasma. A hemispheric plasma shape with a flat side that completely

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covers the top of the substrate is preferred. Substrate temperature is a dependent variable that increases greatly with gas pressure and slightly with increasing microwave energy. Typically, the substrate temperature varied between 800 C - 1100C when the gas pressures range from 50 torr to 80 torr. The input microwave power had a range of 400 W to 900W. A maximum growth rate of 1 $\mu\text{m/hr}$ was achieved.

A major drawback of the side feed reactor design in figure 2.16 is that at higher pressures the plasma tends to be drawn towards the area of the quartz bell jar side wall closest to the probe. This phenomenon is caused by near fields formed at the probe and becomes more prevalent as the input microwave power is increased. While the uniformity and quality of deposited diamond may be unaffected by the near field plasma, an undesirable coating of the quartz does occur near the probe.

The end feed reactor configuration shown in figure 2.17 was developed to eliminate the near field effect of the side mounted probe. The result was that the plasma became cylindrically symmetric but the near field effect was merely relocated to the top of the quartz. The end feed MCPR cavity shell was later lengthened to allow excitation of the TM_{012} and TM_{013} modes. To excite higher TM_{01n} modes the sliding short must be moved away from its TM_{011} mode location which is about 7 cm from the floor and just a few cm from the top of the bell jar. For the TM_{013} mode the theoretical cavity length is greater than 20 cm. When the sliding short is moved away from the top of the quartz bell jar, the near field effect on the shape of the plasma decreases and the coating of the quartz bell jar diminishes.



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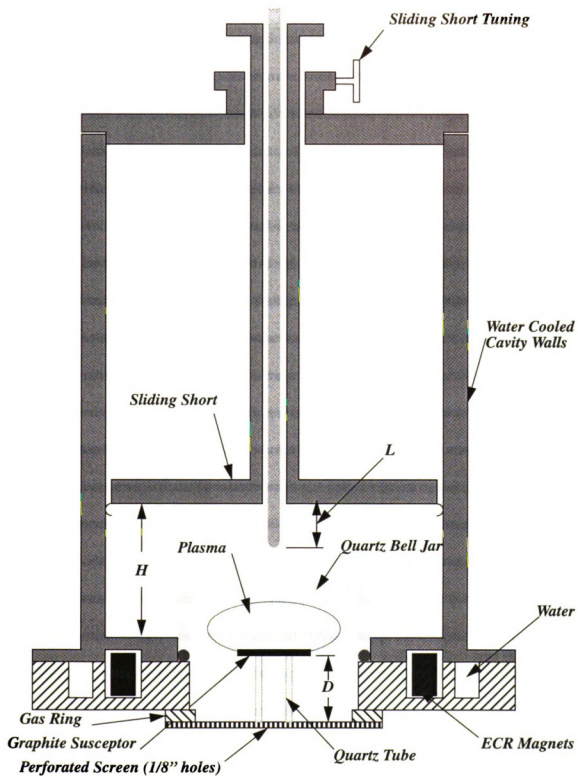


Figure 2.17 End Feed Configuration of the 4" MCPR.

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2.2.2.2.6 5" Microwave Cavity Plasma Reactor (5" MCPR)

The 5" MCPR was developed by J. Zhang and J. Asmussen with the intent of designing a microwave plasma source that could deposit polycrystalline diamond films on substrates with a diameter as large as 4"^[37]. Previously in the 4" reactor, diamond could only be uniformly deposited on substrates with a diameter of 1.5" or less. In the 5" MCPR larger substrates can be accommodated because the outside diameter of the quartz bell jar is increased to 5", however; the basic end feed reactor configuration remains the same.

The diameter of the cavity shell in the 5" MCPR is left unchanged at 7" and the sliding short equipped with a microwave input probe for TM_{01n} resonating modes is still used. The length of the cavity shell was increased to 12", since another objective of the 5" MCPR design was to preclude quartz coating by the near field plasma. The longer shell allows the cavity to be tuned to the TM_{013} mode. Tuning the cavity to a higher TM_{01n} mode moves the tip of the input probe from a few cm from the top of the quartz bell jar to more than 10 cm away. With the microwave input probe located higher in the cavity the height of the quartz bell was then adjusted to insure that the plasma could not come in contact with it.

The base plate for the 5" MCPR was designed to fit the larger bell jar and to incorporate performance improvements for better thermal management, a problem that plagued the 4" reactors. One modification of the base plate was the relocation of the vacuum o-ring used to seal the bell jar to the base plate. A flange was added at the bottom of the bell jar that provided a means of moving the o-ring closer to the water galley running around the

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outer edge of the base plate. This modification allowed the use of higher process gas temperatures without the risk of burning out the o-ring.

Another major design improvement that was implemented in the 5" MCPR reactor was an increase in input power capability of the microwave input probe in the sliding short. The diameter of the coaxial assembly in the sliding short was increased to 1 5/8 inches. This larger diameter allows up to 6 kW of power to flow into the cavity; whereas, the 4" MCPR had a 7/8 inch coaxial feed that was limited to a maximum microwave power capacity of 1 kW.

An initial set of diamond deposition experiments was designed to evaluate reactor performance with 5 different substrate holder configurations. All the configurations used were developed for diamond deposition on a disk shaped substrate area with a diameter between 3 and 4 inches. Specific details and a physical description of each stage is not discussed here, but can be obtained elsewhere^[36]. A summary of the performance evaluation for each substrate holder configuration is listed in table 2.3.

The Forced Flow Configuration is shown in figure 2.18. This assembly can be used to deposit diamond on disk shaped substrates with a diameter of 4" or less. The primary components of the assembly are the substrate holder, the large quartz tube and the interior metal tube.

The substrate holder is a thin disk with a recessed area to positively locate disk shaped substrates. A ring of small holes around its perimeter allows the process gas to flow through the plasma and to the vacuum pump. The holder can be fabricated from a variety of materials including graphite, amorphous carbon, boron nitride and stainless steel. Perhaps the best material is boron nitride since it does not react with the plasma to

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Configuration Name	Performance Results
Basic	4" substrate 20 torr 1% CH ₄ in H ₂ 2 kW Growth Rate <0.2 $\mu\text{m/hr}$
Forced Flow	4" substrate 40 torr 1% CH ₄ in H ₂ 4 kW Growth Rate 0.5 - 0.8 $\mu\text{m/hr}$
Jet	1.5" substrate 95 torr 1.5% CH ₄ in H ₂ 1.67 kW Growth Rate 1.5 $\mu\text{m/hr}$
Lower Cavity Resonance	3" substrate 30 torr 1% CH ₄ in H ₂ 2 kW Growth Rate <0.2 $\mu\text{m/hr}$
Down Stream	3" substrate 15 torr 1% CH ₄ in H ₂ 1.5 kW BN heater 100V _{ac} (60Hz) Growth Rate and uniformity were described as poor.

Table 2.3: Performance of 5" MCPR configurations^[36].



Figure

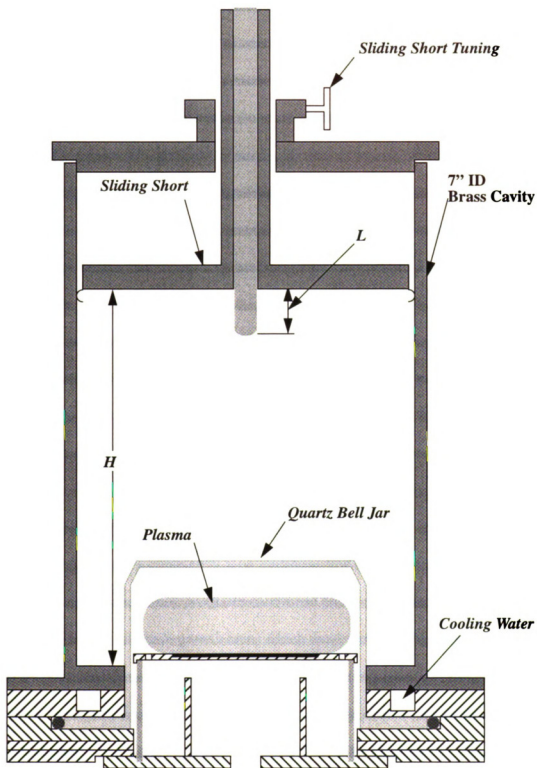


Figure 2.18 End Feed 5" MCPR.

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alter the process chemistry like carbon based materials. Also, boron nitride has a high thermal conductivity. This thermal characteristic of boron nitride means it would be preferred over a poor thermal conducting metal such as stainless steel.

The function of the quartz tube that the substrate holder sits on is to position the substrate in the desired location in the reactor. Besides centering the substrate holder, the length of the quartz tube is used to adjust the height location of the substrate. It turns out that the best location for uniform diamond deposition on large substrates is when the substrate is near a height that is even with the floor of the cavity when the plasma pressure is above 30 torr.

The interior metal tube is set at the bottom of the cavity base plate in a concentric location. It serves to prevent resonance of high intensity EM fields in the bottom of the cavity. This in turn prevents the formation of a plasma discharge in the area below the substrate holder. The metal tube is fabricated from stainless steel stock and is 3" in diameter.

2.3 CVD Diamond Gas Phase Chemistry

There is not yet a completely clear understanding as to what chemical processes are dominant in the deposition processes mentioned previously in section 2.2. It is apparent from the large variance in growth rates, which range from less than 1.0 $\mu\text{m/hr}$ in low pressure plasma systems to greater than 950 $\mu\text{m/hr}$ in the dc plasma jet, that greatly different situations can exist on the substrate in the various processes. Some of the unknowns are what precursors are present in the gas phase, what is the minimal gas phase temperature required to generate the desired chemistry, and what effect does substrate temperature have on diamond seed growth. Of course another large subset of variables in the deposi-

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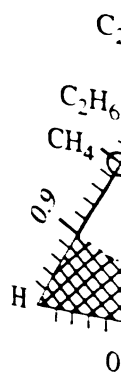
oxygen is too hig

tion process is the input gases and the mixture ratio. Typically, a carbon containing gas such as CH_4 or CO is mixed in a small percentage with H_2 (i.e. $\text{CH}_4 < 2\%$ in H_2). Here the carbon containing gas provides the diamond precursor and the molecular hydrogen provides atomic hydrogen and OH if oxygen is included. In either case, H and OH are necessary in sufficient quantity to etch non-diamond carbon that is deposited during diamond growth. Under some process conditions deposition growth rate and quality are improved when oxygen is added to the mixture. Oxygen can be added via CO , CO_2 and O_2 . There have also been reports that halogen containing gases can promote diamond growth in a non-diamond carbon process.

Recently, a group at Argonne National Laboratory has shown that very smooth nano-crystalline films can be deposited via a mixture of argon and C_{60} in a small amount of H_2 ^[38]. The measured wear rates of diamond grown by this process have two orders of magnitude improvement over those grown by conventional CH_4 - H_2 methods.

2.3.1 Bachmann C-H-O gas phase diagram

Recent publications by Bachmann describe the diamond growth region with a C-H-O gas phase diagram (figure 2.19)^{[39][40]}. Generally, the diamond growth region is found in the center of the ternary diagram surrounding the CO line. From the figure it is apparent that diamond can be grown from a wide range of gases mixed in hydrogen including methane, ethane, ethylene, acetylene and carbon dioxide. A general trend is that the quality of the deposited diamond improves from the carbon rich to the oxygen rich side. Also, no solid carbon, diamond or otherwise, is deposited if the partial pressure of oxygen is too high. Bachmann further concluded that the ability of a certain mixture to



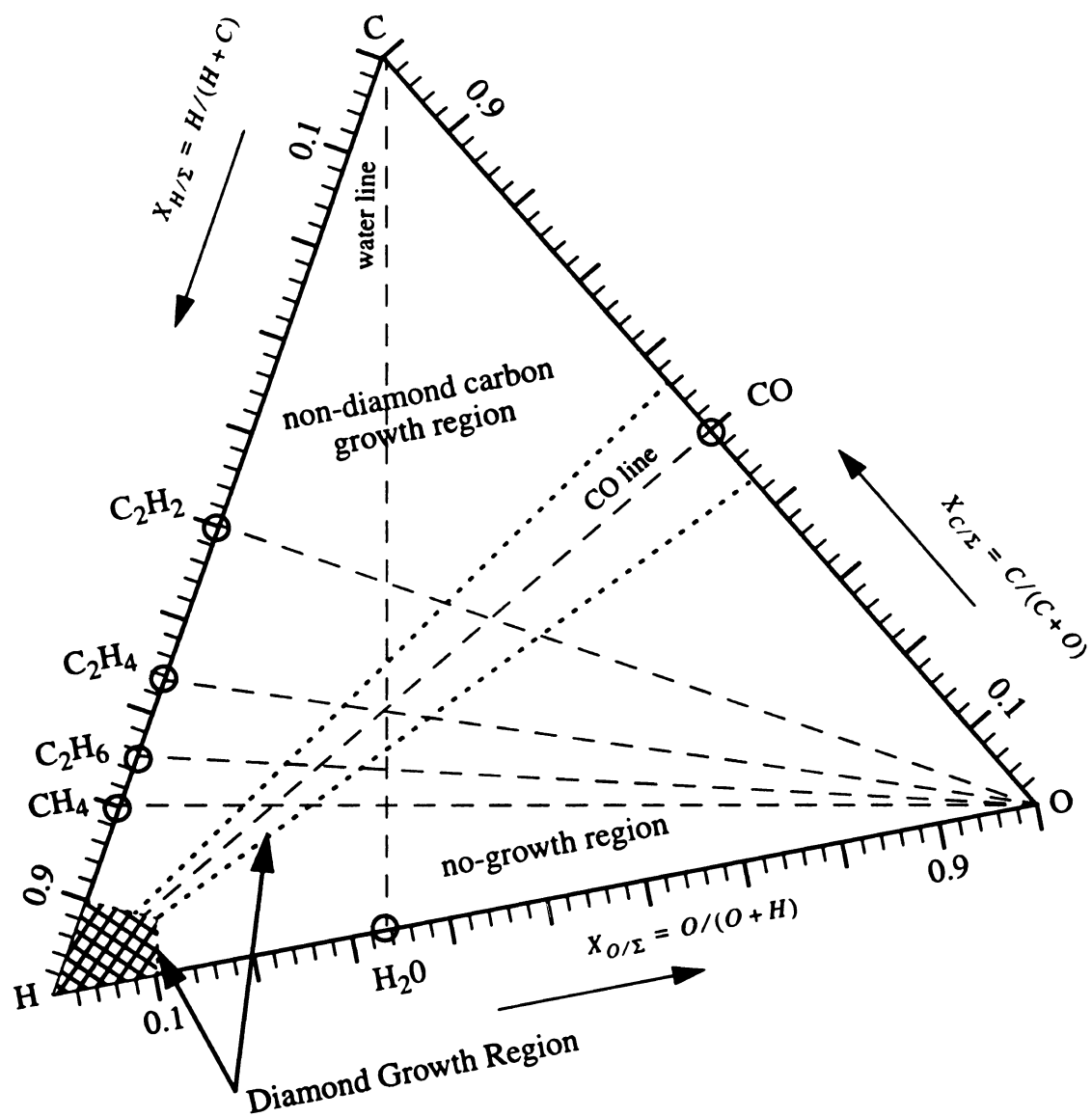


Figure 2.19 Ternary gas phase diagram for C, H, and O.

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yield diamond depends only on the overall content of C, O, and H -- the makeup of the initial chemical species is irrelevant.

The concept of diamond growth based on the overall C-H-O content was later investigated by Morinelli^[41] et. al. The motivation for this work was the high degree of freedom allowed by being able to select among a great number of possible starting mixtures. One might choose the ones most suitable to satisfy one's own conveniences, e.g., the ones being least hazardous, expensive, poisonous or polluting.

The growth mixtures investigated in the study were $\text{CH}_4\text{-CO}_2$, $\text{C}_2\text{H}_2\text{-CO}_2$, $\text{C}_2\text{H}_4\text{-CO}_2$ and $\text{C}_2\text{H}_2\text{-CO}_2$, whose representative lines intersect the assumed diamond domain in figure 2.19. These mixtures are non-conventional in that they contain neither molecular hydrogen nor molecular oxygen. The results were that the qualitative aspects of Bachmann's model were confirmed, meaning that a diamond domain was found to exist in the C-H-O diagram. Quantitatively though, the domain had a different size and shape (figure 2.20). The width of the domain shrinks while moving away from the H vertex. Also, the $\text{C}_2\text{H}_2\text{-CO}_2$ mixture had a single composition (C_2H_2 67.3%, CO_2 37.7%) which results in diamond deposition. Slight variances in the $\text{C}_2\text{H}_2\text{-CO}_2$ mixture as little as 1% result in deposition of non-diamond carbon.

2.3.2 The effect of Oxygen in Microwave Diamond Deposition

Y. Lou et. al. at Penn. State found that the addition of oxygen can improve the deposition process^[42]. When O_2 is added to a methane, hydrogen plasma in the Bell Jar Reactor an increase in growth rate and film quality can occur. They reported that for substrates above 950 C an oxygen to carbon ratio of <1% improves the deposition rate and Raman

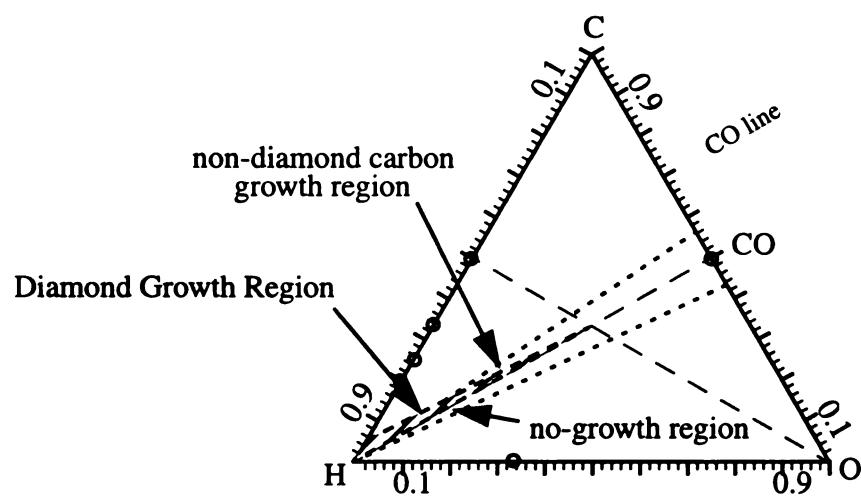


Figure 2.20 Modified C-H-O ternary gas phase diagram

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spectra for deposited films. At temperatures below 700 C the addition of oxygen decreases the deposition rate, but dramatically improves the quality of deposited films. Films deposited at low temperature without oxygen were translucent amorphous carbon material.

Those deposited with oxygen were described as optically smooth, transparent films with a light interference pattern.

Harris and Weiner concluded that at low substrate temperatures oxygen may improve the quality of diamond through selective etching of non-diamond carbon^[43]. They calculated that the removal rates by O₂ and O are relatively low, but the removal rate by OH is about 0.25 μm/hr.

2.3.3 Harris-Goodwin Model

At low substrate temperatures and low pressures, there are two potential bottlenecks for growth. First, lower substrate temperatures result in fewer available surface sites for incorporation of new carbon. Second, the flux of carbon containing species to the substrate decreases as the pressure and power are reduced. The latter can be increased by using high microwave input powers and higher pressures with substrate cooling as mentioned above. Information about the relative roles of substrate temperature and plasma species concentration is obtained by considering the pathway to diamond growth, following Harris^[44] and Goodwin^[45].

First, considering the interaction of hydrogen with a diamond surface, abstraction of surface hydrogen, S:H, by atomic H atoms proceeds as is shown in equation [2.6].

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Equation [2.7] represents filling of a radical surface site by atomic H.



The rate constant for the reverse reaction in equation [2.7], K_{-2} , is negligibly small. In steady state, the rate of production of S^* by the reaction in equation [2.6] will equal the rate of destruction of S^* by the reactions in equation [2.6] and equation [2.7] as is shown in equation [2.8].

$$\text{K}_1[\text{S:H}][\text{H}] = \text{K}_{-1}[\text{S}^*][\text{H}] + \text{K}_2[\text{S}^*][\text{H}_2] \quad \text{eq (2.8)}$$

The concentration of surface sites is then determined to be that shown in equation [2.9].

$$[\text{S}^*] = \frac{\text{K}_1[\text{H}][\text{S:H}]}{\text{K}_{-1}[\text{H}_2] + \text{K}_2[\text{H}_2]} \quad \text{eq (2.9)}$$

The fraction of covered surface sites is given in equation [2.10] and the fraction of uncovered surface sites is given in equation [2.11] and equation [2.12]. The molar fraction of atomic hydrogen $[\text{H}]/[\text{H}_2]$ is expressed as X_H .

$$\Theta = \frac{\text{S:H}}{[\text{S}^*] + [\text{S:H}]} \quad \text{eq (2.10)}$$

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$$1 - \Theta = \frac{K_1[H]}{K_1[H] + K_2[H] + K_{-1}[H_2]} \quad \text{eq (2.11)}$$

$$1 - \Theta = \frac{K_1 X_H}{(K_1 + K_2)X_H + K_{-1}} \quad \text{eq (2.12)}$$

Incorporation of new carbon at the uncovered surface sites proceeds as the attachment of a hydrocarbon species as shown in equation [2.13].



A carbon containing species that is attached to the surface is represented as S:A. Next, there is a competition between a reaction that etches the newly placed non-diamond carbon species, shown in equation [2.14] and a reaction that incorporates the adsorbate into the diamond lattice. The latter is shown in equation [2.15]. It includes the abstraction of adsorbate hydrogen from the surface.



The rate of incorporation and etching of S:A is expressed in equation [2.16]. In the steady state the time derivative is zero. Equation [2.17] shows the steady state solution for S:A.

$$\frac{d}{dt}[S:A] = K_3[CH_m][S^*] - K_{-3}[S:A] - K_4[S:A][H] - K_5[S:A][H] \quad \text{eq (2.16)}$$

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$$[S:A] = \frac{K_3[CH_m][S^\bullet]}{K_{-3} + (K_4 + K_5)[H]} \quad \text{eq (2.17)}$$

The rate of incorporation of new diamond into the lattice R_C can be expressed in terms of K_5 , $[S:A]$ and $[H]$. Then, the growth rate of diamond, G , is simply R_C divided by the carbon atom density in diamond n_C .

$$R_C = K_5[S:A][H] \quad \text{eq (2.18)}$$

$$G = \frac{R_C}{n_C} \quad \text{eq (2.19)}$$

Substituting equation [2.17] and equation [2.18] into equation [2.19], G is expressed in terms of rate constants and molecular concentrations. This is essentially Goodwin's equation (20)^[45].

$$G = \frac{K_5 K_3 [CH_m] [S^\bullet] [H]}{n_C \{ K_{-3} + (K_4 + K_5) [H] \}} \quad \text{eq (2.20)}$$

$$G = \frac{K_5 K_3 [CH_m] [H] n'_o (1 - \Theta)}{n_C \{ K_{-3} + (K_4 + K_5) [H] \}} \quad \text{eq (2.21)}$$

The surface concentration of carbon atoms for diamond is n'_o .

A more detailed model, proposed by Harris and Weiner, requires that radical surface sites must be present in pairs for carbon to be incorporated in the diamond lattice. The

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concentration of paired surface radicals is expressed as $n_o'(1-\theta)^2$. Their modified expression for the growth rate, G^* , of the diamond lattice is shown in equation [2.22].

$$G^* = \frac{K_5 K_3 [CH_m] [H] n_o' (1-\theta)^2}{n_C \{K_{-3} + (K_4 + K_5) [H]\}} \quad \text{eq (2.22)}$$

Harris presents the rate constants as the following.

$$K_1 = (4.15 \times 10^{-10}) \exp(-0.316 / kT) \text{ cm}^3/\text{sec}$$

$$K_{-1} = (4.15 \times 10^{-10}) \exp(-1.17 / kT) \text{ cm}^3/\text{sec}$$

$$K_2 = 1.66 \times 10^{-10} \text{ cm}^3/\text{sec}$$

$$K_3 = 1.66 \times 10^{-11} \text{ cm}^3/\text{sec}$$

$$K_{-3} = 1.66 \times 10^{-10} \exp(-1.01 / kT) \text{ sec}^{-1}$$

The activation energies in the exponential terms are in electron volts and k is Boltzmann's constant, $8.62 \times 10^{-5} \text{ eV/K}$. If it is noted that over the temperature range of interest K_{-3} is very small, and if, following Goodwin, the etch rate constant K_4 is also considered to be negligible, then the expression for G^* can be simplified.

$$G^* = \frac{K_3 [CH_m] n_o' (1-\theta)^2}{n_C} \quad \text{eq (2.23)}$$

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For diamond the atom density is $n_C = 1.79 \times 10^{23} \text{ cm}^{-3}$ and for the (100) surface, $n_o' = 1.57 \times 10^{15} \text{ cm}^{-2}$. The concentration of species, $[CH_m]$, is expressed in cm^{-3} . Consequently, the units of growth in equation [2.23] are cm/sec.

In equation [2.23] the terms n_C , n_o' and K_3 are constants. The two variables are Θ , which depends primarily on temperature, and $[CH_m]$, which depends of the pressure of the plasma and the degree of dissociation of the plasma. The quantity $[CH_m]$ can be increased by increasing the power, which increases the dissociation rate, and by increasing the pressure, which increases the concentration of species to be dissociated. By increasing the power and pressure, cooling of the substrate is required in order to maintain low substrate temperatures.

2.4 Methods of Low Temperature Diamond Deposition

As mentioned earlier, substrates that are temperature sensitive can not be exposed to a typical high temperature diamond deposition process. Three techniques for adapting a plasma CVD process for deposition on a temperature sensitive substrate are (1) lowering the pressure, (2) controlling the substrate temperature and (3) using pulse modulated microwave power.

2.4.1 Low Pressure Plasma CVD Processing

In a plasma CVD process the substrate temperature is highly dependent on the gas pressure. Hence, a method of adapting a plasma CVD process to deposit a diamond film on a temperature sensitive substrate is to lower the gas pressure of the plasma. At lower pressures, the mean free path increases and the plasma expands decreasing the power den-

sity in the plasma. Hence, lowering the plasma pressure is one method for lowering the substrate temperature. It is also believed that a lower plasma pressure may create a more radially uniform plasma density, thus improving deposition uniformity. Unfortunately, lowering the gas pressure also reduces the available carbon precursors in the plasma. This in turn means that the deposition rate of low pressure process will be much lower than the high pressure high temperature process for a given input power.

2.4.2 Manipulation of Substrate Temperature

In a plasma process, it is also possible to heat or cool the substrate. If a low pressure process provides a desired deposition uniformity that a higher pressure process can not achieve the substrate can be heated to maintain the substrate temperature of the high pressure process. Heating the substrate in this case could reduce the diminished deposition rate effect. Another way to achieve a process with a lower substrate temperature is to cool the substrate in a high pressure process to the desired temperature. By employing a substrate cooler in this manner the substrate temperature can be controlled without reducing the carbon radical density in the plasma. However, this approach may have limited value for thick substrates with low thermal conductivity.

2.4.3 Pulse Modulated Microwave Power

A pulse-modulated-microwave-power supply provides a different means to create a low temperature diamond deposition process. The rationale is that the high values of the

electromagnetic field magnitude in a pulsed discharge may provide more efficient dissociation of gases for a given average power load to the substrate.^[46]

Ring and Mantei have reported that this technique produces an order of magnitude increase in the diamond deposition rate of the MAP CVD system^[26]. Their experiments had an average microwave power of 300 W (2.45GHz); generated by a source operating at 0.8 ms pulse width, 120 Hz repetition frequency and 3 kW peak power. Typical MAP operating conditions were used; pressure at 1 - 3 torr, mixtures of CH₄ - H₂ - O₂, and substrate temperature between 300 C and 600 C.

Hatta et. al. advanced the idea further by investigating the dependence of growth rate on repetition frequency in a pulse-modulated-microwave-power CVD diamond deposition system^[47]. Using an MMPA CVD system, they generated pulse-microwave-power with 2 kW peak and a 50% duty cycle (2.45 GHz). The repetition frequency was varied from 500 Hz to 20 kHz: yielding an average power of about 900 W. The maximum deposition rate occurred at 500 Hz and was twice as large as that for diamond grown in a continuous discharge.

Matsumoto and colleagues also investigated the idea of increasing deposition rates by using pulsed-microwave-power with an average equal to the CW power (2.45 GHz)^[48]. The range of repetition rates was within that of Hatta, but the peak power was much less than both Ring and Hatta (400 W). The result was that there was only a slight increase in deposition rate over that of the CW process.

One might conclude from this that pulsed-modulated-microwave-power can be successful in many types of CVD systems as long the peak power is high enough. Furthermore, comparing the results of Ring and Mantei with those of Hatta and colleagues it is

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noted that increasing the peak power in a pulse-modulated process increases the deposition rate.

2.5 Diamond Nucleation

While CVD diamond does nucleate on diamond substrates it does not nucleate on most non-diamond substrates. A nucleation enhancement step is required for deposition of diamond from the gas phase on mirror polished silicon or boro-silicate glass. There are two types of enhancement processes reported in the literature; substrate seeding and process assisted nucleation. Substrate seeding is a pre-deposition process where the substrate surface is either polished or seeded with diamond particles. Process assisted nucleation is a unique CVD process separate from the actual deposition process such as bias assisted nucleation of silicon.

For some CVD applications, such as optical coatings, the quality of the deposition process is proportional to the nucleation density. Transmission through a thin diamond film increases with increasing nucleation density. Therefore, it is necessary for nucleation methods to yield high densities.

It is not yet completely understood why diamond nucleates on substrates that are abraded with diamond powder. Two obvious potential reasons for nucleation are that the surface topography is modified during the scratching and that tiny amounts of diamond are left on the surface from the diamond powder. It has been demonstrated that nucleation of diamond is possible on substrates that are scratched with non-diamond abrasive powders. However, the nucleation density is higher when diamond abrasives are used than when non-diamond abrasives are used. Paul A. Dennig and David A. Stevenson conducted fur-

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ther experiments to investigate whether diamond nucleation can be linked to modifications of the silicon surface. The conclusion was that diamond nucleates on silicon with small, sharp convex features^[49]. Their experiments involved etching V grooves and other features in mirror polished silicon with KOH and then processing the silicon in a diamond deposition process. From this they concluded that it is possible to nucleate diamond on top of the small features, and that frequency of nucleation is greater on features with more acute angles.

2.5.1 Abrasion Seeding

A technique of scratching the substrate as a process of abrasion seeding is described by H. Windischmann^[52] and R. Erz et. al.^[53]. Windischmann describes a simple process. First, a small amount of 1 μm diamond powder is sprinkled on the substrate. Then the substrate is polished by hand with a wipe. The excess powder is removed with methanol. Erz dilutes the diamond powder in aqueous media and polishes the substrate by hand using two sheets of silicon. The substrate is then cleaned in acetone with ultrasound. Erz reports that their process yields increasing nucleation density for decreasing diameter diamond powder. Reportedly, 0.1 μm diamond powder yields 10^9 cm^{-2} and 0.01 μm diamond powder yields 10^{10} cm^{-2} seeding density.

2.5.2 Ultra-Sonic Seeding

Ultrasonic seeding is similar to abrasion seeding except that hand polishing is replaced by ultrasonic agitation. Muranaka et. al. describe a process where the substrate surface is supersonically scratched in a methanol-diamond slurry and then cleaned with

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organic solvents^[54]. Wild and his colleagues describe a similar process where the diamond powder is mixed with ethanol^[57]. The ethanol solution and the substrate are placed in an ultrasonic bath. Afterwards, the substrate is cleaned with methanol in ultrasound. Nucleation density with this process can be as high as 10^{10} cm^{-2} .

2.5.3 Bias Enhanced Nucleation

Diamond nuclei can also be generated on mirror polished silicon by applying a negative bias to the substrate. S. Yugo et.al. report a 10 minute CVD nucleation method where a negative bias is applied to the substrate^[55]. For diamond deposition the percent of methane in hydrogen is 0.5%. During the nucleation process the percentage of methane in hydrogen is as high as 40%. The minimum voltage and methane fraction for generation of diamond nuclei in this process is -70 V and 5%. The substrate temperature is typically 900 C. This process can yield substrate nucleation density as 10^{10} cm^{-2} . B. Sheldon et. al. report a that nucleation does occur at methane concentrations as low as 1.6% if the bias is increased to -200 V^[56].

2.5.4 Photo-Resist Diamond Seeding

Photo-resist diamond seeding (DPR) was developed at MSU and Ford as means of patterning or selectively seeding desired areas of the substrate with diamond powder^[50]. This process involves the following: diamond powder is mixed in a solution of photo-resist and photoresist thinner, the solution is spun on the substrate using a wafer spinner, and the substrate is baked in an oven. Afterwards, the photo-resist can be patterned with normal lithographic masking techniques to selectively remove diamond seeds from areas

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where diamond deposition is not desired. If patterning is not desired diamond can be deposited without any further processing after the photo-resist is dry. Nucleation densities as high as 10^9 cm^{-2} have been reported.

Although techniques such as abrasion seeding, ultrasonic seeding and bias enhanced seeding have the capability of producing higher seeding densities than the current DPR method, DPR is reported to have an advantage over those methods of easier control of nucleation density and grain size. This is due to the fact that only the diamond seed particles form the active nucleation sites. Furthermore, DPR does not damage the surface of the substrate.

Masood reports that the optimum DPR procedure for obtaining a uniformly seeding a substrate with a nucleation density of 10^8 cm^{-2} is as follows^[51]. A quantity of 142.6 mg. of 1mm diamond powder should be mixed with 42 ml of photoresist and 16 ml of photoresist thinner. When spinning the DPR mixture onto the substrate the following spin schedule should be used. The spinner should be spun in three successive steps with revolutions of Ramp-up - 4000 rpm - 500 rpm, for durations of 10 sec - 30 sec - 5 sec.

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Chapter 3

Experimental System, Experimental Procedures, and Measurement Methods

3.1 Introduction

The scope of this chapter is to describe in detail the general experimental setup that was used for diamond deposition, the procedures for depositing diamond on a substrate, and methods for characterizing deposited diamond films. The description of the experimental setup gives specific detail about the computer controlled apparatus that was constructed for depositing diamond films with a MCPR plasma source. It is divided into two sections that cover the hardware in the deposition system and the software that controls it. The experimental procedures section provides the specific details of how substrates are pre-treated prior to diamond deposition. It also includes details of how the deposition system is operated for a general diamond deposition experiment. Some miscellaneous deposition system maintenance procedures are also outlined here. The final section of this chapter describes the methods used to characterize the deposited films. It includes characterization techniques for evaluating the properties of “as-deposited” diamond films such as film thickness, deposition rate, deposition uniformity, surface roughness, adhesion, and film quality. There is also a discussion detailing the method of measuring the transmissivity of diamond films that are deposited on glass substrates.

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3.2 The MCPR Diamond Deposition System

One of the chief tasks required for this dissertation was to construct a semi-automated machine that deposits thin diamond films on substrates using a MCPR plasma source. This was necessary because the growth experiment typically required 10 to 40 hours of continuous operation under precise and repeatable conditions. This section gives detailed information concerning both the hardware used to construct the machine, as well as the design of the windows based program that was written to control it. The hardware section includes information regarding the configuration of components that were common to most diamond deposition experiments. Specific details concerning the exact setup of the MCPR are excluded as they are covered in later chapters as required.

3.2.1 Hardware in the MCPR Diamond Deposition System

As was mentioned earlier, a MCPR plasma source was used for all the diamond deposition experiments that are discussed in later chapters. However, the MCPR is only one component of the whole system that was used. Other essential components include a precision gas flow system, a vacuum system, a microwave power supply, a pressure measurement system, and others. Figure 3.1 is an schematic representation of the complete MCPR diamond deposition system that was constructed for this investigation. The following sections provide details concerning each of the hardware subsystems in figure 3.1.

3.2.1.1 Vacuum and Gas Flow Systems

In order to have a clean, sub-atmospheric CVD process in the MCPR, a supply of gasses must be continuously pumped through the process chamber of the MCPR at a pres-

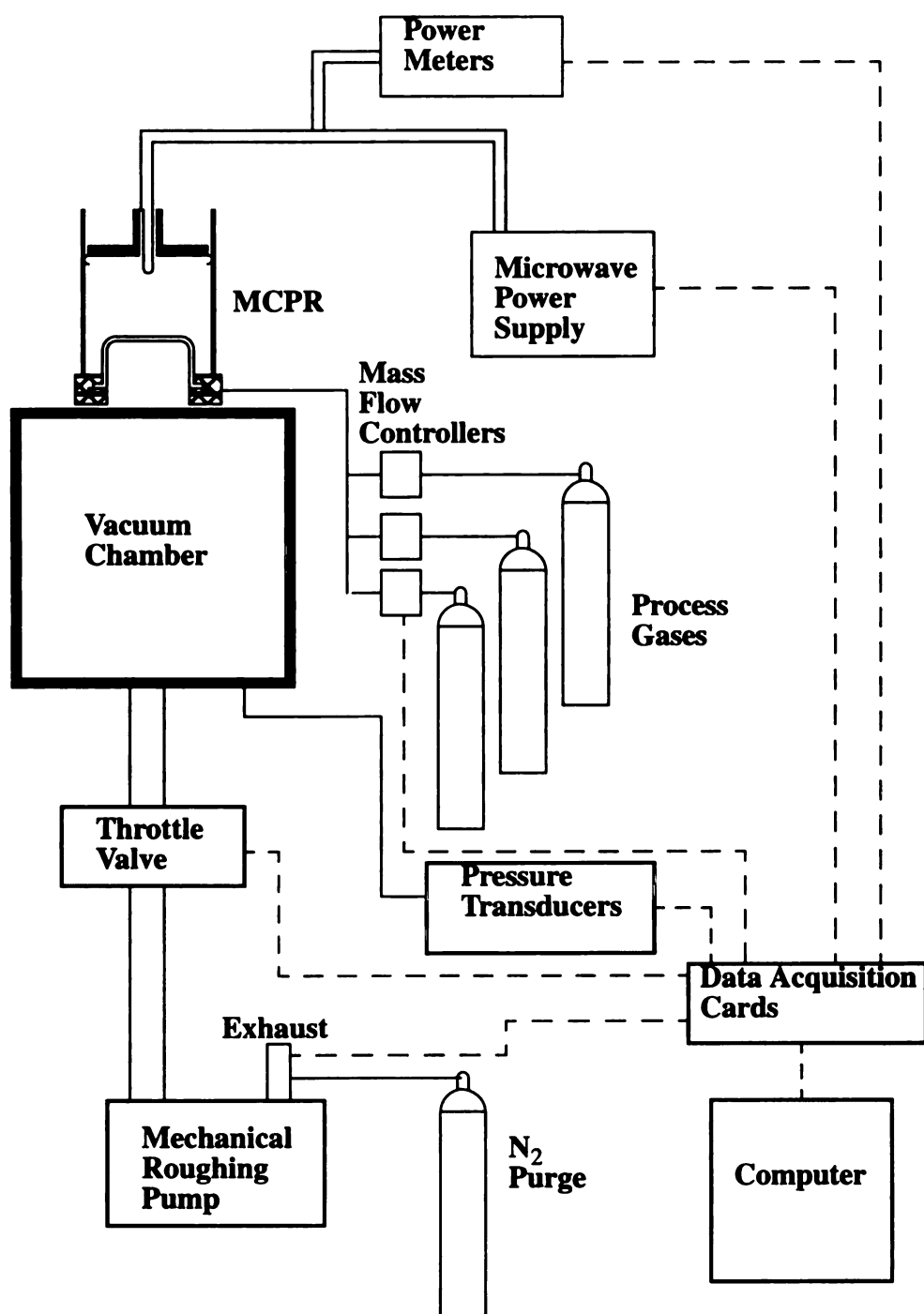


Figure 3.1 The diamond deposition system.

sure below atmosphere. This was achieved by mounting the MCPR on top of a large stainless steel vacuum chamber and routing the gas flow into the MCPR base plate (24), through its process chamber (27) and out to the vacuum chamber (6) as shown in figure 3.2.

The vacuum chamber (6) was constructed from a stainless steel tube with a diameter of 18 inches and an overall length of 16 inches. It has a round 8-inch diameter vacuum tight access door in the front that allows easy access to the chamber when it is not under vacuum. On the sides there are two round 6-inch diameter viewing windows. In the rear there are four $2\frac{3}{4}$ inch conflat feed-through ports which are connected to pressure transducers (26). The vacuum chamber is placed on top of the vacuum chamber base plate (28). On top of the vacuum chamber is the chamber top plate (29) where the MCPR connects to. The chamber base plate has a 10-inch ASA feed through port in the center, and 6 small $1\frac{1}{3}$ inch conflat feed-through ports on a radius of 15 cm surrounding the center port. One of the $1\frac{1}{3}$ inch feed-throughs is used for venting the chamber to atmospheric pressure. This port is connected to a nitrogen cylinder (22) through a manual type Nupro valve (23). The manual valve is connected to the feed-through by stainless steel tubing (11); the nitrogen tank is connected to the manual valve by flexible plastic tubing (30). The vacuum is sealed between the vacuum chamber and its top and base plates by vacuum seal o-rings. The o-rings are located in o-ring grooves located at each end of the chamber. The top and base plate are 1 inch thick, and were fabricated from stainless steel plates. There is also an o-ring between the MCPR and the vacuum chamber top plate. The o-ring groove for this seal was cut into the vacuum chamber top plate.

The vacuum chamber pressure is maintained by an Alcatel Model 2033 CP+

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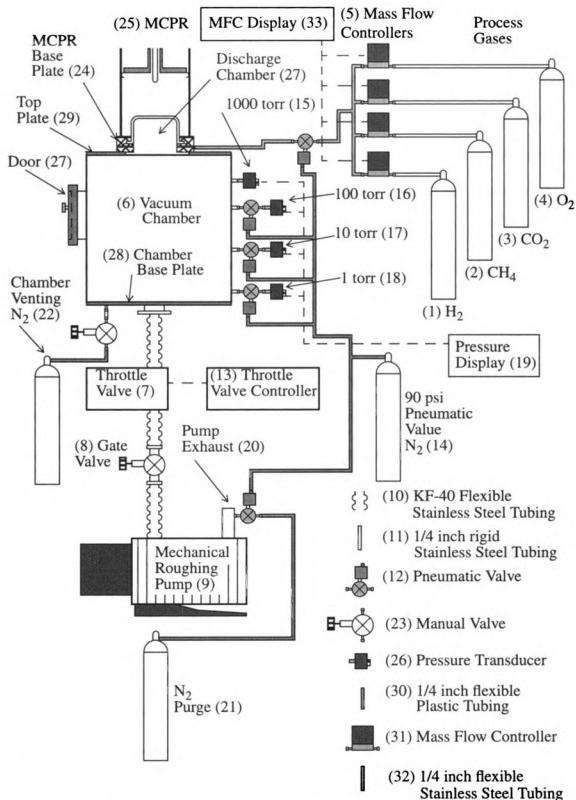


Figure 3.2 The vacuum and gas flow system.

mechanical vacuum pump (9) working in conjunction with a MKS Type 253 Throttling Valve. The throttling valve is connected in series with a mechanical gate valve (8) in the flow path between the vacuum chamber and the mechanical pump by flexible stainless steel tubing (10). Control of the throttling valve is maintained by a MKS Type 152A Exhaust Valve Controller (13). This controller operates the throttle valve by comparing the actual vacuum chamber pressure with the desired chamber pressure and adjusting the position of the throttle valve as needed.

Pressure in the vacuum chamber is measured by four independent pressure transducers (26) and displayed by a MKS Type PDR-5B Power Supply Digital Read-Out (19). The pressure range of each pressure transducer is different. The ranges are 1000 torr (15), 100 torr (16), 10 torr (17) and 1 torr (18). Since the maximum reading of the last three pressure transducers is below atmosphere, a normally-closed $\frac{1}{2}$ inch VCR Nupro pneumatic isolation valve (12) is connected in series between each transducer and the vacuum chamber. Whenever the pressure rises above that of the maximum range of a particular pressure transducer, the corresponding pneumatic isolation valve is automatically closed. The range operating pressure of the pneumatic isolation valves (12) is 60 to 90 psi. They are connected via flexible stainless steel tubing (30) to a nitrogen gas cylinder (14) with a regulator that is adjusted to 90 psi.

The 1 torr transducer is used to monitor the base pressure of the vacuum system and to check for vacuum leaks. The 10 torr and 100 torr pressure transducers are used to monitor the system's pressure during deposition experiments. One is always connected to the throttle valve controller for pressure control. The 1000 torr transducer is used as a safety feature to validate the reading of the 10 torr and 100 torr transducers during experi-

ments. If a pneumatic isolation valve were to fail and close during a deposition experiment, it would isolate the chamber from one of the low pressure valves. This would cause an open loop in the throttle valve control. For this reason, the reading of the 1000 torr transducer, which does not have an isolation valve, is compared to those of lower pressure transducers. More details of safety and other feature of system operation are discussed in later sections.

There are six process gas flow channels in the MCPR system. Each of them routes gases from a gas cylinder through a mass flow controller (MFC) (31) and into the MCPR discharge chamber. Process gases are connected to the MFCs by rigid stainless steel tubing (11) and $\frac{1}{4}$ inch swagelok connectors. The outputs of the MFCs are tied together through flexible stainless steel tubing (32) and $\frac{1}{4}$ inch VCR connectors, and routed to the base plate of the MCPR (24) through a normally closed $\frac{1}{4}$ inch VCR Nupro pneumatic valve (12). The pneumatic valve isolates the MFCs from the MCPR discharge chamber when it is vented to atmosphere. The MFCs are MKS Type 1159B Mass Flow Controllers. The maximum flow rate of the largest MFC is 1000 sccm, and is calibrated to hydrogen. This channel is always connected to a hydrogen gas cylinder (1). The other five MFCs are calibrated to nitrogen and have the following maximum flow rates: 200 sccm, 100 sccm, 100 sccm, 50 sccm, and 20 sccm. Oxygen (4), Carbon Dioxide (3) and Methane (2) are connected to three of these MFCs. Actual flow in each MFC is controlled by MKS type 247C 4 Channel Read Out Mass Flow Controller 1100 Series (33). There are two of these units in the MCPR system. Since the last five MFCs are calibrated to nitrogen, they must be adjusted to accurately flow other gases. Each MFC is re-calibrated for the particular gas it is flowing by a scaling control setting adjustment on the back of MKS 247C. Since each

MKS 247C can control up to four MFCs simultaneously, there are four scaling control setting adjustments on the back of each unit. The adjustment is a rotary knob with a range of 0 to 1000. The setting value of the scaling control knob is determined by the gas correction factor and the gauge factor as shown in equation [3.1]^[58]. The gas correction factors for many types of gases are published by MKS in the back of the manual for the 247C series.

$$\text{Scaling control setting} = \text{Gauge Factor} \times \text{Gas Correction Factor} \quad \text{eq (3.1)}$$

Table 3.1: MKS MFC Gauge Factors^[58]

MFC N₂ Calibrated Maximum Flow Rate	Gauge Factor
1, 10, 100, 1000, 10K	100
2, 20, 200, 2000, 20K	200
5, 50, 500, 5000, 50K	50

3.2.1.2 Vacuum Measurement System

As was mentioned in section [3.2.1.1] the pressure of the vacuum chamber (6) is measured by four pressure transducers (26). These transducers are MKS variable - capacitance sensors. Figure 3.3 is a diagram of the pressure measurement system of the MCPR moderate pressure diamond deposition system. The 1000 torr pressure transducer (15) is a MKS type 224 HA pressure transducer, which has two trigger set points. These set points are used to open and close the pneumatic valves (12) that protect the 100 torr (16) and 10 torr (17) transducers when the pressure in the vacuum chamber (6) exceeds the maximum

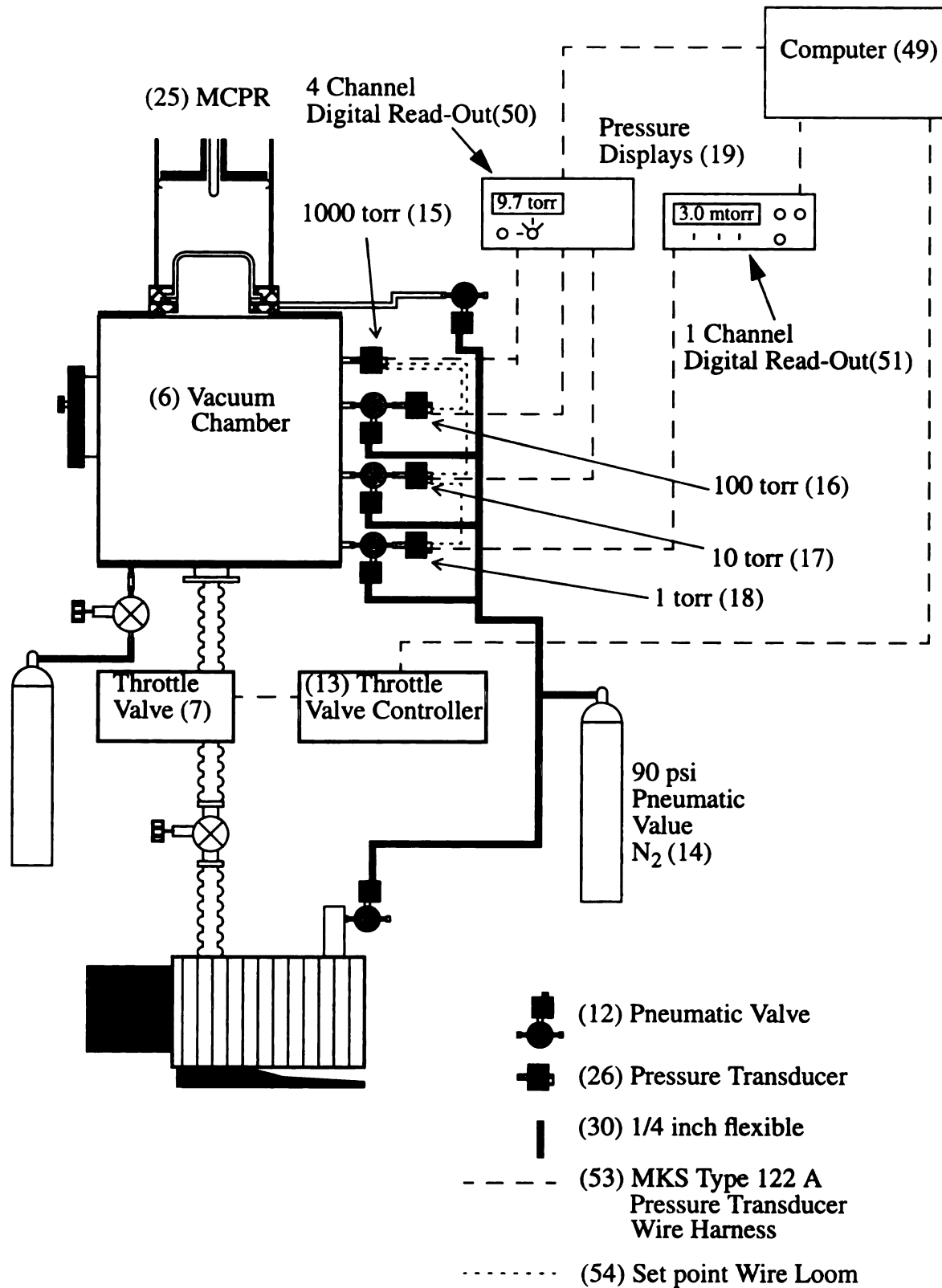


Figure 3.3 The vacuum measurement system.

reading of either transducer. The 100 torr transducer is a MKS Type 122 AA pressure transducer and has no trigger set points. Like the 1000 torr transducer, the 10 torr transducer is a MKS model 224 HA with two set points. One of the set points in the 10 torr transducer is used to open and close the pneumatic isolation valve that protects the 1 torr pressure transducer. All three of the above mentioned > 1 torr pressure transducers are connected to a MKS Type PDR-5B Power Supply Digital Read-Out (19). This unit supplies +/- 15 V to each transducer and displays the pressure reading of each. The 1 torr transducer (18), is connected to a separate display (51), a MKS Type 270 Signal Controller.

3.2.1.3 Microwave Power Supply System

In the diamond deposition MCPR, microwave energy at 2.45 GHz is focused into a TM_{01n} mode (refer to section [2.1]). The electric and magnetic fields of the TM_{01n} mode are such that a hemispherical-shaped, or thick disc-shaped - depending on pressure, plasma is formed above the deposition substrate. Figure 3.4 is a diagram of the microwave power supply system that was assembled for the MCPR diamond deposition experiments of this dissertation.

The microwave power circuit in figure 3.4 was constructed to safely deliver microwave energy up to 1 KW to the MCPR while protecting the power supply (40) from any energy that is reflected back from the MCPR. For most of the experiments discussed in later chapters, the power supply (40) was a Gerling Model GL119 microwave power supply. The Gerling Model GL 119 is a 3 KW 2.45 GHz water cooled power supply. The power flow in figure 3.4 is as follows. Microwave power is transported from the Gerling to

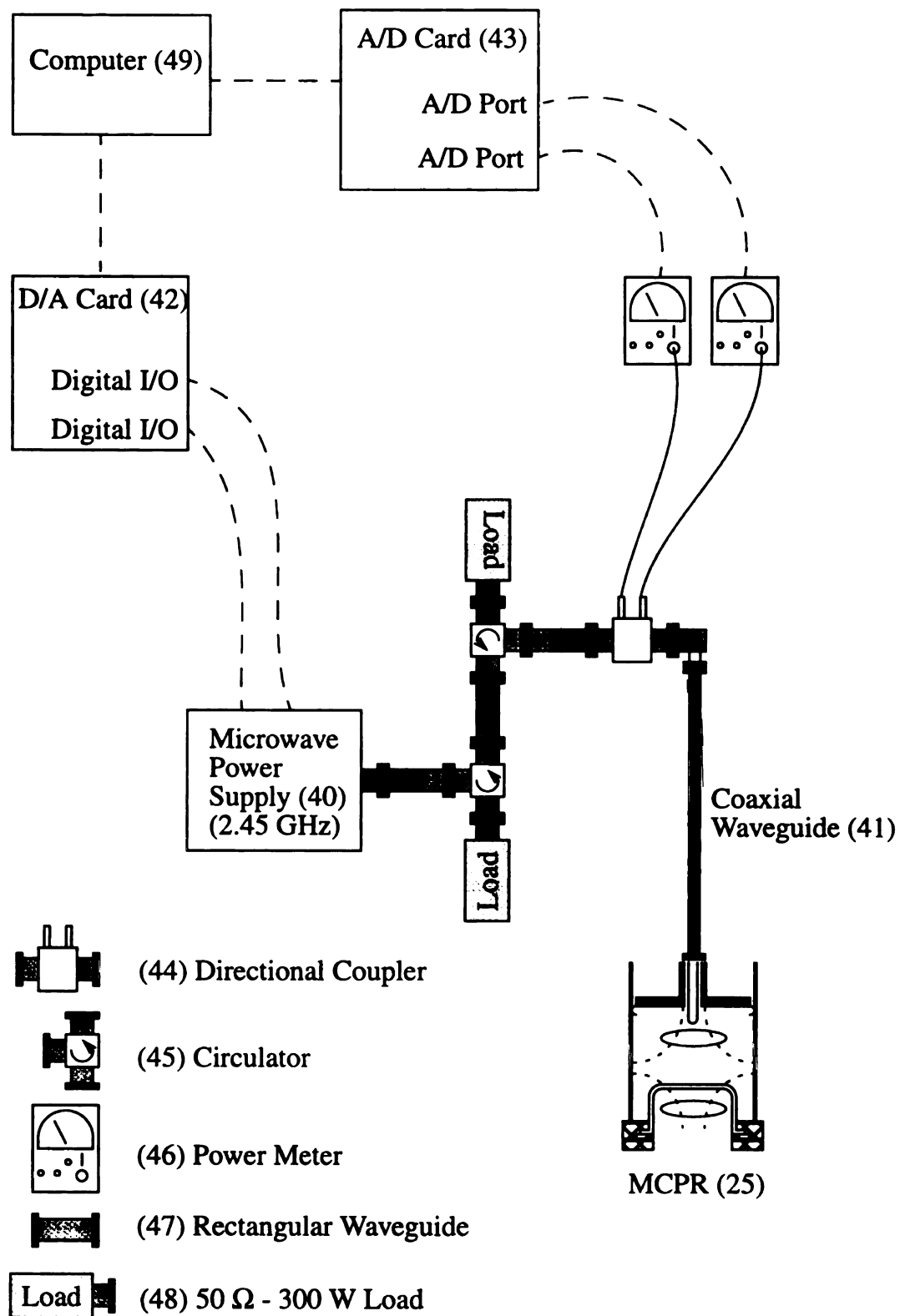


Figure 3.4 The CW microwave power supply system

the MCPR through sections of rectangular (47) and coaxial waveguide (41). The rectangular waveguide is single mode TE_{10} waveguide with a maximum power rating of 10 KW.

Spliced in between the sections of rectangular wave guide, are two circulators (45) and one directional coupler (44). The circulators have three waveguide ports, and serve to guide reflected power away from the microwave power supply, thus protecting it from reflected microwave energy. There is a matched impedance $75\ \Omega$ load (48) attached to each circulator. This load is water cooled and serves to absorb any microwave energy that is directed towards it. Together, the two circulators and matched impedance loads work to protect the microwave power supply from microwave energy that is reflected by the MCPR. The directional coupler (44) diverts a highly attenuated amount of the incident and reflected microwave energy from the waveguide to two HP 432 A power meters (46). These meters convert the milli-watt level power that they receive from the directional coupler to a voltage signal. It should be noted that the HP 432 A power meters monitor CW microwave power and not pulsed microwave power. For experiments using pulsed microwave power, the power level is measured with a power diode and an oscilloscope (refer to section [5.5]). There is a variable scale analog display in each power meter that indicates the amount of milli-watt microwave energy the meter is seeing. On the back of each power meter there is a 0-1 V_{ac} port for electronic sensing of the power meter reading.

From the directional coupler to the MCPR, microwave energy is transported in a TEM mode along flexible circular coaxial waveguide (41). This waveguide is dielectric filled and is rated to 1 KW. This is the lowest rated microwave component in the MCPR microwave system. Hence it limits the amount of microwave energy that can be transported to the MCPR to a CW maximum of 1KW.

Since the matched impedance loads dissipate microwave energy, they along with other components in the MCPR microwave power supply system must be liquid cooled. In this configuration, the Gerling Model GL119, the circulators, and the matched impedance loads are all water cooled. The cooling requirement for the Gerling GL 119 is a minimum of 0.5 gallons per minute.

As is indicated in figure 3.4, the microwave system is connected to the computer (49) that controls the MCPR diamond deposition system in two places. First, the analog outputs of the microwave power meters are routed to the input channels of an analog to digital card in the PC. This allows the PC to monitor the incident and reflected power to and from the MCPR. Secondly, there are two connections from digital I/O ports in the PC to the microwave power supply. This gives the computer on - off control over the microwave power supply. Further details concerning the exact wiring between the PC and the microwave power supply circuit are provided in later sections. Refer to section [3.3.1.3] for detailed instructions for operation of the Gerling Model GL 119 microwave power supply.

3.2.1.4 Computer Hardware

The moderate pressure, low temperature MCPR diamond deposition system that was constructed for this dissertation is a semi-automated experimental apparatus. It was designed such that a computer could start and finish the deposition experiments. The computer also serves to measure and record various system parameters during each experiment. This is all necessary for safety since diamond deposition experiments typically last from just a few hours to several days. During this time the computer is able to reliably

watch over the system and stop an experiment immediately if a critical subsystem is functioning out of tolerance. To accomplish this task of automating the MCPR diamond deposition experiment, a computer with connections to systems hardware and a unique software program were required.

The computer in the MCPR diamond deposition experiment is an Intel 386 based PC. To make the connections to the various subsystems, four ISA slot data acquisition cards were inserted into the PC. In addition, one expansion card that remains external to the PC was added. Table 3.2 has the parts numbers and I/O details of each card. For simplicity and a reduction in cost, all the cards were purchased from Computer Boards Incorporated. The digital I/O channels can be configured either as input or output ports.

Table 3.2: Data Acquisition Cards

Part Number	ISA Card or Expansion	A/D Channels	D/A Channels	Digital I/O Channels	K-type Therm- o couple
CIO-DDA06	ISA		6	24	
CIS-DAC02	ISA		2		
CIO-DAS08	ISA	8		24	
CIO-DAS16/Jr	ISA	8		4	
CIO-EXP32/16	Expansion				16

Collectively, there are three functions that these cards serve. First, system parameters must be monitored such as incident microwave power and system pressure. For this, analog voltages must be converted into 12 bit digital words. The CIO-DAS08 and CIO-DAS16/Jr are used to perform this function. Second, equipment set points must be controlled, e.g. gas flow rates and system operating pressure. The CIO-DDA06 and CIS-

DAC02 are D/A cards that perform this function. Third, most equipment in the MCPR diamond deposition system is turned on and off by digital 0 and 5 volt signals. Digital I/O ports from several of the above mentioned cards are used to perform this function. In addition some experiments required thermocouple temperature measurements. For this the CIO-EXP32/16 card is connected external to the PC to one of the A/D channels of the CIO-DAS16Jr. The expansion card is used to precondition the signals from the k-type thermal conductors. Hence the signal read by the computer is the corrected temperature. With this card the PC can make temperature measurements directly from the thermocouples. Further information regarding the use of these data acquisition cards is provided in the system's software section (section [3.2.2]). System level connections from these cards to system hardware is detailed in the next section.

3.2.1.5 Computer Interface of the MCPR Diamond Deposition System

This section has been included to provide an overview of how the computer interfaces to the system hardware through the data acquisition cards. A few system level sketches of the connections between the computer and the system hardware are included; however, the exact circuitry of these and other circuits in the low temperature MCPR apparatus of this dissertation are omitted.

3.2.1.5.1 Computer Interface to the Microwave Power Supply System

In order for the computer to safely operate the MCPR system, it is imperative that it be able to control both the on and off functioning of the microwave power supply. In this

MCPR system, the computer controls only these functions. The adjustment of the input microwave power level is a manual operation performed by the user.

Figure 3.5 is a diagram of the interface between the computer's data acquisition cards and the microwave power supply (40) and power meters (46). The on - off operation of the power supply is controlled via digital I/O ports in the CIO-DDA06 (61) D/A card. When 5 volts is applied to both the relays (60) from the digital ports of (61), the power supply is turned on. Otherwise it is off. The analog output of the power meters (46) is sensed by the A/D channels of the CIO-DAS16/Jr (62).

3.2.1.5.2 Computer Interface to the Vacuum and Gas Flow System

The computer's interface to the vacuum and gas flow system acts to control what quantities of input gases are flowed into the system during an experiment, and to set and monitor the systems pressure. Figure 3.6 is a diagram of the connections between the computer's data acquisition cards and the pressure display hardware of the low temperature diamond deposition system. In the figure, the signal output of the three highest range pressure transducers (1000 torr, 100 torr, and 10 torr) are connected to the MKS Type PDR-5B Power Supply Digital Read-Out (50). These same signals are also routed to separate A/D inputs in the CIO-DAS08 (63). This allows the computer to monitor the systems vacuum chamber (6) pressure in triplicate. Besides measuring the systems vacuum pressure, the computer also controls the set point of this parameter. The computers CIS-DAC02 (65) D/A card is connected to a throttling valve controller (13) for this purpose. There is also a circuit in figure 3.6 that connects a digital I/O port of the CIO-DDA06 (61) to the pneumatic valve of the mechanical pump nitrogen purge. This circuit is used by the computer

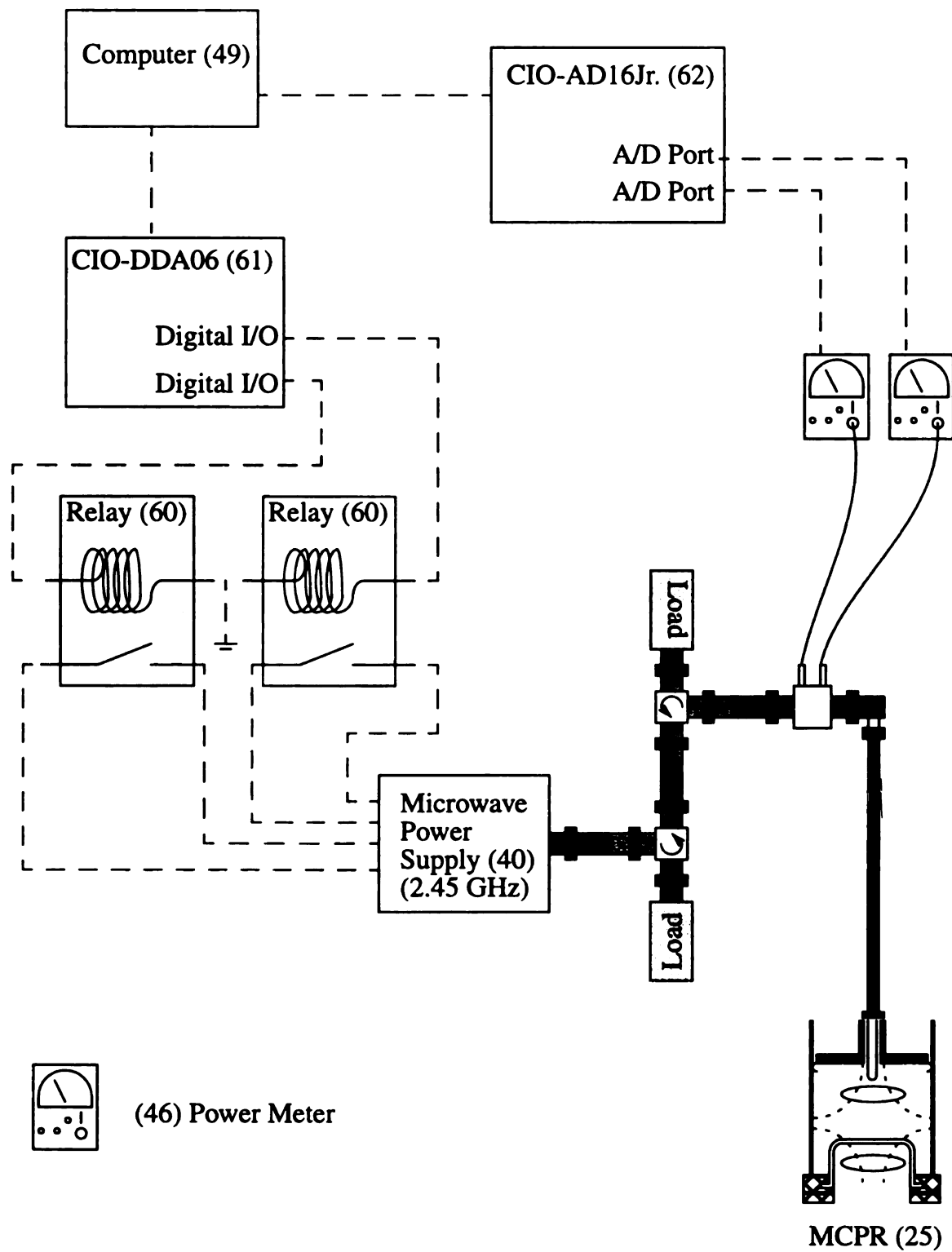


Figure 3.5 Computer Interface to the Microwave Power Supply.



Figure 3.6 Computer Interface to the Pressure Transducers.

to dilute the exhaust of the pump, which generally has a high concentration of hydrogen, with nitrogen.

Figure 3.7 is a diagram of the connections from the CIO-DDA06 (64) to the MKS Type 247C 4 Channel Read Out (33), which controls the flow of gases through the MKS Type 1159B Mass Flow Controllers (5). In the figure, the D/A channels transmit the set point values to the MFC Type 247 C (33), and the digital I/O ports control the on - off functioning of the MFCs.

3.2.2 Software for the MCPR Diamond Deposition System

The software program that controls the semi-automated low temperature MCPR diamond deposition system was created using Microsoft Visual C++ Version 1.51. The uncompiled C++ code that makes up the plasma software is approximately 5,000 lines long. Visual C++ programs contain a great deal of C++ code which is necessary to create and manage the program's user friendly interface which is presented in each programs window frames and document views. The details concerning these operations need not be discussed when presenting the MCPR system's hardware control algorithm that is executed by the program, named plasma.exe. What is presented in this section in a flow chart format is what is necessary to understand the algorithm that is executed each time a diamond deposition experiment is run. The details have been simplified to reduce the complexity of several thousand lines of code down to a four page flow chart.

Figure 3.8 through figure 3.11 shows the flow of the software algorithm for a typical diamond deposition run. There may be a slight variation in this procedure based on what hardware control features the systems administrator has installed. The shaded col-

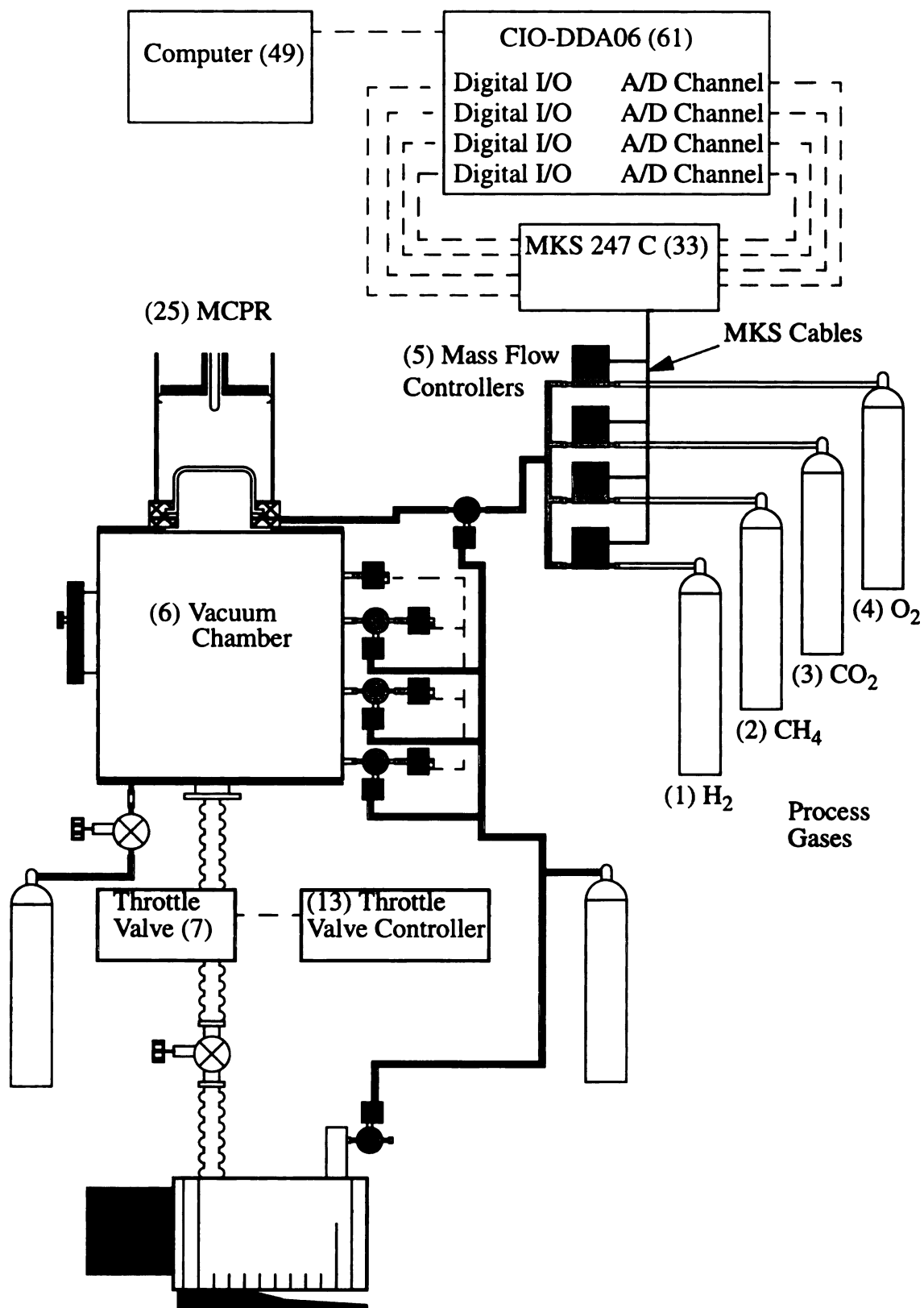


Figure 3.7 Computer Interface to the MFCs.

umn on the left of each figure shows the points in the algorithm where user input is required. While these figures do not cover every feature in the plasma.exe software, they do provide a complete systems level representation of the steps that are executed whenever a diamond deposition experiment is run.

There are two levels of users in the plasma.exe program, the basic user and the master user. The master user has access to every feature of the program. Persons with master user access can add and delete users to the password list, configure the systems hardware interface, and execute automated deposition experiments. The basic user's password does not allow access to the system's password list or the hardware interface configuration; however, they can run automated experiments.

As was mentioned in section [3.2.1.5] the computer interfaces to several components of the MCPD diamond deposition system through data acquisition cards. Whenever the software requests a measurement from one of these cards it must provide a list of parameters such as board number, channel number, voltage range, and others. This information is stored by the plasma.exe program in a group of files on the computer's hard drive. This allows the versatility of changing the configuration of the hardware, i.e. installing new data acquisition cards, without revising the software. The main window frame of plasma.exe has six buttons in a group labeled *systems configuration* that the master users can select them to change the hardware interface configuration whenever the system's hardware is altered. These hardware interface configuration menus allow some functions such as substrate thermocouple measurements to be disabled.

The flow chart in figure 3.8 through figure 3.11 assumes that all the system's hardware interface features of the plasma.exe program are being executed. If a feature is not

installed the program will just skip that step. Installation of some hardware control features is mandatory for execution of the program. If they, or any optional software control features are not properly configured, a hardware error will be relayed by the data acquisition cards, and program execution will terminate.

3.3 Experimental Procedures

3.3.1 Operation of the Low Temperature MCPR System

As was stated earlier, the experimental apparatus used for this dissertation is a semi-automated machine. During a deposition experiment, the computer monitors, measures and records many of the system parameters. However, the start-up procedure requires that some steps be completed by the system's user. The next sections outline the procedure for start-up, shut-down and operation of the Gerling Model GL119 microwave power supply.

3.3.1.1 The Start-Up Procedure for Running a Deposition Experiment

The procedure outline here for start-up of the low temperature diamond deposition apparatus is listed in figure 3.12. This procedure assumes that the apparatus is being operated in the semi-automated deposition mode with the Plasma version 3.0 software or later. It is further assumed that prior to beginning the start-up procedure, the system is in a vacuum state with no substrate inside the MCPR. There are some variations to this procedure for experiments mentioned in later sections; however, for most experiments this procedure applies.

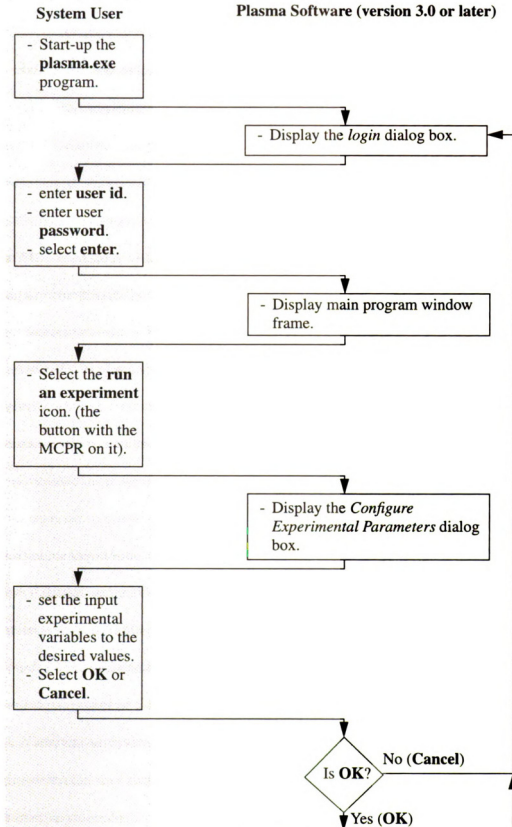


Figure 3.8 Steps to run an experiment with *plasam.exe*.

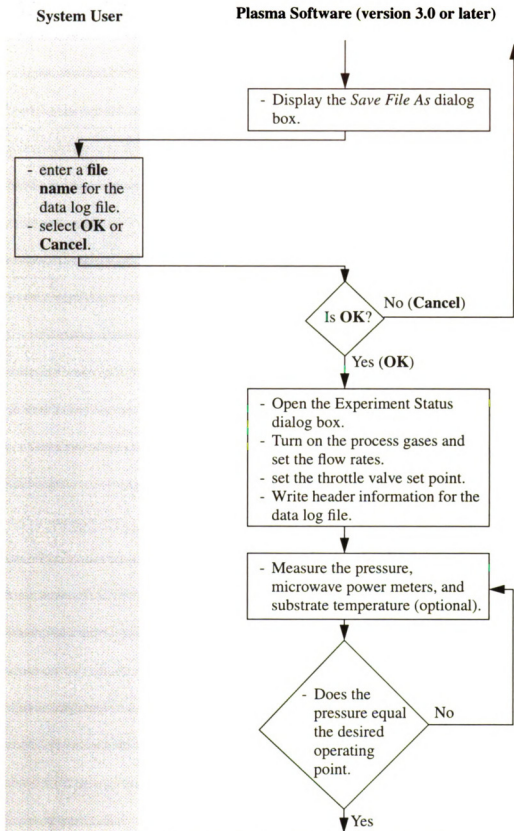


Figure 3.9 Steps to run an experiment with *plasam.exe*.

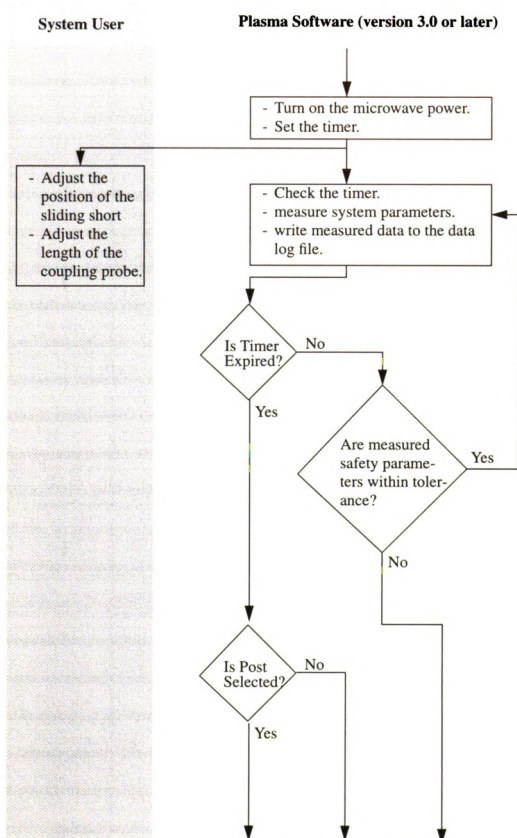


Figure 3.10 Steps to run an experiment with *plasam.exe*.

System User

Plasma Software (version 3.0 or later)

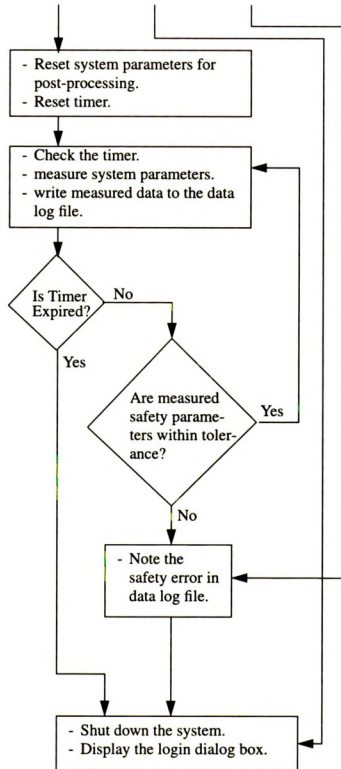


Figure 3.11 Steps to run an experiment with *plasam.exe*.

I Insert the substrate into the MCPR system

- 1) turn the switch labeled *MFCB* to **Closed**.
- 2) set the switch labeled *throttle valve* **Manual Closed**.
- 3) close the *manual gate valve* (turn knob clockwise until tight).
- 4) open the valve labeled *N₂ purge* (turn counter-clockwise slowly) let the vacuum system fill with N₂ until the 1000 torr Baratron reads 760 torr.
- 5) close the valve labeled *N₂ purge* (turn clockwise until tight).
- 6) open the vacuum door.
- 7) insert the substrate and substrate holder assembly into the MCPR base plate and tighten the 7/16" retaining nuts.
- 8) close the vacuum door.
- 9) turn the switch labeled *throttle valve* to **Open**.
- 10) open the *manual gate valve* fully (turn counter clockwise slowly).
- 11) let the system pump to vacuum until the 1 torr Baratron reads below 1 mtorr.

II Start the Experiment

- 1) set the *throttle valve* switch to **auto**.
- 2) set the switch labeled *MFCB* to **Open**.
- 3) turn on the MCPR and microwave power supply load water cooling and check flow rate.
- 4) turn on the MCPR internal and external forced air cooling.
- 5) perform the Gerling Model GL119 warm-up procedure (refer to section [I.1]).
- 6) open the valves to all the gas cylinders connected to the system.
 - mechanical pump N₂ purge (minimum of 600 psi).
 - pneumatic valve N₂ (regulator set to 60 - 90 psi, minimum of 300 psi).
 - all gases connected to the MFCs that will be used for this experiment.
- 7) login to plasma (version 3.0 or later) software, configure system parameters and begin experiment (refer to section [3.2.2]).
- 8) wait for the plasma software to turn on the microwave power supply, then adjust the output microwave power level to the desired value (refer to section [I.2]).
- 9) adjust the sliding short location in the MCPR and the length of the coupling probe until the measured reflected power is at a minimum and the plasma has the desired shape.

Figure 3.12 Generic System Start-Up Procedure.

3.3.1.2 The Shut-Down Procedure for a Deposition Experiment

The shut-down procedure for a deposition experiment that is controlled by the system software plasma version 3.0 or later is a mostly automatic procedure. The few steps that must be completed by the user include shutting off cooling systems and system components after the system has had time to cool down. This cool down time is critical to many components of the MCPR because the MCPR system is typically operated at temperatures above 200°F. Furthermore, some individual components in the MCPR low temperature system have a minimum required cool down period after normal operation. The manual MCPR system shut-down steps are listed in figure 3.13.

For an **emergency system shut-down** during a deposition experiment, press the return (enter) key on the computer key board, or click on the stop sign on the computer screen with the mouse.

3.3.1.3 Operation of the Gerling Model GL 119

The procedures outlined in the following sections provide the details of operating the Gerling Model GL 119 in the semi-automated mode. This information follows the system configuration that was outlined in section [3.2.1]. The Gerling Model GL119 is a liquid cooled magnetron based microwave generator. It is capable of producing up to 3 KWatts of microwave energy at a stable operating frequency of 2.45 GHz. It can be operated in both the CW and Pulsed mode. Important details as to the warm-up procedure, adjustment of microwave power level, and shut down procedure, are contained in Appendix I.

- 1) after the computer has stopped the experiment the login dialog box will appear (refer to section [3.2.2]). **wait at least 1 hour before proceeding further.**
- 2) turn off the internal and external forced air cooling for the MCPR.
- 3) turn off the water cooling for the MCPR and the microwave loads.
- 4) turn off the Gerling's Neslab cooling unit.
- 5) turn off the Gerling Model GL119 (refer to section [I.3]).
- 6) close the valves to the gas cylinders connected to the MFCs.

Note, the system cool down time must always be adhered too!

Figure 3.13 Generic System Shut-Down Procedure.

3.3.2 Substrate Pre-treatment Methods

In section [2.5], which was titled *Diamond Nucleation Methods*, several nucleation techniques were reviewed. From that list, two methods were utilized for pre-treating the deposition substrates that were coated with diamond films by the methods of chapters 5 and 6. The first method that was used was the photo-resist seeding method, which was developed by Masood et.al. at Michigan State University. Since this low temperature diamond deposition study was an extension of on-going high temperature MCPR diamond film deposition, it was appropriate to begin the work with this method. Later on, when a higher seeding density and smaller grain films were desired as a means to reduce film surface roughness, the nucleation method was switched to abrasion seeding. This was in response to a suggestion by Henry Windishman of Norton Diamond Films Inc. In the following sections the procedure for pre-treating the substrate with these methods is outlined. Regardless of which pre-treatment method was used, the diamond powder type was always a grade where the particles had a diameter of 0.25 μm or less.

3.3.2.1 Preparation of substrates prior to Seeding

Before any substrate was seeded for diamond deposition it was first cleaned and weighed. The substrate cleaning procedures removed dirt and contaminants from the substrates prior to seeding. Whenever continuous diamond films were deposited such that the film completely covers one side of the substrate, the weight gain of the substrate from before the deposition to after deposition was used to approximate the average thickness of the deposited film. Hence each substrate was weighed prior to being seeded by either seeding process.

The cleaning procedure for silicon substrates had just three steps. To clean a silicon substrate it was rinsed in acetone for 2 minutes, rinsed in methanol for 2 minutes, rinsed with de-ionized water for 3 minutes, and dried with a nitrogen blow gun.

The cleaning procedure for glass substrates was a three part process. First, the substrates were cleaning in an ultrasonic bath in a 1000 mL beaker filled with 5 mL of Liquinox cleaning solution and 800 mL of de-ionized water. After 15 minutes in the ultrasonic bath the substrates were rinsed with de-ionized water for 1 minute. Second, the substrates were placed in boiling hydrogen peroxide. After 20 minutes in the boiling H_2O_2 , the substrates were rinsed with de-ionized water for 1 minute. Finally, the substrates were dried in an oven for 20 minutes at a setting of 125 C to 170 C.

3.3.2.2 Photo-Resist Seeding of Silicon and Glass Substrates

The process for seeding a substrate with the DPR seeding method was as follows. After the substrate is cleaned and weighed, the diamond powder - photoresist solution is mixed. First the appropriate amount of diamond powder is measured into a 60 mL bottle which is then placed in an oven for 1 hour with a temperature setting of 125 C to 170 C. This step removes moisture from the diamond film and helps to preclude clumping later. Second 16 mL of Microposit Type P thinner is added to the 60 mL bottle. Third, the bottle containing the mixture of thinner and diamond-powder is placed in an ultrasonic bath for 30 minutes. Note: to avoid damaging the ultrasonic bath the bottle should always be placed in the baths suspension basket, and should never be in contact with the walls or floor of the bath. After a few minutes the mixture will have a milky white appearance. Fourth, over the course of 1 hour equal portions of the 42 mL of Shipley 1813 photoresist

are added to the mixture in the ultrasonic bath. Fifth, the appropriate size chuck is inserted into the spinner and the spinner is configured to spin at 3000 rpm for 30 seconds. With the DPR solution still in the ultrasonic bath, a dropper is filled with a quantity of photoresist that can completely cover the surface of the substrate. Then the entire surface of the substrate is coated with the solution in the dropper. After 10 seconds, the spin cycle is started. Finally, the coated substrate is baked in the oven for 30 minutes at a temperature setting of 125 C to 170 C. Further information about seeding results vs. diamond powder concentration is contained in Appendix.

3.3.2.3 Abrasion Seeding of Silicon and Glass Substrates

The process for seeding a substrate with the abrasion seeding method was as follows. After the substrate is cleaned and weighed it is placed on a Kim Wipe™. Next, a quantity of diamond power is sprinkled onto the surface of the substrate in a uniform manner. While carefully holding the substrate in place on the Kim Wipe™ with the left hand, the substrate is polished with the right hand index finger for about 2 minutes. For this step the index finger is wrapped in a Kim Wipe™. The polishing technique was a counter-clockwise circular manner that was evenly applied to the entire surface of the substrate. Polishing was done with a fair amount of downward force exerted on the substrate. While polishing the surface with the right hand, the substrate is slowly rotated in a clockwise direction with the left hand. This is done to achieve a uniform seeding process. Afterwards, the remaining diamond powder on the surface of the substrate is wiped away with a clean Kim Wipe™. Next the substrate is blown clean for 2 minutes with a nitrogen gun.

Then the substrate is rinsed with acetone, methanol and de-ionized water for 2 minutes for each step. Finally, the substrate is blown dry with a nitrogen gun.

3.4 Characterization of the Diamond Deposition Process and Diamond Film

The remaining sections of this chapter are devoted to describing the methods of characterization for both the low temperature diamond deposition process and the deposited films. As was stated in section [2.3.3] the rate of deposition of a diamond film in a subatmospheric CVD process is strongly dependent on the temperature of the substrate. Hence, the methods that were used to determine the in-situ substrate temperature are described here. As a means of understanding how well a particular CVD diamond deposition process works, one must measure a group of relevant characteristics of the deposited diamond film. This list includes the quality of the diamond film, the thickness of the film, the deposition rate, and the deposition uniformity. Furthermore, when diamond is deposited on glass substrates additional measurements such as the film surface roughness, the optical transmissivity of films deposited on glass substrates, and film to glass substrate adhesion are required. These measurements provide further data that is useful in characterizing the diamond CVD process as it is applied to glass substrates. The following sections address how these parameters were measured.

3.4.1 Substrate Temperature Measurements

The temperature of the substrate during most diamond deposition experiments was measured in situ by one of two methods (1) optical pyrometer, or (2) thermocouple. In most experiments, an OS1200-HTS Omegascope pyrometer was used. This device is sen-

sitive to infrared radiation with a wavelength of $2.2\text{ }\mu\text{m}$, and can measure temperatures between $400\text{ }^{\circ}\text{C}$ and $1200\text{ }^{\circ}\text{C}$. During some experiments the location of the substrate in the MPCR precluded use of an optical pyrometer. In these instances, the temperature of the substrate was measured by a thermocouple measurement.

The Omegascope HTS head has a spot size of 0.1 inches and a focal length of 12 inches. In the MCPR setup, the pyrometer senses infrared energy from the substrate that radiates out of the cavity through the cavity viewing window (refer to figure 3.14). Before being detected by the pyrometer, the substrate's radiated infrared energy passes through the plasma, the quartz bell jar, and the screen on the MCPR viewing window. For the diamond deposition experiments of this dissertation the substrate temperature range is between $400\text{ }^{\circ}\text{C}$ and $550\text{ }^{\circ}\text{C}$, which is at the low end the sensitivity spectrum of the OS1200 Omegascope. It might appear that a pyrometer that measures infrared radiation in the range of $3\text{ to }5\text{ }\mu\text{m}$ would be more appropriate; however, radiation of this wavelength is absorbed by the quartz bell jar and would not be detected. Hence, a pyrometer with a sensitivity of radiation below $3\mu\text{m}$ is necessary.

Whenever substrate temperature measurements could not be acquired by optical pyrometry, they were sometimes obtained with thermocouples. The thermocouples measured either the backside temperature of the substrate, or the temperature of the substrate holder in the MCPR (refer to figure 3.14). The thermocouples were K type and can measure temperatures in a range of 200°F to 1000°F .

Cross-Section of the MCPR

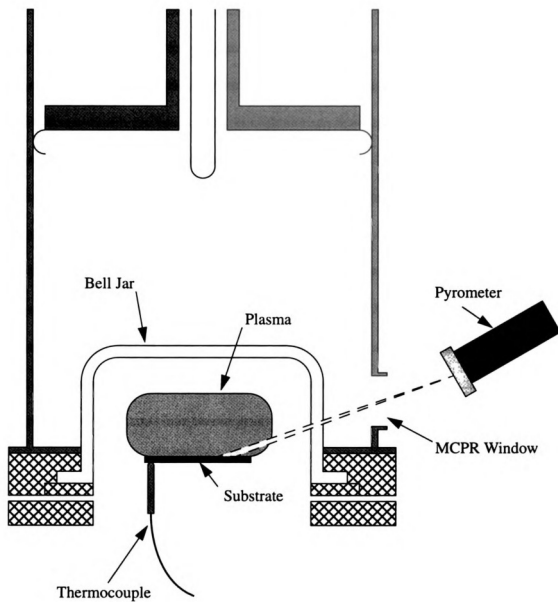


Figure 3.14 Substrate temperature measurements in the MCPR.

3.4.2 Optical Transmission Measurements

The spectral optical transmission of light with wavelengths between 400nm and 1600 nm was measured for diamond films that were deposited on glass substrates. An Oriel Monochromator with a 1200 line diffraction grating was used to produce monochromatic light with a bandwidth of approximately 20 nm for these measurements. A Newport silicon detector (Model 818SL) was used to detect transmitted light with wavelengths from 400 nm - 1100 nm, and a Newport germanium detector (Model 818IR) was used for wavelengths from 800nm - 1600nm. As is shown in figure 3.15, the optical detector was located at a distance of 2.5 cm from the diamond coated glass. To reduce the effects of scattering from the rough surface of the diamond film, the substrate was placed with the film closest to the detector. The diameter of the exit slit was approximately 10nm. As is shown in figure 3.15, monochromatic light is produced by filtering it prior to entry into the monochromator. Various filters were used along with the multiple detectors for each segment of the light spectrum. Table 3.3 lists the filter and detectors that were used for each wavelength segment.

Table 3.3: Transmission Arrangements

λ range (nm)	Filter	Detector
360 - 440	clear glass	818 SL
400 - 800	3-74	818 SL
700 - 1100	2 - 64	818 SL
900 - 1600	7 - 56	818 IR

The measured radiation is converted to a voltage signal by a Newport Model 825 Optical Power Meter. The analog output of the Newport Model 825 scales the detected radiation to a relative scale of 0 to 1 volts ac. This signal is measured by a 386 PC via a

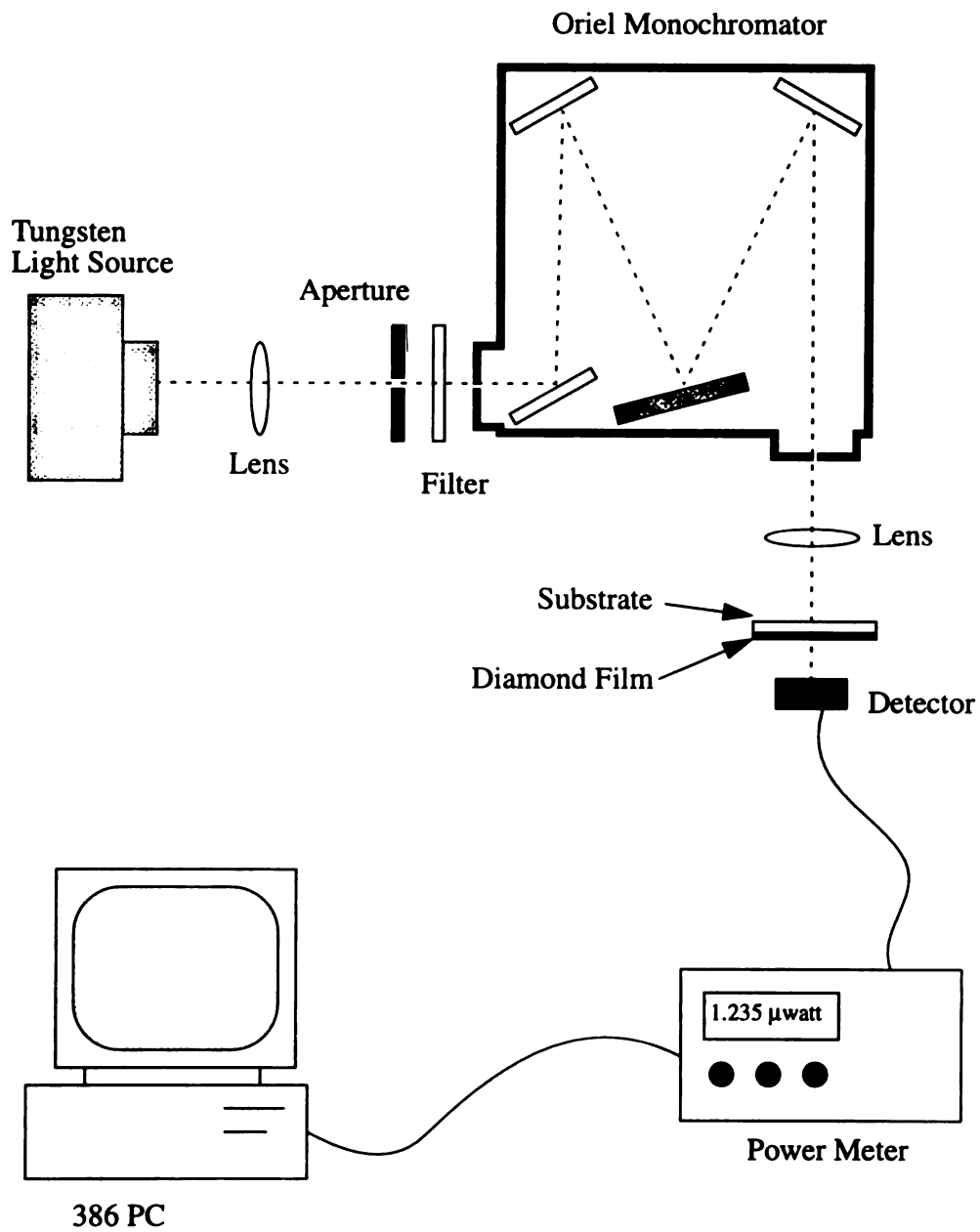


Figure 3.15 Measurement of spectral optical transmission.

Computer Boards Incorporated CI0-DAS16/Jr analog to digital data acquisition card. The software that acquires the transmission data is a windows based program named Optics version 1.0 that was written for this dissertation with Microsoft Visual C++. For details regarding the operation of this software program refer to Appendix.

3.4.3 Film Thickness Measurements

Film thickness measurements are important for two reasons; determining the deposition rate, and determining the uniformity of deposition. For this dissertation the thickness of as-grown films was determined by three methods (1) weight gain, (2) optical transmission, and (3) scanning electron microscopy (SEM). The uniformity of the as-grown film was determined by SEM.

3.4.3.1 Weight Gain Determination of Film Thickness

The process of film thickness measurements by weight gain is accomplished by simply measuring the weight of the substrate before and after deposition. Subtraction of the former from the latter gives the amount of carbon that was deposited by weight. The resulting film thickness is then determined by equation [3.2] where t is the average film thickness in cm, w is the amount of carbon deposited by weight in mg, and A is the area of the substrate in cm. The coefficient 3.515 g/cm^3 is the density of diamond.

$$t = \frac{w}{3.515 \times A} \quad \text{eq (3.2)}$$

3.4.3.2 Scanning Electron Microscopy

Another method of measuring the thickness of a diamond film is to use a scanning electron microscope (SEM). Images of fine grain diamond films studied in this dissertation can not be obtained with an optical microscope since the grain size and thickness of them are in the range of 0.1 μm to 1 μm , and the upper limit of the magnification of an optical microscope is about 2000 X. Furthermore, at its highest magnification, the depth of field in an optical microscope is too small to effectively image the cross section of these films. Even when imaging with an SEM is done within the range of a light microscope, an SEM is often preferred because it has a much higher depth of field. This is because the wavelength λ_e of the electron beam in a SEM is much smaller than that of light. Besides being a useful tool for measuring the thickness of a diamond film, an SEM image can also be used to analyze the morphology of a film and its nucleation density.

The principle concept of the operation of an SEM is that it focuses an electron beam into a very small spot size on the surface of the sample being imaged. Inelastic collisions with this electron beam generate a variable quantity of secondary electrons from the weakly bonded electrons in the conduction band of the sample. These emitted secondary electrons are collected by a Faraday cage and multiplied by a photomultiplier tube. During operation, the beam of incident electrons is scanned across the surface of the sample in the same manner that a CRT rasterizes its screen. As the beam travels across peaks and valleys on the surface of the substrate the quantity of emitted secondary electrons varies, thus creating light and dark regions in the SEM image. These light and dark areas resolve into clear images that show the texture of the image being scanned.

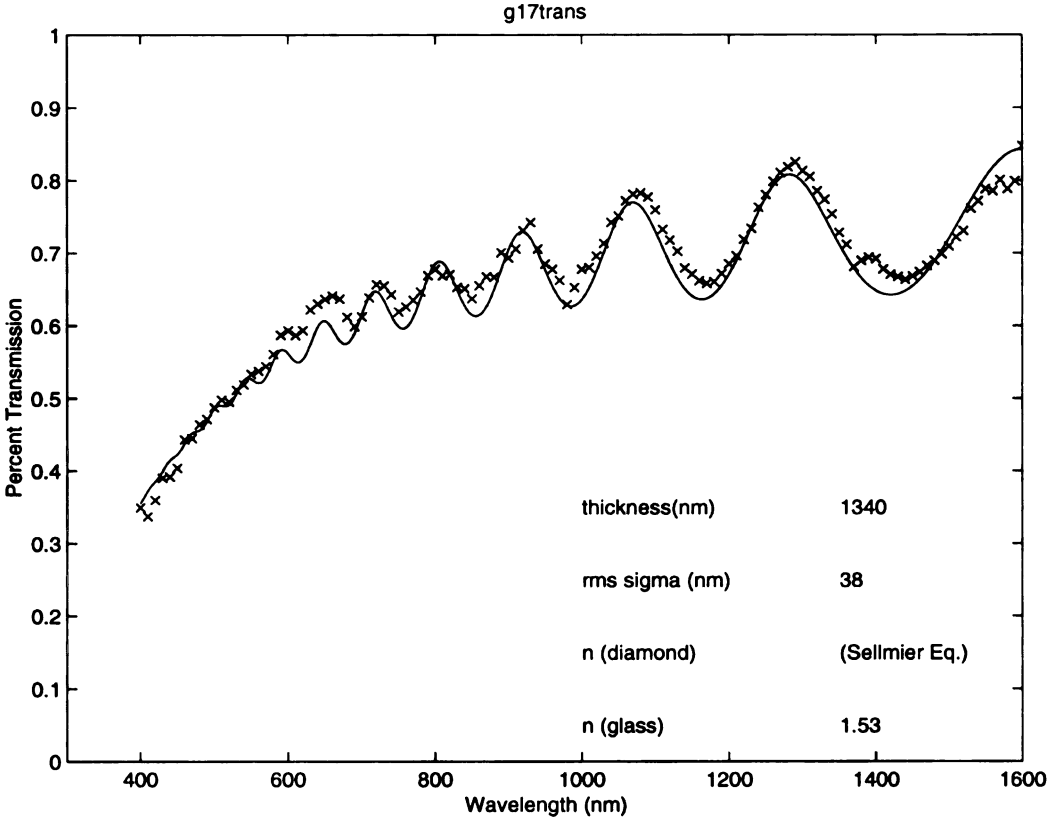
In this dissertation, SEM images were used to study film thickness, film morphol-

ogy and in some cases film uniformity. Since the SEM generates its images by creating a beam of secondary electrons from the conduction band of materials, it works best on conducting samples. Whenever an insulator is to be imaged with an SEM, a few nanometer thick film of gold is sputtered coated onto the sample. The gold is thick enough to preclude surface charging on insulating substrates, but thin enough to avoid distorting the true surface texture of the sample. Since diamond films are inherently electrically insulating, the films imaged with SEM for this dissertation were all sputter coated with gold for 3 minutes in an Argon plasma.

3.4.3.3 Determination of Film Thickness by Coherent Interference

Another method of measuring the thickness of a diamond film is to determine its thickness from a measurement of the transmissivity of the diamond film. A method of measuring the transmissivity of diamond films on glass substrates was described in section [3.4.2]. Figure 5 shows a theoretical transmission spectrum of 1 μm thick diamond film on a thick glass substrate that might result from the measurements of section [3.4.2]. The assumptions of the plot are that there is no absorption in the film or scattering at either interface of the film. The refractive index of the glass was chosen to be 1.5 and the refractive index of the diamond film was determined by the Sellmeier equation (refer to section [6.4.1.1]).

As is observed in the figure, smooth thin films with negligible optical absorption or optical scattering, exhibit coherent interference in the range of light previously mentioned. The data from the location of these peaks and valleys can be used to extract the average thickness of the film by two methods.



Theoretical optical transmission of a 1 μm diamond film.

One method of extracting the thickness of a diamond film from its transmissivity data is to fit a curve to the measured data that has the thickness of the film as its only variable. This can be accomplished by the classic relation for the intensity of transmitted normally incident light through a thin film on a glass substrate as is defined in equation [3.3].^[60]

$$T = \frac{(1 - (r_{01})^2)(1 - (r_{12})^2)}{1 + (r_{01})^2(r_{12})^2 + 2r_{01}r_{12}\cos\left(\frac{4\pi n_1 d}{\lambda}\right)} \quad \text{eq (3.3)}$$

The r_{mn} terms in the equation are the fresnel reflection coefficients at the air-glass interface, the glass-diamond interface, and the diamond-air interface. The subscripts 0, 1 and 2 designate air, diamond and glass respectively. The term n_1 is the refractive index of the diamond film, and λ is the wavelength of light in air. This technique may also be used for thin non-absorbing diamond films that have an rms surface roughness below 40 nm. While this roughness of these films does create scattering at the air-diamond interface, coherent interference is still present in the measured transmissivity data. In this case the rms surface roughness of the film must be measured prior to applying this method. To include the effects of surface roughness, the effects of light scattering by the rough diamond surface are included in equation [3.3] and the result is defined in equation [3.4].

$$T_R = \frac{(1 - r_{21}^2)(1 - r_{10}^2)S_T}{1 + (r_{21})^2(r_{10})^2S_R + 2r_{21}r_{10}\sqrt{S_R}\cos\left(\frac{4\pi n_1 d}{\lambda}\right)} \quad \text{eq (3.4)}$$

The terms S_n in equation [3.4] are the correction factors for the transmitted and reflected power at the diamond interfaces. They include the rms surface roughness of the film. For

further development of these equations refer to section [6.4.1.2]. Appendix A contains the matlab “.m” files for a program that was used to generate all the plots of theoretical and measured transmission of diamond films on glass substrates for this dissertation.

The thickness of a thin diamond film on a glass substrate can also be estimated from it's transmission spectrum by the simple formula described in equation [3.5]^[61]. Here, the fringes of the film's transmission spectrum are used to determine the approximate thickness of the film.

$$d = \frac{N}{2n_d(\nu_1 - \nu_2)} \quad \text{eq (3.5)}$$

It is assumed however, that its refractive index is a known quantity n_d with an average value throughout the spectrum. The term N is the number of fringes, d is the thickness of the film and $(\nu_1 - \nu_2)$ is the difference in wavenumber from the first to last fringe.

3.4.4 Film Quality Analysis by Raman

For this dissertation, a qualitative analysis of the quality of the deposited diamond films was accomplished by evaluation of the Raman spectrum of the as-deposited films. Raman spectroscopy has been widely used to characterize diamond thin films grown by various depositions, and to compare CVD diamond films to natural diamond. Raman spectroscopy is an ideal method for characterizing the quality of diamond because it is sensitive to many forms of carbon besides diamond such as graphite and diamond-like-carbon (DLC).

The principle theory of Raman spectroscopy is based on the phenomenon of

inelastic scattering of radiation by a medium. When a beam of monochromatic light with a frequency of ν_0 is focused on a sample, radiation is scattered from the sample that contains three frequency components. Besides containing Rayleigh scattered light with the excitation frequency ν_0 , there are inelastic components of scattered radiation which are due to phonon interactions, that have frequencies of $\nu_0 + \nu_m$ and $\nu_0 - \nu_m$. These inelastic components are referred to as Stokes scatter ($\nu_0 - \nu_m$) and anti-Stokes scatter ($\nu_0 + \nu_m$). For most Raman systems, the spectrum of radiation from the anti-Stokes scatter is taken collectively as the Raman spectrum, and is measured in wavenumbers. A high quality diamond film shows a sharp characteristic first order Raman peak that is reported to be in the range of 1332.1 cm^{-1} - 1332.6 cm^{-1} with a width at half maximum (FWHM) on the order of 1.8 cm^{-1} ^[62]. This is associated with the sp^3 bonds present in diamond. There is also a second order diamond peak in the Raman spectrum at 2450 cm^{-1} ^[63]. In contrast a broad peak around 1600 cm^{-1} is attributed to well ordered graphite^[64]. Graphitic carbon phases also produce peaks around 1355 cm^{-1} (D band) and 1582 cm^{-1} (G band)^[65]. Another carbon phase peak that is sometimes present in Raman analysis is at 1550 cm^{-1} ^[66]. This was thought to be associated with a graphite phase, but has recently been attributed to DLC films. It should be noted that the ratio of the intensities of the diamond peak at 1332 cm^{-1} and the graphite peak at 1600 cm^{-1} is not proportional to the ratio of diamond to non-diamond components present in the film. This is due to the fact that Raman scattering is typically about 50 times more sensitive to sp^2 bonded (non-diamond) carbon than sp^3 (diamond) bonded carbon^[67]. The Raman analysis experiment used to characterize diamond for this dissertation uses an Argon laser with a wave length of 514 nm which is reported to be more sensitive to fine grain film than a 632.8 nm He laser. The configuration

and operation of this Raman apparatus has been well documented^[68].

Besides analyzing the quality of CVD diamond films, Raman analysis has been successfully used to analyze the internal strain in them^{[62][67][69]}. It has been reported that the diamond Raman peak shifts linearly with film strain. From this shift of the 1332 cm^{-1} Raman diamond peak, information about the strain type, i.e. tensile or compressive, and strain magnitude may be obtained. If the net stain in the diamond film is compressive, the position of the 1332 cm^{-1} Raman peak shifts to a higher wavenumber. For tensile strain, the peak shifts to a lower wavenumber.

Recent publications indicate that it is also possible to measure the Raman spectrum of a diamond film during the deposition process^{[70][71]}. In situ Raman has been shown to work well in both microwave plasma-assisted CVD reactors and hot filament systems. The reported capability of these in situ Raman systems are (1) measurements of the actual film temperature, and (2) on-line control of film quality in terms of non-diamond species and crystallite sizes.

As was stated earlier, one of the chief goals of this dissertation is to develop a process for depositing very fine grain ($<0.25 \mu\text{m}$ diameter) diamond films^[63]. Raman analysis is typically very sensitive to the average grain size of a diamond film. It has been reported that for Raman excitation of 488 nm the intensity of the peak at 1332 cm^{-1} decreases and the broadens as the average grain diameter decreases. It also shifts to a lower wavenumber. These effects have been misinterpreted by some to indicate that fine grain films are poor in quality as compared to those of larger grain sizes ($>10 \mu\text{m}$). Furthermore, the shift of the 1332 cm^{-1} Raman peak to a lower wavenumber does not mean the film has internal strain.

In addition to grain size, Raman is also sensitive to the frequency of excitation^[65].

Most Raman studies use an excitation in the visible and near-UV region. It has been reported that shorter wavelength Raman is more sensitive to the 1332 cm^{-1} peak than longer wavelength Raman. In fact, the intensity of the 1332 cm^{-1} diamond peak relative to that of the 1580 cm^{-1} non-diamond peak dramatically increases with UV excitation as compared to the excitation in the visible and near-UV region. The intensity of the ratio of diamond to non-diamond carbon peaks for 244 nm Raman is about 25 times greater than that of the 488 nm Raman ratio.

3.4.4.1 Definition of Raman A spectra and Raman B spectra

The diamond film deposition experiments and subsequent film characterizations that are discussed in the later chapters of this dissertation were carried out over a period of four years. During that time the Raman spectroscopy measurement setup was re-configured to include new measurement features. The Raman spectra, which are presented in later chapters, were acquired with these different Raman spectroscopy configurations. Differences between Raman spectroscopy configurations cause changes in the appearance of the Raman spectrum from a particular sample. Specifically, the shape, position, height and width of each individual peak changes as the Raman spectroscopy operating wavelength, spot size and resolution are altered. Hence, the spectrum that was acquired from these two Raman configurations should not be analyzed comparatively.

To denote what Raman spectroscopy configuration was used for the acquisition of each Raman spectrum that is reported in later chapters of this dissertation, the following nomenclature was adopted. Raman spectra that were acquired with the early Raman configuration are labeled as type *Raman A* and the more recent Raman measurements are labeled

as type *Raman B*. These two Raman configurations differed in that they had different optical arrangements and different operating wavelengths. The wavelength of *Raman A* was 488 nm, and the wavelength of *Raman B* was 514 nm. For comparison, the *Raman A* spectrum and *Raman B* spectrum from the film on substrate G2-32 are shown in figure 3.16 and figure 3.17. The film on G2-32 is fine grained and has an approximate thickness of 530 nm. It is observed from the figures that the Raman A spectrum has a higher sensitivity to the diamond in the film.

3.4.5 Surface Roughness Measurements by Dektak and AFM

Measurement of the rms surface roughness of deposited diamond thin films was accomplished by two surface profilometry systems. They were the Sloan Dektak II and an atomic force microscope (AFM). Both of these systems measure the profile of a material by dragging a stylus tip across its surface.

The Dektak measures the profile of a materials surface by using a linear variable differential transformer to convert the vertical motion of a diamond stylus to electrical signals. Dektak surface profile measurements are two dimensional in that the movement of the stylus is only in the y and z directions i.e. its measurements are taken in succession along a single line. To measure the rms surface roughness of a diamond film with the Dektak, the profile of the film is first recorded by the instrument and then stored to an ASCII data file. The rms surface roughness is then calculated from the data in the file.

Another popular method for investigating small features of diamond films such as nucleation sites that is often used is atomic force microscopy (AFM)^{[72][73]}. Like the Dektak, the AFM uses a diamond stylus to measure the surface profile of a material; however,

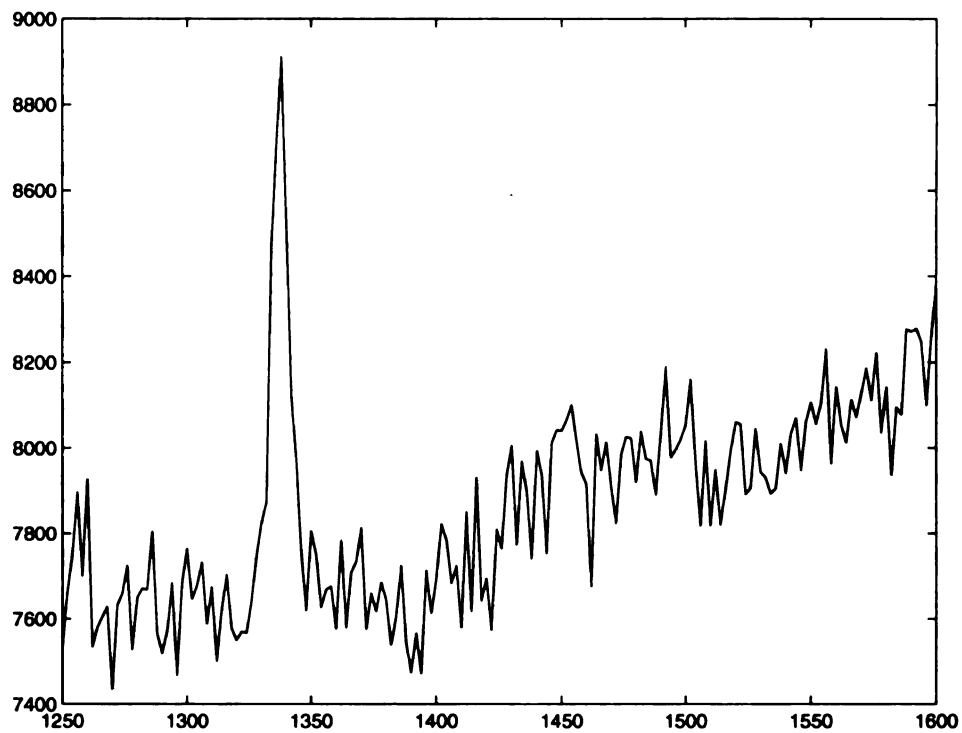


Figure 3.16 The Raman A spectrum from G2-32, dated 17 April 1997.

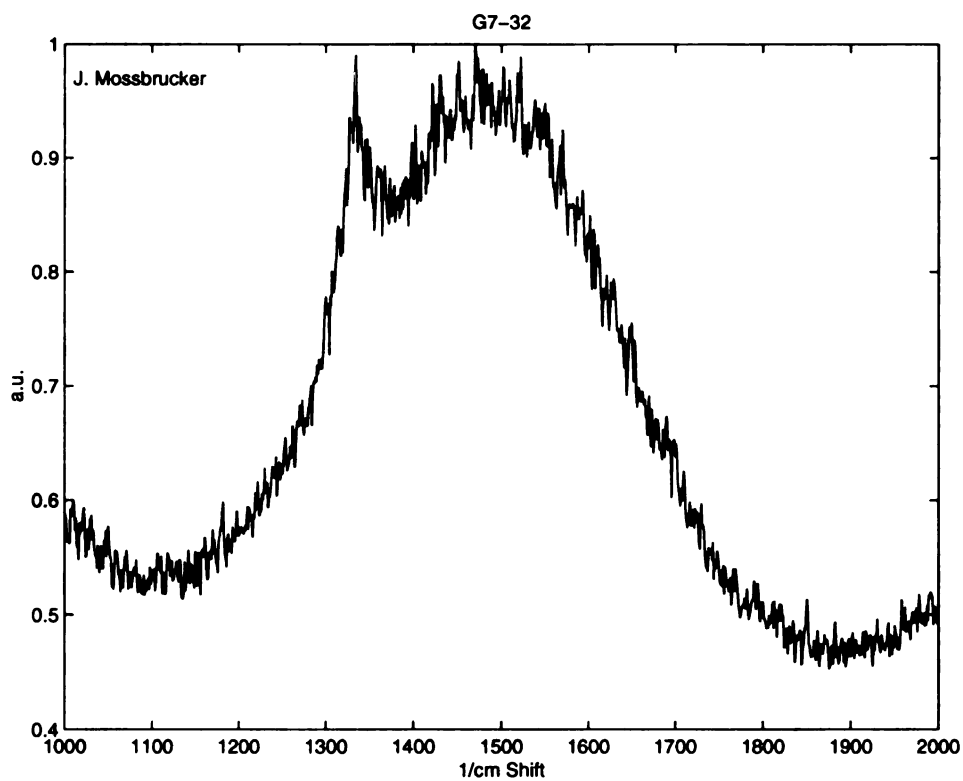


Figure 3.17 The Raman B spectrum from G2-32, dated 1 April 1998.

there are many differences between them. Unlike the Dektak, the AFM automatically rasters in the x-y plane and thereby measures surface profiles in three dimensions. Surface profile images can be generated from this 3D surface data that show the exact molecular make-up of the surface. Also, AFM systems calculate and display many quantities from the measured surface data in real time, such as the Ra and rms averages of the surface roughness. The AFM operates by shining a laser on the backside of the stylus. The reflected light is directed towards a pair of photo-diode detectors. As the stylus moves vertically while moving across the surface of the material the distribution of the reflected light on the two photo-diodes varies. This change in signal intensity at the diodes is used to form the surface profile image by the AFM. A typical AFM has a resolution down to about 0.1 nm.

3.4.6 Film to Substrate Adhesion Tests

The large mismatch between the thermal expansion coefficients of the glass substrates and that of diamond was expected to generate an appreciable amount of compressive stress in the films that were deposited on glass substrates for this dissertation. As a result, film to glass adhesion was predicted to be problematic. Therefore it was necessary to test the adhesion of those films. This was done by subjecting the films to various thermal cycles. Further test for resilience to chemical attack by HF and the effects of exposure to water of various temperatures were also conducted on selected films.

The steps of the thermal cycling tests were: (1) place the sample in an oven at temperature T for a time t , (2) remove the sample and observe cool down, and (3) apply and remove a piece of 3M Scotch Magic tape to the film. The film was observed after each step

for possible delamination.

The steps of the HF etch test were: (1) dip the sample into an HF to water mixture with a ratio of $R_{(H_2O/HF)}$ for a duration of time t_1 , and (2) rinse the sample in DI water at a temperature of T for a duration of t_2 . The film was observed after each step for possible delamination. Both continuous and patterned diamond films were tested with this method.

3.4.7 Carbon Conversion Efficiency

Another method of characterizing a particular diamond thin film CVD process is to analyze its carbon conversion efficiency (CCE). CCE is the percent amount of carbon that is put into the process that is actually incorporated into the diamond film. It is calculated by determining the amount of carbon in the film C_{film} (in atoms per hour), determining the amount of carbon provided in the feed gas C_{feed} , and then dividing the former by the latter (equation [3.8]).

Equation [3.6] is used to determine C_{feed} (in Carbon atoms supplied per hour) where C_{in} is the sccm of carbon that is supplied in the feed gas, e.g. 5 sccm CH_4 .

$$C_{feed} = (C_{in}) \times (60 \text{ min / hour}) \times \left(\frac{6.024 \times 10^{23} \text{ atoms}}{22400 \text{ cm}^3} \right) \quad \text{eq (3.6)}$$

The amount of carbon C_{film} that is incorporated into the film (in atoms per hour) is determined by equation [3.7], where wg_f is the time averaged weight gain of the film (in grams per hour).

$$C_{\text{film}} = (wg_f) \times \left(\frac{\text{cm}^3}{3.515 \text{ grams}} \right) \times \left(\frac{1.79 \times 10^{23} \text{ atoms}}{\text{cm}^3} \right) \quad \text{eq (3.7)}$$

$$\text{CCE} = \frac{C_{\text{film}}}{C_{\text{feed}}} \% \quad \text{eq (3.8)}$$

Chapter 4

Description of Reactor Configurations

4.1 Introduction

In pursuit of the goal of this dissertation, which was to develop a low-temperature diamond deposition process, many concepts were investigated. Included among them were conjectures for methods that might improve process measurables such as deposition rate, quality and area. While these variables have dependencies on the various MCPR input parameters, e.g. chemistry and microwave power, they are also influenced by the substrate's temperature distribution and its location with respect to the plasma. For diamond deposition in the MCPR, a substrate receptor assembly of some kind is always used to place the deposition substrate in the proper location inside the MCPR. Besides controlling the substrate's location in the MCPR these assemblies play an important role in controlling the shape of the plasma and in the substrate's temperature distribution. Thus many design issues arise during the development of an MCPR substrate receptor.

As has been previously noted, this dissertation was an exploration as to whether diamond could be deposited at temperatures below 500 C using MPCR technology. Previously, MCPR work was aimed at high temperature diamond deposition in two different MCPR reactors (refer to section [2.2.2.2.5] and section [2.2.2.2.6]). The primary difference between the reactors was the size of the quartz bell-jar, the resonant microwave tun-

ing modes, and maximum allowable area for diamond deposition. In all cases however, the substrate's temperature ranged from 700 C to 1100 C.

At the beginning of this project it was not known if either of the MPCR designs would yield a better low-temperature diamond deposition process. So low-temperature diamond deposition processes were investigated in both reactors. While the first goal was to show that MCPR technology could be used to deposit diamond at substrate temperatures below 500 C, there was also a desire to investigate ways to maximize the deposition measurables -- namely rate, quality, area and in some cases adhesion. To investigate how these deposition properties are influenced by variables such as input chemistry, gas pressure, input microwave power, substrate temperature, and substrate location; several substrate receptor assemblies, i.e. MCPR configurations, were developed. Included among them were assemblies with a dc bias, liquid substrate cooling, and variable independent substrate heating. Many interesting traits were noted during the development of these MCPR configurations, and are reported in later sections of this chapter.

This chapter summarizes the resulting characteristics of the substrate receptor assemblies that were developed during this dissertation for the MCPR's with the 4-inch and 5-inch bell-jars. A total of nine different MCPR configurations were investigated, each having a unique substrate receptor assembly. Four of the MCPR configurations had substrate assemblies that were developed for the 4-inch bell-jar MCPR and the other five had assemblies that were developed for the 5-inch bell-jar MCPR. The differences between the various MCPR configurations include maximum deposition area -- typically 20 - 80 cm², inclusion of a dc substrate bias, impact on microwave tuning --reflected power varied between 0 and 50%, thermal conductivity -- variable when liquid cooled, and variable

independent heating.

This chapter begins with an introductory section that provides definitions of MCPR terms that define a few of the relevant components and areas inside the MCPR. Most of these terms are common to all nine of the MCPR configurations, and are necessary for the detailed MCPR configuration discussions that are contained in later sections. Following the definition of MCPR terms is a section titled, *MCPR Substrate Receptor Design Considerations*. It outlines the rationale and design criteria that were considered during the development of the nine MCPR configurations. Following these two introductory sections there are nine sections that describe the relevant physical details and characteristics of each MCPR configuration. They include what components were in them, how they were operated, performance measurables (such as observed plasma distribution, microwave tuning and substrate temperature) and in some instances their diamond deposition limitations. The second to last section of this chapter is a description of MCPR microwave tuning methods for plasma ignition. It provides a short discussion about the techniques that were used to tune the nine MCPR configurations that are described in this chapter. This includes MCPR reactor tuning that was performed before and after plasma ignition -- there was a difference. The final section of this chapter is a summary of the performance measurables of the nine configurations.

4.2 Definition of MCPR Terms

For discussions in this and subsequent chapters, several terms that describe regions of interest inside the MPCR are defined (refer to figure 4.1). They are the MCPR's (1) discharge chamber, (2) discharge chamber well, (3) discharge chamber floor, and (4) the res-

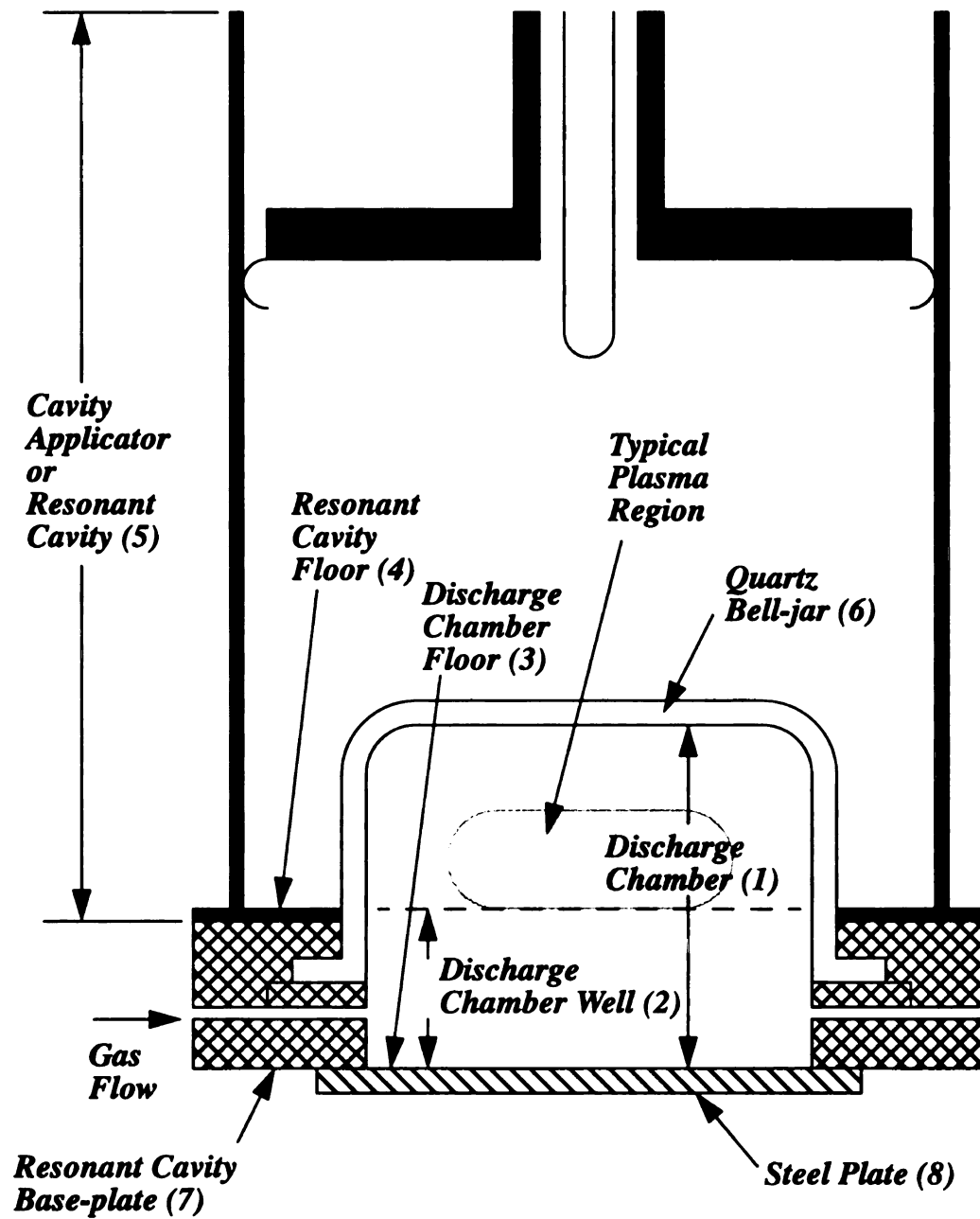


Figure 4.1 Definition of regions inside the MCPR.

onant-cavity floor. The discharge chamber is the evacuated region of the MCPR where plasma processing was performed for this dissertation. Its top half is inside the cylindrical resonant cavity (5) and is bordered by the inside surface of the quartz bell-jar (6). The lower half of the discharge chamber is referred to as the discharge chamber well (2). The chamber well is bordered on its sides by the inside surface of the inside surface of the quartz bell-jar (6) and by the resonant cavity's steel base plate (7). The bottom of the discharge chamber well is bordered by a steel plate (8). The top surface of the steel plate (8), which is the bottom of discharge chamber, is termed the discharge chamber floor (3). Similarly, the flat surface at the bottom of the resonant cavity is termed the cavity floor (4).

4.3 MCPR Substrate Receptor Design Considerations

At pressures of interest for this work, plasma formation in an empty MCPR operated in a TM_{01n} mode (refer to figure 2.1.2) takes place in a region that is close to the top inside surface of the quartz bell jar, and far from the floor of the discharge chamber (refer to figure 4.1). In most instances, the distance from the bottom edge of the plasma to the floor of the well is greater than the diffusion length of the molecular species necessary for diamond deposition. Hence, very little of the chemical species that are created in the plasma reach the bottom of the discharge chamber. Additionally, the components of the MCPR must be maintained at a temperature far less than that required for low-temperature diamond deposition to avoid damaging them. In most MCPRs the cavity components are cooled by forced air and/or liquid cooling. Since the substrate is heated by the plasma to a temperature that would be detrimental to most of the components of the MCPR, it is necessary to provide enough thermal insulation between the substrate and the cooler compo-

nents of the MCPR such that in the steady-state the substrate temperature is adequate for diamond growth. Consideration of these issues means that the floor of the discharge chamber is not a good location for efficient diamond deposition. If one were to place the substrate on the bottom of discharge chamber well, there would be little or no deposition of diamond-bonded carbon on it.

To deposit diamond on disk shaped substrates in a uniform manner with the highest possible deposition rate, the substrate must be elevated above the discharge chamber floor such that it is in direct contact with the plasma. This problem is often solved by using an apparatus that places the substrate in contact with the plasma in a location above the bottom of the discharge chamber, and thermally insulates the substrate from the cooler components of the MCPR. However, the apparatus must be designed such that it does not adversely affect the performance of the MCPR.

During the development of the nine MPCR configurations, which are described in later sections, four design specifications were considered. First, the substrate receptor assembly must place the substrate as close as possible to a location in contact with the plasma where the flux of chemical species and the substrate's temperature profile are most uniform. As was stated earlier, this is necessary to achieve the best possible deposition uniformity. Second, the placement of the substrate receptor inside the discharge chamber should not alter the resonating electromagnetic fields in a way that causes the plasma to form with a non-uniform shape in the region near the substrate or causes the plasma to shift to undesirable locations in the discharge chamber. A non-uniform plasma shape is one where the plasma is un-evenly distributed throughout the space adjacent to the substrate. An undesirable plasma location would be one where the plasma comes in direct

contact with the inside walls of the quartz bell-jar. When this happens, a coating of the bell-jar usually ensues. Third, the receptor assembly should not reduce the load matching performance of the MCPR. Due to the power limitations of the coaxial waveguide and the dummy loads in the microwave circuit, the impedance match of the MCPR should be such that the amount of reflected microwave power is as close to zero as possible. Finally, the thermal resistance of the substrate receptor should be high enough to preclude uncontrollable cooling of the substrate during deposition. This is necessary because as the flow of heat from the substrate increases the steady-state temperature of the substrate decreases.

4.4 The Side Feed 4" MCPR

Initial diamond deposition experiments for this dissertation were conducted with the 4-inch MCPR. The next two sections describe plasma performance results for two configurations of the side-feed 4-inch MCPR. The primary achievement of the experiments conducted with these two configurations was the development of a method for uniformly depositing diamond on circular disk-shaped substrates with a diameter up to 2 inches at a pressure below 16 torr.

4.4.1 MCPR Configuration 1

The first reactor configuration that was used for exploratory low-temperature diamond deposition experiments was a side-feed version of the 4-inch bell jar MCPR. The substrate receptor in this case was a simple design that was reported to be successful by Zhang^[36] and Huang^[35]. As is shown in figure 4.2, the substrates were seated on a graphite disk with a recessed area in the middle for positive location of the substrate. The graph-

ite was centered in the discharge chamber on a quartz tube of variable height.

The primary difference between the work of Zhang and Huang and this investigation was the pressure regime. They investigated a regime where the gas pressure was between 30 and 80 torr. Here it was lowered until a desirable substrate temperature was achieved. The result was that at pressures below 15 torr, this MCPR configuration yields substrate temperatures that are below 600 C.

4.4.1.1 Operation and Tuning

The three MCPR variables for this configuration are (1) the length of the cavity h , (2) the insertion length of the probe l , and (3) the height of the quartz tube d . The first two, h and l , serve to match the impedance of the plasma and the substrate loads in the MPCR to that of the microwave transmission line. The third d , influences the tuning of the cavity and the resulting induced plasma by varying the location of the lossy graphite disk.

At pressures below 15 torr, a uniform hemispherical shaped plasma forms over the substrate when h and l are tuned such that a TM_{011} resonant mode is excited. Typically, this mode is excited when the short is tuned to a cavity height h of about 7 cm, and the insertion length into the cavity l of the coupling probe is tuned to near 2 cm. In order for the substrate to be in contact with the plasma the height d should be at least 3 cm. The maximum height of d for which a plasma that uniformly contacts the substrate may be maintained is 4 cm. Above this height the plasma forms in locations beneath the substrate and near the walls of the quartz dome bell-jar. In all cases, microwave tuning capability was excellent, with less than 2% reflected power.

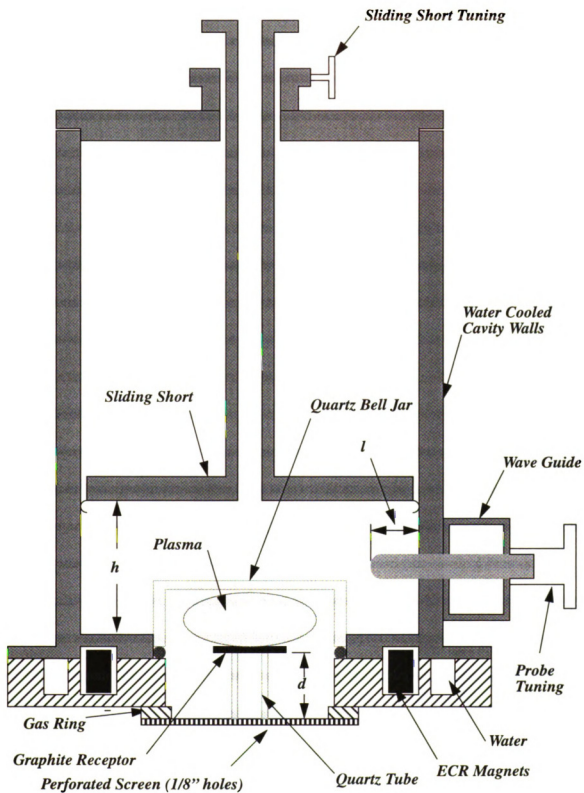


Figure 4.2 Cross-section of MCPR configuration 1.

4.4.1.2 Concerns and Limitations

The major difficulty of this configuration is that it is limited to processing substrates with diameters smaller than 1.5 inches. If the diameter of the graphite is increased to accommodate substrates with a diameter of 2 inches, the location of the plasma is altered. When 2 inch diameter substrates are inserted into this configuration the plasma shifts to a position below the substrate. In order for a useful plasma to be induced in the center of the discharge chamber in this configuration with a 2 inch substrate the height d must be reduced to 1 cm. Unfortunately, at this height the plasma is stable but is not in contact with the substrate. Hence, uniform deposition of diamond on a 2 inch diameter substrate was not possible.

4.4.2 MCPR Configuration 2

To improve upon the size limitations on the diameter of the substrate that resulted from MCPR configuration 1 at pressures below 15 torr, a second MCPR side-feed configuration was created. In this configuration, a graphite insert disk was added to the substrate receptor between the top graphite receptor and the perforated plate at the bottom of the discharge chamber (refer to figure 4.3). Also, the quartz tube was divided into two sections so that the insert disk could be placed between the receptor and the bottom of the discharge chamber. Varying the heights d_1 and d_2 of the quartz tubes allows the locations of the receptor and the graphite disk to be adjusted independently. This approach led to a U.S. patent [5,736,818].

The cross-section of the substrate receptor that is shown in figure 4.3 has two distinguishing features. One is that there is a recessed area in the top of the receptor that pos-

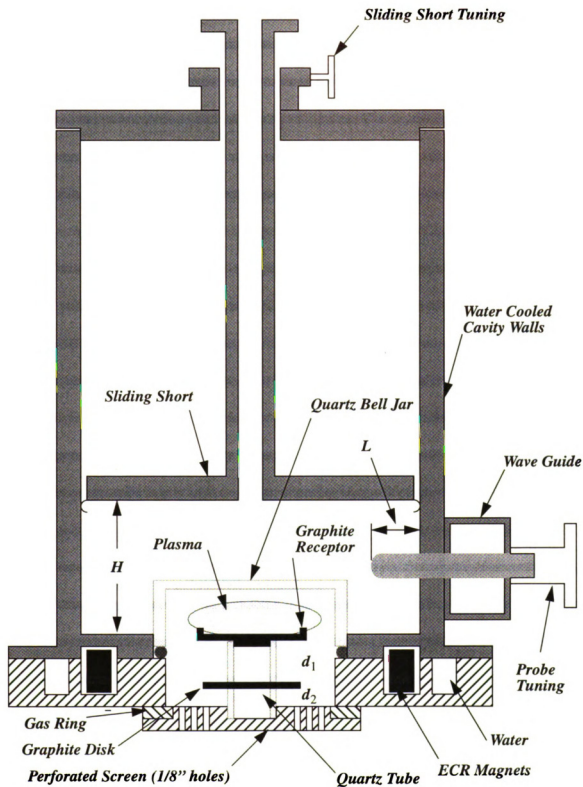


Figure 4.3 Cross-section of MCPR configuration 2.

itively locates the substrate. The other is a small projection from the bottom of the receptor that locks the part into the quartz tube. Together these features work to prevent the substrate from shifting away from the center axis of the cavity during processing. The inner diameter of the substrate recessed area is $2\frac{1}{32}$ inches. The fractional part is necessary to compensate for thermal expansion of the substrate during deposition. The outer diameter of the part is $2\frac{5}{32}$ inches. This provides a $\frac{1}{8}$ inch wide border around the outer edge of the part.

4.4.2.1 Operation and Tuning

With these modifications the resulting plasma forms with an elliptical, cross-sectional shape that evenly covers the top surface of the substrate. Similarly to MCPR configuration 1, the resonant mode of the cavity is the TM_{011} mode. The cavity tuning for this mode remains at 7 cm for the cavity height h , and 2 cm for the probe insertion length l . A combined quartz tube height of 4.0 cm for d_1 and d_2 is an adequate location for the substrate.

The shape and location of the plasma are not greatly influenced by the location of the insert disk. This is an important feature since it is not possible for quartz tube sections to be cut with a high degree of accuracy. Also, the plasma is not greatly influenced by the location of the substrate receptor; however, deposition rates can be influenced by the material of the receptor.

4.4.2.2 Temperature Measurements

Figure 4.4 shows the dependence of the measured substrate temperature on the gas

pressure and the input microwave power. These measurements were observed with a 2.2 μm single wavelength optical pyrometer through the tube in the center of the sliding short. The measurements were made with a 2 inch silicon wafer in the receptor, and with the heights of d_1 and d_2 at 16 mm and 24 mm respectively. The horizontal axis of the graph is the input microwave power in watts, and the vertical axis is the measured substrate temperature in degrees Celsius. The three curves in the graph show data that was measured at pressures of 6, 8 and 10 torr. It is observed that unlike the high pressure measurements of Zhang^[36] there is a strong dependence of the substrate temperature on both the microwave power and the gas pressure.

4.4.2.3 Concerns and Limitations

While MCPR configuration 2 is an adequate solution to the problem of depositing diamond on substrates with a diameter of 2 inches, it does create a new concern. When creating a plasma that is large enough to uniformly cover a 2 inch substrate with the side feed antenna, a small plasma discharge is always formed in contact with the side of the quartz bell jar. Its location is always on the side of the bell jar that is nearest to the coupling probe. As would be expected, a coating of the bell jar occurs and it is difficult to remove. As the amount of film deposited on the inside of the bell-jar increases the shape and location of the plasma begins to change. If a sufficient amount of film is present, it becomes impossible to induce an axially symmetric plasma. At that point the MCPR can not uniformly deposit diamond on a 2-inch diameter substrate. Excitation of this small unwanted discharge is caused by evanescent near-fields of the probe since the radius end of the probe projects to within 1 cm of the inside wall of the bell jar. Besides depositing

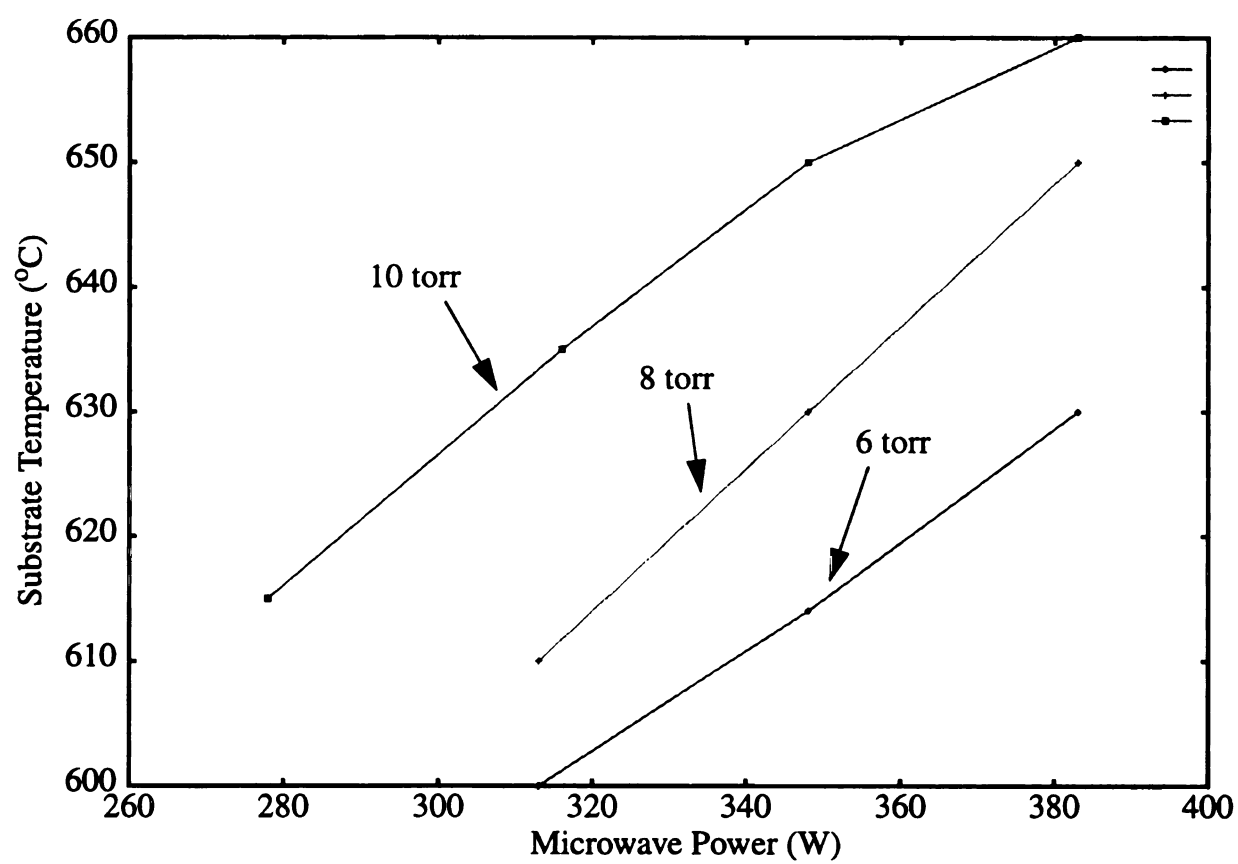


Figure 4.4 Temperature vs. pressure and power for MCPR-C2.

coatings on the quartz bell-jar, the small discharge also contributes to over heating of the bell-jar's vacuum o-ring. Over time, this leads to vacuum leaks.

Another drawback of this configuration is that the substrate receptor was fabricated from graphite. Since CVD diamond processes with H_2 and CH_4 have a strong temperature dependence, it is imperative that the surface of the substrate have a uniform temperature distribution. Hence, graphite was chosen because it has a high thermal conductivity, which might help distribute the heat in the substrate so that the temperature profile is more uniform. Unfortunately, the graphite is noticeably etched during deposition experiments. The severity of the etching is such that the outer edges of the receptor disappear after 5 to 10 deposition experiments, or 100 to 200 hours of operation. Furthermore, the data presented in chapter 5 indicates that the carbon that is etched from this receptor has a positive influence on the diamond deposition rate. This makes it difficult to determine the precise percentage of carbon containing feed gas that is required for the desired diamond film.

4.5 The End-Feed 4" MCPR

A process for uniformly depositing diamond on substrates with a diameter up to 2 inches was achieved with MCPR configuration 2; however, it was necessary to switch to an end-feed MCPR arrangement to preclude coating of the sides of the bell-jar and over heating of the bell-jar o-ring. The next two sections of this chapter describe the reactor performance of two additional 4-inch bell-jar MCPR configurations. The first is a thermally isolated configuration similar to configuration 2 (refer to section [4.4.2]). The second is a bias enhanced configuration -- where a positive dc bias is applied to the substrate.

4.5.1 MCPR Configuration 3

To overcome the concerns that arose from MCPR configuration 2 two more changes were implemented. To alleviate the issue of erosion of the graphite receptor during diamond deposition the material of the receptor was changed to stainless steel. The dimensions of the part remained the same however. Second, the side-feed microwave coupling probe was removed and replaced with an end feed coupling probe (refer to figure 4.5).

While the change of substrate receptor material alleviated the graphite erosion problem, a new deposition uniformity issue did arise. Since the thermal conductivity of stainless steel is very low ($\sim 21 \text{ W/m} \cdot ^\circ\text{K}$ for SAE type 304 at 400°C) it was likely that this switch would cause a reduction in the deposition uniformity. To offset this effect inserts were used between the stainless steel and the substrate. The effects these inserts have on deposition uniformity are reported in Chapter 5.

The advantage of the end-feed probe is that the evanescent electromagnetic fields that it induces in the MCPR have a axially symmetric distribution. Thus the small, side discharge is eliminated. Unfortunately, with this microwave power coupling configuration substrate temperatures can no longer be measured through the short at a normally incident angle. Instead they were observed through the cavity's front viewing window as was shown in section [3.4.1].

4.5.1.1 Operation and Tuning

Similar to MCPR configuration 1, the resonant mode of the cavity for this configuration is the TM_{011} mode. The cavity tuning remains at 7 cm for the cavity height h , and 2

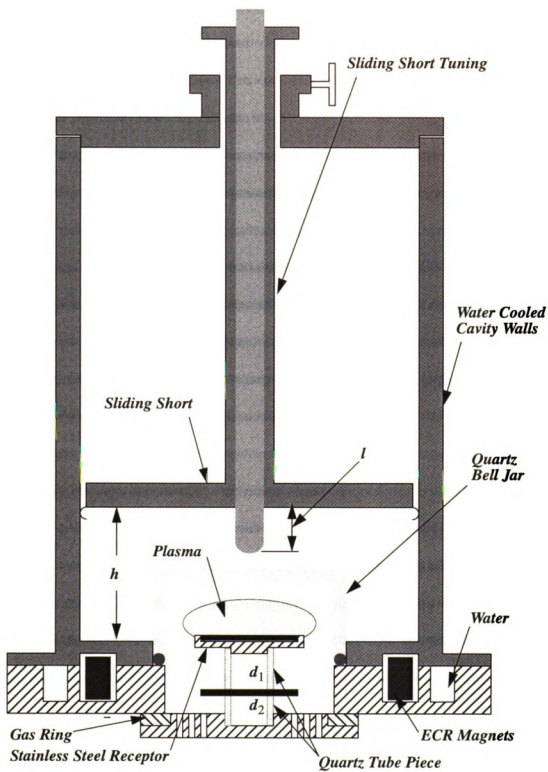


Figure 4.5 Cross-section of MCPR configuration 3.

cm for the probe insertion length l . A combined quartz tube height of 40 cm for d_1 and d_2 is an adequate location for the substrate.

4.5.1.2 Concerns and Limitations

In configuration 3, the resulting plasma remains the same as it was in configuration 2 with the exception of the small evanescent discharge. Moving the probe from the side to the top of the cavity provided no additional separation between the quartz bell-jar and the radius end of the probe. Hence the small discharge merely shifted to a new position that is centered in the top of the bell jar. As would be expected, coating of the quartz during processing remained a problem. The amount of quartz coating was reduced by increasing the height of the bell jar by 1 cm. It would later be resolved by changing the resonant mode of future MCPR configurations from TM_{011} to TM_{013} .

4.5.2 MCPR Configuration 4 -- dc Bias Enhanced

In previous MCPR configurations the substrate was thermally and electrically insulated from the walls of the MCPR discharge chamber by the quartz tube on which the receptor is placed. There have been some reports of improvements to deposition processes by controlling the electric potential of the substrate. Mantei et. al. concluded that some low pressure plasma assisted CVD processes can be improved by adding a positive dc bias to the substrate. Through the addition of a bias, the quality and deposition rate of the Magneto-Active Plasma System are improved upon (refer to section [2.2.2.2.4]). Additionally, recent publications by other investigators also indicate that the nucleation density on some substrates may be increased with a dc bias (refer to section [2.5.4]). Such bias enhanced

nucleation is accomplished by adding an additional step to the diamond deposition process.

Since this dissertation is an investigation searching for the best low temperature MCPR diamond deposition process, the idea of improving the quality and rate of deposition by applying a bias was included among possible solutions. Bias enhanced nucleation was not investigated however.

Two bias-enhanced substrate receptors were included in this work -- one for each MCPR. The bias-enhanced receptor for the 4" bell jar MCPR is discussed in this section. A discussion of the other one is deferred to section [4.6.2].

The bias-enhanced substrate receptor that was constructed for the 4" bell jar reactor is shown in figure 4.6. Its appearance is similar to that of previously detailed receptors. It includes a stainless steel substrate receptor that is a dimensional replica of previous receptors; however, there is a pole in the bottom for the bias circuit. The positive bias wire enters the discharge chamber through a ceramic feed through and connects to the bottom of a stainless steel substrate receptor that is seated on a variable height quartz tube. The negative bias wire is connected to the base plate of the cavity. Hence the metallic walls of the discharge chamber are used to complete the bias circuit.

4.5.2.1 Concerns and Limitations

Although the graphite mode enhancing disk is not shown in figure 4.6, it was included for part of the investigation of biasing in the 4" bell jar MCPR. With the graphite disk in the stage however, a suitable plasma could not be induced with any variation of quartz tube heights d_1 and d_2 . The only configuration of the bias receptor that produced a

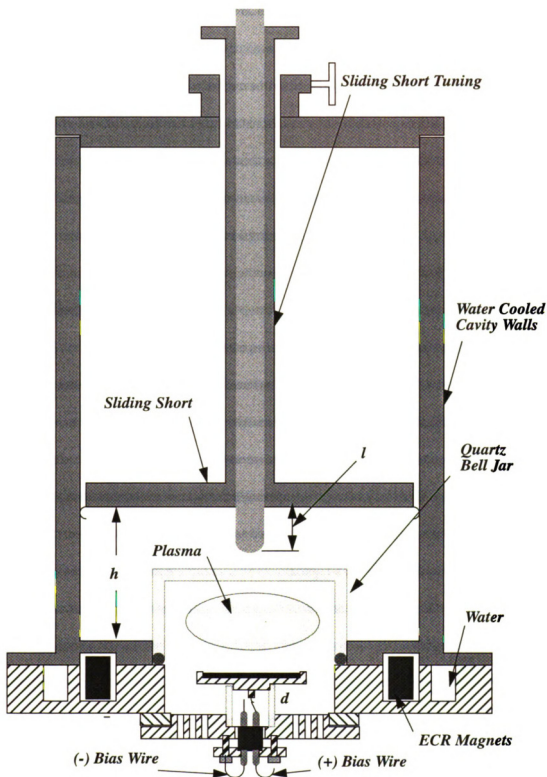


Figure 4.6 Cross-section of MCPR configuration 4.

symmetric plasma in the 4" bell jar MCPR is the one shown in the figure 4.5. Unfortunately, even in this instance the arrangement is not a useful one. In order that a symmetric plasma form in the discharge chamber with this bias assembly the height of the quartz tube had to be below 2 cm. At this height the substrate is very low in the discharge chamber and the induced plasma is not in contact with it. As a result no appreciable diamond deposition occurs on the substrate with this cavity configuration. Hence no deposition results are reported in later chapters for this configuration.

4.6 The End-Feed 5" MCPR

The issues of limited substrate processing area and process coating of the quartz bell-jar in the 4" MCPR were resolved by Asmussen and Zhang by the design of a new reactor -- one with a larger diameter bell-jar and a longer length cavity shell (refer to section [2.2.2.2.6]). The new bell-jar has an inside diameter of 4.6 inches, which allows processing of substrates with a circular diameter up to 4 inches. The longer length cavity shell provides new modes of tuning such as the TM_{013} . When tuned to this resonant electromagnetic mode, the sliding short is approximately 14 cm further from the inside surface of the quartz bell-jar than the TM_{011} mode, however the distribution of the electromagnetic field pattern in the region of the discharge chamber remains the same (refer to section [2.1.2]). Hence, the evanescent fields from the probe are further attenuated and can no longer distort the shape of the plasma such that it is drawn towards the bell-jar. The shape of the plasma though, is still symmetric and capable of processing large area substrates.

In order that this investigation of plasma assisted low-temperature CVD diamond MCPR processes be complete several configurations of the 5" bell-jar MCPR were

included in it. Among them were electrically and thermally isolated configurations, electrically biased configurations, and thermally controlled substrate temperature configurations.

The following sections discuss the operation and characteristics of the 5" MCPR configurations. A description of the unique components that make-up each configuration is provided. In addition, dependent system parameters such as substrate temperature, percent of incident absorbed microwave power, and the resulting size, shape and location of the plasma are discussed.

The sliding short that was used with the 5-inch MCPR was the one that was used with the 4-inch MCPR configurations. Measurements of the cavity height h are determined by a scale on the short's coaxial feed. When this short is used with the taller cavity of the 5-inch MCPR the actual cavity height h is always 6.3-cm higher than the number indicated on the scale. The cavity heights h reported in the remaining sections of this chapter are those taken from the scale on the short, the correction factor is not included.

4.6.1 MCPR Configuration 5

The substrate receptor assembly of MCPR configuration 5 is a thermally isolated configuration for substrates with an outside diameter of 4 inches or less. It is similar to that of MCPR configuration 2 with the exception that a metal ring is included at the bottom of the stage. The addition of this new part is necessary to preclude plasma formation under the substrate, and is similar to that used by Zhang^[34]. Experiments indicate that without it the plasma forms under the substrate receptor and near the top of the bell-jar. A typical arrangement for low-temperature, diamond deposition on 2 inch diameter substrates is

shown in figure 4.7.

Two additional modifications that were included in MCPR configuration 5 are that the material of the graphite insert disk was changed to stainless steel, and a new quartz tube was included. The material of the insert disk was changed to stainless steel to make it more durable and less susceptible to damage during handling. Experiments with insert disks made of both materials were conducted and no difference in the operation of the MCPR was observed. The new quartz tube, which is named the quartz flow tube (QFT), was added to improve the flow of gas in the MCPR discharge chamber. This is necessary because in the 5" bell-jar MCPR the input gases enter the discharge chamber at the very bottom. The QFT forces the input gases to flow up towards the substrate before exiting the discharge chamber.

4.6.1.1 Operation and Tuning

The typical plasma that is induced in MCPR configuration 5 forms approximately an elliptical, cross-sectional shape (as opposed to ball-shaped or hemispherical shaped) and evenly covers the top surface of the substrate. The typical tuning points for this MCPR configuration are 16 cm for the cavity height h , and 3.2 cm for the probe insertion length l . This cavity length corresponds approximately to the TM_{013} cavity resonant mode. At pressures between 5 and 9 torr the amount of reflected microwave power is below 30%, which is much worse than the that of 4-inch MPCR configurations.

The combined heights of the quartz tubes d_1 and d_2 can be varied between 3.0 cm and 6.0 cm without significantly altering the shape of the plasma. Data presented in chapter 5 however, indicates that more uniform deposition takes place when the substrate is

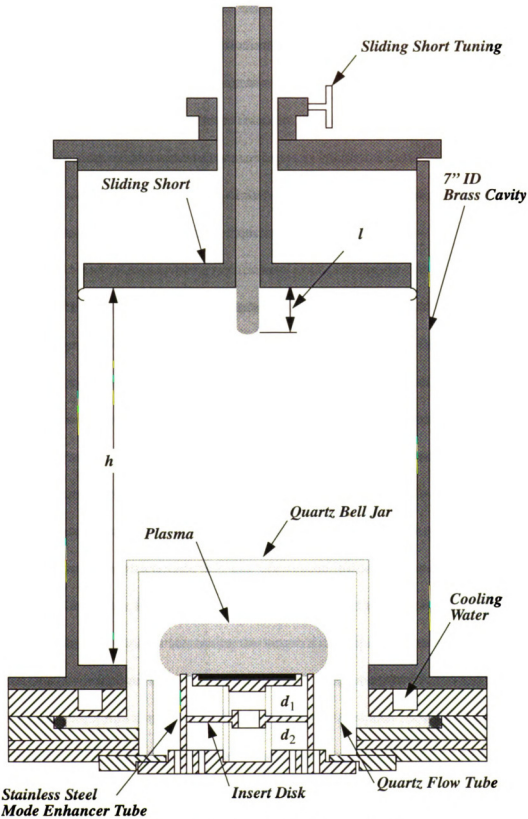


Figure 4.7 Cross-section of MCPR configuration 5.

positioned at a height nearly equal to that of the cavity floor. In this configuration, the vertical distance between the floor of the cavity and the bottom of the recessed area in the substrate receptor assembly where the lower quartz tube sits was approximately 62-mm. The thickness of the insert disk was 1.5-mm, and the thickness of the substrate receptor between the bottom of the substrate and the upper quartz tube was 2-mm. With these components, a total of heights d_1 and d_2 of 58.5-mm would place the underside of the substrate in a location that was level with the floor of the brass-cavity.

4.6.1.2 Processing Large Area Substrates

One notable feature of the 5" bell-jar MCPR is that its discharge chamber is large enough to provide processing of substrates with a circular diameter of up to 4". MCPR configuration 5 was easily adapted for processing large area substrates. The only changes required were that the diameter of the stainless steel receptor be increased and that the height d_1 of the upper quartz tube be lengthened.

Since substrate receptors for 3 and 4 inch substrates are larger than the inner diameter of the mode enhancer tube they can't be placed inside it like the 2 inch one shown in figure 4.7. To correct for this, they were positioned in the MCPR discharge chamber above it. This was easily done by increasing the length d_1 of the upper quartz tube. The typical total height for the quartz tubes d_1 and d_2 was 46 mm, which places the bottom of the substrate receptor 2 mm above the mode enhancer tube. A typical arrangement for 3 inch substrates in MCPR configuration 5 is shown in figure 4.8.

Substrate receptors with an outer diameter as large as 4.25 inches were utilized for low-temperature, diamond deposition on substrates with diameters as large as 4 inches.

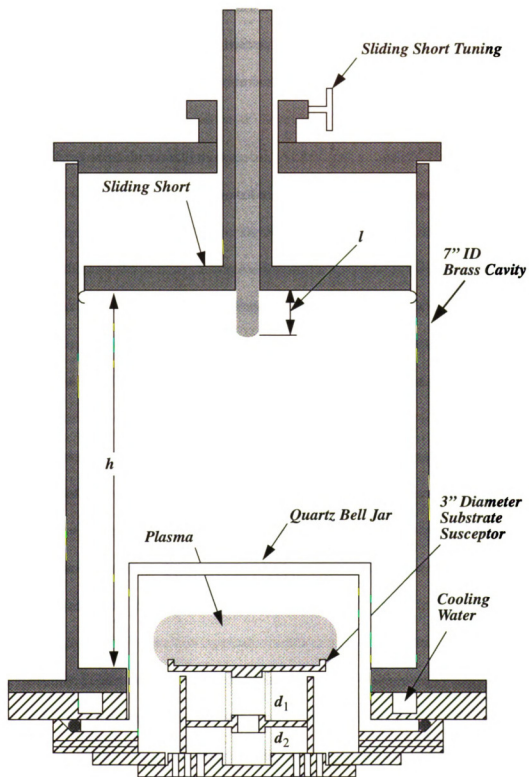


Figure 4.8 Cross-section of MCPR configuration 5.

The use of these components did not alter the tuning or the size, shape and location of the plasma. The tuning improved slightly with their use such that the amount of reflected microwave power at 9 torr was reduced to below 25 percent.

4.6.1.3 Temperature Measurements

Figure 4.9 shows the dependence of the measured substrate temperature on the gas pressure and the input microwave power for MCPR configuration 5. These measurements were observed with a 2.2 μm single wavelength optical pyrometer through the window in the front of the MCPR (refer to section [3.4.1]. The horizontal axis of the graph is the gas pressure in torr. The vertical axis is the temperature in degrees Celsius. The two curves in the graph show data that was measured at input microwave powers of 750 Watts and 1000 Watts.

As was the case with MCPR configuration 2, the temperature of the substrate in this configuration has a strong dependence on the pressure and the input microwave power. The curves appear to diverge for decreasing pressure. This may be an indication that at lower pressures the substrate temperature in the 5 inch bell-jar MCPR becomes more dependent on the input microwave power.

4.6.2 MCPR Configuration 6 -- dc Bias Enhanced

Although deposition with the aide of a dc bias could not be successfully investigated in the 4" MCPR, there was some success in incorporating it into the 5" MCPR. The design of the biased-substrate-receptor-assembly of MCPR configuration 6 was a simple modification of the substrate receptor that is used in MCPR configuration 5.

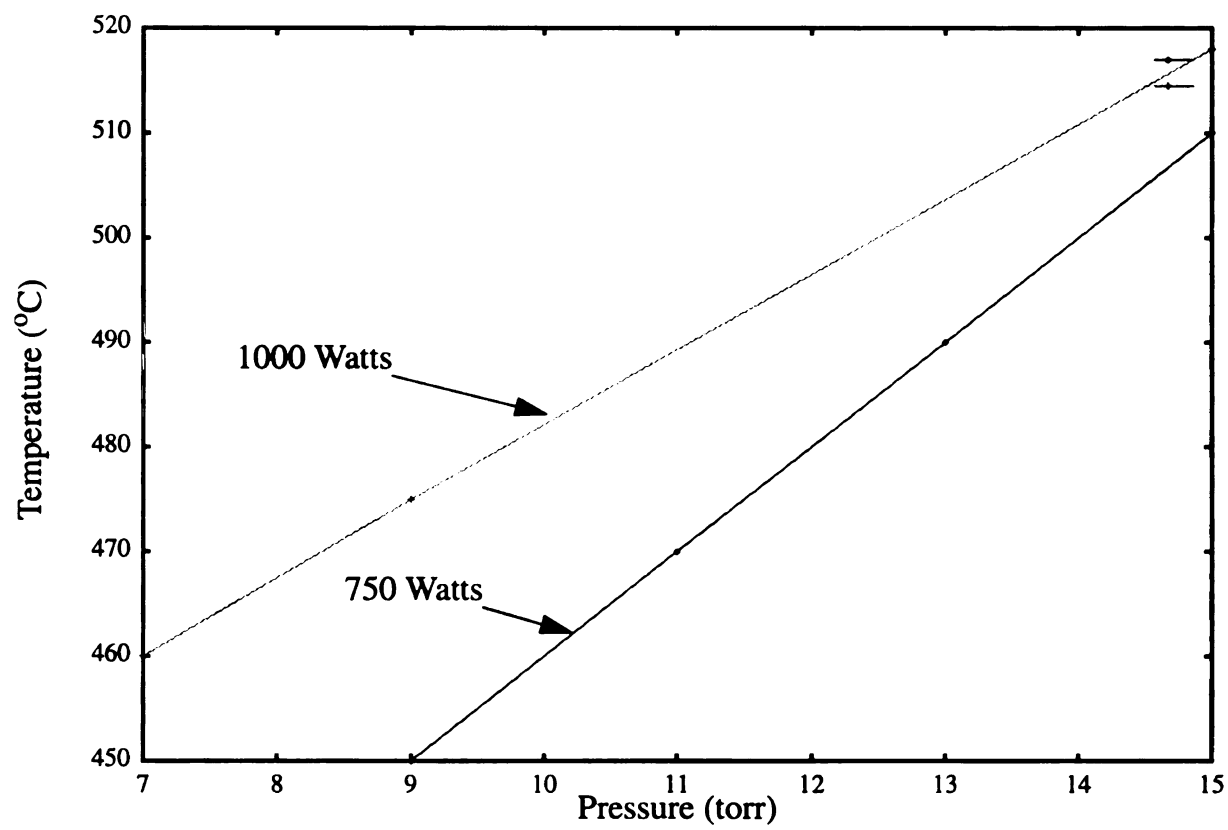


Figure 4.9 Temperature vs. pressure and power for MCPR-C5.

To apply a bias to the substrate, a two wire ceramic feed-through was added in the center of the discharge chamber bottom plate. The positive wire was connected to the stainless steel substrate receptor (refer to figure 4.10) and the other to the MCPR cavity and the outer metal tube of the substrate receptor assembly. As is the case for MCPR configuration 5, the substrate receptor is thermally and electrically isolated from the other metallic components in the discharge chamber by the quartz tube on which it sits. In the bias-enhanced configuration, the outer metal tube that is used to preclude plasma formation under the substrate doubles as the cathode for the bias circuit. The stainless steel substrate receptor is the circuit anode.

4.6.2.1 Operation and Tuning

Operation of the MCPR with the bias-enhanced substrate receptor is unchanged from that of MCPR configuration 5. The tuning and other variables of the MCPR remain the same; however, a small amount of microwave energy is transported out of the cavity by the bias wires. The cavity tuning was typically 16-cm for the cavity height h , and 3.2-cm for the coupling probe insertion length l . For most bias experiments, the quartz tube heights d_1 and d_2 were 2.0-cm and 2.4-cm. With these heights, the top surface of the anode and cathode are at the same height. Since the dimensions of the components of this assembly were the same as those of MCPR configuration 5, quartz tube heights d_1 and d_2 of 20-cm and 2.4-cm placed the underside of the substrate 1.45-cm below the floor of the cavity. At 15 torr and in incident microwave power of around 1 KW the magnitude of reflected microwave power is below 20 percent.

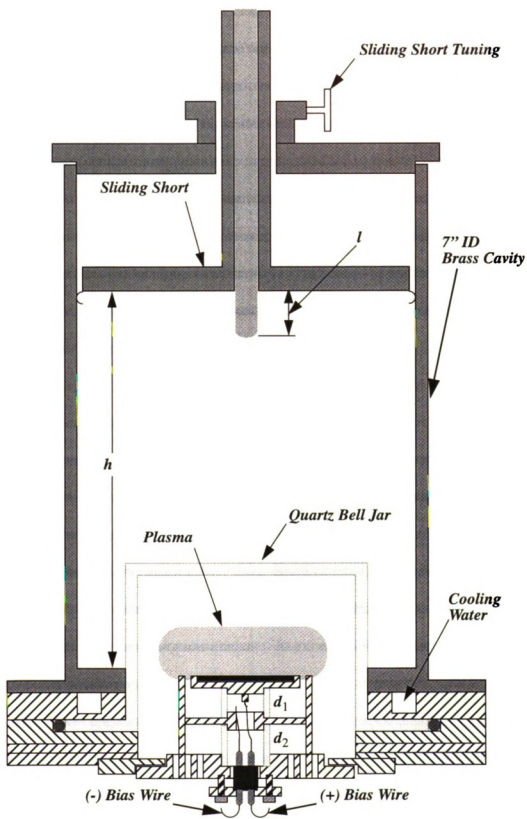


Figure 4.10 Cross-section of MCPR-C6.

4.6.2.2 The dc Bias Circuit

The dc power supply that was used for all the bias enhanced deposition experiments that are discussed in this dissertation was a NJE Model QRP-160-3. Its rated maximum output is 200 V at 3 Amps. The positive and negative output terminals of the NJE power supply are connected to a two-wire ceramic feed through in the bottom the vacuum chamber by two rubber-insulated stranded copper wires. The bias circuit is completed by two fiber-glass-insulated, stranded copper wires that connect the terminals of the ceramic feed-through in the vacuum chamber to the one in the bottom of the substrate receptor assembly. The current and voltage that were applied to the substrate were measured by two Fluke Model 77 multi-meters as is shown in figure 4.11.

4.6.2.3 Bias Current Measurements

Measurements of the magnitude of the bias current were taken at various pressures and amounts of input microwave power. The data was collected in a random order over a period of two hours for pressures ranging from 4 torr to 15 torr. At each pressure data point, the bias current was measured for three values of input microwave power (1040 W, 870 W, and 700 W). A seeded silicon substrate with a diameter of 2 inches was placed in the substrate receptor for these measurements. At the end of the measurements there was no apparent deposition on the wafer.

The lower pressure limit of 4 torr was the lowest point for which the plasma appeared to remain stable. At pressures below 4 torr the distribution of the plasma does not appear to be uniform -- bright spots begin to appear in random locations in the plasma. During visual observation of the plasma, it was noted that the diameter of the plasma

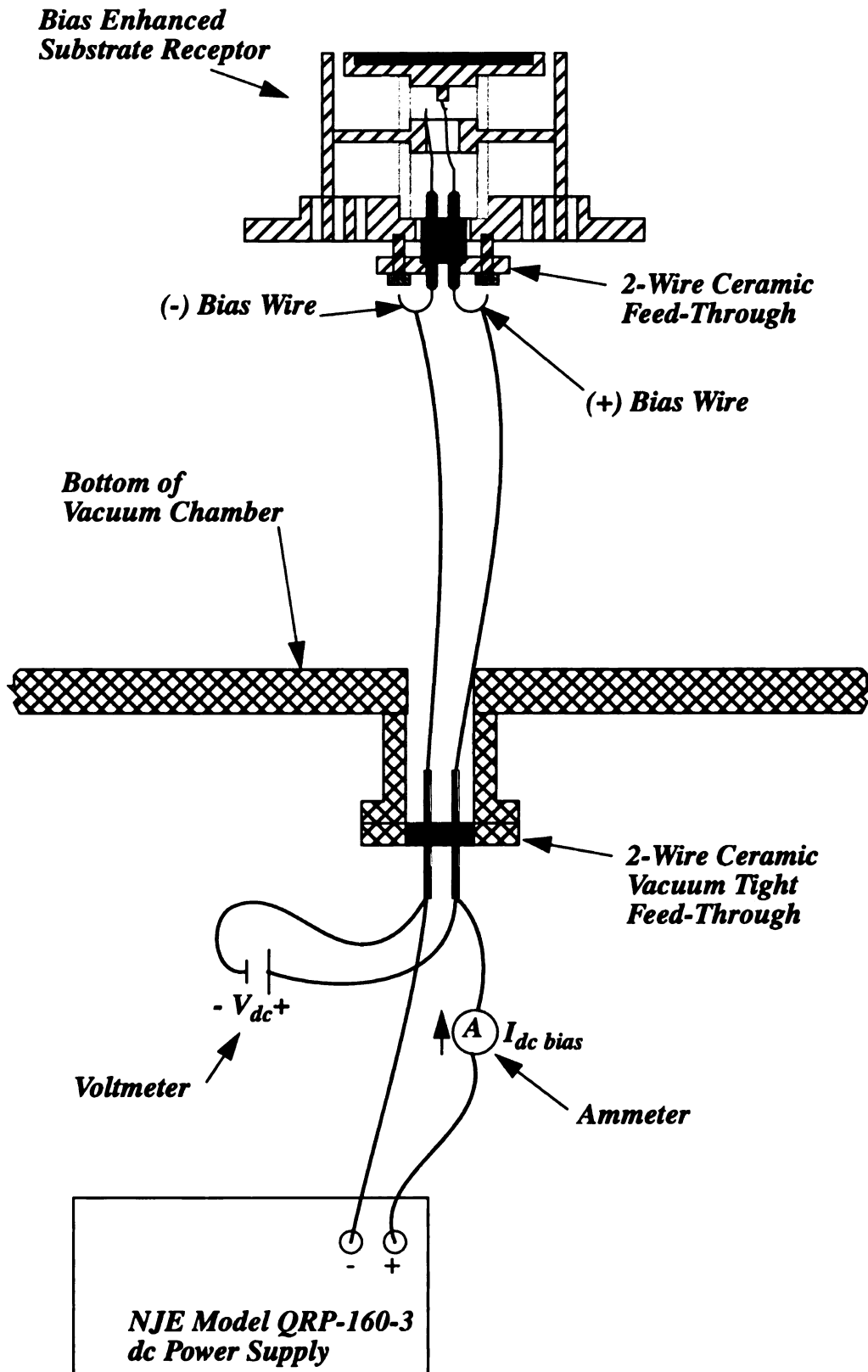


Figure 4.11 Electrical Connections of the bias-enhanced MCPR-C6.

increases with decreasing pressure. Conversely, its diameter decreases with increasing pressure. This dependence of plasma size on the system pressure is the reason for the upper pressure limit of 15 torr. The maximum input power that can be transported by the microwave coaxial waveguide is 1 KW. With this power limit, the maximum pressure where the plasma is still in contact with the bias cathode is approximately 15 torr.

Figure 4.12 shows a graphical representation of the measured bias current versus gas pressure for three values of input microwave power. The x-axis of the plot is the gas pressure, and the y-axis is the measured bias current. The bias voltage was +100 V_{dc} for all of these measurements.

Two things to note about the data in figure 4.12 are that (1) the bias current decreases with increasing pressure, and (2) the bias current increases with increasing input microwave power. The first characteristic coincides with the effect that increasing the pressure has on the size of the plasma. When the pressure is increasing, the bias current and the plasma's radial diameter both decrease. Similarly, when the input microwave power is increased the bias current and the observed radial diameter of the plasma increase. These two observations indicate that bias current is very sensitive to the size of the plasma, and possibly its location. Conditions that cause the plasma to grow and shrink in size cause similar changes in the bias current. This may be an indication that shrinking the plasma's size causes it to become less in contact with the anode and cathode of the bias circuit.

One might expect that at higher pressures the bias current should increase. This would coincide with the higher power density of a higher pressure plasma. Since the plasma size decreases with increasing power, the power density, in W/cm³, increases.

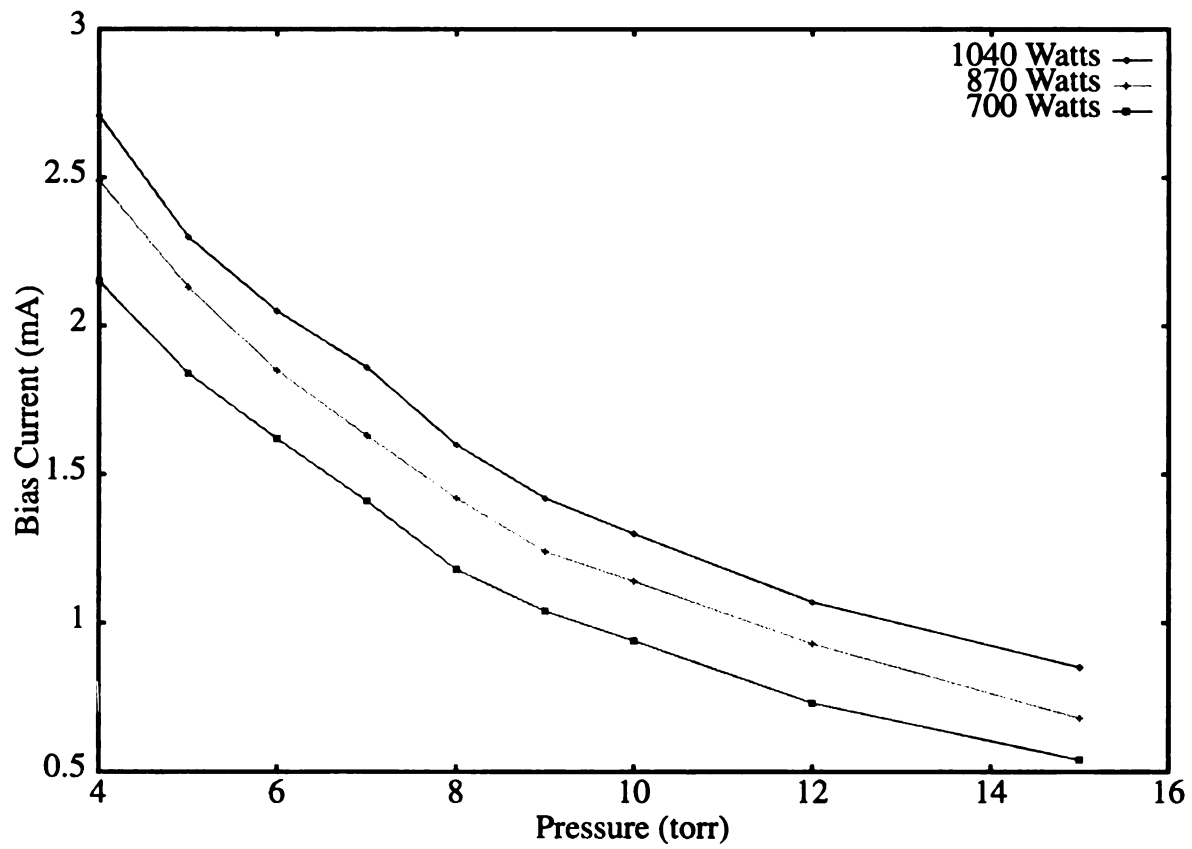


Figure 4.12 Electrical Connections of the bias-enhanced MCPR-C6.

Higher power densities create larger densities of species in the plasma. This should lead to a greater flux of electrons to the substrate; however, the location of the substrate in these experiments may have contributed to the overall trends of the measured dc bias current.

The data of figure 4.12 was measured with a total quartz tube height of 44 mm. At this height, the substrate is 40 mm above the bottom of the MCPR discharge chamber. This places the substrate about 15 mm below the floor line of the MCPR brass cavity. With the substrate so low, it is possible that only the center of the substrate is in good contact with the substrate. If that were the case, the outer edges of the substrate and the surrounding anode would not be in good electrical contact with the plasma.

It is difficult to determine how much of the substrate is in contact with the plasma. The window in the brass-cavity is the only place available for viewing items inside the MCPR. From this vantage point, one can only observe the approximate shape and location of the plasma. The substrate can be seen by looking through the plasma; however, one cannot determine how much contact there is between the plasma and the substrate from this vantage point.

As the plasma's diameter is increased it may also descend deeper into the well of the discharge chamber and become more in contact with the bias-stage components. Experiments with the substrate positioned closer to the MCPR brass-cavity floor were not conducted because of extensive machining requirements for the cathode tube. So it is not known what influence the substrate's location had on the resulting dc bias current.

4.6.2.4 Influence of Seeding

One question that arises regarding the bias currents of figure 4.10 is how much of

the measured dc bias current is actually conducted through the substrate. This question arises because the substrate does not constitute the sole path between the two electrodes. Also, there is a short gap of approximately 2 mm between the inner and outer edges of the concentric anode and cathode. No experiments were conducted to specifically address this issue; however, some insight can be obtained from the data acquired during the various bias enhanced deposition experiments. It was noted that the magnitude of the bias current varied proportionally with the seeding nucleation density of photo-resist seeded silicon. In one experiment where the seeding density was poor, there was an order of magnitude increase in the bias current at the beginning that slowly decreased with time.

4.6.3 MCPR Configuration 7 -- Deposition on 3" and 4" Substrates

Another MCPR configuration for depositing diamond on large area substrates is one that was developed by Zhang. MCPR configuration 7 of this dissertation was an approximate replica of that assembly. Figure 4.13 shows a cross-section of configuration 7. The components in the assembly are (1) the stainless steel receptor, (2) the quartz flow tube, (3) the mode-enhancer tube, and (4) the base-plate.

Components (1) and (2) are dimensionally the same as those used by Zhang. The stainless steel receptor (1) is a disk with an outer diameter of 4.6 inches. Its features include a ring of gas flow holes near the outer edge, a recessed area for substrate retention in the middle, and a groove on the back side for connection to the quartz tube (2). Two different receptors (1) were used for diamond deposition. They were dimensionally identical except for the diameter of the recessed substrate retention area. One was cut for retention of 3 inch substrates and the other for 4 inch ones. Like previous MCPR configurations, the

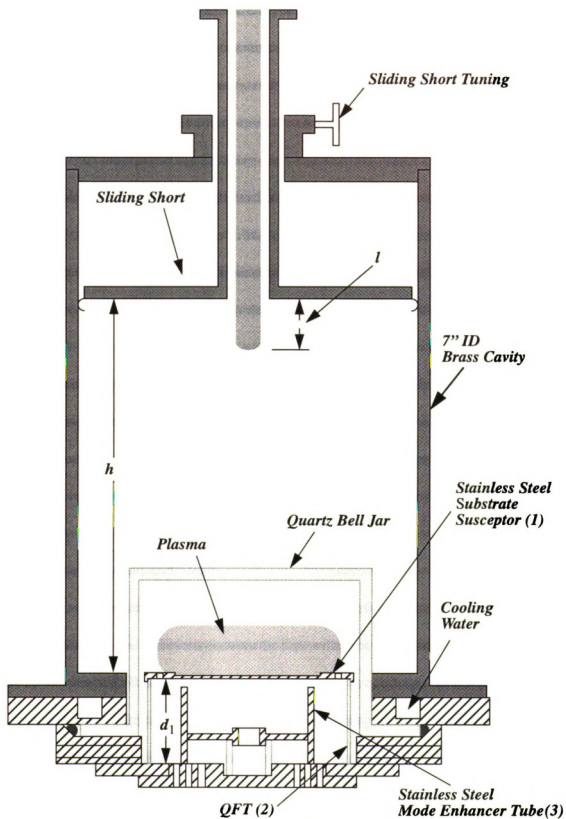


Figure 4.13 Cross-section of MCPR-C7.

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quartz flow tube forces the input process gases to flow up to the top of the discharge chamber before exiting to the vacuum chamber. It also creates a large thermal resistance between the substrate and the water cooled brass-cavity, base plate. In this configuration, the quartz tube is also used to locate the substrate receptor in the discharge chamber. The location of the substrate in the chamber can be adjusted by varying the length of d_f .

The mode-enhancer tube (3) and the base plate (4) are the same components that were used in MCPR configuration 5. The mode-enhancer tube is similar to that used by Zhang and is necessary to preclude plasma formation under the substrate receptor. The idea of using such a metallic tube to control the regions of plasma formation was first reported by Zhang. The base plate is a two piece assembly that supports the substrate receptor components in the MCPR. It differs from the one used by Zhang for large area diamond deposition in that gas flows to the vacuum chamber through concentric rings of 1/8 inch gas flow holes. The one used by Zhang had a single 1 inch diameter hole in the center.

4.6.3.1 Operation and Tuning

The typical plasma that is induced in MCPR configuration 5 forms an elliptical, cross-sectional shape and evenly covers the top surface of the substrate. The typical tuning points for this MCPR configuration are 16 cm for the cavity height h , and 3.2 cm for the probe insertion length l . This cavity length corresponds approximately to the TM_{013} cavity resonant mode. At pressures between 5 and 9 torr the amount of reflected microwave power is below 30%.

The shape and location of the plasma is influenced by the length of the quartz flow

tube (2) because it alters the location of the steel substrate receptor (1) in the discharge chamber. Diamond deposition experiments with lengths ranging from 48 mm to 63 mm were conducted to observe the affects of the substrate location. If the length of the tube was 55-mm the bottom of the substrate was level with the floor of the brass-cavity. If the length of the tube was 63-mm, the underside of the substrate was more than 8-mm above the cavity floor. At the 63-mm receptor location, a plasma could not be induced with a uniform cross-section that evenly covers the substrate. Instead the plasma formed in a region adjacent to the quartz tube side walls and in areas below the substrate. At quartz tube heights of 58 mm and below however, the plasma had the shape and distribution that was described in the preceding paragraph.

4.7 Thermally Adjustable End-Feed 5" MCPR Configurations

The Harris - Goodwin growth models indicate that diamond deposition in a hydrogen - methane plasma has a strong dependence on the temperature of the substrate as well as the flux of atomic hydrogen and methyl radicals to the substrate surface (refer to section [2.3.3]). The model predicts that it is unlikely that diamond deposition will be uniform if the temperature profile of the substrate and the flux of reactive chemical species to the substrate are not. At low pressures, substrates in the MCPR are heated by recombination of hydrogen atoms on the substrate surface. So the Harris - Goodwin model has two dependencies for atomic hydrogen flux -- substrate temperature, and surface chemistry reactions.

One method for increasing the deposition rate in the MPCR is to create higher fluxes of reactive chemical species to the substrate surface by increasing the gas pressure

and the input microwave power. This also increases the temperature of the substrate, which contributes to the increasing growth rates. A technique for increasing deposition uniformity in the MCPR may be to make the distribution of hydrogen flux to the surface more uniform by lowering the gas pressure. Growth rates would decrease though as lower overall atomic hydrogen concentrations would yield lower substrate temperatures.

Two thermally adjustable MCPR configurations were included in this dissertation to study the effects of substrate temperature and chemical species flux on the uniformity and deposition rate of diamond. One configuration had a independently heated substrate receptor assembly and the other had an independently cooled one. The heated substrate receptor allowed the temperature of the substrate to be increased at low pressures where substrate heating due to hydrogen recombination is reduced. This provided a means by which the temperature of the substrate could be maintained at levels near that of higher pressure plasmas. Conversely, the cooled substrate receptor reduced the temperature of the substrate at high pressures. This created a deposition environment where higher pressure plasmas could be used without increasing the temperature of the substrate. Such a process was necessary for diamond deposition on temperature sensitive substrates. While it was preferred that deposition processes be developed without the added complexity of externally connected components such as electric heaters, it was necessary to investigate the effectiveness of such an items.

4.7.1 MCPR Configuration 8 -- Heated Substrate

One of the chief goals of this investigation was to develop a low-temperature diamond deposition process with the best possible deposition uniformity. In pursuit of that

goal an investigation of deposition uniformity was conducted with an electrically heated substrate receptor. The conjecture was that the flux distribution of chemical species including atomic hydrogen has a better uniformity at lower pressures. This improvement would create a more uniform temperature profile across the substrate and improve deposition uniformity. A heater is necessary, because at lower pressures heating of the substrate by the plasma in the MCPR is reduced as a result of a reduction in chemical species flux to the substrate. This in turn causes growth rates to decrease. The heater in MCPR configuration 8 is used to independently heat the substrate. The desired result is that with this configuration a heater in conjunction with lower gas pressures provide better uniformity at equivalent growth rates to other higher pressure configurations.

There are two issues that arise when an electric heater is inserted into the MCPR. First, the heated substrate receptor assembly must be manufactured with metallic parts such that microwave energy is not transported out of the MCPR by the heater wires. This metallic assembly will undoubtedly increase the flow of heat from the substrate to the water cooled brass-cavity base plate. The second issue is that the heater must supply enough power to offset the increased heat losses to the substrate by the lower plasma pressure and higher thermal conduction through the metallic components of the substrate assembly.

A cross section of MCPR cavity configuration 8 is shown in figure 4.14. The substrate receptor assembly is constructed entirely from stainless steel -- no quartz tubes are used. The components of the assembly are (1) a hollow stainless steel tube, (2) a stainless steel disk, (3) a stainless steel base plate, and (4) a boron-nitride heater. The stainless steel disk supports both the heater and the substrate. A small circular recessed area with a diam-

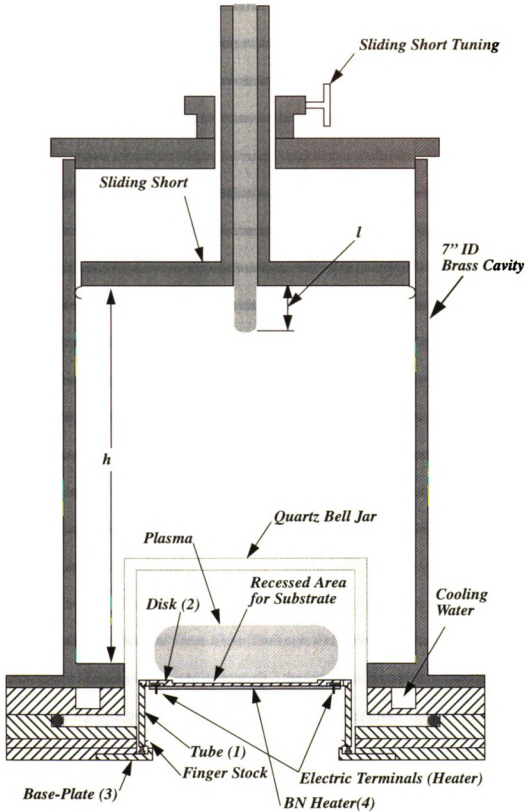


Figure 4.14 Cross-section of MCPR-C8.

eter of 3 inches was machined in the top of this part to locate the substrate. A pair of small tabs were added to the bottom the part to hold the BN heater firmly in place. A circular pattern of 1/16 inch holes was machined around the outer edge of the steel disk. These holes allow the process gases to exit the discharge chamber from an area surrounding the substrate.

Unlike previous configurations, the 1 inch diameter quartz tube that supports the assembly was replaced by the larger diameter stainless steel one. This was added so that microwave energy would not couple out of the reactor via the two wires that connect to the heater. This had been somewhat of an issue with the bias configurations and it was anticipated that it would be even more problematic with the heater configuration. Together the steel tube, base-plate and disk form an electric short circuit in the bottom of the discharge chamber and preclude microwave leaks. The joint between the tube and the base plate was electrically sealed by copper finger stock. The finger stock was connected to the base plate and presses firmly against the inside of the steel tube. The joint between the disk and the tube was electrically sealed by a press fit that was created by thermal expansion of the two parts.

4.7.1.1 Calculations of Heat Flow Through the Substrate Receptor

In MCPR configurations 1 through 7 the substrate is positioned in the discharge chamber on top of a quartz tube. Heat is transported away from the substrate by four means, (1) conduction and (2) convection by the neutral gas, (3) radiation losses and (4) conduction through the substrate receptor assembly. The first three are negligibly affected by the addition of heated substrate assembly. Thermal conduction through the metallic

components does require consideration however.

The thermal conductivity k of quartz is ~ 1 W/m - C, which is quite low compared to stainless steel ($k_{304} > 21$ W/m - C at 400 C). The low thermal conductivity of the quartz tube creates a high thermal resistance and serves to reduce the amount of heat that is conducted from the substrate to the water cooled base-plate of the MCPR brass-cavity. Essentially, the substrate is thermally isolated from the cooler components of the MPCR. In the steady state heat conducted to the substrate by the plasma is equal to that lost by the substrate through radiation and neutral gas cooling. If the quartz tube is replaced by a material with a higher thermal conductivity, the temperature of the substrate will decrease because of the additional heat transfer through that material.

The equation for heat diffusion in an incompressible medium is shown in equation [4.1]^[74]. This relation assumes that convection is not present in the medium. The term T is the temperature, and q' is the volumetric heat release W/m³. The constants ρ and c are the density and specific heat of the material.

$$\nabla \cdot k \nabla T + q' = \rho c \frac{dT}{dt} \quad \text{eq (4.1)}$$

If variations of k and T are small with respect to space and time, equation [4.1] can be simplified to an ordinary-differential-equation, the result is shown in equation [4.2].

$$\nabla^2 T = \frac{q'}{k} \quad \text{eq (4.2)}$$

The term $\nabla^2 T$ in equation [4.2] is a “Lapacian”, which in Cylindrical coordinates can be expressed as is shown in equation [4.3].

$$\nabla^2 T = \frac{1}{r} \frac{d}{dr} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \Theta^2} + \frac{\partial^2 T}{\partial z^2} \quad \text{eq (4.3)}$$

When equation [4.2] is used in conjunction with Fourier’s law, which is shown in equation [4.4] for heat q in W/m^2 in the z -direction, the temperature distribution and heat flux in objects can be determined.

$$q = -k \frac{\partial T}{\partial z} \quad \text{eq (4.4)}$$

Using equation [4.2] and equation [4.4] one can approximate the temperature gradient and the heat flow for the quartz tube in MCPR configurations 1 through 7 as follows. First since there is no volumetric heat release inside the quartz tube the term q' in equation [4.2] is zero. Second, assume that the length of a typical quartz tube is 40-mm, its diameter is 25-mm, and its wall thickness is 2-mm. Since the wall thickness small as compared to the length, and the quartz is homogeneous throughout, one can assume that T does not have a gradient in the directions of r and Θ . Hence equation [4.2] can be simplified to the form shown in.

$$\frac{\partial^2 T}{\partial z^2} = 0 \quad \text{eq (4.5)}$$

The general solution of equation [4.5] is shown in

$$T = C_1 z + C_2 \quad \text{eq (4.6)}$$

In the steady state, the temperature at the ends of the quartz tube are T_1 and T_2 . Applying these boundary conditions to equation [4.6] the resulting expression for the temperature distribution, T , from one end of the tube to the other is simply

$$T = T_1 + \frac{T_2 - T_1}{L} z \quad \text{eq (4.7)}$$

where L is the length of the tube. To determine the flux of heat, q in W/m^2 , through the tube for a particular temperature gradient, T_1 and T_2 , equation [4.4] is solved for q using the expression for T from equation [4.7].

$$q = (-k) \frac{d}{dz} \left(T_1 + \frac{T_2 - T_1}{L} z \right) \quad \text{eq (4.8)}$$

The result is shown in equation [4.9] and equation [4.10].

$$q = k \left(\frac{T_2 - T_1}{L} \right) \quad \text{eq (4.9)}$$

$$q = k \frac{\Delta T}{L} \quad \text{eq (4.10)}$$

If the top of the tube is at $T_2=500$ C and the bottom of the tube is at $T_1=100$ C, the heat flux through the tube would be $q=10,000$ W/m². The circular, cross-sectional area of the tube is 145.0×10^{-6} m² (i.d. of 21-mm and o.d. of 25-mm). Hence, the total heat flow, Q , through the 40-mm long tube with a temperature gradient, ΔT , of 400 C is 1.45 Watts. This is far less than the 700 W of microwave power that is typically absorbed by the plasma.

In comparison to the small quartz tubes of previous configurations, the heat conduction through the new larger cross-section steel tube is considerably larger. It has a diameter of 10-cm, a length of 3.8-cm and a wall thickness of 4-mm. All of the stainless steel components used for this thesis were made from type 304 stainless steel. The thermal conductivity k of type 304 stainless steel at 400 C is ~ 21 W/ m - °K. This along with the increased cross-section of the part reduces the thermal resistance between the substrate and the water cooled MPCR base-plate by as much as 2 orders of magnitude over that of the small quartz tubes. Using equation [4.10], if the thermal gradient, ΔT , across the length of the steel tube is 400 C, then the heat flux through it would be approximately 221,053 W/m². The cross-sectional area of the tube is $1,206 \times 10^{-6}$ m². Hence, the total heat flow, Q , through the 38-mm long steel tube with a temperature gradient, ΔT , of 400 C is 267 Watts, which is nearly 200 times that through the 40-mm quartz tube. To produce a thermal gradient of 400 C across the steel tube independent of plasma heating, the BN heater must generate more than 200 W of heat.

4.7.1.2 The Heater Circuit

The BN heater (4) was powered by a 60 Hz ac electric power supply that uses a variable transformer to attenuate 120 volts rms from the line to between 0 and 120 V rms. The heater was connected to the ac power supply by a circuit identical to that shown in figure 4.11 for the bias circuit. The input voltage and current to the heater was measured by a Fluke Model 88 multi-meter as is shown in the figure. The only difference was that the dc power supply of the bias circuit was replaced by the ac power supply. Table 4.1 shows the measured power delivered to the heater by the ac power supply for a voltage range of 40 to 70 volts. These are representative values that were determined by measuring the voltage and current to the heater with a plasma in the discharge chamber. Under some conditions, the current can vary by as much as 10 to 15 percent depending on the temperature of the heater. For example, if the discharge chamber is at vacuum the measured current at 60 Vac is 2.6 A. With hydrogen flowing at 200 sccm and no input microwave energy, the heater stops glowing -- an indication it is cooler. At this point the current drops to below 2.2 A. With a plasma present at pressures between 5 and 9 torr however, the values in the table are a close approximation.

4.7.1.3 Operation and Tuning

Igniting a plasma in MPCPR configuration 8 is somewhat difficult. At pressures below 15 torr microwave leaks from the discharge chamber to the vacuum chamber in any MPCPR configuration can often prevent plasma formation. This configuration is no exception. When the components of the heated substrate receptor assembly are at room temperature, the joint between the tube (1) and the disk (2) is not electrically sealed. Thus, at

Voltage (Vac)	Current (Amps)	Power (Watts)
70	3.0	210
60	2.5	150
50	2.0	100
40	1.5	60

Table 4.1: Measured values of voltage, current and power.

room temperature microwave leaks were detected and the plasma did not ignite. The solution to this issue was that the BN heater (4) was used to heat the assembly and seal it for microwave leaks. Prior to each deposition experiment, the BN heater was turned on for 30 to 40 minutes to allow the assembly to warm up.

Once the assembly is heated, ignition of the plasma is routine. Typical tuning points for the MCPR at pressures between 4 and 9 torr are 14.5 cm for the sliding short length h and 3.3 cm for the insertion probe length l . The amount of microwave energy that is reflected is higher in this configuration than in the first seven. It typically varies between 40 and 50 percent. Considering the limits of the coaxial wave guide and the matched loads, this high reflection percentage limits the incident microwave power to a maximum of about 850 Watts.

During initial operational experiments with this assembly it was noted that a dense toroidal plasma with a cross-section of a few milli-meters appeared around the edge of the disk (2). It formed in a area near the edge of the part where the top outer corner was machined at a 90 degree angle. This issue was resolved by machining a 2mm radius all the way around the part.

Like all MCPR configurations the location of the substrate was a critical variable that could greatly influence diamond deposition rates and uniformity. With this configuration the maximum length of the steel tube (1) where a plasma could still be ignited that had a uniform distribution above the substrate was 3.4 cm. Above this height, the plasma usually formed in the bottom of the discharge chamber between the quartz bell-jar and the steel tube (2). With a steel tube length of 3.8-cm, the underside of the substrate was approximately 1.6-cm below the floor the brass-cavity.

4.7.1.4 Temperature Measurements

Since the substrate in this configuration was approximately 2.0-cm below the floor for the brass-cavity, it was often not possible to measure the temperature of the substrate by optical means as was outlined in section [3.4.2]. Furthermore, the location of the 3 inch diameter BN heater beneath the substrate precluded measurement of the substrate temperature from the back-side. The only means available for temperature measurements was to record the temperature of the outer edge of the disk (2) with a thermocouple. To do this a K-type thermocouple was inserted into one of the 1/16 inch gas flow holes near the edge of the disk. Figure 4.15 shows the placement of a thermocouple in the disk and its connection to a temperature meter outside the vacuum chamber through a thermocouple vacuum feed-through.

The actual surface temperature of the substrate could not be determined from these measurements; however, this data provided insight regarding the influence of the plasma and the BN heater on the temperature of the disk. As conditions caused changes in these measurements, it was assumed that the surface temperature of the substrate followed proportionally.

A collection of temperature measurements was acquired for a range of heater voltages and gas pressures for a typical heater configuration. The resulting data is shown in graphical form in figure 4.16. These data points were collected in random order for pressures ranging from 0 to 9 torr, and heater voltages ranging from 0 to 60 volts ac. The chemistry for all the measurements was a mixture of hydrogen, carbon dioxide, and methane with flow rates of 200-8-3 sccm respectively. A 1.1 mm thick glass substrate with a diameter of 1.5 inches was inserted into the substrate receptor.

**Thermocouple Joint
Inserted in Gas Flow Hole
(temperature measured here)**

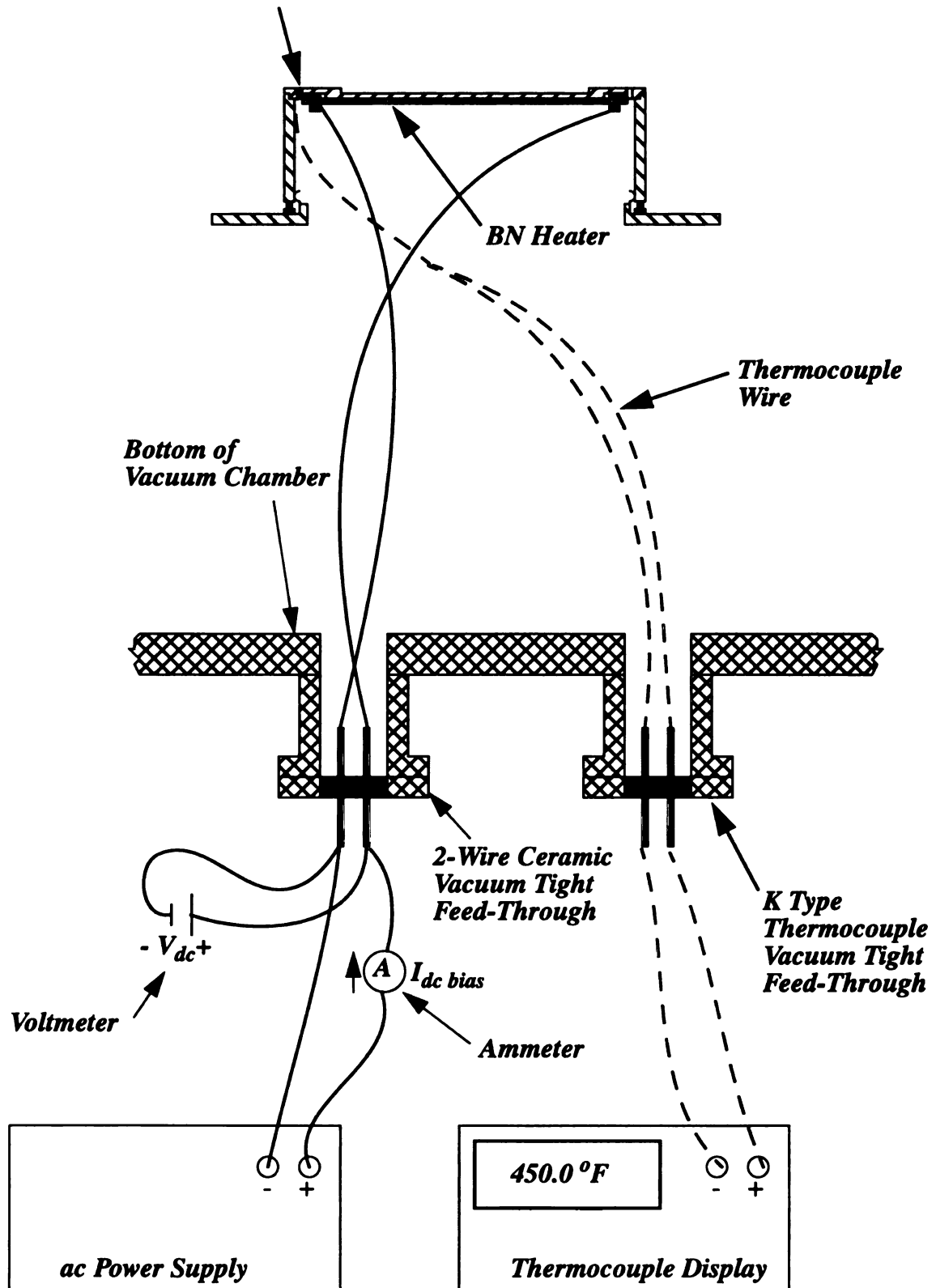


Figure 4.15 The BN-heater circuit.

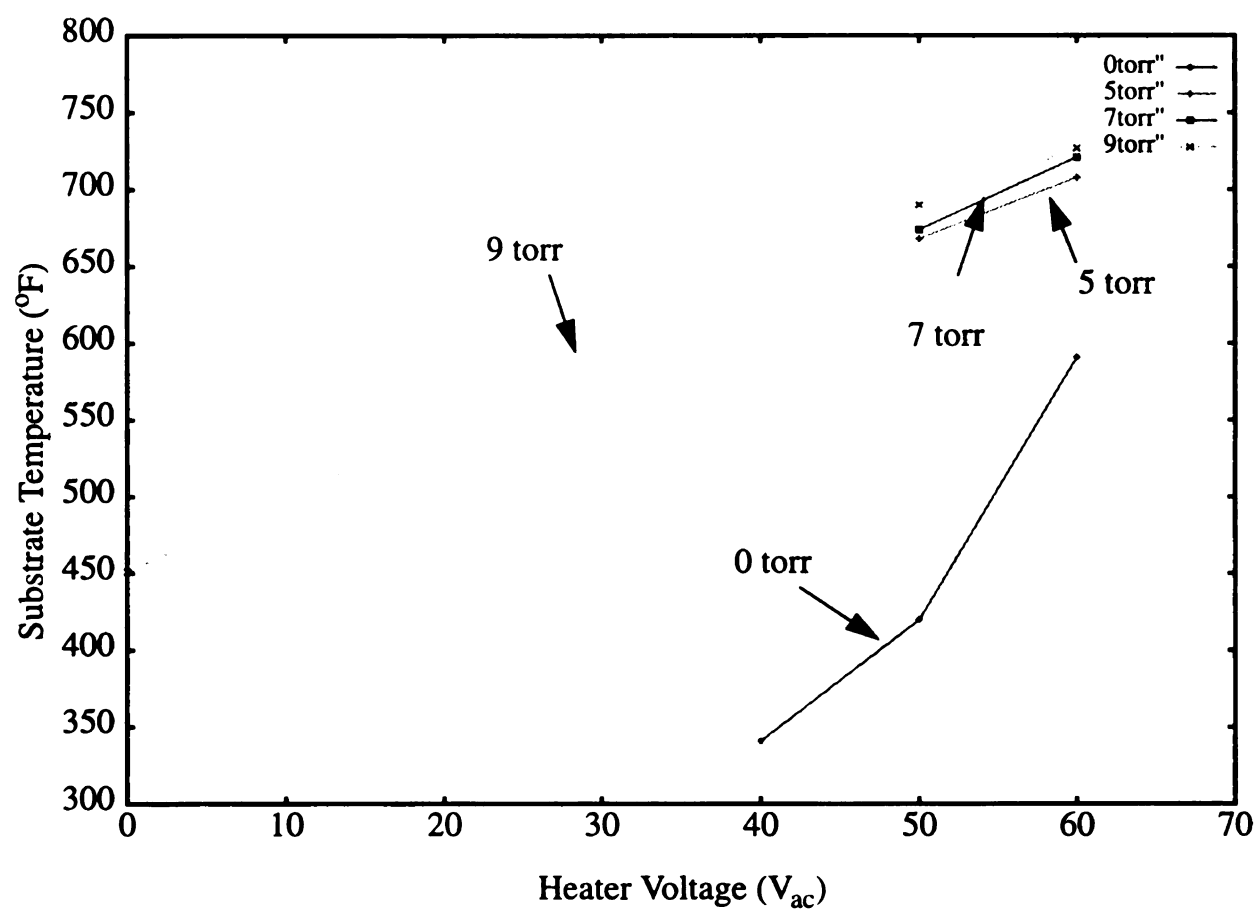


Figure 4.16 Temperature vs. pressure and heater voltage for MCPR-C7.

Measurements labeled “0 torr” were acquired with the system under vacuum. No gasses were flowing and there was no plasma present. The “0 torr” measurements show heating of the substrate receptor by the heater alone. The temperature data lines with the pressure greater than zero were acquired with a plasma present in the system.

There is a single data point at 9 torr where the heater is turned off ($0 V_{ac}$). The temperature at this point is 451°F or 233°C , which is several hundred degrees below that of the substrates in MCPR configuration 5. This is an indication that the high thermal conductivity of the stainless steel components reduces the steady state temperature of the substrate. It should also be noted that no diamond is deposited at 9 torr with the heater turned off. In contrast, the temperature of the disk at 9 torr rises to 727°F (386°C) when $60 V_{ac}$ is applied to the heater. At this point diamond does grow however. A complete discussion of diamond deposition with this MCPR configuration at low temperatures is provided in section [6.3.2] of chapter 6. Operation at voltages of $70 V_{ac}$ and higher are not reported here because at these values diamond films deposited on glass substrates peel, an indication the substrate was too hot.

4.7.1.5 Concerns and Limitations

A drawback of this configuration is that the stranded copper wire in the heater circuit becomes brittle from excessive heating and cooling. Measurements of the current during deposition experiments indicate that this does not reduce the current flow over time. After most experiments though, these wire must be replaced to prevent breakage. To do this the heater must be removed from the assembly.

4.7.2 MCPR Configuration 9 -- Cooled Substrate

The second thermally adjustable MCPR configuration that was included in this dissertation was one with a liquid cooled substrate receptor. The conjecture for the cooler was that the temperature of the substrate could be lowered by adjusting the conductive heat losses from the substrate with a liquid cooled substrate receptor. If the conductive flow of heat from the substrate could be controlled, then temperature sensitive substrates could be processes in higher pressure plasmas -- possibly resulting in higher growth rates. At higher pressures, with the substrate held at a constant temperature, higher growth rates might be achieved if the bottle neck to diamond growth at lower pressures is the availability of atomic hydrogen and diamond precursors and not the substrate temperature.

Heretofore, the substrate in MCPR configurations 1 through 7 was cooled by conductive and convective losses to the neutral gas and radiative losses. In those configurations the substrate was thermally insulated from the water cooled components of the MCPR by the quartz tube on which it sat. Under these conditions the steady state temperature of the substrate varied accordingly with the recombination rate of atomic hydrogen on the surface of the substrate. In these instances there was no means for varying the heat loss from the substrate. If the pressure of plasma was increased so did the power density, and the substrate temperature.

The liquid cooled substrate assembly provides a substrate heat loss mechanism in addition to that of the neutral gas cooling and radiative losses. The cooler uses a large capacity for heat exchange and thermal gaps in spacer materials to control the amount of conductive heat flow from the substrate. A liquid coolant flows through the cooler housing at a controlled rate and has a controlled temperature. This maintains the cooler at a con-

stant and controllable temperature regardless of the amount of heat flowing from the substrate. Furthermore, layers of spacer material with a high thermal conductivity k are placed between the substrate and the cooler. The high k of the spacer material allows even lateral heating of each layer, while the spaces between the layers provides the vertical thermal resistance necessary to control the amount of heat that flows from the substrate to the cooler (see figure 4.17). The heat flux from the substrate to the coolant can be varied by increasing the number of spacers, or by varying the temperature of the coolant in the cooler assembly.

The cooler assembly used for deposition experiments in this dissertation was manufactured from type 304 stainless steel, and was based on the design by Zhang and suggestions from Brian Klein at Norton Corporation. Four notable differences between this cooler and the one used by Zhang are a change in the thickness of the cooler housing, the weld locations, the size of the coolant lines, and the inclusion of thermocouple probes. The first two modifications were changes to the cooler's outer shell. The basic outer shell of the coolant reservoir in the cooler assembly for this dissertation was comprised of two components that were welded together -- making it water and vacuum tight. The components were the housing (1), and the base plate (2). The difference was that Zhang's housing was itself comprised of two parts that were welded together. One failure mode of the Zhang design was that the weld between those two components of the cooler housing had the potential for leaks and did create concerns. Thus for this dissertation, the part was machined as a single piece in the shape of a hollow metal tube with a flat, closed end. Additionally, the flat end of the Zhang cooler had a variable thickness to allow greater cooling in the middle than at the edges. Since the control of heat flux from the substrate is

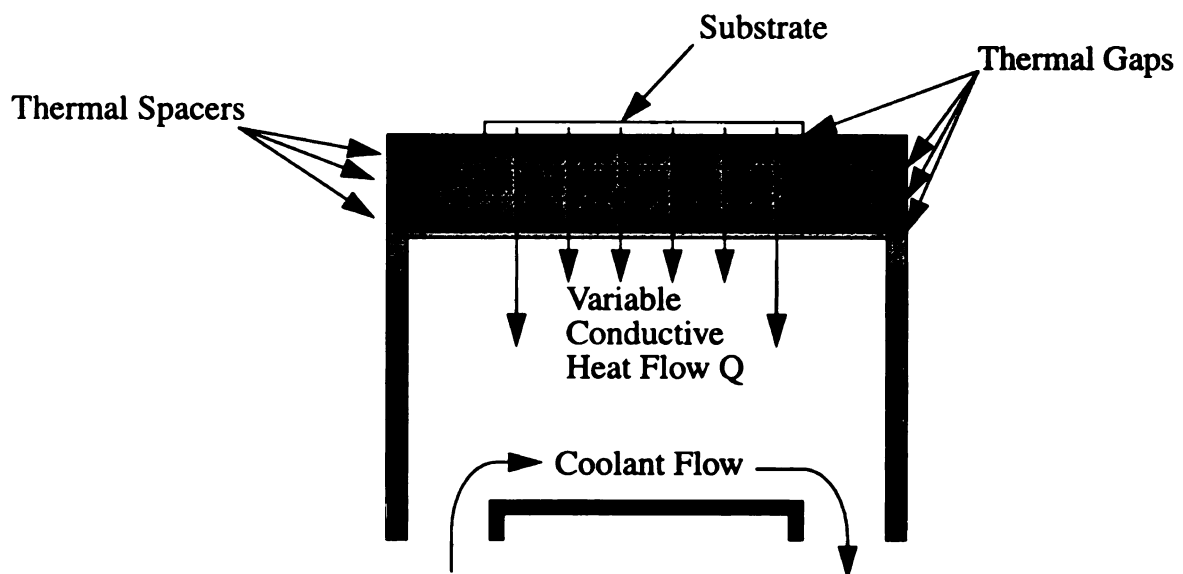


Figure 4.17 Variable conductive heat flow in a substrate cooler.

controlled by the gaps in the spacer material, the flat end of the cooler housing was machined with a constant thickness for this dissertation. A third modification of the Zhang design was to increase the diameter of the coolant flow lines from 1/4-inch to 3/8-inch diameter. This was done to preclude over-heating of the cooler itself. Finally, four thermocouple ports (3) were added to the design to allow placement of thermocouple probes inside the cooler. They were used to measure the temperature of the top surface of the cooler. This allowed the system's computer to monitor the cooler assembly for the possibility of over-heating.

A typical cross-section of the substrate cooler assembly as it was configured for this dissertation is shown in figure 4.18. In addition to the cooler itself, there is a quartz flow tube (QFT) (4), a molybdenum gas plate (5), molybdenum spacers (6), and BN substrate receptors (7). Like other MCPR configurations, the QFT was used to force the process gases to flow up to the substrate before being pumped out to the vacuum chamber. The molybdenum gas plate locks onto the QFT which is centered in the chamber by a groove in the cooler base-plate. To assure that the molybdenum gas plate and the cooler housing were in contact the height of the QFT was 1-mm below that of the cooler's housing. Since the top of the cooler has no grooves or recessed areas, the gas plate is used to locate the interlocking thermal spacers and substrate receptors. Figure 4.19 shows a cross-section of the MCPR with the cooler assembly in it.

4.7.2.1 Operation and Tuning

The MCPR cooler configuration was operated as a closed-loop cooling system. It was filled with a mixture of de-ionized water and ethylene-glycol. The temperature and

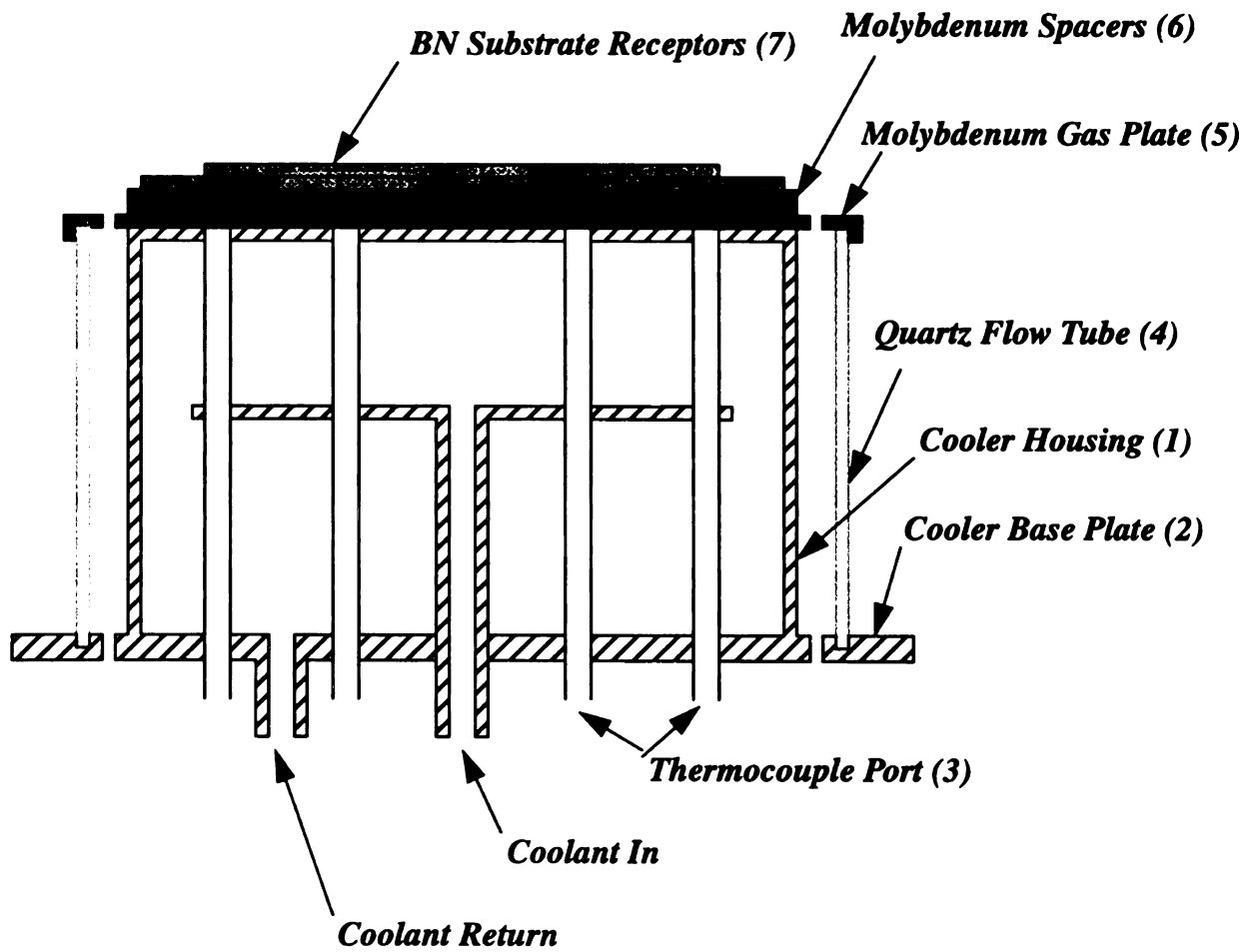


Figure 4.18 Cross-section of the cooler assembly.

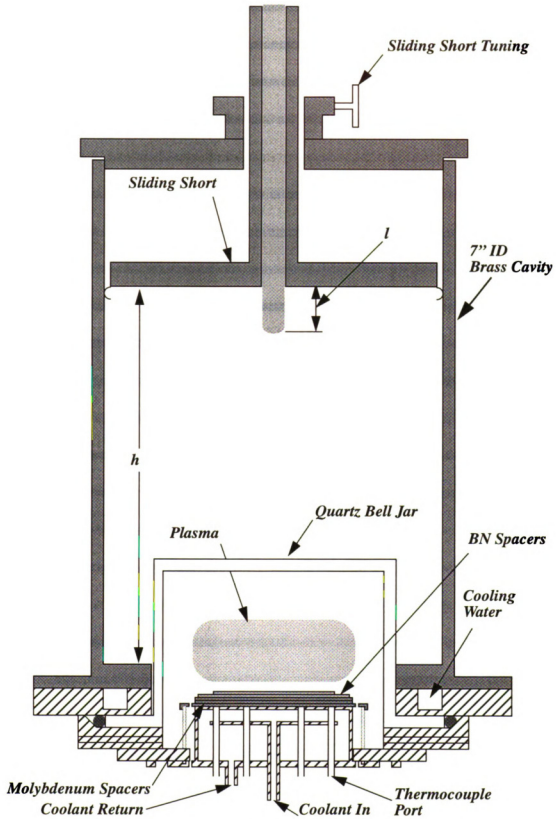


Figure 4.19 Cross-section of MCPR-C9.

flow of the coolant mixture was maintained by a Neslab Model CFT-75 laboratory chiller. This unit has an adjustable temperature range of -17 C to 47 C and a maximum heat capacity of 2100 Watts. It's flow rate varies between 4 gpm at 0 psi and 3 gpm at 60 psi. The temperature of the Neslab was set to 45 C for all deposition experiments reported in this thesis.

Besides the temperature and flow rate of the coolant, there are two additional operation variables for the cooler assembly -- the insertion depth of the cooler in the MCPR, and the thickness and amount of molybdenum spacers that were used. The height of the top of the cooler's housing was approximately 2-inches above its base-plate. So the cooler could be inserted up to 2-inches into the MCPR. The insertion length could be reduced by placing large ring washers between the cooler's base-plate and that of the MCPR cavity. That was not done for this dissertation however. The cooler was inserted the full 2-inches so that the substrate could be positioned as close to the floor of the cavity as possible. The molybdenum spacers were all disk shaped and had an outer diameter of 3.25 inches. They had varying thicknesses so that different configurations could be experimented with, and were machined such that each spacer could lock into the one above it or below it (refer to figure 4.20).

The molybdenum spacers used for this work were provided by Norton Corporation. A selection of four parts were provided, with thicknesses of 60 mils, 60 mils, 120 mils, and 240 mils. Additionally, two BN substrate receptors were donated -- one for 3-inch substrates and the other for 2-inch ones. They were designed such that the 3" BN receptor sits firmly in any of the molybdenum spacers. The 2-inch one though was smaller and only fit in the 3-inch receptor. So to process 2-inch substrates both BN components

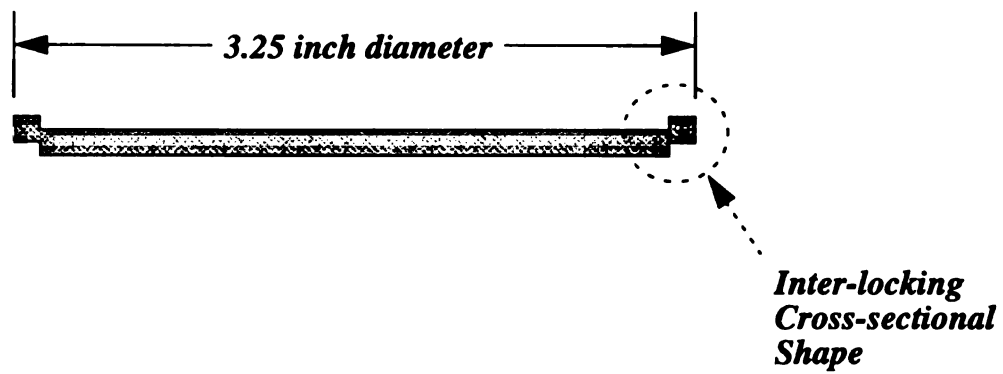


Figure 4.20 Cross-section of a molybdenum spacer.

were used.

The initial experiments with the cooler were conducted to investigate how the inclusion of the spacers influences formation of the plasma in the MCPR. If the cooler assembly is inserted in the MCPR without them, a plasma can be induced without any difficulty. Various arrangements of molybdenum spacers were tested with varying degrees of success. Table 4.2 lists the results of eight different arrangements that were seated separately on the cooler. Some of them included the previously mentioned large ring washers that lower the cooler assembly in the MCPR discharge chamber. A summary of the results is as follows. When the total thickness of the spacers was equal to or less than 240 mils a uniform hemispherical shaped plasma formed above the substrate retention area in the BN receptor. This was true for plasma pressures at or below 30 torr. If more than 240 mils of molybdenum was included, then the plasma could not be induced at any pressure below 30 torr. This was true even when washers were used to lower the location of the cooler. The pressure range for those experiments was kept below 30 torr because that was the maximum pressure where the diameter of the plasma appeared to be at least 2-inches. To achieve this at 30 torr, the input microwave power was approximately 1.2-KW. In the pressure range of 20-torr to 30-torr the reflected power was below 10 percent.

4.7.2.2 Temperature Measurements

For diamond deposition experiments using the cooler assembly, temperatures were measured in 5 locations. Four measurements were taken from the thermocouples in the cooler and the fifth was a measurement of the substrate temperature by optical means as was described in section [3.4.2]. The thermocouple data was recorded every minute by the

Spacer Configuration Number	60 mil spacer	60 mil spacer	120 mil spacer	240 mil spacer	1/32-inch washer	1/32-inch washer	1/16-inch washer	1/8-inch washer	Plasma @ 25-torr	Plasma @ 30-torr
1	X	X	X	X					No	No
2	X	X	X	X	X	X	X	X	No	No
3	X	X	X				X	X	No	No
4				X					Yes	Yes
5	X	X	X						Yes	Yes
6	X	X		X					No	No
7	X		X						Yes	Yes
8	X	X							Yes	Yes

Table 4.2: MCPR cooler assembly spacer configurations

system's computer, the optical measurements were recorded manually 4 or 5 times during a typical 15-hour deposition experiment.

The thermocouple probes were located in the cooler such that their tips contacted the flat, top surface of the cooler's housing (refer to figure 4.18). Two were placed in locations 1-inch from the center of the housing's flat edge, and two were placed in locations 2-inches from the center. The thickness of the top surface of the housing was reduced to less than 30-mil in the region directly above each thermocouple so that measurements could be acquired near the top surface of the housing. Data from the thermocouples was used to monitor the temperature of the cooler's top surface for over-heating, and to observe its temperature profile. The measured data for all the diamond deposition experiments with the cooler was a consistent profile of 45 °C, the same as the operation set point on the Neslab chiller. This is an indication that the chiller was always able to maintain the substrate cooler assembly at the set point temperature.

The 240-mil molybdenum limitation for plasma excitation and the limited selection of spacers meant that the maximum number of thermal gaps that could be placed between the substrate and the cooler was seven. The seven gaps are those between the cooler, the molybdenum gas plate, three molybdenum spacers, two BN receptors, and the substrate. With this arrangement however, the temperature of the substrate at 25 torr is below 400 °C, and the deposition rate is very low. The desired substrate temperature for diamond deposition experiments with the cooler assembly was chosen to be between 450 °C and 500°C, which was adequate for deposition of glass substrates in other MCPR configurations. Since the experimental apparatus was power limited to 1.2-KW for the cooler assembly, the pressure was limited by the minimum allowable plasma size to 30 torr. This

meant that increasing the substrate's temperature by raising the pressure was not an option. Additionally, the Neslab's was already operating at its upper limit of 45 °C. The only means for increasing the temperature of the substrate was to reduce the flux of heat from the substrate to the cooler by increasing the thermal resistance, which meant increasing the number of thermal gaps. Additional gaps were created by placing polished 15-mil silicon wafers in the gaps between the BN receptors and the substrate. For some experiments as many as six silicon wafers were used, three between the BN receptors and three beneath the substrate. In some instances, gaps were created by inserting a 1.1-mm thick Corning 7059 or a graphite disk beneath the substrate instead of silicon. Table 4.3 is a listing of temperature measurements for several cooler arrangements where silicon, graphite and 7059 inserts were used. The data indicates that as the number of thermal gaps between the substrate and the cooler increased so did the substrate temperature. All the measurements in the table were recorded under identical operating conditions with the coolant chiller set at 45 °C and the pressure at 25 torr.

Note that the substrate temperature of molybdenum spacer arrangement 5.1 was 476 °C. The thermally insulated MCPR configurations achieved this temperature at pressures below 10 torr. Here, the substrate cooler assembly can maintain that temperature at 3 times that pressure.

4.7.2.3 Concerns and Limitations

It's obvious by the need to include inserts in addition to the molybdenum and BM spacers that the temperature of the coolant is too low for operation at 30 torr with only 1.2 KW of incident power. The cooler would probably function better with a higher thermal

Spacer Configuration	3-3" Silicon inserts between the BN Receptors	3-2" Silicon inserts beneath the substrate	1-2" 7059 insert beneath the substrate	1-2" Graphite insert beneath the substrate	Total Number of Gaps	Measured Substrate Temperature
4					5	---
5					7	---
5.1			X		8	467 C
5.2	X		X		11	511 C
7.1			X		7	450 C
8.1	X		X		10	502 C
8.2	X			X	10	492 C
8.3	X	X			12	550 C

Table 4.3: Substrate temperature verses thermal gaps.

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gradient between the substrate and the coolant, which could be created by a higher operating pressure regime. The power limitation of the system precluded operation above 30 torr however.

4.8 Tuning the MCPR for Plasma Ignition

In the several *Operation and Tuning* sections of this chapter the tuning points, cavity height h and coupling probe insertion length l , of the various MCPR configurations are reported. These measured data points were an average of the final tuning of the MCPR where the reflected power was minimized after the plasma was ignited. For general low pressure operation however, MCPR tuning has a beginning point prior to the presence of the plasma and an ending point after the plasma is ignited. As was mentioned in section [2.1.2], the impedance of an empty cavity and a plasma loaded cavity are not the same. To ignite a plasma in the empty cavity, it must first be tuned to a matched resonance load. After the plasma ignites the impedance of the cavity changes and the MCPR length h must be re-tuned to improve the load match and increase the amount of microwave power that is absorbed by the plasma. For MCPR configurations 1 through 9, the initial tuning of the MCPR cavity length h was generally 0.5-cm to 1.0-cm longer than the final tuning point. For example, to excite the TM_{013} mode in the 5-inch MPCR the initial height h was typically 15-cm indicated (23.3-cm actual). After the plasma was ignited and the cavity was re-tuned the final cavity height was typically 16-cm indicated (22.3-cm actual). When the initial tuning of the empty MCPR cavity was correct, a small discharge ignited with just 200 to 300 Watts of incident microwave power.

4.9 Summary

The previous sections of this chapter provided descriptive details regarding parameters and performance characteristics for the nine MCPR configurations that were developed for this low temperature diamond deposition dissertation. Data presented in later chapters will show that all but one of these, configuration 4, could be used for diamond deposition at substrate temperatures below 550 °C. The other eight configurations could generate plasmas and diamond deposition environments such that circular disk shaped substrates could be evenly coated. In some configurations diameters up to 4-inches could be processed.

Table 4.4 summarizes the deposition processing areas, and the availability of a dc biased or thermally controllable substrate receptor assembly for MCPR configurations 1 - 9. In configurations 1, 2 and 3, which were the thermally and electrically insulated configurations of the 4-inch MCPR, the diameter of the substrate processing area was limited to 2-inches by the characteristics of the reactor. The diameter of the processing area of configuration 6, which was a dc biased configuration in the 5-inch MCPR, was also limited to 2-inches by design. The thermally insulated and thermally adjustable configurations of the 5-inch MCPR, which were named configurations 5, 7, 8 and 9, could all process substrates with diameters up to 3-inches. Diamond deposition on 4-inch diameter substrates could only be achieved with modified versions of configurations 5 and 7, neither of which had a bias or any thermal adjustments.

In seven of the MCPR configurations the substrate was placed in a receptor that was seated on top of a quartz tube. The quartz tube was a critical component in these assemblies for two reasons. First its transparency to microwaves precluded it from altering

MCPR Configuration	2" Substrates	3" Substrates	4" Substrates	Variable dc bias	Variable Thermal Conductance	Variable Substrate Heating
1	< 1.5"					
2	X					
3	X					
4	X			X		
5	X	X	X			
6	X			X		
7	X	X	X			
8	X	X				X
9	X	X			X	

Table 4.4: Summary of MCPR Configurations.

the resonant electromagnetic fields in the MCPR cavity. Second, its extremely low thermal conductivity k created a large thermal resistance between the substrate receptor and the MCPR's water cooled base plate. If the material used had a higher thermal conductivity than that of quartz, the temperature of the substrate might have been reduced below that necessary for diamond deposition.

In addition to the seven thermally insulated configurations with quartz tubes supporting the substrate receptor, there were two thermally adjustable ones. MCPR configuration 8 had a heated substrate receptor assembly where a BN heater was used to provide heat to the substrate in addition to that provided by the plasma. This configuration was designed with the intent of achieving the ability to maintain a constant substrate temperature over a range of pressures. It allowed the temperature of the substrate to be controllable independent of the pressure, a feature not available in the seven thermally insulated configurations.

MCPR configuration 9 had a closed-loop, liquid cooled substrate receptor assembly that could vary the conductive heat flux from the substrate to the MCPR base-plate. It was created so that diamond films could be deposited on temperature sensitive substrates, e.g. Corning 7059 glass, at pressures above 20 torr -- a condition where the substrate would overheat in configurations 1 through 8.

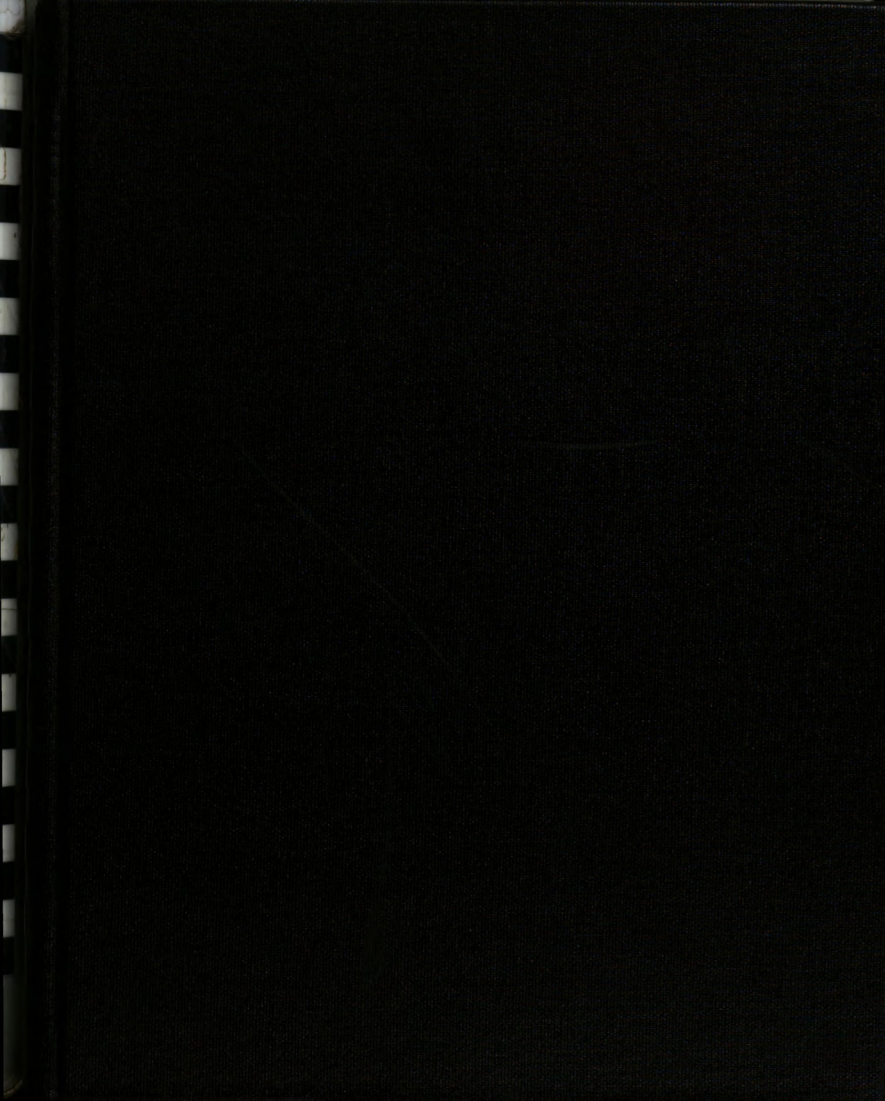
For low temperature diamond deposition with MCPR configurations 1 through 9, the plasma was excited by tuning the microwave power in the cavity to one of two TM_{01n} modes, the TM_{011} mode in the 4-inch MCPR and the TM_{013} mode in the 5-inch MCPR. The measured tuning points for the TM_{011} mode where the reflected power is minimized while a plasma is present were generally 7-cm for the cavity height h and 2-cm for the

coupling probe insertion length l . At 15 torr the reflected power for this mode was typically 5 percent or less. For the TM_{013} mode the measured MCPR tuning points were approximately 16.0-cm indicated (22.3-cm actual) for the cavity height h , and 3.2-cm for the probe insertion length l . For the non-thermally adjustable configurations in the 5-inch MCPR, which were operated at 15 torr and less, the reflected power of the TM_{013} mode was 30 percent or less. For the heated substrate receptor configuration however, the reflected power was as high as 50 percent. The best tuning match for the TM_{013} mode in the 5-inch MCPR was achieved with the liquid cooled configuration -- the reflected power was generally less than 10 percent. The variations of load matching of the TM_{013} mode are characteristic of how the 5-inch MCPR reacts to changes in pressure. At lower pressures the reflected power is always higher than at higher pressures. Since the heated substrate receptor assembly was operated at pressures substantially lower than that of the cooled or thermally insulating ones the load matching was worst.

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**LOW-TEMPERATURE DEPOSITION OF
TRANSPARENT DIAMOND FILMS WITH A
MICROWAVE CAVITY PLASMA REACTOR**

VOLUME II

By

Michael J. Ulczynski

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

DOCTOR OF PHILOSOPHY

Department of Electrical Engineering

1998

Chapter 5

Low-Temperature Diamond Deposition Results on Silicon

5.1 Introduction

The goal of this dissertation was to explore the development of a useful low-temperature diamond deposition process with existing MCPR technology. A useful process was defined as one that deposits quality material at a reasonable deposition rate over areas at least as large as 20 cm². Traditionally, CVD diamond-deposition-process development with MCPR and other plasma sources is carried out with silicon wafer substrates. Likewise, benchmarking for this dissertation was conducted with silicon substrates. Afterwards, useful deposition processes were applied to temperature sensitive substrates, which were typically Corning 7059 glass. The silicon substrates that were used for the benchmark, low-temperature process development were p-type (100) silicon substrates that were polished on one side. They had a thickness of 8-17 mils and diameters of 2, 3, and 4 inches.

The scope of this chapter is to report the benchmark results of diamond deposition on silicon substrates with many of the MCPR configurations that were presented in Chapter 4. Included in the results are measurements of deposition rates, measurements of approximate deposition areas, measurements of surface roughness, SEM photos, and Raman spectrum. Additionally, there are some comparisons of the deposition results with

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the growth models that were summarized in chapter 2. The deposition results and film characterization of diamond films that were deposited on glass substrates are presented later in Chapter 6.

Remember, the Raman spectra in this dissertation are labeled as type *Raman A* and type *Raman B* as was noted in section [3.4.4]. It may appear that a *Raman B* spectrum has a higher graphitic and amorphous content than a *Raman A* spectrum, which is not necessarily the case. Raman of these types were acquired with different methods and should not be analyzed comparatively.

The remaining sections of this chapter are organized into four topics. The first contains sections where measured, experimental substrate weight gains are compared to growth models. In these sections, experimental results for growth rate and/or film quality are compared with predictions by growth models that were developed by Harris-Goodwin and Bachmann. Specifically, comparisons are presented for experiments with varying substrate temperatures, gas compositions and gas pressures. In the second topic, experimental results are presented for depositions where a dc bias was applied to the substrate. The results of these experiments are evaluated in comparison with non-biased deposition experiments for changes in growth rate, film quality, and morphology. Thirdly, experimental results are presented for depositions where the substrate temperature was controlled via the aid of a substrate cooler. This is a continuation of the investigation of how the gas pressure influences the deposition rate. A comparison to the Harris-Goodwin model is included. Finally, the chapter concludes with additional observations from deposition experiments with silicon substrates. They include an investigation of nucleation density with photo-resist seeding, measurements of film surface roughness, deposition on 3-inch

and 4-inch substrates

5.2 Comparison

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5.2 Comparison of Deposition Results to Growth Models

Two models for diamond growth from CVD processes were presented in Chapter 2. One was the Harris-Goodwin growth model, which predicts diamond growth rates from hydrogen-methane processes. The other was the Bachmann C-H-O gas phase diagram, which predicts trends for CVD processes where gases containing hydrogen, carbon and oxygen are used. In section [5.2.1] and section [5.2.2] discussions are presented for comparison of the predictions of these models with actual deposition results that were obtained with the MCPR configurations and experimental techniques that were outlined in Chapter 3 and Chapter 4.

5.2.1 Comparison to the Harris-Goodwin Growth Model

A model for diamond growth from atomic hydrogen and methyl radicals, which was developed by Harris and Goodwin, was outlined in Chapter 2 (refer to section [2.3.3]). It predicts that the three variables that influence the growth rate of diamond are (1) the substrate temperature, (2) the concentration of atomic hydrogen at the substrate's surface, and (3) the concentration of methyl radicals at the substrate's surface. In the MCPR however, the substrate's temperature and the chemistry at it's surface are internal variables that are themselves dependent on the input variables of the MCPR. They vary with the input chemistry, the gas pressure, the microwave power, the substrate receptor, the substrate location in the discharge chamber, and the ambient temperature of the MCPR.

The equations

(2.12) are repeated here

$$\dot{G} = \frac{K_1 [CH_4]}{1 + K_1 [CH_4]}$$

$$(1 - \theta) = \frac{1}{1 + K_1 [CH_4]}$$

The terms in equation

$[CH_4]$ the concentration

density of diamond, ρ_d

the atomic density of

rate for abstraction of

gen $[H]$ to molecular

face site by atomic hydrogen

$$K_1 = (4.15 \times 10^4) \exp \left(\frac{-10,000}{T} \right)$$

$$K_{-1} = (4.15 \times 10^4) \exp \left(\frac{-10,000}{T} \right)$$

$$K_2 = 1.66 \times 10^4 \exp \left(\frac{-10,000}{T} \right)$$

$$K_3 = 1.66 \times 10^4 \exp \left(\frac{-10,000}{T} \right)$$

The equations for diamond growth from the model (equation [2.23] and equation [2.12]) are repeated here as equation [5.1] and equation [5.2].

$$G^* = \frac{K_3[CH_m]n'_o(1-\Theta)^2}{n_C} \quad \text{eq (5.1)}$$

$$(1-\Theta) = \frac{K_1 X_H}{(K_1 + K_2)X_H + K_{-1}} \quad \text{eq (5.2)}$$

The terms in equation [5.1] are defined as G^* the diamond deposition rate in cm/sec, $[CH_m]$ the concentration of methyl radical at the surface of the diamond, n'_o the surface density of diamond, $(1-\Theta)$ the percent of surface sites not terminated by hydrogen, and n_C the atomic density of diamond. The terms in equation [5.2] are defined as K_1 the reaction rate for abstraction of surface hydrogen by atomic hydrogen, X_H the ratio of atomic hydrogen [H] to molecular hydrogen [H_2], and K_2 the reaction rate for filling an available surface site by atomic hydrogen. The rate constants were defined as follows

$$K_1 = (4.15 \times 10^{-10})\exp(-0.316 \text{ eV}/kT) \quad [\text{cm}^3/\text{sec}] \quad \text{eq (5.3)}$$

$$K_{-1} = (4.15 \times 10^{-10})\exp(-1.17 \text{ eV}/kT) \quad [\text{cm}^3/\text{sec}] \quad \text{eq (5.4)}$$

$$K_2 = 1.66 \times 10^{-10} \quad [\text{cm}^3/\text{sec}] \quad \text{eq (5.5)}$$

$$K_3 = 1.66 \times 10^{-11} \quad [\text{cm}^3/\text{sec}] \quad \text{eq (5.6)}$$

where k is Boltzmann's constant in degrees Kelvin.

In the next three paragraphs, the measurement of the diameter of the model. The predicted methyl radical concentration trends of actual experiments from changes the MCPH between the model and sure, and methane flow rate. parameters were held constant. the model's predicted methane flow rate, the methane flow rate, radical concentration. I approximately constant proportional changes in

5.2.1.1 Influence of

Figure 5.1 shows the results of the experiments (denoted as circles) and the model (denoted as a solid-line) for temperatures up to 530 C. The graph shows

where k is Boltzmann's constant ($k=1.38 \times 10^{-23}$ J/K) and T is the substrate temperature in degrees Kelvin.

In the next three sections, experimental substrate weight gains, which are a measurement of the diamond deposition rate, will be compared with the Harris-Goodwin model. The predicted influence of the model's variables, i.e. substrate temperature and methyl radical concentration, on the diamond deposition rate will be compared to the trends of actual experimental deposition rates, for which changes in growth rates arise from changes the MCPR's input parameters. Specifically, comparisons will be made between the model and deposition experiments where the substrate temperature, gas pressure, and methane flow rate were varied independently while the other MCPR input parameters were held constant. Varying the substrate's temperature has a direct impact on the model's predicted growth rate since it is a variable in the model. The gas pressure and the methane flow rate however, affect the model indirectly through changes in the methyl radical concentration. In these instances the substrate temperature was maintained at an approximately constant value so that changes in growth rates would only be as a result of proportional changes in methyl radical concentrations.

5.2.1.1 Influence of the Substrate's Temperature

Figure 5.1 shows a graph of the measured weight gains for nine experiments (denoted as circles) and the Harris-Goodwin model's predicted weight gain, wg_{HG} , (denoted as a solid-line) for substrate temperatures, T_s , ranging from approximately 440 C to 530 C. The graph shows that for this range of substrate temperatures the rate of increase

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$$w_{HG} = t_p \times 3$$

For calculations of G^* ,

following equations.

$$[CH_m] = [CH$$

of the diamond deposition rate with increasing substrate temperature corresponds well with predictions by the Harris-Goodwin model.

The experimental data in figure 5.1 was acquired from deposition on 2-inch diameter silicon wafers using MCPR-C3. For these experiments the gas pressure was 7 torr, the incident microwave power was 350 W, the input chemistry was 200-8-3 ($\text{H}_2\text{-CO}_2\text{-CH}_4$) and the deposition duration was 40 hours. Variations in substrate temperature were due to slight variations in the lengths of the quartz tubes in the substrate receptor (+/- 2mm) and run-to-run differences in the ambient temperature of the MCPR.

The model's predicted weight gain, w_{HG} in mg, was determined from the model's predicted deposition rate, G^* , as follows. First, the predicted thickness of the diamond film, t_p , was determined from G^* .

$$t_p = \text{duration of deposition [hrs]} \times 3600 \left[\frac{\text{sec}}{\text{hr}} \right] \times G^* \quad [\text{cm/deposition}] \quad \text{eq (5.7)}$$

Then the model's predicted weight gain, w_{HG} , was determined from t_p as was described in section [3.4.3.1].

$$w_{\text{HG}} = t_p \times 3.515 \times \pi \times r^2 \times 1000 \quad [\text{mg}] \quad \text{eq (5.8)}$$

For calculations of G^* , the concentration of methyl radicals $[\text{CH}_m]$ was determined by the following equations.

$$[\text{CH}_m] = [\text{CH}_4] \times \text{percent dissociation of methane} \quad [\text{cm}^{-3}] \quad \text{eq (5.9)}$$

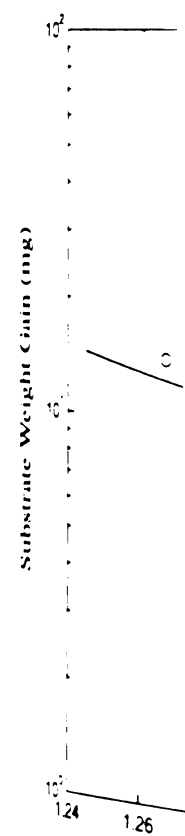


Figure 5.1

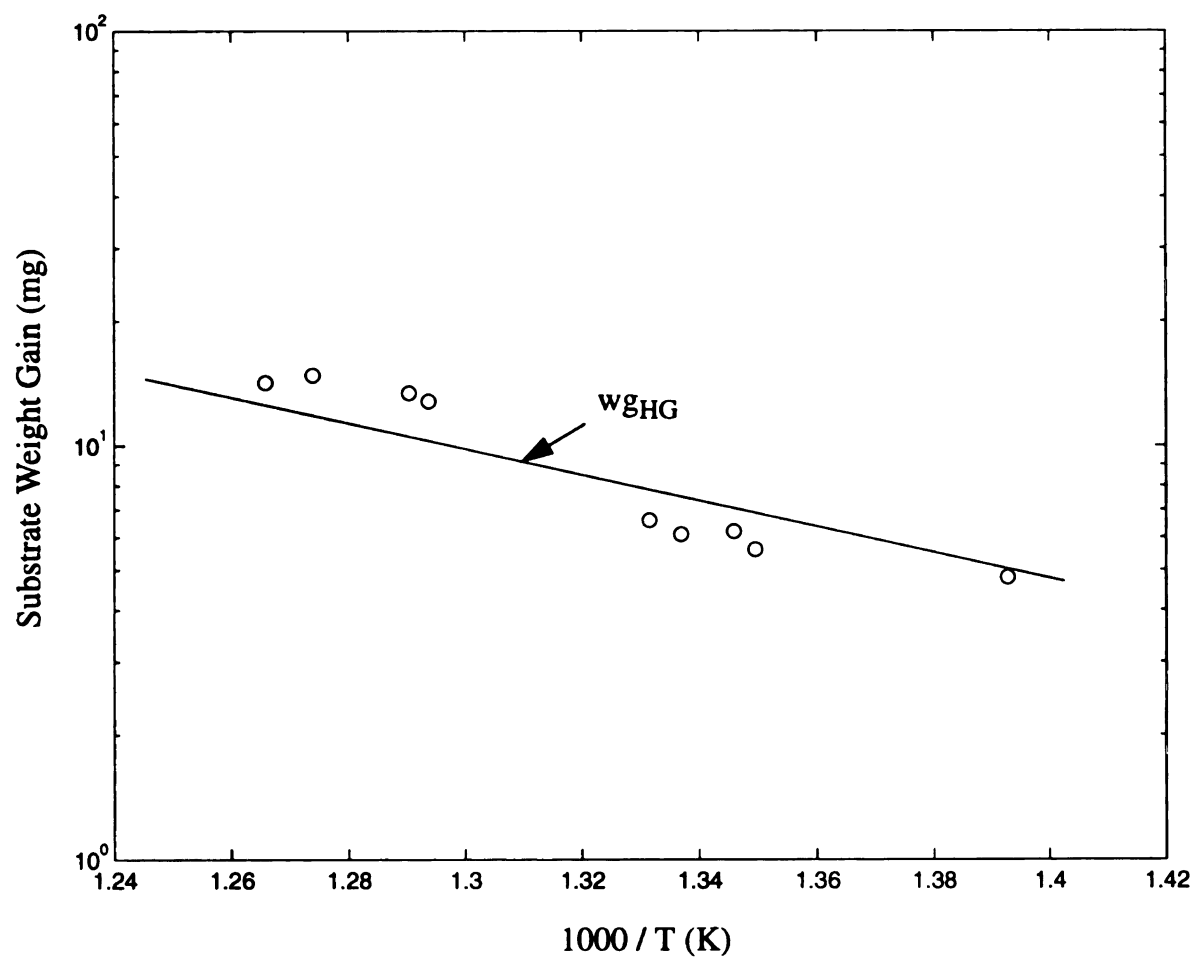


Figure 5.1 Predicted influence of the T_s on the deposition rate.

$$[\text{CH}_4] = \frac{P}{kT}$$

$$n = \frac{P}{kT} \times 10^{23}$$

The terms $[\text{CH}_3]$ and $[\text{CH}_2]$ are the concentrations of the methyl and methylene radicals. The terms $[\text{CH}_4]$ and $[\text{H}_2]$ are the concentrations of methane and hydrogen. The terms P and T are the gas pressure (in Pa) and the gas temperature (in degrees Kelvin). Additional terms σ_{CH_3} and σ_{CH_2} are the collision cross-sections for the methyl and methylene radicals, which are $1.57 \times 10^{-15} \text{ cm}^2$ for CH_3 and $1.57 \times 10^{-15} \text{ cm}^2$ for CH_2 .

For the graph in figure 5.6, the concentration of the methyl radicals was varied by varying the percent of methane in the gas mixture. In figure 5.6, the methane dissociation rate is plotted against the concentration of the methyl radicals. The data points accurately reflect the data obtained from the experiments. The data points were created without the use of the Raman experiments. The data points show a linear dependence however.

A measurement of the weight gains of the samples through figure 5.6, and the data points from the Raman data, are shown in figure 5.7. The data points have a distinct peak at 1.57 eV. The data points of all the spectra show a distinct peak at 1.57 eV.

$$[\text{CH}_4] = \frac{\text{CH}_4}{\text{CH}_4 + \text{H}_2} n \quad [\text{cm}^{-3}] \quad \text{eq (5.10)}$$

$$n = \frac{P}{kT} \times 10^{-6} \quad [\text{atoms/cm}^{-3}] \quad \text{eq (5.11)}$$

The terms $[\text{CH}_4]$ and $[\text{CH}_m]$ in equation [5.9] are the concentration of methane and methyl radicals. The terms CH_4 and H_2 in equation [5.10] are the gas flow rates, in sccm, of methane and hydrogen. The terms n , P , k , and T in equation [5.11] are the gas density (in cm^{-3}) the gas pressure (in Pa), Boltzmann's constant (in J/K), and the substrate temperature (in degrees Kelvin). Additionally, the surface site density, n'_o , and the density of diamond, n_C , are $1.57 \times 10^{15} [\text{cm}^{-2}]$ for the (100) surface and $1.79 \times 10^{23} [\text{cm}^{-3}]$ respectively.

For the graph in figure 5.1, the solid-line was adjusted to fit the experimental data by varying the percent dissociation of methane in equation [5.9]. For the solid-line in the figure, the methane dissociation percentage was chosen to be 0.45%. This value does not accurately reflect the actual dissociation percentage of methane because the line in the figure was created without including the effects of the CO_2 , which was used for the deposition experiments. The data in the graph is useful for analysis of substrate temperature dependence however.

A measurement of the Raman spectrum was recorded for four of the diamond films who's weight gains are shown in figure 5.1. The Raman spectra are shown in figure 5.2 through figure 5.6, and the corresponding, calculated FWHMs, which were determined from the Raman data, are listed in table 5.1. All five of the Raman spectrum in the figures have a distinct peak at 1335, which indicates that the films contain diamond. De-convolution of all the spectra showed that there is a very low amount of amorphous carbon and

Substrate	MCP
S12	3
S15	3
S16	3
S18	3
S31	3

Table 5.

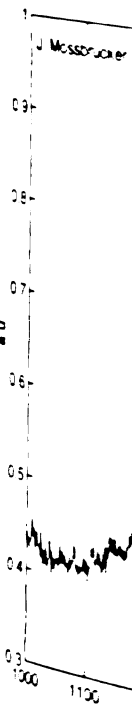


Figure S.2

Substrate	MCPR-Cn	Seeding	Chemistry $\text{H}_2\text{-CO}_2\text{-CH}_4$ (sccm)	wg (mg)	T (°C)	FWHM
S12	3	PR	200-8-3	14.2	517	8.9
S15	3	PR	200-8-3	13.4	502	10.1
S16	3	PR	200-8-3	6.2	470	9.5
S18	3	PR	200-8-3	6.1	475	9.1
S31	3	PR	200-8-3	6.6	478	10.2

Table 5.1: Measurements of the Raman B Spectra FWHM.

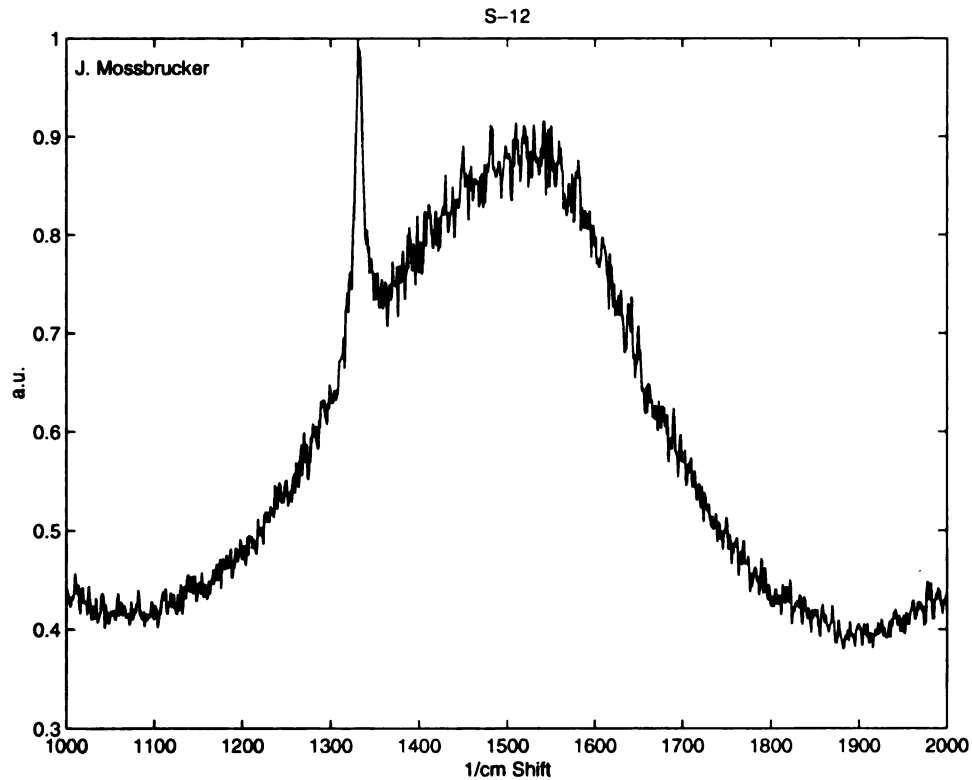


Figure 5.2 The Raman B spectrum recorded from substrate S12.

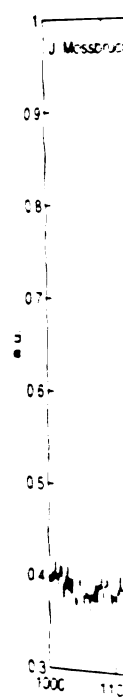


Figure 5

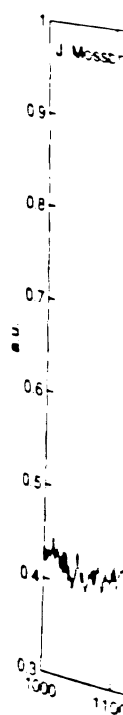


Figure 5.

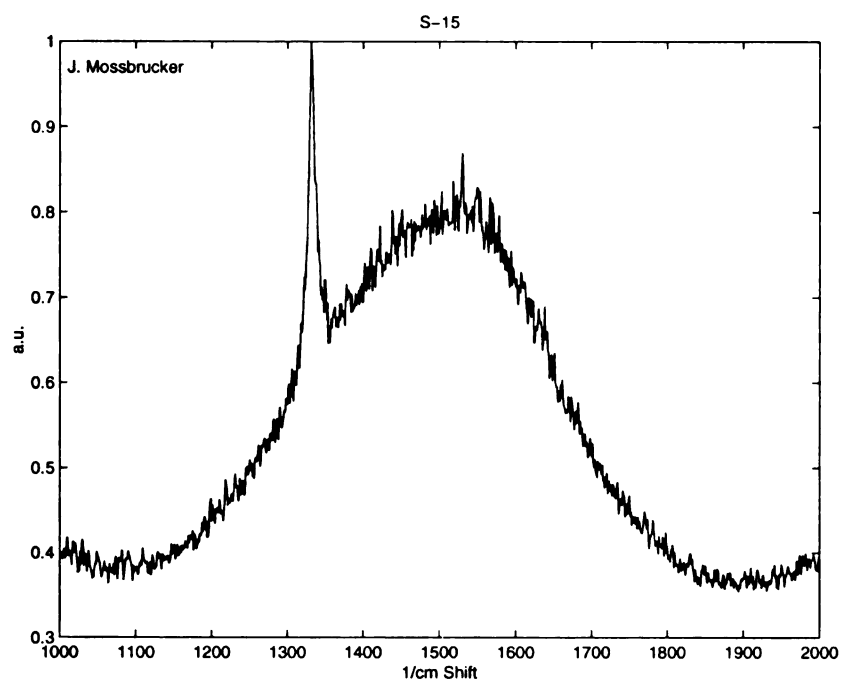


Figure 5.3 The Raman B spectrum recorded from substrate S15.

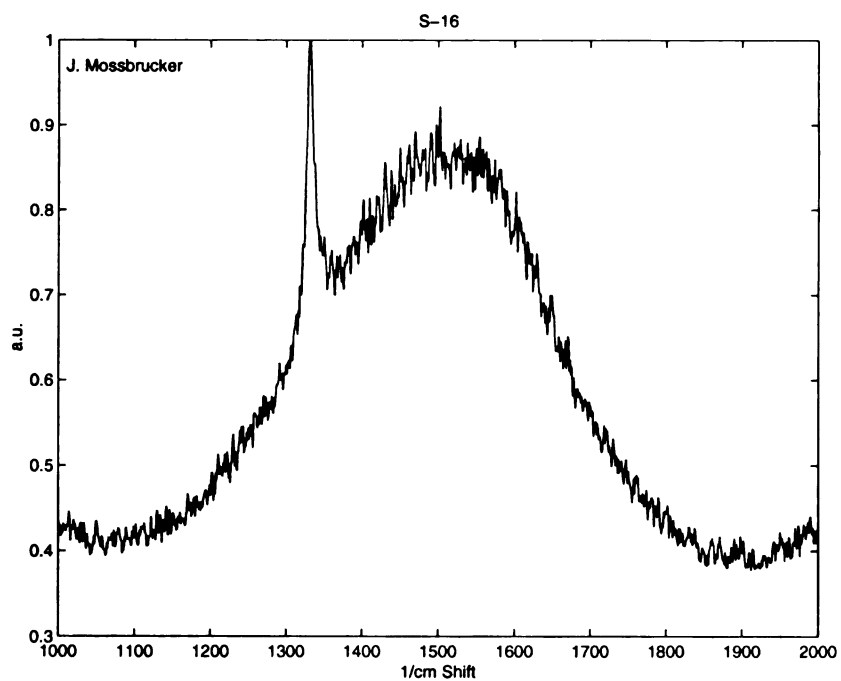


Figure 5.4 The Raman B spectrum recorded from substrate S16.

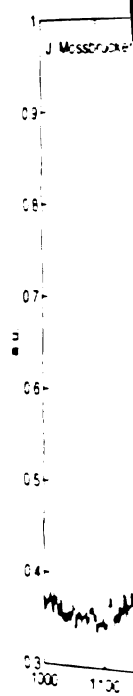


Figure 5.5

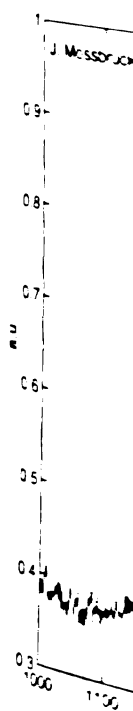


Figure 5.6

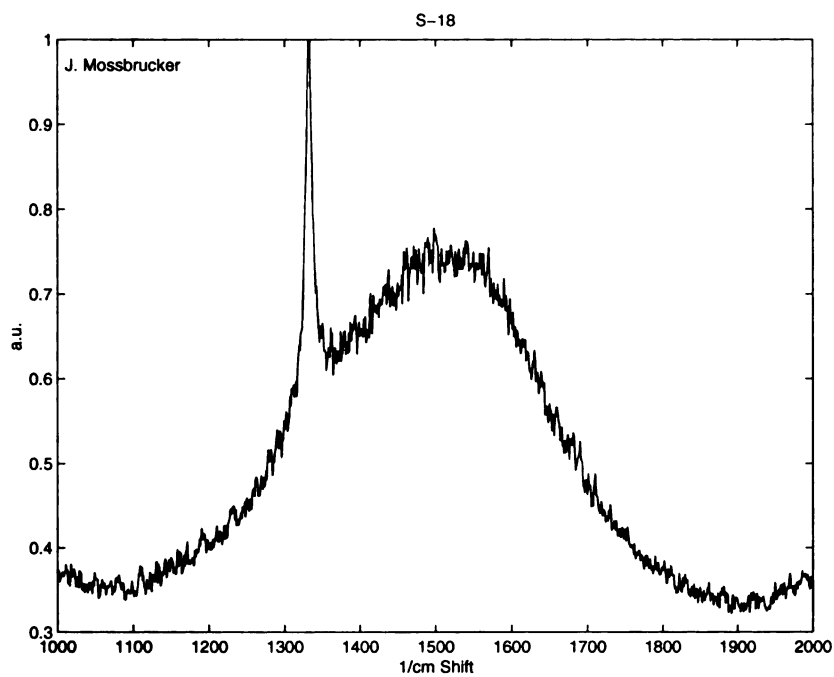


Figure 5.5 The Raman B spectrum recorded from substrate S18.

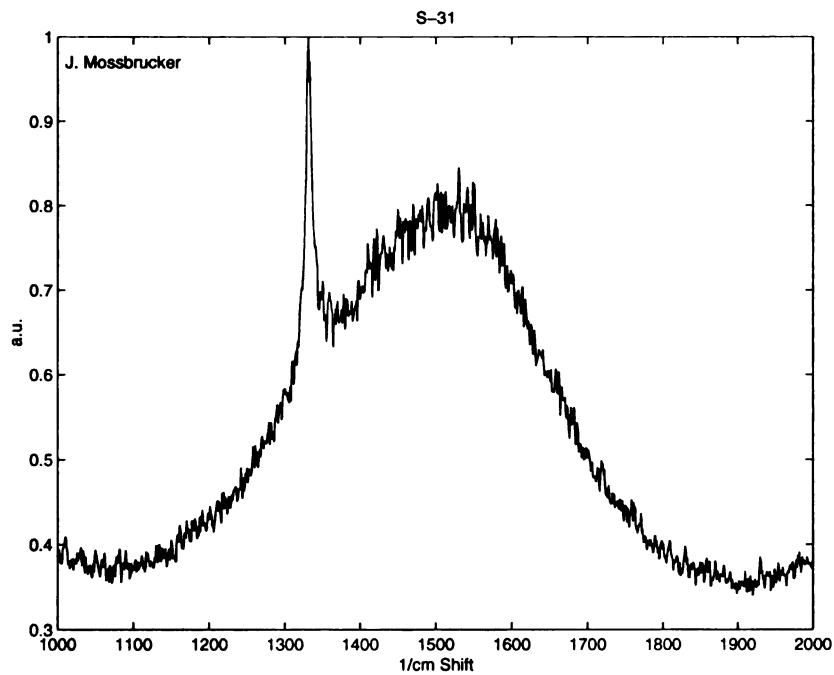


Figure 5.6 The Raman B spectrum recorded from substrate S31.

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5.2.1.2 Influence

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graphite in these films. From the data in table 5.1 it is observed that there are no distinguishing differences between the FWHM over the temperature range of 470C to 517C. Hence while the diamond deposition rate is observed to decrease with decreasing substrate temperature, the quality of the deposited diamond appears to be unchanged.

5.2.1.2 Influence of Deposition Chemistry

A second MCPR input variable that can be compared to the Harris-Goodwin growth model is the deposition chemistry. Since the model has a dependency on the flux of methyl radicals (denoted as $[CH_m]$) to the substrate's surface, any MCPR input parameters that influence $[CH_m]$ whether directly or indirectly should be investigated. One such variable is the concentration of methane, $[CH_4]$, in the discharge chamber. From the model it appears that if the substrate temperature and the methane dissociation percentage are held constant while the methane concentration is increased, there will be an proportional increase in the methyl radical concentration, $[CH_m]$, and thus a proportional increase in the deposition rate G^* . One way to increase the methane concentration is to increase the flow rate of the methane (denoted as CH_4 in equation [5.10]) while maintaining a constant flow rate of hydrogen (denoted as H_2 in equation [5.10]).

Figure 5.7 shows a graph of the measured weight gains (denoted as shapes) and the model's predicted weight gains (denoted as a solid-line) for methane flow rates ranging between 3 sccm and 10 sccm while the hydrogen flow rate, the gas pressure and the substrate's temperature were held constant at 200 sccm, 9 torr and 470 C respectfully. The graph shows that for methane flow rates below 2.5% (methane in hydrogen) the measured experimental weight gains appear to correspond well to the models predicted growth rate,

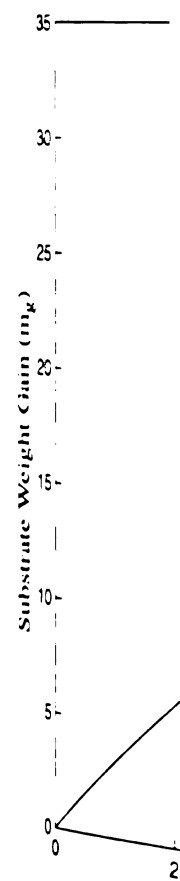


Figure 5.7

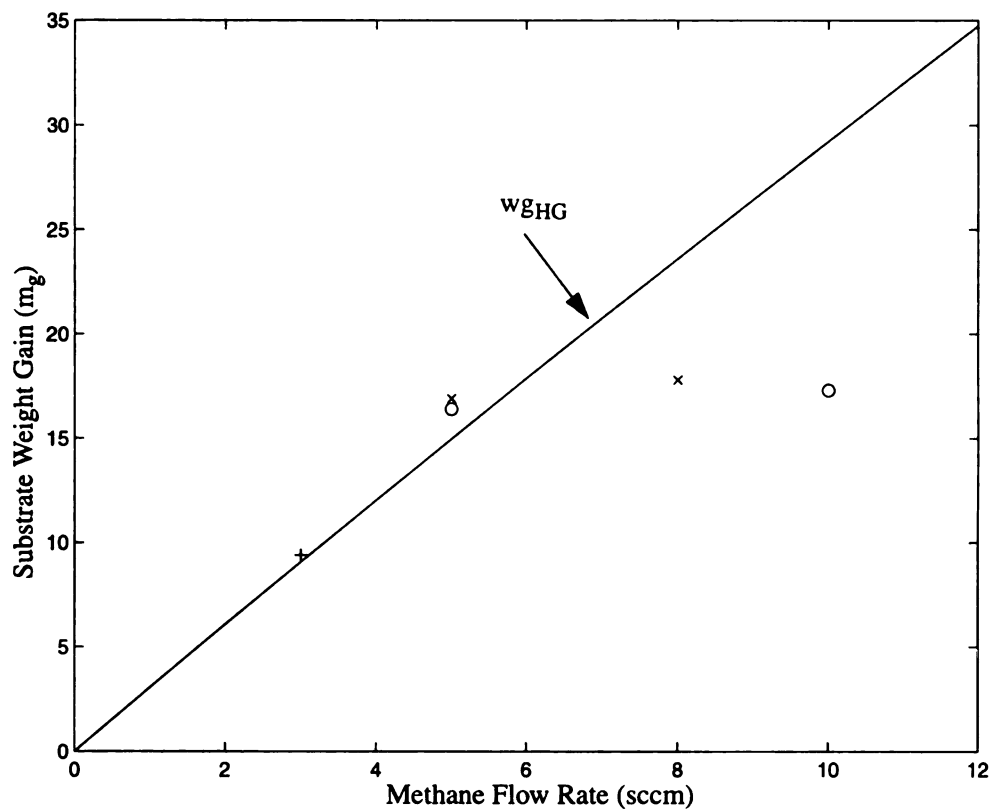


Figure 5.7 Predicted influence of the CH_4 flow rate on the deposition rate.

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A measurement of

w_{HG} . For percentages of methane higher than 2.5% however, the weight gain saturates, there is no more deposition at 5% methane than at 2.5%. This phenomenon is consistent with the results of Zhang^[36]. Figure 5.8, figure 5.9 and figure 5.10 show SEM photos of the films from figure 5.7, which were S83, S84, and S85, for methane flow rates of 5, 8, and 10 sccm respectively. The photos show that the films consist of poly-crystalline diamond; however, there appears to be more twinning in the films grown with a methane flow rates of 8 and 10 sccm than the one grown at 5 sccm.

The model's predicted weight gain, w_{HG} in mg, that is shown in figure 5.7 was determined using the equations that were outlined in section [5.2.1.1]. Again, the solid-line in the figure was adjusted to fit the experimental data by varying the percent dissociation of methane in equation [5.10], which was chosen to 0.45% for this figure.

The measured weight gains in figure 5.7 were recorded from deposition experiments where diamond films were deposited on silicon substrates with a 2-inch diameter. Deposition was conducted with MCPR-C5, the quartz tube lengths were $d_1=22\text{mm}$ and $d_2=24\text{mm}$. All the experimental films were grown under identical conditions except for slight variations that occurred during pre-treatment, i.e. seeding. The substrates were seeded with the photo-resist, diamond-powder method that was outlined in section [3.3.2.2]. Three different quantities of diamond seed (measured in mg) were used for pre-treatment of the substrates though. As will be discussed in section [5.6.1] seeding variations can have a dramatic effect on the weight gain, i.e. deposition rate; however the quantities used for the experiments shown in figure 5.7 cause only slight variations in deposition rates.

A measurement of the Raman spectrum was recorded for the diamond films on



Figure 5.1



Figure 5.1

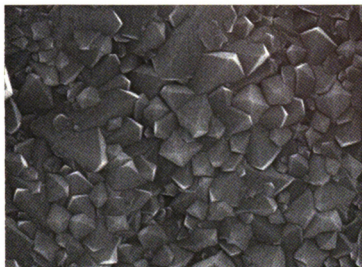
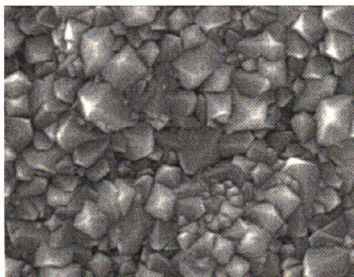


Figure 5.8 An SEM photo of S83.



— 1μ

Figure 5.9 An SEM photo of S84.

Figure 5.1

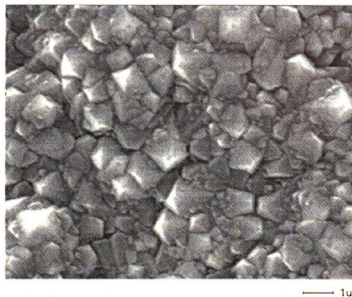


Figure 5.10 An SEM photo of S78 (200 sccm of H_2 and 10 sccm of CH_4)

substrates S78, S83 and S84. The Raman spectra are shown in figure 5.11 through figure 5.13, and the corresponding, calculated FWHMs, which were determined from the Raman data, are listed in table 5.2. All three of the Raman spectrum in the figures have a distinct peak at 1335, which indicates that the films contain diamond. De-convolution of the spectra showed that there is a very low amount of amorphous carbon and graphite in these films. From the data in table 5.2 it is observed that there are no distinguishing differences between the FWHM. It has been stated that the SEM photos, which were taken of the films on S78, S83 and S84, indicate that the film's morphology changes with increasing quantities of methane gas flow. The quality of the deposited diamond however, appears to be unchanged with increasing methane flows.

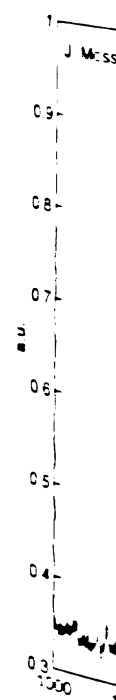
5.2.1.3 Influence of Deposition Gas Pressure

A second way to increase the methane concentration, CH_4 , is to increase the gas pressure, P in equation [5.11]. Again if the substrate temperature and the methane percent dissociation remain the same, the model predicts there will be an increase in the diamond deposition rate, G^* .

Figure 5.14 shows a graph of measured weight gains from several experiments (including those in figure 5.1) where the gas pressure and temperature were varied (denoted as shapes). The shapes in the figure indicate weight gains from diamond films that were deposited with one of four conditions. Data points from films grown at 7 torr with MCPR-C3 are denoted as circles (the same as those in figure 5.1). Those from films grown at 9 torr and 15 torr with MCPR-C5 are represented by x's and boxes respectively. There is one additional data point at 15 torr from MCPR-C6, which is represented by the

Substrate
S78
S83
S84

Ta



Figure

Substrate	MCPR-Cn	Seeding	Chemistry H ₂ -CO ₂ -CH ₄ (sccm)	wg (mg)	T (°C)	FWHM
S78	5	PR (8x)	200-0-10	17.3	473	9.9
S83	5	PR (16x)	200-0-5	16.9	471	9.2
S84	5	PR (16x)	200-0-8	17.8	470	8.7

Table 5.2: Measurements of the Raman B Spectra FWHM.

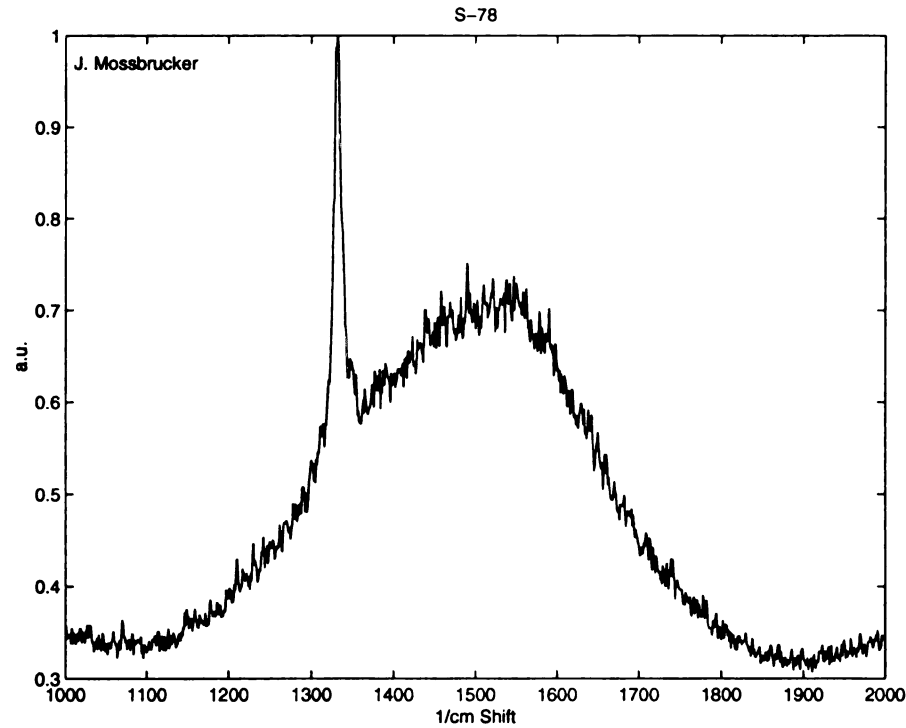


Figure 5.11 The Raman B spectrum recorded from substrate S78.

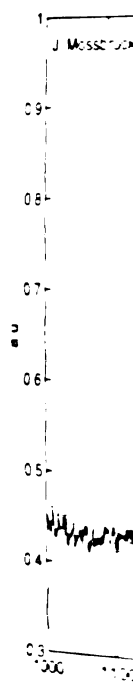
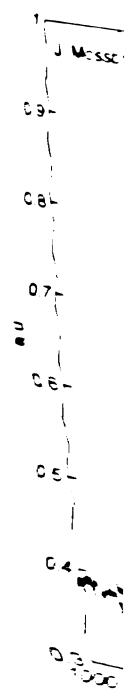


Figure 5



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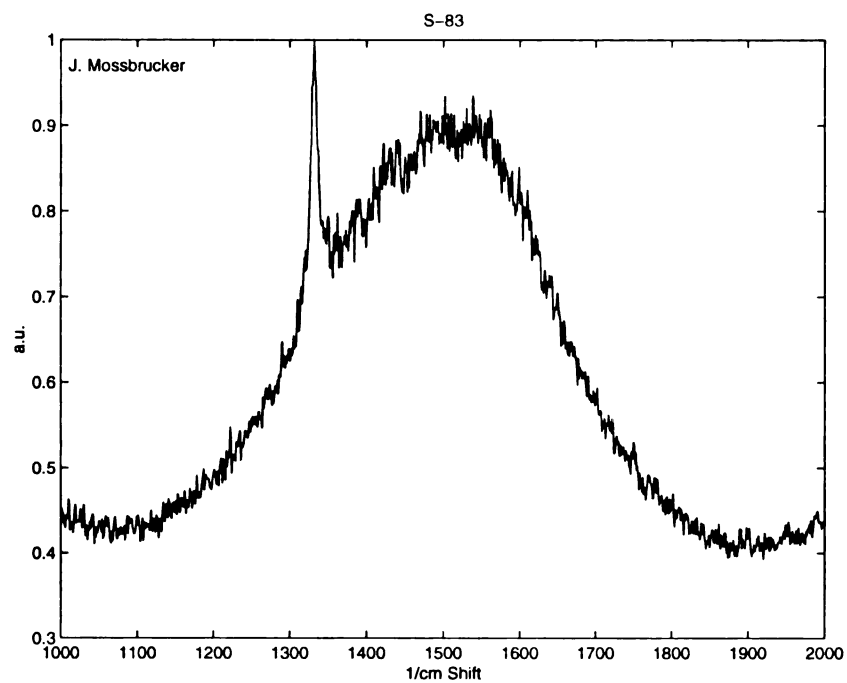


Figure 5.12 The Raman B spectrum recorded from substrate S83.

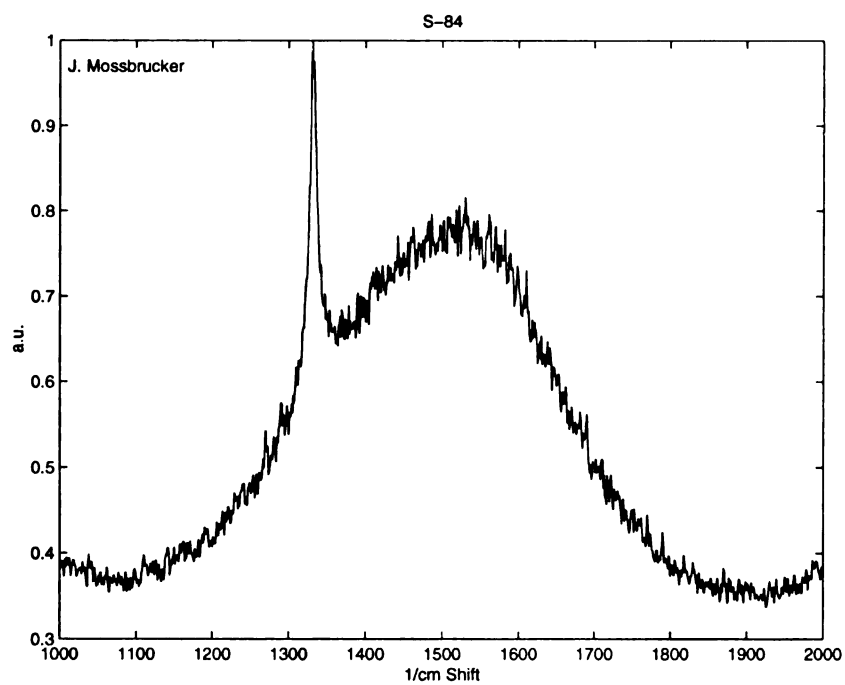


Figure 5.13 The Raman B spectrum recorded from substrate S84.

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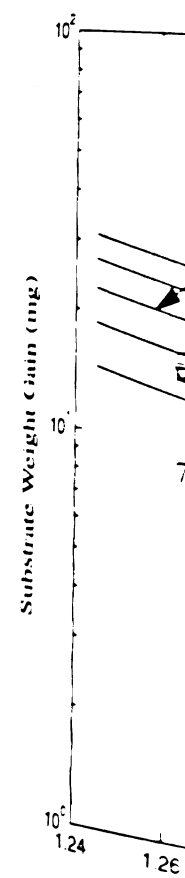
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inverted triangle. Also shown in figure 5.14 are solid-lines, which denote the model's predicted growth rate for pressures ranging from 7 torr to 15 torr. The solid-lines were calculated using the equations from section [5.2.1.1]. For the calculation of each solid-line, the model's variables were the same except for the pressure, P , in equation [5.11]. The methane dissociation rate was chosen to be 0.45% in each case.

From figure 5.14 one can see that with these assumptions, the experimental results do not correlate to the model's predicted growth rates. All of the experimental data points lie around the model's 7 torr line. From this, it appears that either the methane dissociation percentage, i.e. dissociation rate, in the experiments is decreasing with increasing pressure, or the flux of species to the substrate is decreasing with increasing pressure. A possible cause for a reduction of the dissociation rate of methane with increasing pressure is lower electron temperatures, T_e . Since the rate constants for dissociation processes, K_{diss} , of diatomic and polyatomic gases are a function of T_e , changes that affect T_e also influence K_{diss} . If increasing the gas pressure in the MPCR results in lower T_e , one would expect a decrease in K_{diss} . There is some evidence to suggest that this may in fact be happening. Data from Raizer shows that T_e in a hydrogen plasma decreases with increasing gas pressure^[75]. With regards to the flux of neutral species to the surface of the substrate, e.g. $[H]$ and $[CH_m]$, increasing the pressure was observed to reduce the dimensions of the plasma. This may cause the plasma to retract away from the substrate, which would affect the diffusion of neutral species. Additionally, increasing the pressure inherently reduces the mean free path of the neural species, and their diffusion length.



Figure

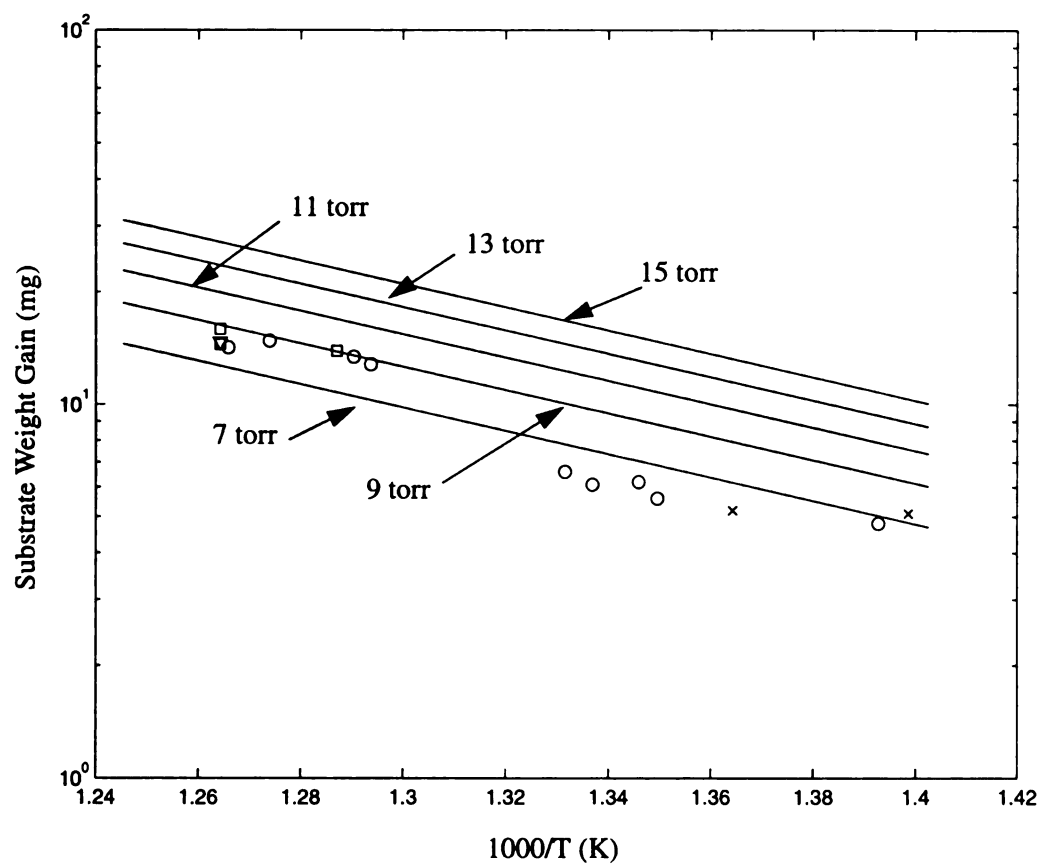


Figure 5.14 Predicted influence of the gas pressure on the deposition rate.

5.2.2 Comparison

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5.2.2 Comparison to the Bachmann C-H-O Gas Phase Diagram

The Bachmann C-H-O gas phase diagram, which was outlined in section [2.3.1], provides trends for diamond CVD. The model qualitatively describes how the diamond growth rate and film quality are affected by various mixtures of gases containing carbon, hydrogen and oxygen. Specifically, there is a region in the diagram surrounding the CO-line where diamond-growth exists (refer to figure 2.19). The diamond-growth region is bordered on the oxygen rich side by a no-growth region, and on the carbon rich side by a non-diamond-growth region. As process gas compositions vary from the non-diamond region towards the no-growth region, the growth rate diminishes from a maximum value to zero. At the same time however, the diamond quality of the deposited material generally improves. Substrate temperatures were also noted to have an affect on the diamond growth region. As the temperature increases, the width of the diamond growth region diminishes until at around 1300 C it disappears.

Experimental data is presented in the following sections for deposition with varying gas composition percentages, which containing mixtures of methane and carbon dioxide in hydrogen. The resulting growth rates (measured in weight gain) and film quality (measured by Raman) are compared to the predictions of the Bachmann model. Three types of experiments are presented, (1) variable CH₄ flow rates with constant flow rates of H₂ and CO₂, (2) variable CO₂ flow rates with constant flow rates of H₂ and CH₄, and (3) deposition experiments with mixtures of CH₄ and CO₂ only.

5.2.2.1 Variations

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5.2.2.1 Variations in the Flow of Methane

Figure 5.15 shows a graph of measured deposition rates (in mg) for deposition experiments where the CH_4 flow rate was varied between 3 and 8 sccm while the flow of H_2 and CO_2 were maintained at constant flows of 200 sccm and 8 sccm respectively. These experiments were conducted using MCP-CC5 with $d_1=22\text{-mm}$ and $d_2=24\text{-mm}$. The pressure was 9 torr, the incident microwave power was 1 KW, the substrate temperature was approximately 470 C, and the duration of the experiments was 25 hours.

The data in figure 5.15 correlates with the Bachmann model. Increasing the flow of CH_4 from 3 sccm to 8 sccm while maintaining constant flow of H_2 and CO_2 changes $X_{C,\Sigma}$ from 0.41 to 0.50. The model predicts that such a transition from an area near the no-growth region towards the CO-line should result in an increase in the deposition rate as is indicated qualitatively in figure 5.15.

It was noted in section [5.2.1.2] that there was a distinct increase in the measured weight gains of comparable deposition experiments when the CH_4 flow rate was increased. This phenomenon was reported to hold true for CH_4 flow rates that were equal to or less than 2.5% of the flow rate of H_2 . For higher mixtures, the measured weight gains were nearly identical, indicating that the deposition rate saturated at methane concentrations greater than 2.5% in H_2 . It is interesting to note that contrary to the observations from figure 5.7, there does not appear to be a weight gain saturation with increasing flow rates of CH_4 when CO_2 is used. In figure 5.15, the CH_4 flow rates range from 1.5% to 4% of the flow of H_2 , and a weight gain saturation is not observed. The recorded weight gains in figure 5.15 are considerably less than those in figure 5.7.

In addition to the reported trend of increasing deposition rates, Bachmann also

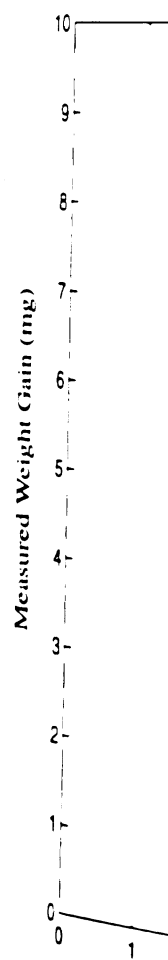


Figure 5.1.

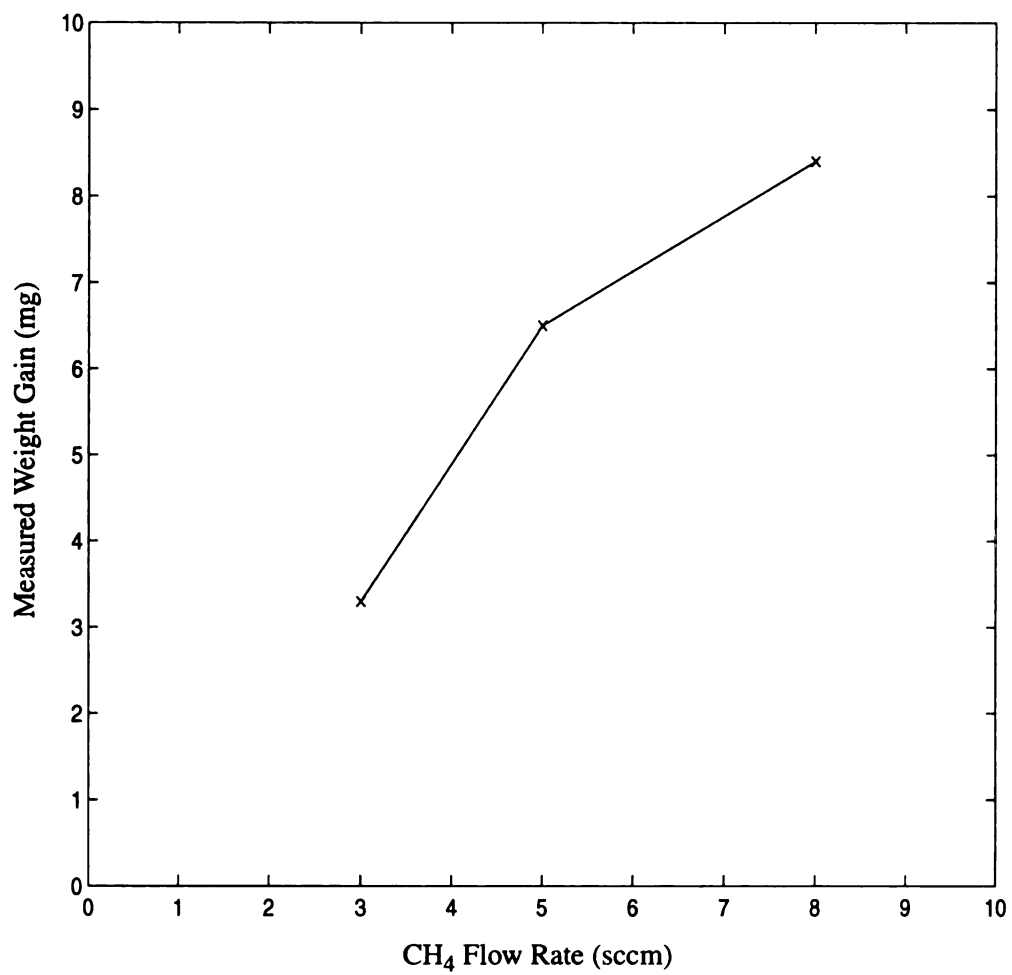


Figure 5.15 Measured weight gain for gas compositions of CH₄ in CO₂ and H₂.

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noted that the diamond quality was reported to decrease when the percent of carbon in oxygen, $X_{C:\Sigma}$, is increased. The FWHM, which was calculated from the Raman spectra of the diamond films that are shown in figure 5.15, is listed in table 5.3, and the corresponding Raman spectra are shown in figure 5.16 through figure 5.18. It is observed from the data in table 5.3 that there is no apparent change in the FWHM with an increase in the flow of CH_4 . This is an indication that in the range of mixtures shown in figure 5.15, which were all on the oxygen rich side of the CO line, the diamond film quality does not decrease with an increasing percentage of carbon in oxygen, $X_{C:\Sigma}$.

5.2.2.2 Variations in the Flow of Carbon Dioxide

Figure 5.19 shows a graph of measured deposition rates (in mg) for deposition experiments where the CO_2 was varied between 0 and 16 sccm while the flow of H_2 and CH_4 were maintained at constant flows of 200 sccm and 3 sccm respectively. These experiments were conducted using MCPR-CC5 with $d_1=22$ -mm and $d_2=24$ -mm. The pressure was 9 torr, the incident microwave power was 1 KW, the substrate temperature was approximately 470 C, and the duration of the experiments was 40 hours. The data in figure 5.19 correlates with the Bachmann model in that increasing the flow of CO_2 from 0 sccm to 16 sccm while maintaining constant flow of H_2 and CH_4 changes $X_{C:\Sigma}$ from 1.0 to 0.37. The model predicts that such a transition from C-H axis, across the CO-line and towards the no-growth region should result in a diminishing deposition rate as is indicated in qualitatively figure 5.19.

Substrate
S89
S92
S100

T



Figure 5.16

Substrate	MCPR-Cn	Seeding	Chemistry $\text{H}_2\text{-CO}_2\text{-CH}_4$ (sccm)	wg (mg)	T (°C)	FWHM
S89	5	scratch	200-8-3	5.8	476	10.2
S92	5	scratch	200-8-5	6.5	470	9.4
S100	5	scratch	200-8-8	8.4	457	9.5

Table 5.3: Measurements of the Raman B Spectra FWHM.

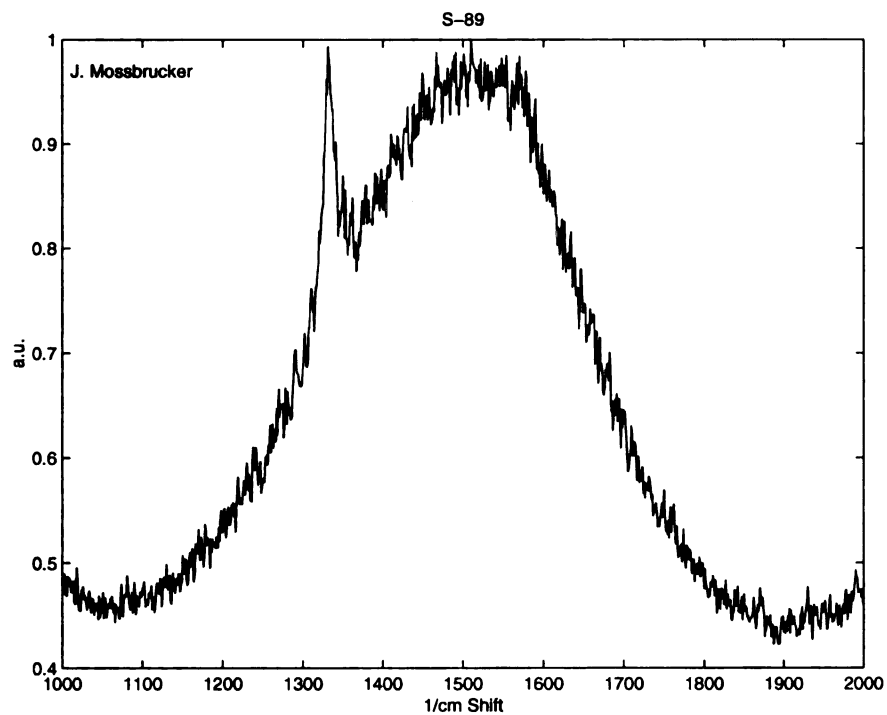


Figure 5.16 Raman B spectrum recorded from substrate S89.

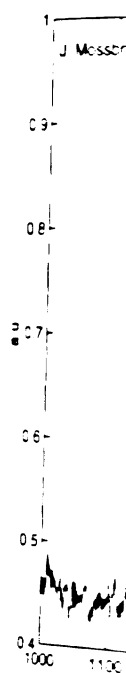


Figure 5.1

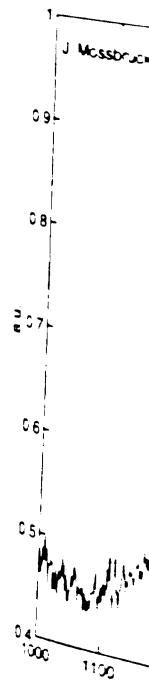


Figure 5.18

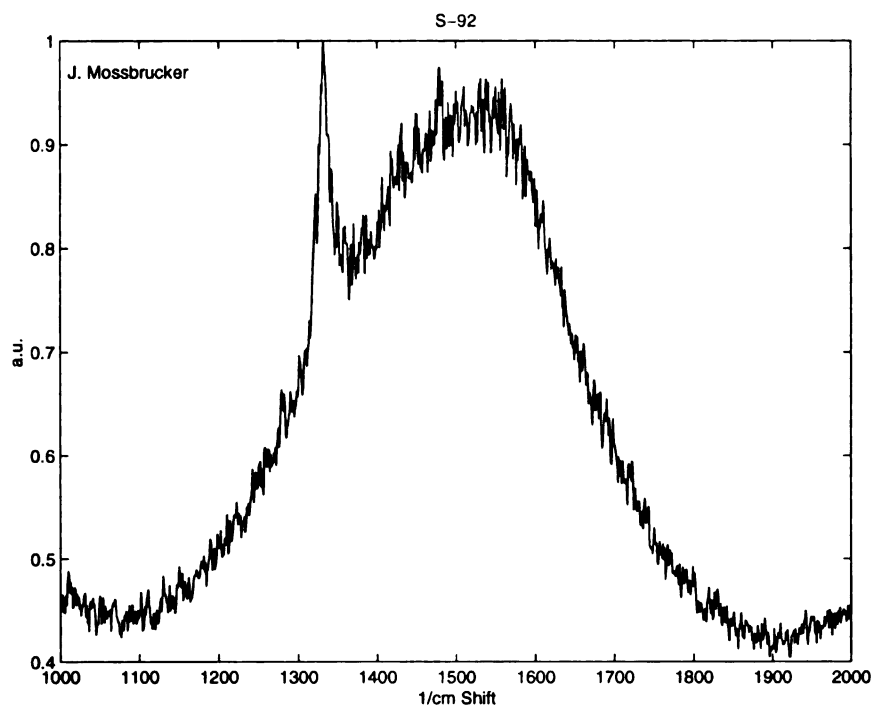


Figure 5.17 Raman B spectrum recorded from substrate S92.

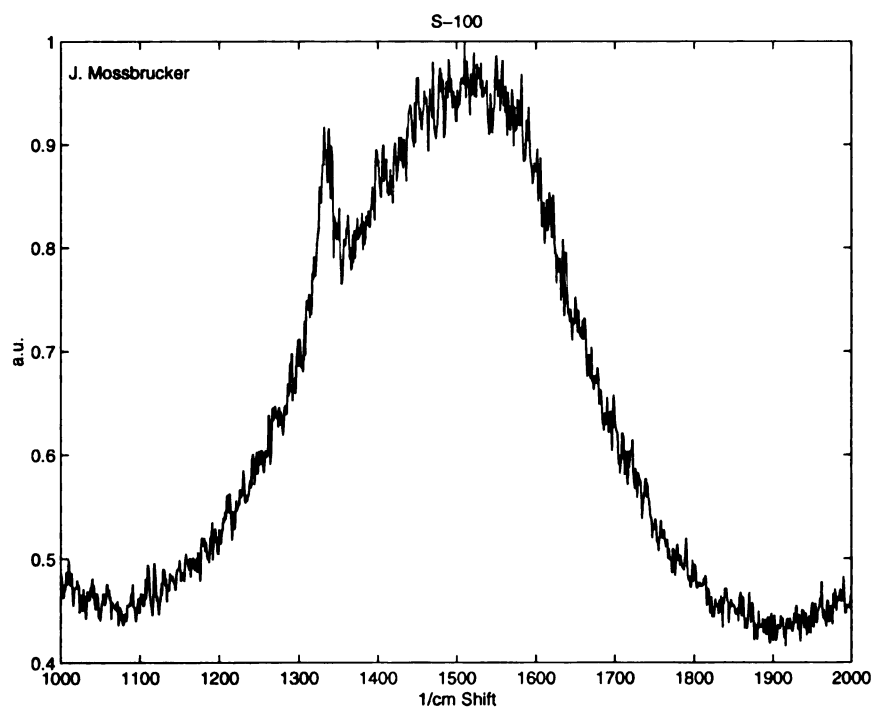


Figure 5.18 Raman B spectrum recorded from substrate S100.

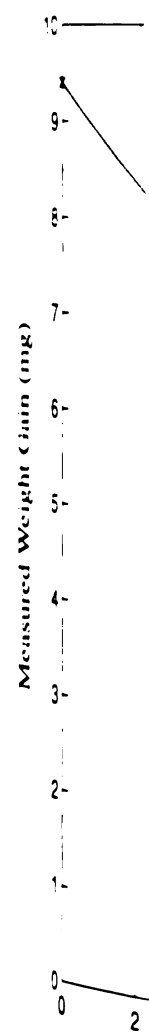


Figure 5.

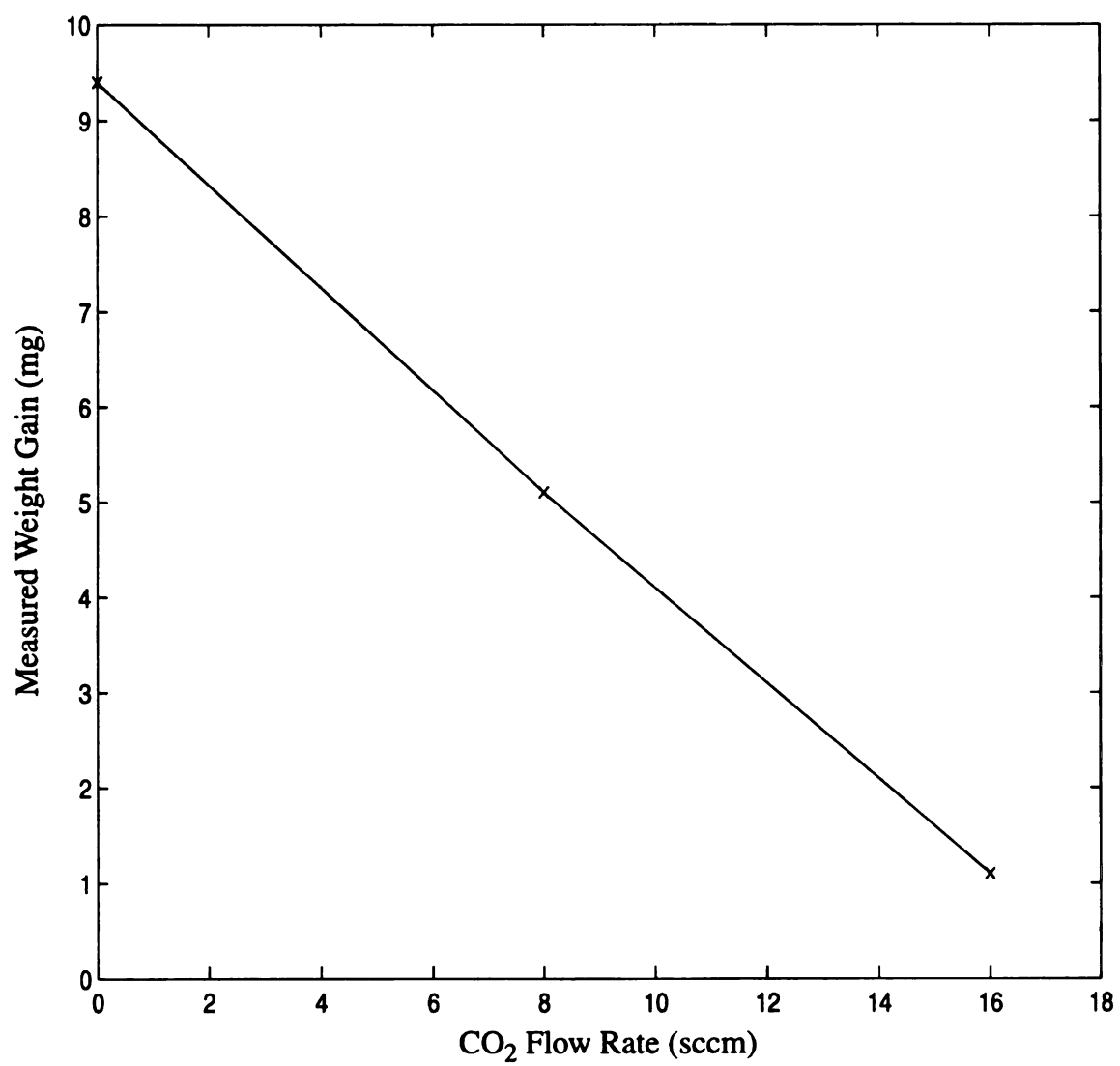


Figure 5.19 Measured weight gain for gas compositions of CO₂ in CH₄ and H₂.

In addition to the model predicts that diamond containing hydrogen, carbon, use of specific gases such as certain hydrogen and carbon all refer to section [2.3.1], could be deposited from C flow rate to the CH_4 flow rate

Figure 5.20. figure Raman data for S122, S60 CH_4 and CO_2 were used. T C5. The quartz tube dimension the input microwave power for the first experiment, S-ratio of 1:1. As can be seen deposited under these conditions were 30 sccm and 60 sccm Mornelli ratio of 2:1. From be deposited without the use indicate that the quality, as grown with hydrogen. Further possible to those of experim

5.2.2.3 Diamond Deposition with mixtures of CH_4 - CO_2

In addition to the trends of diamond growth rate and film quality the Bachmann model predicts that diamond deposition can be achieved with any mixture of gases containing hydrogen, carbon, and optionally oxygen -- diamond can be deposited without the use of specific gases such as molecular hydrogen and methane as long as the process gases contain hydrogen and carbon. This concept was confirmed in publications by Morinelli et. al. (refer to section [2.3.1]). They reported that among many mixtures of gases, diamond could be deposited from CH_4 and CO_2 without the addition of H_2 if the ratio of the CO_2 flow rate to the CH_4 flow rate was 2:1.

Figure 5.20, figure 5.21 and figure 5.22 show SEM photos from S60 and S122 and Raman data for S122. S60 and S122 were processed in deposition experiments where only CH_4 and CO_2 were used. These two deposition experiments were conducted with MCPR-C5. The quartz tube dimensions were $d_1=22\text{-mm}$ and $d_2=24\text{-mm}$, the pressure was 9 torr, the input microwave power was 1 KW, and the duration was 40 hours. The gas flow rates for the first experiment, S-60, were 15 sccm for both CH_4 and CO_2 , which has a $\text{CO}_2\text{-CH}_4$ ratio of 1:1. As can be seen by the SEM photo in figure 5.20, no-diamond appears to be deposited under these conditions. For the second experiment, S-122, the gas flow rates were 30 sccm and 60 sccm for the CH_4 and the CO_2 respectively. This corresponds to the Morinelli ratio of 2:1. From the SEM photo in figure 5.21 it is observed that diamond can be deposited without the use of hydrogen in the MCPR; however, figure 5.22 appears to indicate that the quality, as measured by Raman, is not as good as the best films that were grown with hydrogen. Furthermore, it was observed that the growth rate of S-122 is comparable to those of experiments where H_2 was used. No real benefit was observed for this



Figure 5.20



Figure 5.21 S

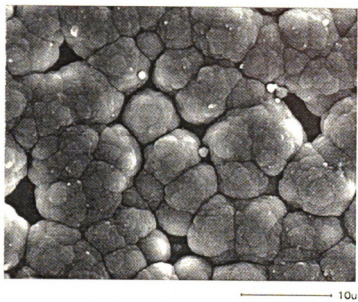


Figure 5.20 SEM photo of S-60.

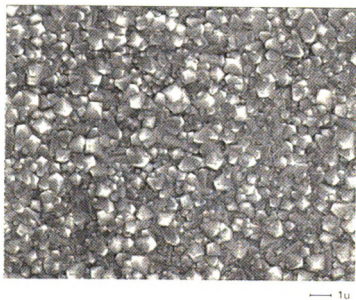


Figure 5.21 SEM photos for S-122.

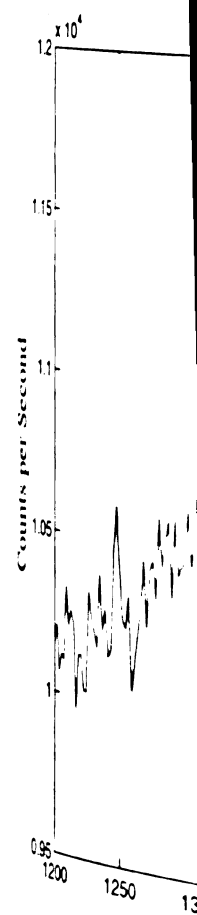


Figure 5.22 7

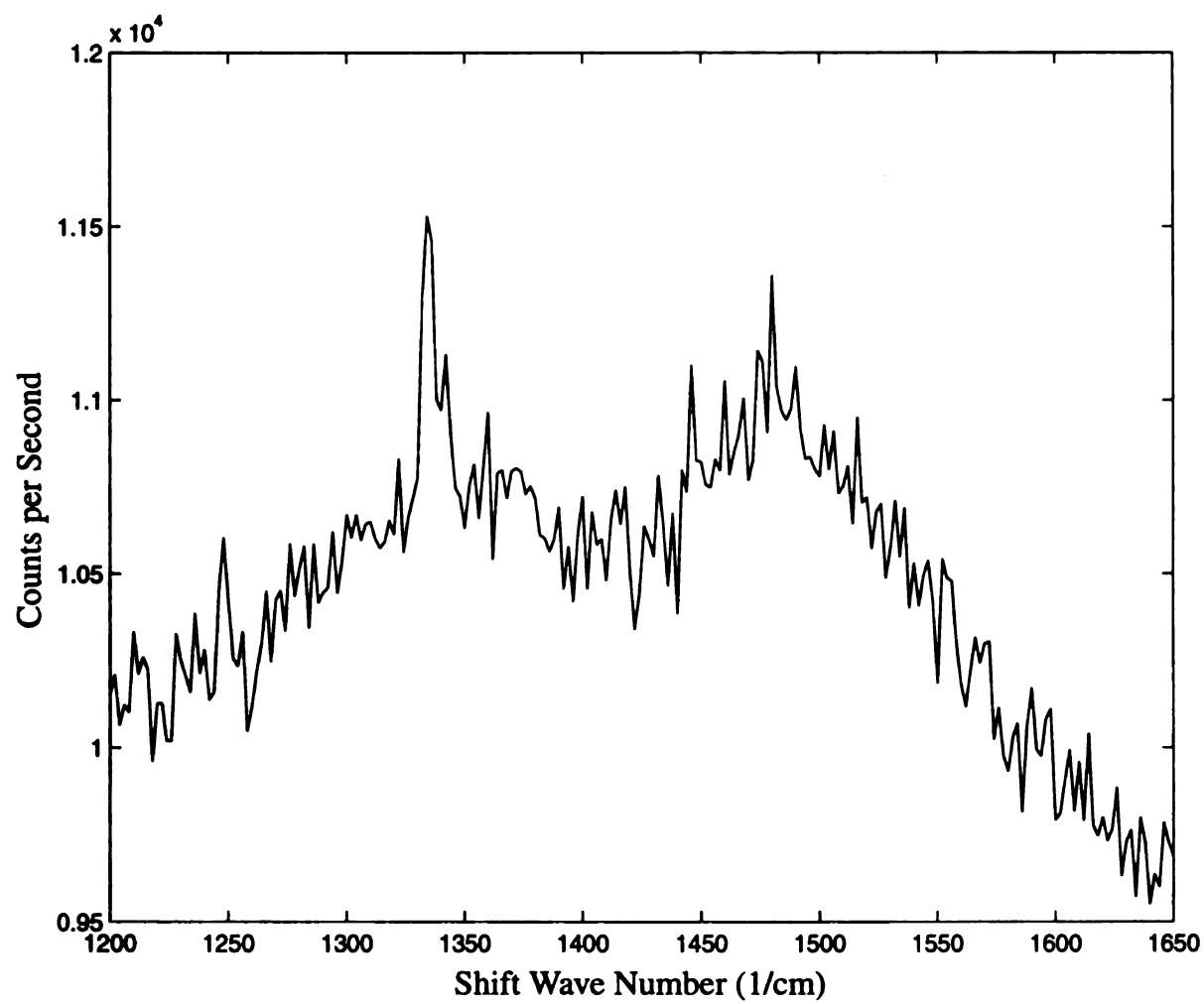


Figure 5.22 The Raman A spectrum from S-122.

gas composition other than
methane and carbon dioxide
MCPR.

5.3 An Investigation

Reports by Mantel

when a dc bias is applied

reactor (refer to section 1)

MCPR-CC6 to investigate

at low pressures in the M

five of them had a +100V

V_d bias. The gas flow rates

and CH_4 respectively, the

The measured substrate te

The results of the

ence between films that w

bias. The film that was de

deposition however. This

that were attracted to the

Figure 5.23 through

had a +100 V_{dc} bias and S

spectra for the films on S-4

observed that there is no s

gas composition other than molecular hydrogen, which is usually more expensive than methane and carbon dioxide, is not critical for diamond deposition at low pressures in the MCPR.

5.3 An Investigation of Deposition with a dc bias

Reports by Mantei et. al. indicate that the quality and deposition rate improve when a dc bias is applied to substrates that are processed in the Magneto-Active Plasma reactor (refer to section [2.2.2.2.4]). A collection of experiments was conducted with MCPR-CC6 to investigate how the application of a dc bias influences diamond deposition at low-pressures in the MCPR. A total of eight substrate bias experiments were completed, five of them had a $+100V_{dc}$ substrate bias, two of them had no bias, and one had a $-100V_{dc}$ bias. The gas flow rates for all the bias experiments were 200-8-3 sccm for H_2 , CO_2 , and CH_4 respectively, the pressure was 15 torr, and the input microwave power was 1KW. The measured substrate temperature was approximately 500 C.

The results of the substrate bias experiments were that there was no obvious difference between films that were deposited with a $+100V_{dc}$ bias and those that did not have a bias. The film that was deposited with the $-100V_{dc}$ bias peeled from the substrate during deposition however. This destruction of the film may be a result of bombardment of ions that were attracted to the substrate from the plasma by the bias.

Figure 5.23 through figure 5.28 show SEM photos for substrates S48 and S52. S48 had a $+100V_{dc}$ bias and S52 had no bias. Figure 5.29 and figure 5.30 show the Raman spectra for the films on S48 and S52. From the SEM photos and the Raman spectra, it is observed that there is no significant difference in the morphology or quality of films that

Figure 3.

Figure 5.

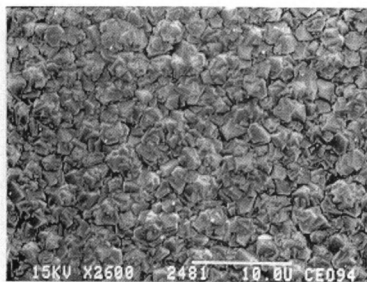


Figure 5.23 SEM photo of S48.

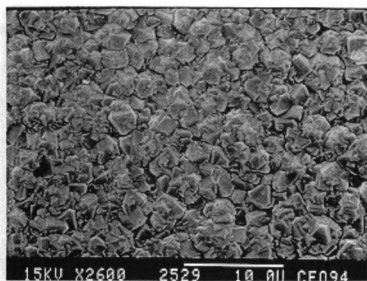


Figure 5.24 SEM photo of S52.



Figure 5.



Figure 5.

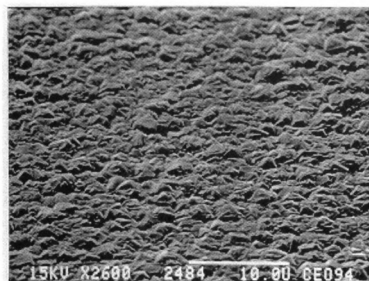


Figure 5.25 SEM photo of S48 taken at a 60° angle.

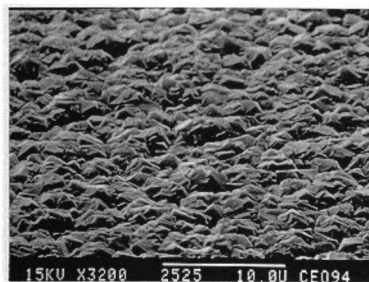


Figure 5.26 SEM photos of S52 taken at a 60° angle.



Figure 5.



Figure 5.

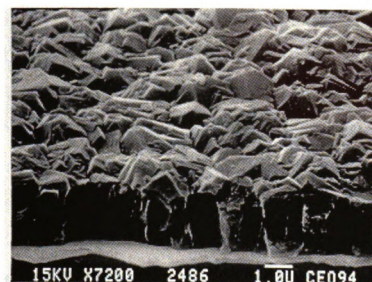


Figure 5.27 SEM Photo of S48 taken at a 60° angle.

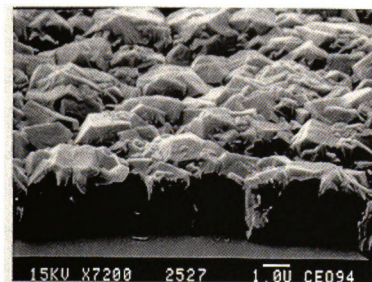


Figure 5.28 SEM Photo of S52 taken at a 60° angle.

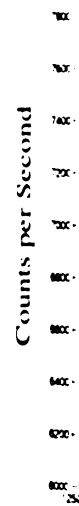


Figure 5.29

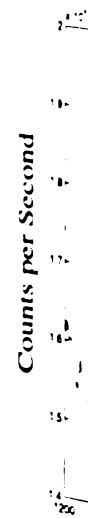


Figure 5.30

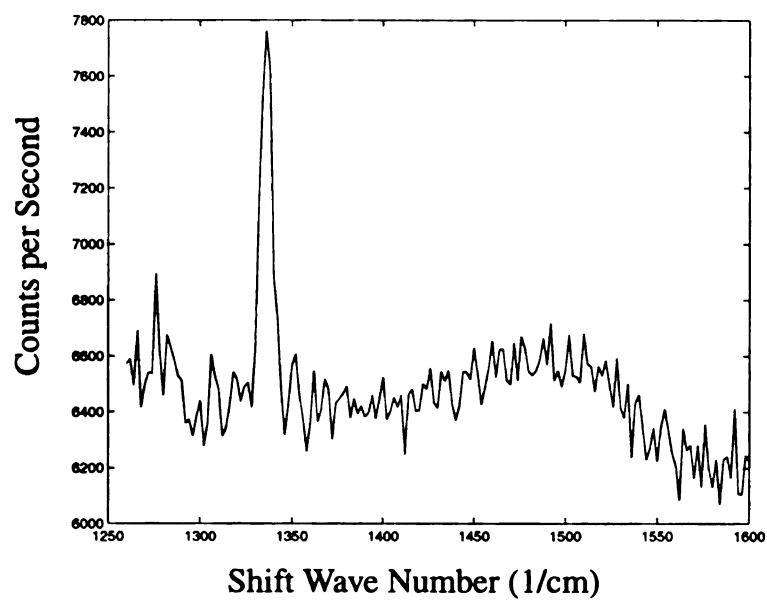


Figure 5.29 The Raman A spectrum from S48.

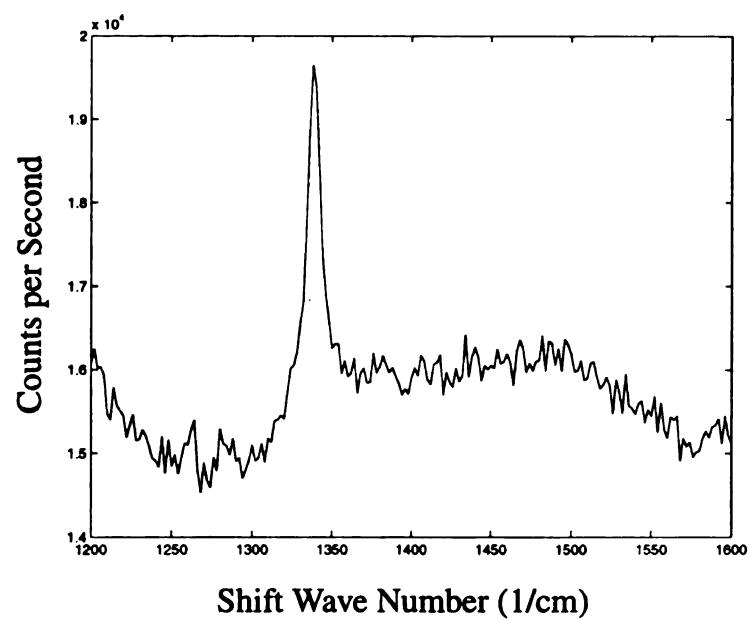


Figure 5.30 The Raman A spectrum from S52.

are deposited with and
also unaffected by the
deposited with a bias w
age weight gain was 1-4

These bias depo
ferent reactor. One poss
tion in the Magneto-Acc
substrate. Alternatively,
MCPR-C6 may have neg
may have been that the b
on the negative results of
experiments were not pu

5.4 An Investigation

In section [5.2.1.1]
gas pressures ranging fro
model. Although the mo
constant substrate temper
cess, the result was that th
concept was further inve
thermally-adjustable sub
MCPR-C9 provides cont
substrate temperature bel

are deposited with and without a bias in the MCPR. Furthermore, the deposition rate is also unaffected by the use of a substrate bias. The average weight gain for films that were deposited with a bias was 14.0 mg, for films that were deposited without a bias, the average weight gain was 14.1 mg.

These bias deposition results are in contrast to those obtained by Mantei in a different reactor. One possible explanation for the disparity is that the bias aided the deposition in the Magneto-Active plasma reactor in ways such as pulling the plasma closer to the substrate. Alternatively, the concentric anode-cathode configuration that was used in MCPR-C6 may have negated the affects of a bias. With the configuration in MCPR-C6, it may have been that the bias current was concentrated at the edges of the substrate. Based on the negative results of bias-enhanced diamond deposition with MCPR-C6, further bias experiments were not pursued.

5.4 An Investigation of Deposition with a Substrate Cooler

In section [5.2.1.3] data was presented from deposition experiments, which had gas pressures ranging from 7 torr to 15 torr, for comparison to the Harris-Goodwin growth model. Although the model predicts that increasing the gas pressure while maintaining a constant substrate temperature could increase the diamond deposition rate in a CVD process, the result was that the deposition rate appeared to be unaffected by gas pressure. This concept was further investigated at higher pressures, e.g. 15 to 25 torr with the aide of a thermally-adjustable substrate cooler, MCPR-C9. The substrate cooler assembly in MCPR-C9 provides controllable substrate cooling, which provides a means to maintain a substrate temperature below 550 C at pressures above 15 torr.

Figure 5.31 shows a graph of measured weight gains vs. substrate temperature for three experiments where MCPR-C9 was used (denoted as o's) and a comparable experiment where MCPR-C5 (denoted as an x) was used. The solid lines in the figure represent the predicted weight gains, w_{HG} , from the Harris-Goodwin model for pressures ranging from 5 torr to 30 torr. The four experimental weight gains in the figure were acquired from silicon substrates with diameters of 2-inches that were processed for 15 hours with gas flow rates of 200 sccm of H_2 and 5 sccm of CH_4 . The predicted weight gains, w_{HG} , were calculated with the equations that were presented in section [5.2.1.1]. For comparison, the methane dissociation rate was again chosen to be 0.45%. Similar to the results of section [5.2.1.3], the experimental results do not appear to coincide with the predictions of the model. At pressures up to 25 torr, deposition appears to be independent of pressure, and highly dependent on the substrate's temperature. Also, they are somewhat less than those obtained at lower pressures with a non-cooled substrate.

For the silicon substrates that were processed in MCPR-C9 the gas pressure was 25 torr, and the temperature of the liquid coolant was 45 C. The substrate temperature, which varied from 492 C to 550 C, was adjusted by placing inserts of various materials between the substrate and the BN substrate holder. MCPR-C9 spacer configurations 8.1, 8.2, and 8.3 (which contain inserts made of Corning 7059 glass, graphite, and silicon) were used (refer to table 4.3). For the benchmark substrate that was processed with MCPR-C5, the gas pressure was 9 torr, and the quartz tube length were $d_1=22\text{-mm}$ and $d_2=28\text{-mm}$.

A measurement of the Raman spectrum was recorded for the diamond films on substrates S112, S113 and S114 whose weight gains were shown in figure 5.31. The

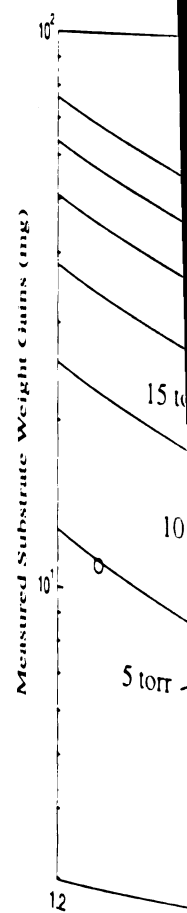


Figure 5.31

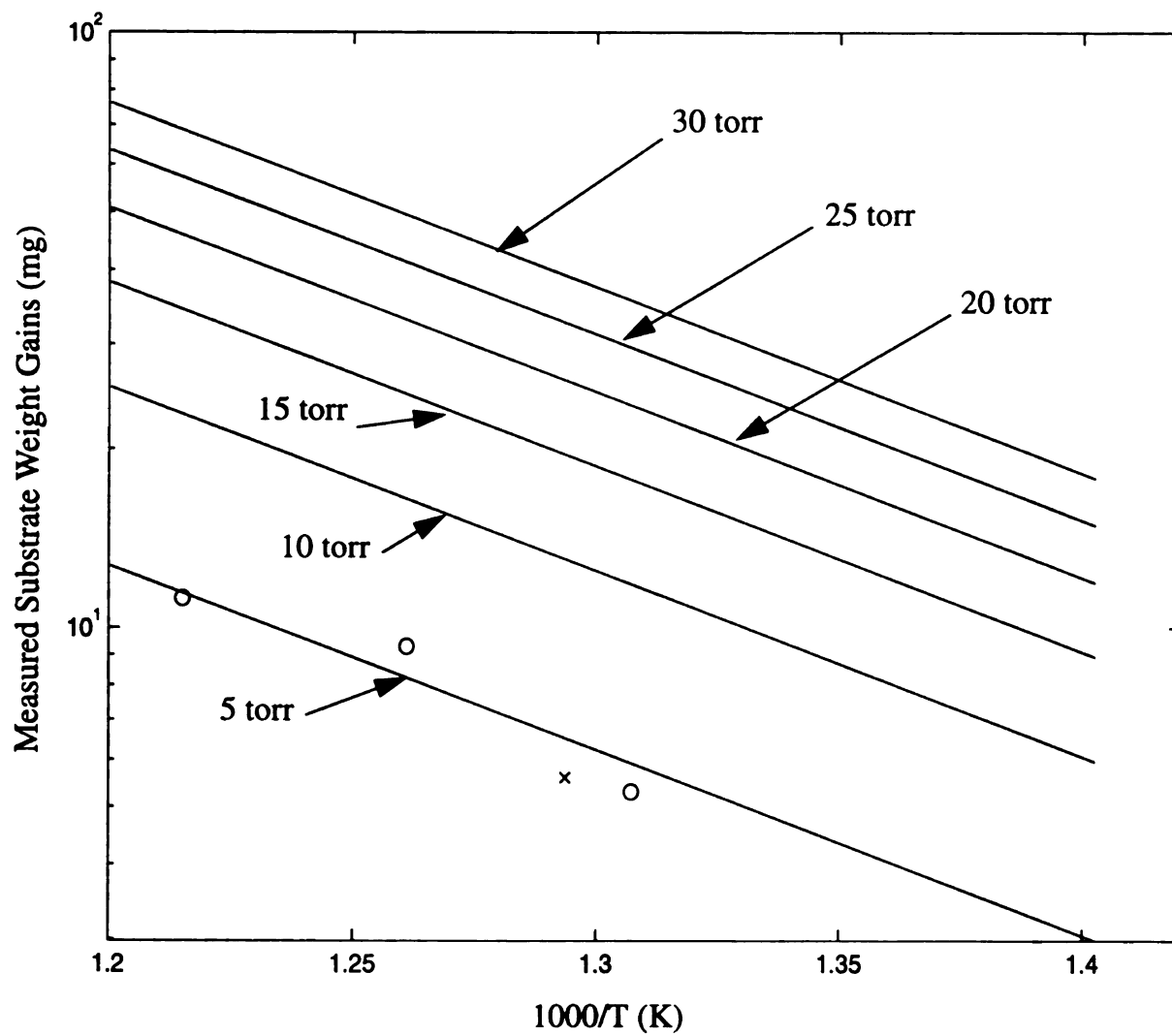


Figure 5.31 Experimental weight-gains for liquid cooled substrates.

Raman spectra are shown

lated FWHMs, which

three of the Raman spectra

that the films contain

low amount of amorphous

is observed that there are

55 An Investigation

As was discussed

power in a microwave-p

improvement in the depo

in some instances pulsed

gases, which results in a

presented for pulsed pow

d=58mm. The gas flow

and 1.5 sccm of CH_4 .

For these experim

2KW Sairem pulsing m

controlled externally by app

Packard model HP3312C

square-wave with a 2.5 V

generator was variable b

the experiments reported

Raman spectra are shown in figure 5.32 through figure 5.34, and the corresponding, calculated FWHMs, which were determined from the Raman data, are listed in table 5.4. All three of the Raman spectrum in the figures have a distinct peak at 1335, which indicates that the films contain diamond. De-convolution of the spectra showed that there is a very low amount of amorphous carbon and graphite in these films. From the data in table 5.4 it is observed that there are no distinguishing differences between the FWHM.

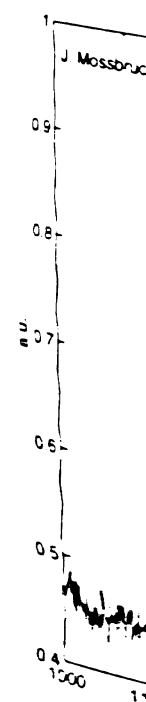
5.5 An Investigation of Deposition with Pulsed Microwave Power

As was discussed previously in section [2.4.3], there are reports that using pulsed power in a microwave-plasma, diamond CVD process sometimes leads to a substantial improvement in the deposition rate. The advantage of pulsed power over CW power is that in some instances pulsed power is reported to increase the dissociation rate of process gases, which results in an increase in the diamond deposition rate. In this section, data is presented for pulsed power experiments that were conducted with MCPR-CC7 with $d_1=58\text{mm}$. The gas flow rates for all the pulsed power experiments were 100 sccm of H_2 , and 1.5 sccm of CH_4 .

For these experiments, pulsed microwave power was generated with a 2.45 GHz, 2KW Sairem pulsing microwave power supply. The pulse rate of the Sairem was controlled externally by applying an analog square-wave signal to the Sairem with a Hewlett Packard model HP33120A wave generator. The output of the wave generator was a 5 V_{p-p} square-wave with a 2.5 V_{dc} offset and a frequency of 60 Hz. The duty cycle of the wave generator was variable between 20% and 80%. It was varied between 50% and 67% for the experiments reported here. Although the frequency and duty cycle of the Sairem were

Substrate	MO
S112	
S113	
S114	

Table



Figure

Substrate	MCPR-Cn	Seeding	Chemistry $\text{H}_2\text{-CO}_2\text{-CH}_4$ (sccm)	wg (mg)	T (°C)	FWHM
S112	9	scratch	200-0-5			9.2
S113	9	scratch	200-0-5			10.2
S114	9	scratch	200-0-5			9.8

Table 5.4: Measurements of the Raman B spectra FWHM.

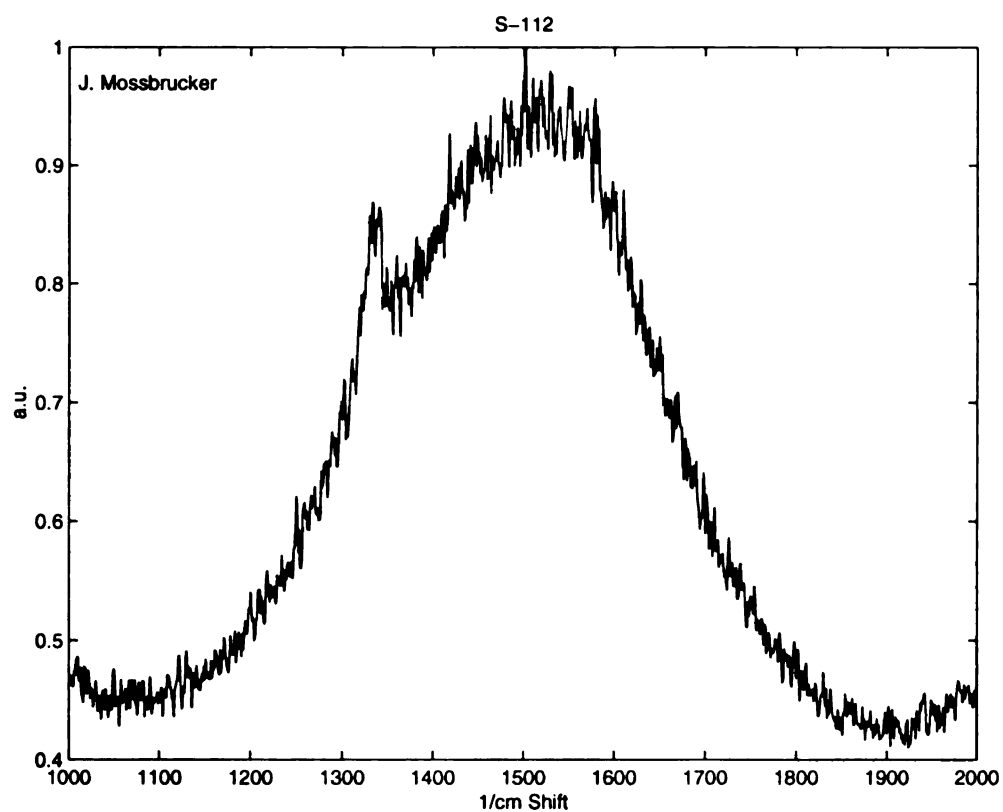


Figure 5.32 The Raman B spectrum from substrate S112.



Figure 5.3



Figure

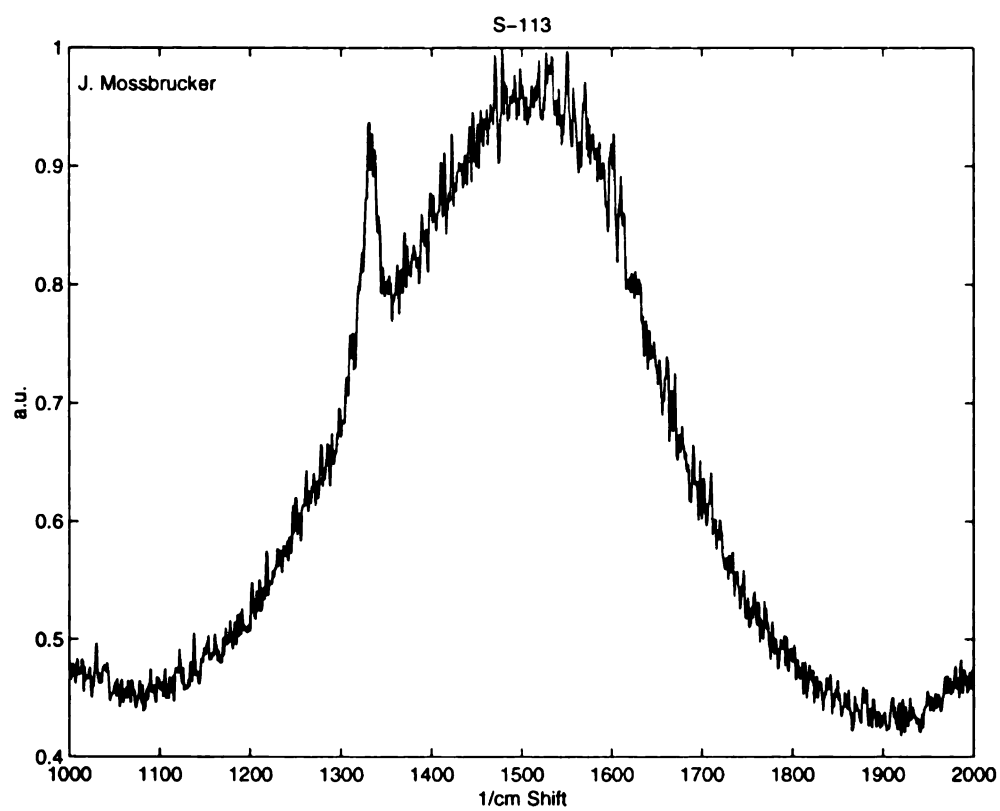


Figure 5.33 The Raman B spectrum from substrate S113.

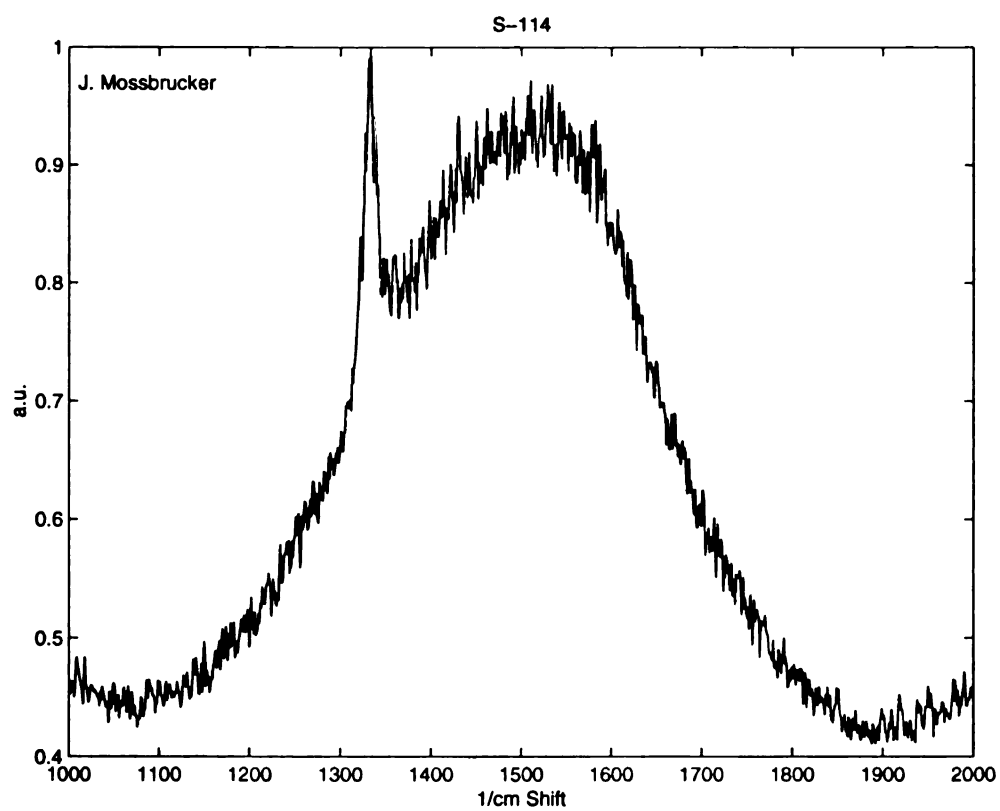


Figure 5.34 The Raman B spectrum from substrate S114.

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The microwave

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detectors were used in

scope. Typical wave

ure 5.36. Figure 5.35

with a peak of $\sim 2\text{KV}$

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5.36, the ground refe

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Sairem does not go t

Figure 5.37 s

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The x-axis in the fig

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1KW, CW depositi

controlled externally, the actual peak power output was controlled internally by the Sairem's own circuitry.

The microwave power meters, which were described in section [3.2.1.3], can only measure CW microwave power levels. Hence for the pulsed power experiments, diode detectors were used instead. The output of the diodes was recorded with an analog oscilloscope. Typical wave forms for 33% and 50% duty cycles are shown in figure 5.35 and figure 5.36. Figure 5.35 shows the incident and reflected power wave-forms for pulsed power with a peak of ~ 2KW and a duty cycle of 33%. The upper wave-form is the reflected power, the lower wave-form is the incident power. Figure 5.36 shows a similar picture of incident and reflected power wave-forms for pulsed power with a peak of ~2KW and a duty cycle of 50%. For all the wave-forms that are shown in the figure 5.35 and figure 5.36, the ground reference is the closest line above each waveform. It is observed from both photos that the wave-forms are not square-waves as is desired, and the output of the Sairem does not go fully off during the off portion of the cycle.

Figure 5.37 shows a graph of the measured substrate weight gains for experiments that were conducted at 15 torr (denoted as x's) and 20 torr (denoted as o's) using pulsed power with an average of 1KW. The peak power magnitude and duty cycle for the pulsed power experiments were 1.5 KW with a duty of 67%, and 2.0 KW with a duty of 50%. The x-axis in the figure represents the peak-power, and the y-axis is the weight gain in mg. The solid-line in the figure indicates the measured weight gain for a 20 torr, 1KW, CW deposition experiment that was conducted under the same conditions as the pulsed power experiments. Similarly, the dashed line represents the measured weight gain for a 15 torr, 1KW, CW deposition experiment. These quantities are the benchmark, CW weight gains

Figure

Figure

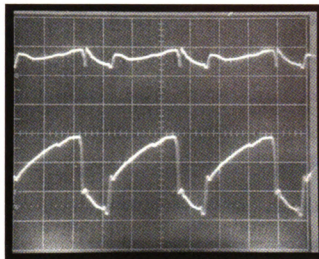


Figure 5.35 Pulsed power wave-forms for a 33% duty cycle.

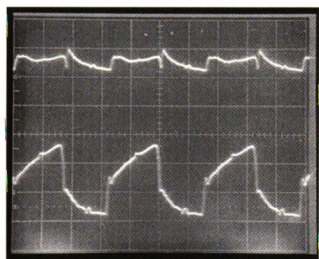


Figure 5.36 Pulsed power wave-forms for a 50% duty cycle.

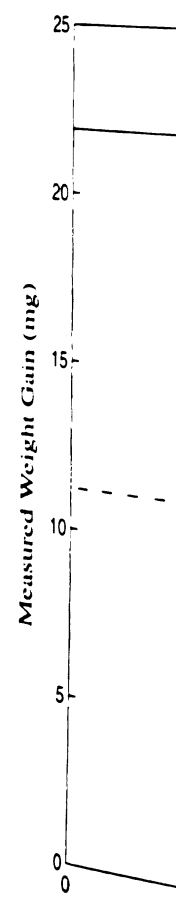


Figure 5.

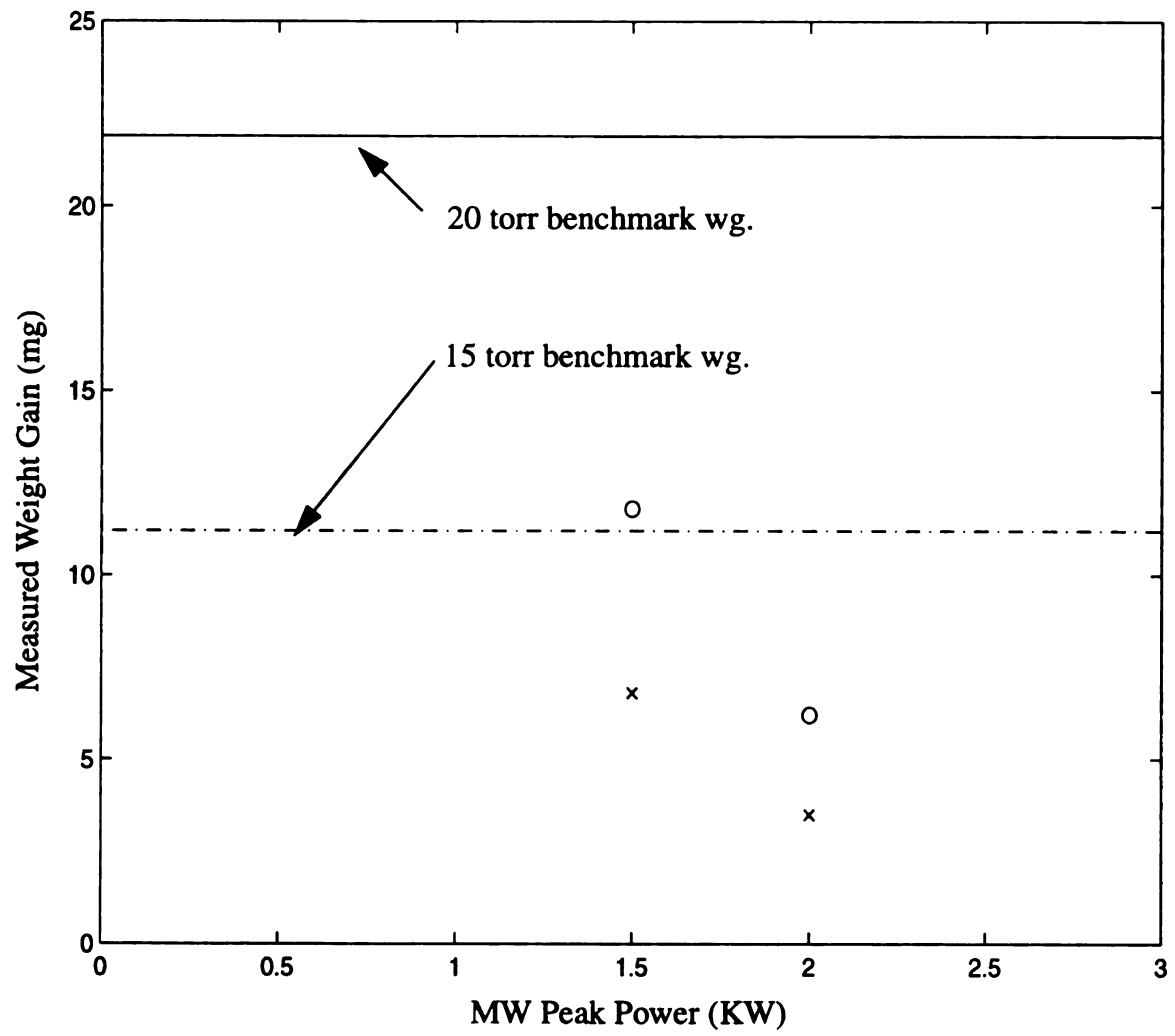


Figure 5.37 Substrate weight gains for pulsed-power experiments.

that the pulsed-power

As is indicated

seems to diminish with

contributed to the low

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Two trends to

increasing peak power

power deposition ex

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drifted away from the

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state as well as a ten

that the pulsed-power experiments must exceed to produce a higher deposition rate.

As is indicated in figure 5.37, the deposition rate with pulsed power in the MCPR seems to diminish with increasing peak power at 15 and 20 torr. One factor that could have contributed to the lower deposition rates with pulsed power is that the substrate's temperature was slightly lower during pulsed power deposition experiments than it was during the CW experiments. For example, the substrate's temperature during the 20 torr, CW experiment, CW-1, was 557 C, during the 20 torr pulsed power experiment, PP-11, which had peak microwave power of 2.0 KW and a duty cycle of 67%, the substrate's temperature was 550 C. This difference in temperature does not explain growth rate differences entirely though. The difference in weight gains for the afore mentioned experiments was 15.7 mg, which is more than 3 times the weight gain of PP-11. In section [5.2.1.1], an adaptation of the Harris-Goodwin model was presented that had a good correlation to the rate of change of the experimental growth rates with increasing substrate temperature. It is clear from the model that an increase in the substrate's temperature of less than 10 C does not triple the deposition rate. Hence, there were other factors that affected the growth rates.

Two trends that may have contributed to the decreasing deposition rate with increasing peak power were noted by visual observation of the plasma during the pulsed power deposition experiments. First, the plasma's size increased as the peak power increased, which might have lower the power density. Second, the plasma appeared to drifted away from the substrate as the peak power increased. These changing physical properties of the plasma could cause a reduction in the flux of neutral species to the substrate as well as a temperature change. In either case, the hypothesized increase in deposi-

tion rate would not

A measure

substrates PP-13 and

spectra are shown in

FWHMs, which were

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diamond. De-convol

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5.6 Additional C

Heretofore, t

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5.6.1 Variations i

It was report

nucleation density a

tion rate would not be realized in the MCPR.

A measurement of the Raman spectrum was recorded for the diamond films on substrates PP-13 and PP-15 whose weight gains were shown in figure 5.37. The Raman spectra are shown in figure 5.38 and figure 5.39, and the corresponding, calculated FWHMs, which were determined from the Raman data, are listed in table 5.5. The Raman spectra in the figures have a distinct peak at 1335, which indicates that the films contain diamond. De-convolution of the spectra showed that there is a higher amount of amorphous carbon and graphite in these films than those that were reported in earlier sections of this chapter. From the data in table 5.4 it is observed that the FWHM for the films grown with pulsed-power is also greater than those of earlier sections in this chapter.

5.6 Additional Observations

Heretofore, the data presented in this chapter has primarily pertained to deposition growth rates and film quality, which were the major emphasis of this dissertation. In addition to growth rate and film quality, observations were recorded regarding variations in seeding density with photo-resist seeding, measurements of film surface roughness, measurements of deposition area and uniformity, and diamond film deposition on silicon ICs that contain aluminum. The next four sections are devoted to discussions regarding these topics.

5.6.1 Variations in Photo-Resist Seeding

It was reported by Masood et. al. that the photo-resist seeding method could yield a nucleation density as high as 10^9 cm^{-2} [51]. This corresponds to a diamond-seed spacing of

Substrate	MC
PP-13	
PP-15	

Table 3

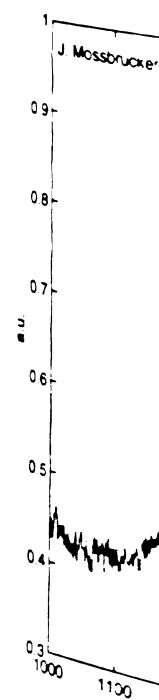


Figure 5.38

Substrate	MCPR-Cn	Seeding	Chemistry $\text{H}_2\text{-CO}_2\text{-CH}_4$ (sccm)	wg (mg)	T (°C)	FWHM
PP-13	7	scratch	100-0-1.5	6.8	496	11.1
PP-15	7	scratch	100-0-1.5			13.2

Table 5.5: Measurements of the Raman B spectra FWHM.

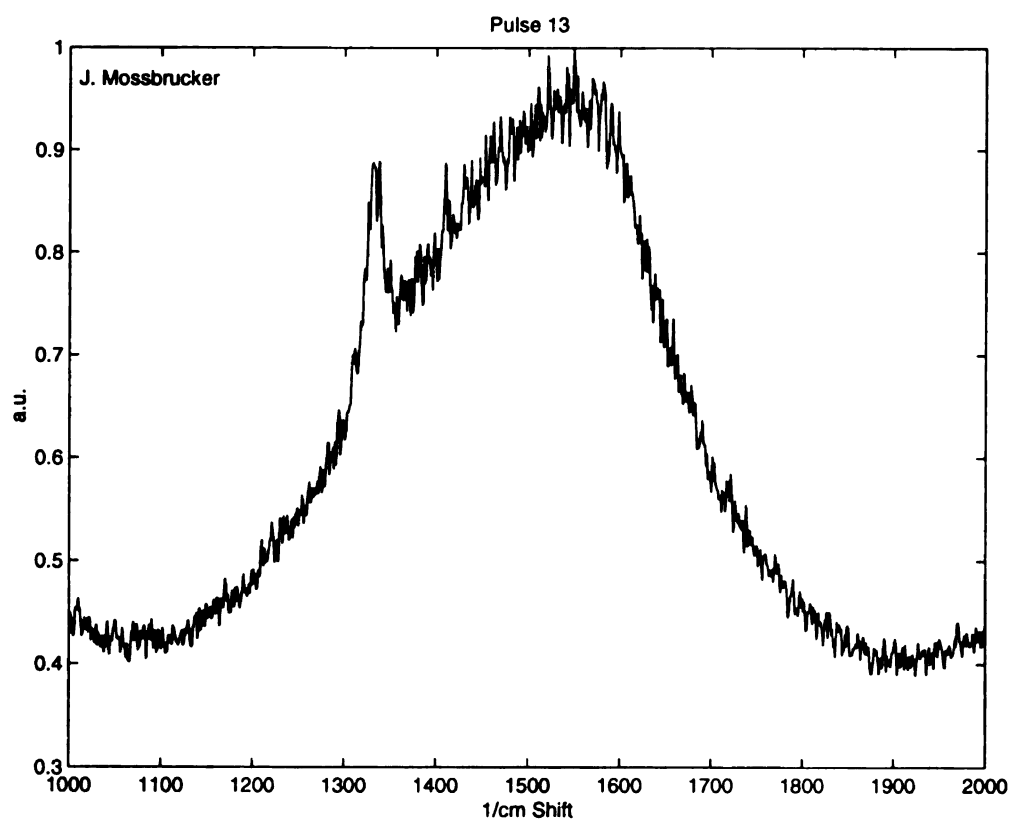


Figure 5.38 The Raman B spectrum from substrate S112.

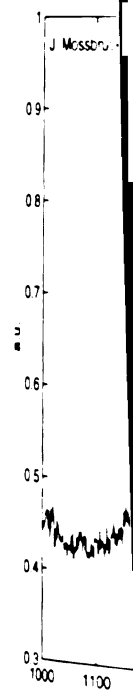


Figure 5.39

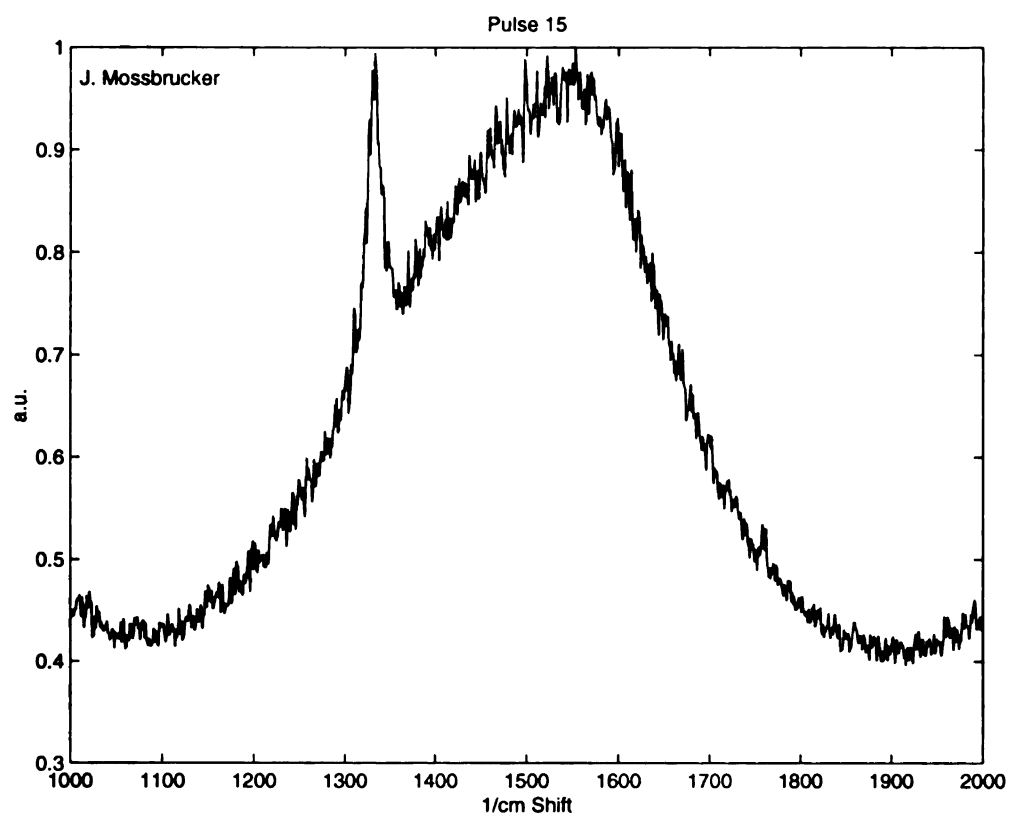


Figure 5.39 The Raman B spectrum from substrate S113.

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approximately 0.3 μm . Early deposition experiments that were conducted for this dissertation with substrates that were seeded by this method had distances between diamond seeds on the order of 1 to 10 μm , which correspond to nucleation densities of between 10^6 cm^{-2} and 10^8 cm^{-2} . This was an indication that while this method could achieve nucleation densities as high as 10^9 cm^{-2} , it was somewhat operator dependent.

Two process variables that Masood reports can affect the seeding density are the amount of diamond powder in the solution, and the spin speed. Increasing the former was reported to increase the seeding density maximum, and decreasing the latter was reported to increase the seeding density uniformity across the substrate.

A set of experiments was conducted with quantities of diamond powder that were larger than those used by Masood in an effort to find a seeding process with a nucleation density that would be high enough to form a continuous diamond film when the film's thickness was 0.5 μm or thicker. For these experiments, the quantities of photo-resist and photo-resist thinner were the same as those used by Masood, which was 42 ml of photo-resist and 16 ml of photo-resist thinner. The diamond powder quantity was increased to between 2 and 16 times that used by Masood. The size of the diamond seeds that were used for these experiments was $<0.25 \mu\text{m}$.

Early observation of the diamond films by optical microscope were that nearly continuous diamond films with a thickness of approximately 0.5 μm were grown when the quantity of diamond powder in the photo-resist solution was 3 times that of the Masood recipe. For quantities less than 3x, spaces between seeds as large as 5 μm were observed.

SEM photos of diamond films on substrates S69, S72 and S71, which were seeded with 1x, 2x and 3x the Masood recipe, are shown in figure 5.40 through figure 5.42. These

Figure

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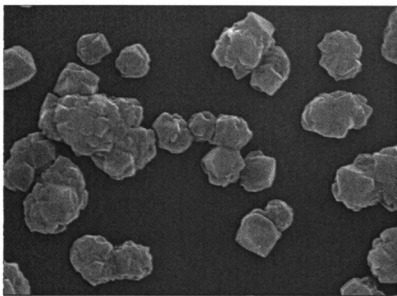


Figure 5.40 SEM photo of S69

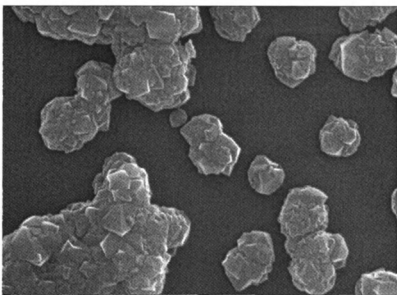


Figure 5.41 SEM photo of S72



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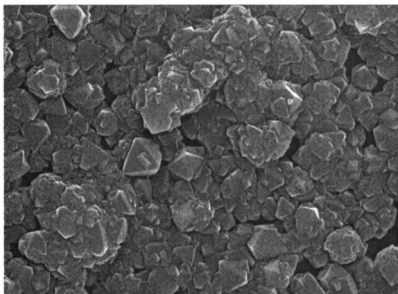


Figure 5.42 SEM photo of S71

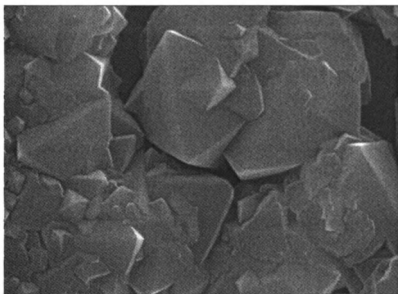


Figure 5.43 SEM photo of S73.

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three films were grown in 10 hours with MCPR-C5, at a pressure of 9 torr. The gas flow rates were 200 sccm of H_2 and 5 sccm of CH_4 , the magnitude of the incident microwave power was 1 KW, and the measured substrate temperature for the three substrates was in the range of 460 C to 470 C. Their respective weight gains were 1.2 mg, 1.8 mg and 3.2 mg, which correspond to average film thicknesses in the range of 160nm to 450nm. It is observed from the SEM photo in figure 5.40 that there are spaces as large as $3\mu m$ in the diamond film on S69. Similarly, it is observed from the SEM photo in figure 5.41 there are large regions on S72 where diamond nucleation did not take place. The film on S71, which is shown in figure 5.42, appears to be nearly continuous however. Only a few pin holes appear to be present in the film, and they are less than $0.5\mu m$ in diameter.

SEM photos for diamond films that were grown on substrates S73, S75 and S83, which were seeded with diamond powder quantities of 3x, 4x, and 16x the Masood recipe, are shown in figure 5.43 through figure 5.45. Besides having been seeded with higher quantities of diamond powder than S69 - S72, these films were grown to a much greater thickness. Their respective weight gains were 14.1 mg, 14.9 mg and 16.9 mg, which correspond to average thicknesses of between approximately $2\mu m$ and $2.4\mu m$. They were each grown for 40 hours with MCPR-C5 at a pressure of 9 torr. The gas flow rates were 200 sccm of H_2 and 5 sccm of CH_4 , the magnitude of the incident microwave power was 1 KW, and the measured substrate temperatures were approximately 470 C. It is observed from the SEM photo of S73 in figure 5.43 that the film on S73 has small pin holes in it. Hence, at a film thickness of $2\mu m$, a diamond powder quantity of 3x the Masood recipe still does not yield a completely continuous film. From the SEM photo of S75 in figure 5.44 it appears that the film is continuous although there are a few deep crevices in the

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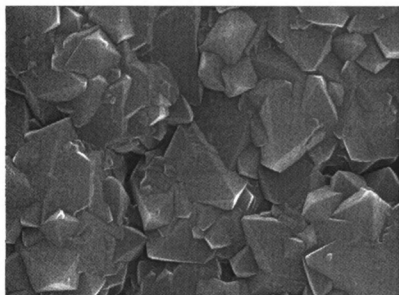


Figure 5.44 SEM photo of S75.

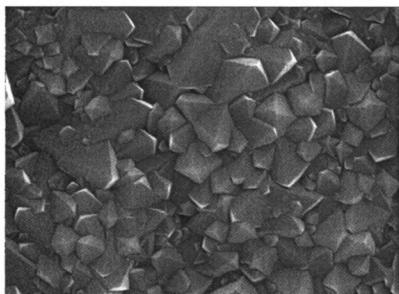


Figure 5.45 SEM photo of S83.

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film. Contrary to the films on S69 through S75, the film on S83, which is shown in figure 5.45, does appear to be continuous. By the method of linear intercepts, the nucleation density of the film on S83 is on average approximately $2.7 \times 10^8 \text{ cm}^{-2}$.

From the SEM photos of S69 - S83, it appears that 16x the Masood recipe is adequate for deposition of continuous diamond films with a thickness of $2 \mu\text{m}$. Furthermore, it was observed from the SEM photos in figure 5.43 through figure 5.45 that the average grain size decreases with increasing quantities of diamond powder. This is evidence that once the seeding density is sufficient for growth of a continuous diamond film, further increasing the diamond powder quantity causes increased competition between grains and thus reduces the average grain size.

Data presented in this section thus far has shown the increase in nucleation density for diamond powder quantities of between 1x and 16x the Masood recipe; however, there remains the question of what influence if any, would quantities of diamond powder greater than 16x the Masood recipe have on diamond nucleation on silicon substrates. Specifically, one may be interested to know how small do the grain sizes become, and how smooth are the films when the substrate is seeded with diamond powder quantities greater than 16x. For some applications, it is critical that diamond films be either fine grained or smooth.

Data that will be presented in the next section, titled *Measurements of Film Surface Roughness*, will show that the photo-resist, diamond-powder seeding method is not the preferred method of substrate pre-treatment for deposition of smooth diamond films. For smooth diamond films, the preferred substrate pre-treatment method is scratching the substrate with fine grain diamond powder, because it produces a much smoother diamond film

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Some insight into the question of the effects of diamond powder quantities in excess of 16x the Masood recipe can be acquired from an analysis of the growth rates on substrates that were seeded with 16x and less. Figure 5.46 shows a graph of the measured weight gains for diamond films that were grown on silicon substrates that were seeded with between 1x and 16x the Masood recipe. The data in the figure shows that there is a large increase in weight gain when the diamond powder quantity is increased from 1x to 8x and there is a slight increase in weight gain from 8x to 16x. One would expect an increase in weight gain whenever the area of the growth surface is increase. Such is the case for films grown on substrates with increasing seeding densities, which are shown in figure 5.46. The convergence of weight gain from 1x to 16x in the figure is an indication that the films are becoming continuous, and further increasing the diamond-powder quantity is not necessary for production of continuous films. A further increase in the quantity of diamond-powder in the photo-resist solution should increase the nucleation density and reduce the average grain size in the film however. So there is the possibility that diamond powder quantities greater than 16x would yield ever finer grain films than that of S83; however, the diamond powder scratching method was chosen as a better method for producing fine grain films.

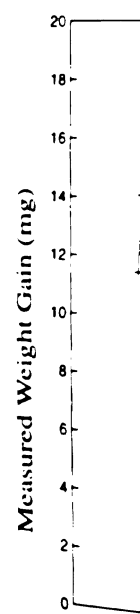


Figure 5

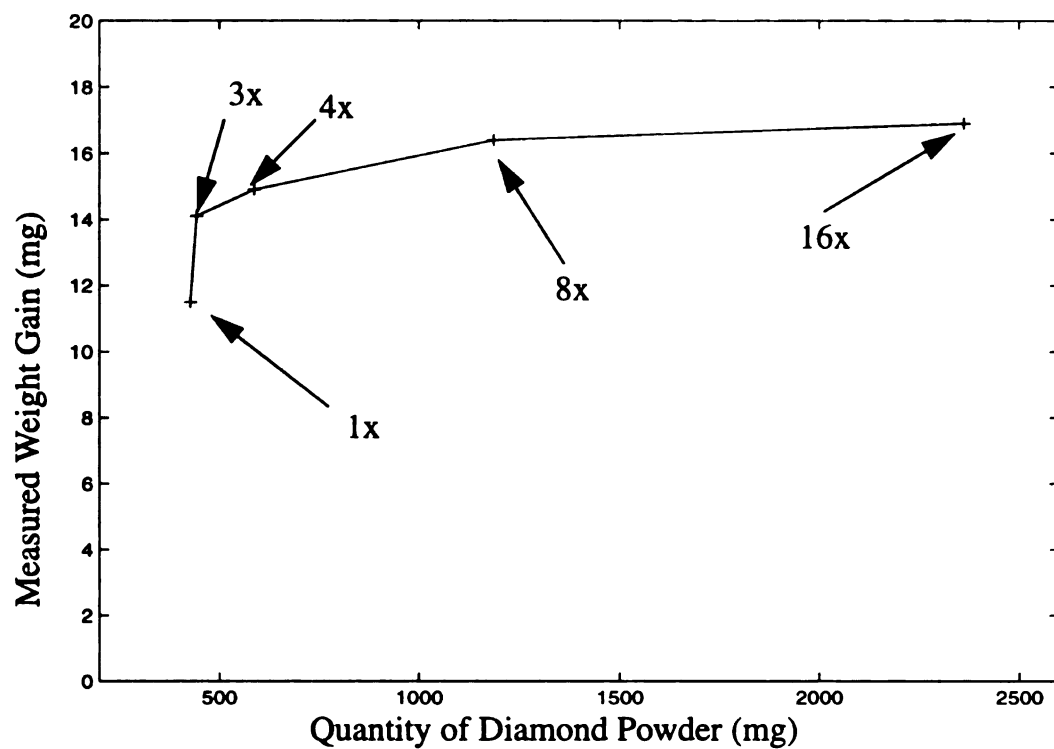


Figure 5.46 Weight gain vs. diamond powder concentration.

5.6.2 Measurement

5.6.2.1 Introduction

In addition to the smooth films, some diamond thin films are deposited on these instances, the results in Chapter 6 that the surface with increasing surface area are present at intermediate results, and the amount of diamond that are deposited on the substrate that causes light scattering.

One way to measure the nucleation density of diamond on silicon. As was shown in the nucleation density on silicon, the nucleation density on silicon has been reported to be on the order of 10^8 cm⁻² on silicon substrates is also important to consider the fine grain diamond.

Data is presented in this section considering two

5.6.2 Measurements of Film Surface Roughness

5.6.2.1 Introduction

In addition to investigating deposition rates and film quality, it is important for some diamond thin-film applications that a process be developed for deposition of very smooth films. One such application is when diamond films are used as optical materials. In these instances, the film's surface roughness becomes a critical variable. It will be shown in Chapter 6 that the transmission of light through a thin-film decreases monotonically with increasing surface roughness. This phenomenon occurs because when rough surfaces are present at interfaces between materials of varying refractive indices scattering of light results, and the amount of light that is transmitted is reduced. In the case of diamond films that are deposited on glass substrates, the diamond film - air interface is a rough surface that causes light scattering.

One way to reduce the surface roughness of a diamond film is to increase the nucleation density; however, there are several variables that affect the nucleation density on silicon. As was discussed in earlier sections, a dominant factor for increasing the nucleation density on silicon substrates is the substrate pre-treatment method. Additionally, it has been reported that the surface smoothness of diamond films that are deposited on silicon substrates is also affected by substrate temperature and gas chemistry^{[76][77]}. Hence it is important to consider all of these variables when developing a deposition process for fine grain diamond films.

Data is presented in the next two sections for measurements of film surface roughness considering two process variables, substrate pre-treatment method and gas chemistry.

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In the first section measurements of surface roughness are discussed for films that were grown on substrates that were pre-treated with the photo-resist seeding method. In the second section, surface roughness measurements are presented for diamond films on substrates that were scratch seeded. Additionally, surface roughness measurements are included in the second section for films grown with various gas mixtures of H_2 , CH_4 and CO_2 .

The measured surface roughness that are presented here are averages of five measurements that were taken from the center of each particular substrate. The actual film surface roughness were measured with a Dektak IIA. For each Dektak measurement, the scan length was $100\mu m$, the scan speed was slow, the range was set to auto, and the profile was set at peaks and valleys. For a scan length of $100\mu m$, the Dektak takes a measurement every $100nm$, which corresponds to 1000 measurements per scan.

5.6.2.1.1 Substrates Pre-Treated with the Photo-Resist Method

It was observed from the SEM photos shown earlier in this chapter that the average grain size of diamond films decreased with increasing quantities of diamond powder for diamond films that were grown on substrates that were pre-treated by the photo-resist method. For example, the films on substrates S73, S75, and S83 (SEM photos were shown in figure 5.44 through figure 5.45) were seeded with diamond powder quantities of 3x, 4x and 16x the Masood recipe. From the SEM photos it was apparent that while they were nearly equal in thickness the film on S83, which was pre-treated with a diamond quantity of 16x, had much finer grains than S73 and S75.

Table 5.6 lists the average surface roughness for five films that were grown on sub-

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strates that were pre-treated with the photo-resist, diamond powder method. The first observation from table 5.6 is that the surface roughness of S73 is greater than that of S71. This is significant because these two films were grown under identical conditions. The only difference is that S73 is 4 times as thick as S71. One would expect that the surface roughness increases as the films grows thicker, as is the case with S71 and S73. The second observation from table 5.6 is that the surface roughness of S83 is approximately 40% less than that of S73, which is a slightly thinner film. Again, S83 and S73 are both continuous film that were grown under identical conditions; however, their pre-treatment was different. S73 was seeded with a diamond powder quantity of 3x the Masood recipe, and S83 was seeded with 16x. This shows that higher quantities of diamond powder produce finer grain films. The final observation from table 5.6 is that the films on S78 and S84 have smaller surface roughness than S83. This is significant because the primary difference between their deposition processes was the flow of methane. S78 had a higher methane flow rate, which was 8 sccm, than S83. Likewise, S84 had an even higher methane flow rate, which was 10 sccm. So it appears that higher methane flow rates result in films with lower average surface roughness. One might expect this because as the Bachmann model predicts, higher flow rates result in more twinning and hence the appearance of smaller grains.

In Chapter 6, data will be presented that shows that a film surface roughness of the magnitude in table 5.6 can reduce the transmission of light to below 10% for wavelengths at 1600nm and shorter. Hence, the data in the table indicates that films grown on substrates that are pre-treated with the photo-resist, diamond-powder method are not adequate for optical coatings.

Substrate	
S71	
S73	
S83	
S78	
S84	

Table 5.6:

Substrate	Average Measured Surface Roughness σ_{rms} (nm)	Measured Substrate Weight Gain (mg)	Film Thickness (μm)	Process Gas Composition $\text{H}_2\text{-CO}_2\text{-CH}_4$	Measured Substrate Temperature
S71	179.0	3.2	0.45	200 - 0 - 5	468 C
S73	242.6	14.1	1.98	200 - 0 - 5	473 C
S83	155.6	16.9	2.37	200 - 0 - 5	471 C
S78	124.2	17.3	2.43	200 - 0 - 10	472 C
S84	112.1	17.8	2.50	200 - 0 - 8	470 C

Table 5.6: Measured Surface Roughness for Photo-Resist Seeded Substrates.

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5.6.2.1.2 Substrates Pre-Treated with Diamond-Powder Scratch Seeding

Table 5.7 lists the average surface roughness for four substrates that were pre-treated with diamond powder scratching method (refer to section [3.3.2]). As was stated in section [2.5.1] this technique can achieve nucleation densities as high as 10^{10} cm^{-2} . Additionally, SEM photos for the films in table 5.7 are included in figure 5.47 through figure 5.50.

Comparison of the surface roughness of S85 from table 5.3 to that of S71 shows that S85 has a surface roughness that is 80% lower than that of S71. This is significant because the films on these two substrates were grown under identical conditions. The only difference between them was the pre-treatment method. Hence, it is apparent that the scratch seeding method can produce much smoother diamond films.

To further investigate the potential for producing fine grain films with scratch seeding, it is important to include the effects of gas chemistry. Hence, CO_2 was added to the chemistry. The three remaining films listed in table 5.7 were all processes with 200 sccm of H_2 and 8 sccm of CO_2 . The only process variable between them was the flow rate of CH_4 , which was varied from 3 sccm to 8 sccm.

When CO_2 was added to the gas mixture, one particular gas flow ratio resulted in an average surface roughness that was far less than that of others. It was also less than the surface roughness of films that were grown without CO_2 . It was observed from the SEM photos in figure 5.48 through figure 5.50 that when the flow rate of CO_2 and CH_4 were equal, which was the case for S100, the average grain size appeared to be much smaller than that of any other film. The measured surface roughness of S100, which is listed in table 5.7, was approximately 11-nm. It is also interesting to note that S92 had a lower σ_{rms}

Substrate	
S85	
S89	
S92	
S100	

Table 5

Substrate	Average Measured Surface Roughness σ_{rms} (nm)	Measured Substrate Weight Gain (mg)	Film Thick- ness (μm)	Process Gas Composition $\text{H}_2\text{-CO}_2\text{-CH}_4$	Measured Substrate Temperature
S85	35.5	4.7	0.66	200 - 0 - 5	472 C
S89	561.5	5.8	0.81	200 - 8 - 3	476 C
S92	24.7	6.5	0.91	200 - 8 - 5	470 C
S100	10.9	8.4	1.18	200 - 8 - 8	470 C

Table 5.7: Measured Surface Roughness for Scratch Seed Substrates

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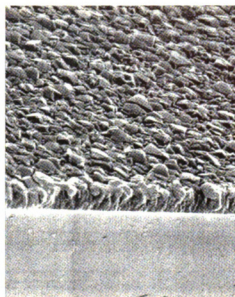


Figure 5.47 SEM photo of S85.

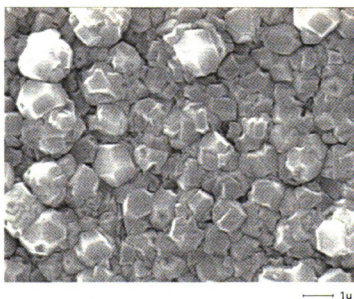


Figure 5.48 SEM photo of S89.

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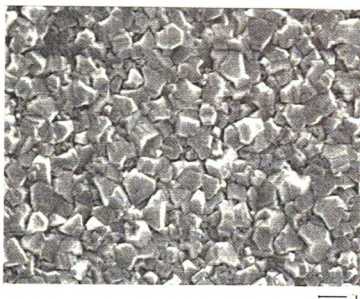


Figure 5.49 SEM photo of S92.

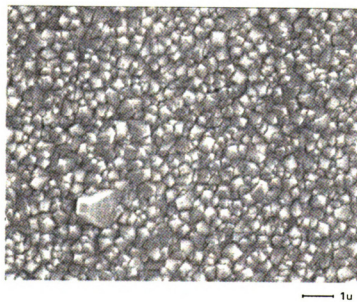


Figure 5.50 SEM photo of S100.

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All of the substrates listed in table 5.7 were pre-treated, i.e. seeded, by the same method, scratch seeding. Hence, one might expect that they should all have the same nucleation density, and that the thinner films would have finer grain films, which would result in smaller surface roughness. Since the film on S100 is thicker than the ones on S85, S89 and S92 and it has smaller grain sizes, it is apparent that the deposition chemistry has a strong influence on the resulting surface roughness of the deposited diamond films. In this case, the lower surface roughness is due to the addition of a specific amount of CO_2 to the gas chemistry.

5.6.2.1.3 Summary of Surface Measurements

The data presented in this section indicates that the nucleation density and grain size of diamond films has a dependency on the substrate pre-treatment method as well as the deposition gas composition. Furthermore, the gas composition of 200 sccm of H_2 , 8 sccm of CO_2 and 8 sccm of CH_4 yields a very low diamond film surface roughness. An investigation of the transmission of light for films deposited with the gas compositions mentioned here will be provided later in Chapter 6.

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5.6.3 An Investigation of Deposition and Uniformity on 3" and 4" Substrates

In addition to growth rate, film quality, and surface roughness, two other process variables of interest for the benchmark silicon diamond deposition experiments were the deposition area and deposition uniformity. A few pilot experiments were conducted with 3" and 4" silicon substrates to investigate these properties. For these experiments, deposition was conducted with MCPR-C5 and MCPR-C7. The results were that continuous diamond films could be deposited over the entire surface of substrates as large as 4 inches in diameter with both MCPR configurations. Deposition rates were observed to be as high as 0.9mg/hr at 470 C for 40 hour deposition experiments with 3 inch substrates, and 0.75 mg/hr at 490 C for 15 hour deposition experiments with 4 inch substrates. The deposition chemistry was 200 sccm of H_2 and 5 sccm of CH_4 and the pressure was varied between 5 and 9 torr. Pretreatment of the substrates consisted of abrasion seeding with 0.25 μm diamond powder.

Observations of film uniformity were made by viewing the colors of the deposited diamond films. As the thickness of a transparent film changes, the color of the film changes. An area of a film that has a single color has a uniformity on the order of 50 nm. In some cases, 15 to 20 color changes were observed over the radius of a 3 inch silicon wafer. For films that were grown on 4 inch silicon substrates with MCPR-C7, it was observed that films could be grown to within one color over an area as large as 3.0 inches at 7 torr if the substrate location was between 0 mm and 3 mm above the floor of the brass cavity. At 5 and 9 torr, the single color area decreases to as little as 2.1 inches.

These observations were later applied to 2 inch silicon and 2 inch glass substrates with excellent results. With MCPR-C7 and a quartz tube height $d_1=58mm$ films were rou-

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5.6.4 Deposition on Silicon IC Substrates

In addition to its many potential mechanical applications, diamond films may also be useful for several electronic applications. One possible electronic application is an over-coating on substrates that contain micro-electronic circuits. Diamond over-coatings might function as thermal conductors, which would spread out heat from thermal hot spots, or they may be used as a passivation layer, which could lengthen the life of the underlying devices.

In previous work, hot-filament CVD was used to deposit a 2 μm thick diamond film on a silicon wafer that contained circuitry that was designed for use in thermal transfer printing devices^[94]. It was noted that these diamond coated devices exhibited superior lifetime. The substrate temperature was reported to have been 850 C during deposition of the diamond passivation layer however. This temperature is too high for conventional microelectronic devices. Such devices contain aluminum, which has a melting point of 660 C, and if it were exposed to such an extreme temperature the devices would be damaged.

The low melting point of the aluminum layers in microelectronic circuits dictates that diamond film over-coatings must be deposited at temperatures below those of conventional CVD diamond processes. Consequently, a pilot study of low-temperature diamond deposition on silicon integrated circuits was included in this dissertation^[95].

Silicon substrates with a (100) orientation were processed to fabricate resistors and bipolar junction transistors. Boron diffusion through oxide windows was used to form dif-

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fused resistor and p-type base regions for the transistors. A subsequent phosphorus diffusion was used to form the n-type emitter regions for the transistors, and ohmic contacts to the n-type collectors. Contacts cuts were made to the underlying silicon and aluminum was deposited by thermal evaporation. The aluminum layer was patterned and etched by conventional photolithography to form contact pads for device testing purposes. An oxide passivation layer was not used.

The IC substrates were pre-treated, i.e. seeded, with the photo-resist diamond seeding method. The abrasive seeding techniques were not used since it would undoubtedly damage the delicate metallization patterns.

A continuous diamond film was deposited at 9 torr over the entire surface of a 2 inch diameter silicon IC wafer with MCPR-C5. The gas flow rates were 200 sccm of H_2 , 8 sccm of CO_2 , and 3 sccm of CH_4 . The pressure was 9 torr the input microwave power was 1 KW, and the substrate temperature was measured by optical pyrometry to be 465 C. The resulting film had a weight gain of 4.8 mg, which corresponds to an average film thickness of 0.67 μm .

Figure 5.51 shows a 100x optical micrograph view of details of the IC structure beneath the transparent diamond film. Figure 5.52 shows a second micrograph, which is at a higher magnification. From these photos it is observed that the diamond film is continuous and polycrystalline. The light, square-shaped features in the figures correspond to aluminum patterns that are approximately 200- μm wide. The other varying patterns are oxide layers of varying thicknesses.

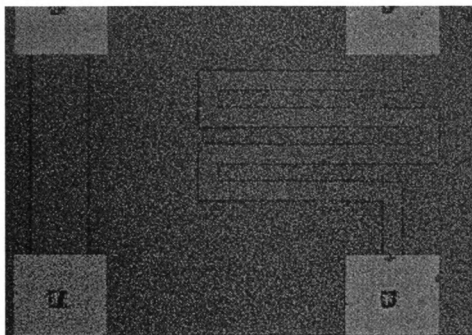


Figure 5.51 A photo of diamond coated devices.

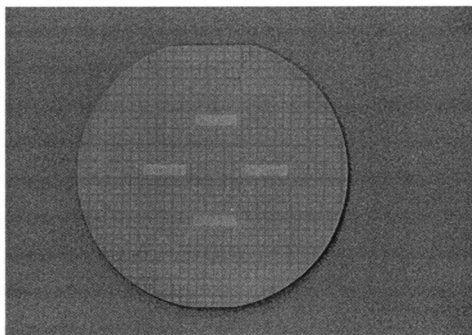


Figure 5.52 A photo of a diamond coated IC.

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5.7 Summary

Data has been presented in this chapter that demonstrates that the MSU developed MCPR technology is capable of producing continuous, thin diamond films on silicon substrates at temperatures in the range of 400 C to 550 C. Furthermore, it has been shown that the low-temperature MCPR diamond deposition process, which was developed during this dissertation, is capable of depositing diamond films on disk shaped substrates with diameters up to 4-inches. Deposition rates, which are highly dependent on the substrate's temperature and the gas chemistry, were in the range of 10 nm/hr to 100 nm/hr.

Presented first in this chapter were comparisons between actual experimental deposition results and the predictions of two growth models. The first model was the one that was developed by Harris and Goodwin. It predicts changes in diamond film deposition rates that occur due to variations in the substrate temperature and the methyl radical concentration. The second model was the Bachmann C-H-O gas phase diagram. This model is generic in that it predicts the trends of the deposition rate and the film quality independent of the CVD process and the input gas chemistry.

It was reported that the experimental, diamond-film deposition-rate did not always correlate with the predictions of the Harris-Goodwin growth model. For deposition at varying substrate temperatures, experimental results correlated well with the model; however, when gas pressure and methane flow rate were examined as independent process variables the data did not always match the predictions of the model. The model's prediction of increased diamond film deposition rate, w_{HG} , with increasing substrate temperature was matched very well by the experimental results.

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the model again predicts an increase in deposition rate, w_{HG} , with increasing pressure. In this instance, experimental data did not show an increase in growth rate with increasing pressure, it remained essentially the same for pressures in the range of 7 torr to 15 torr. One possible explanation for the difference between the model and experimental results for varying gas pressures was that increasing the gas pressure in the MPCR may reduce the distribution of electron temperatures, T_e . A reduction in the distribution of T_e would in-turn cause a reduction in the dissociation rate of CH_4 . It was assumed in the application of Harris-Goodwin model to this range of operation of the MCPR, that increasing the gas pressure produces higher concentrations of methyl radicals, $[\text{CH}_m]$.

When the methane flow rate was singled out as a process variable, the results were mixed. The applied model predicts that if the methane dissociation rate remains the same while the methane concentration is increased, that the deposition rate, w_{HG} , will increase with increasing methane concentration. At methane flow rates equal to and less than 2.5% of the flow rate of hydrogen, the experimental results showed that there was an increase in the deposition rate, which correlated well with the model. For methane flow rates in the range of 2.5% to 5% of the flow rate of hydrogen however, the experimental deposition rate saturated and no additional increase was observed. While the saturation at flow rates higher than 2.5% is not predicted by the model, it is similar to the results that were reported by Zhang^[36].

A comparison of experimental deposition results with the predicted trends of the Bachmann C-H-O gas phase diagram was also included in this chapter. Included in this discussion were experiments where diamond films were deposited from mixtures of hydrogen, methane, and carbon dioxide. Unlike the Harris-Goodwin model, the qualitative

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predictions of the Bachmann model correlated well with the experimental results. The model's prediction that growth rates diminish with decreasing $X_{C/\Sigma}$ matched the results of deposition experiments. Furthermore, a pilot experiment that used only CH_4 and CO_2 had agreement with the model's prediction that diamond can be grown from a CVD process without the use of H_2 .

Data from investigations of three methods for improving the deposition rate in the plasma CVD process was also presented in this chapter. In the first case, a dc bias was added to the substrate to investigate how it might affect diamond deposition at low substrate temperatures in the MPCR. The result was that the growth rate and film quality were essentially unaffected by the addition of the dc bias. Second, a thermally-adjustable substrate cooler was investigated to determine if deposition rate would increase at higher pressures, which were in the range of 15 torr to 30 torr, while the substrate's temperature was maintained below 550 C. Here the cooler was necessary to control the flow of heat from the substrate. At pressures of 15 torr and above, the substrate's temperature would exceed the 550 C point without the aid of the cooler. The results from the cooler experiments were that there seemed to be no clear improvement to the deposition rate. The deposition rate at 25 torr and 500 C was the same as that below 10 torr. Third, deposition with pulsed microwave power was investigated for improvements to the deposition rate. Again, no clear advantage was observed. In fact the deposition rates for experiments with pulsed microwave power were less than those with CW microwave power.

Lastly, data was presented for experiments that investigated the photo-resist seeding method, measurements of surface roughness, deposition on large area substrates, and deposition on silicon ICs. The investigation of the photo-resist seeding method was initi-

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ated because the procedure that was outlined by Masood did not yield a high enough nucleation density to produce a continuous diamond film with a thickness of 0.5 μm or greater. The result was that continuous diamond films were deposited by the Masood method with only one change to the process. It was determined that increasing the diamond powder quantity to 16 times that of the Masood recipe was sufficient to produce continuous diamond films. The measurement data for diamond film surface roughness revealed three interesting facts. First, the surface roughness of diamond films that were deposited on substrates, which were pretreated with the photo-resist method, is on the order of 100 nm and greater. This is predicted to be too high for optical applications at wavelengths below 1600 nm. Second, the surface roughness of diamond films that were deposited on substrates, which were pretreated with the diamond powder scratching method, were as low as 10nm. This low surface roughness is predicted to meet the needs of optical applications at wavelengths above 400 nm. Third, the low surface roughness of 10 nm was dependent on two variables, the substrate pretreatment method and the deposition gas chemistry. It was learned that when the flow rates of CH_4 and CO_2 were equal, a very smooth, fine-grained film was deposited. The data that was presented from the large area deposition experiments showed that the deposition area at low temperatures with the MCPR was sufficient to coat substrates with diameters as large as 4 inches. Furthermore, the deposition of 1 μm and 2 μm films with a uniformity to within 100nm was achieved to a diameter as large as 3 inches. Finally, data was presented for a pilot experiment where a diamond film was deposited on a 2 inch silicon IC, which contained components made of aluminum. SEM photos were presented that showed that the aluminum components suffered no damage during the diamond deposition process. This indicates that diamond films

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can be deposited on temperature sensitive substrates with the low-temperature diamond deposition process that was developed during this dissertation with the current MCPR technology.

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Chapter 6

Characterization of Diamond Films on Glass Substrates

6.1 Introduction

To this point, the thrust of this dissertation has been to describe the investigation of low-temperature diamond deposition in the MCPR. Included in these discussions were presentations of the various MCPR configurations that were investigated and the results of the benchmark silicon experiments. It was concluded in previous chapters that diamond films could be deposited on flat disk-shaped substrates at temperatures below 550 C with MCPR technology; however, the growth rates were rather low. For example, at 470 C and gas flows of 2.5% CH₄ in H₂ the measured weight gain of a 2 inch silicon substrate was approximately 17 mg. This weight gain was for an experiment that was 40 hours long. Hence, it translates to a deposition rate of approximately 60 nm/hr. Additionally, it was observed that the substrate pre-treatment method and the deposition process had a strong influence on the resulting film morphology and grain size. This was noted to cause large variations in measured film surface roughness.

After it was concluded that diamond could be grown at low-temperatures with MCPR technology, the direction of the lab work was switched to glass substrates. The results of these experiments are what is presented in this chapter. Analysis of the diamond films on glass substrates in this chapter is divided into three areas. They are (1) the deposi-

tion results, which include measured weight gains and film quality, (2) the transmission characteristics, which include measurements of optical transmission and film surface roughness, and (3) the film to substrate adhesion, which is more relevant for glass substrates than for silicon ones.

The glass substrates were Corning code 7059 and Corning code 7050. The former is a borosilicate glass composition with near zero alkali content that was originally developed for thin film electronic circuits. The latter is a borosilicate glass in wide spread use. It is commonly known by the trademark Pyrex. A particular historical application for the 7059 glass has been as a substrate material for liquid crystal displays.

The outline of the chapter is as follows. The remainder of the chapter is comprised of five topics. The first topic is an overview of the physical properties of diamond, with an emphasis on those that relate to its use as an optical coating. Specifically, discussions address diamond properties such its optical transmission and thermal expansion. Since the thermal expansion of diamond does not match that of most materials, delamination of diamond as a result of thermal strain is often a concern. Techniques for improving the diamond film adhesion to optical materials are also included. The second topic presents deposition results for diamond films that were grown at low-temperatures with the MCPR configurations outlined in chapter 4 and the methods developed in chapter 5. It includes measured weight gains, observations of uniformity, and observations of how the seeding method affects the film's optical transmission. The third topic compares the measured optical transmission of films that were deposited on glass substrates with theoretical equations for transmission of monochromatic light through a thin film. This discussion includes an investigation of how the surface roughness of a diamond film effects the opti-

cal transmission through the film for wavelengths between 400 nm and 1600 nm. The fourth topic addresses the adhesion of diamond films that were deposited on glass substrates. The thermal expansion mismatch between the glass substrates used here and that of diamond induces significant strain at the film-substrate interface. Hence, it is necessary to discuss how this affects the film's adhesion to the substrate. Finally, the chapter concludes with a summary of the glass deposition experiments and the corresponding diamond film characterization measurements.

6.2 An Overview of Diamond as an Optical Coating

Diamond is predicted to be a promising optical material because of its wide spectral optical transmission range, its extreme hardness and its chemical inertness. The optical transmission range of nitrogen-free, pure type IIA diamond spans from UV light (~230 nm) to IR light (~2.5 μm) and also from 6.5 μm to >100 μm in the far infrared^[89]. The UV edge of the spectrum is where photon absorption due to band gap transition begins (~5.4 eV). At the IR edge of diamond's optical-transmission spectrum, absorption, which is due to C-C bond vibrations, extends from about 2.5 μm to 6 μm . This absorption is weak and may be negligible in films that are thinner than 0.25 mm.

Besides its good transmission, the hardness and chemical inertness of diamond make it an ideal optical material for applications in harsh environments. Consequently, it is of interest as a protective-coating material for optical materials that are less resilient to hostile environments. One of the most common optical materials is silica based glasses. Hence, these glasses are candidates for such protective coatings. Diamond is also of potential interest as a glass coating in the form of field emission pixels for flat panel displays.

CVD diamond has been grown by various groups in free standing films and on optical substrates in recent years. Experimenters have deposited thin polycrystalline diamond films on optical materials such as sapphire^[78], quartz^{[79][80]}, Corning 7059 boro-silicate glass^[81] and IR materials including ZnS, ZnSe and Ge^[82]. Besides the predicted low optical transmission due to its high refractive index, further transmission losses due to scattering, and photon and phonon absorption at the grain boundaries have been observed^{[52][57]}.

6.2.1 Film to Glass Adhesion

As with many diamond deposition processes, adhesion of the diamond film to the underlying glass can sometimes be problematic. First, there is a potential to induce strain at the boundary between the substrate and the deposited film whenever there is a mismatch in the thermal expansion coefficients of the two materials. Second, the problem becomes further compounded when depositing on glass substrates, because of the possibility of heat induced strain in the glass. Internal strain is generally not introduced into glass that is heat treated at less than its strain temperature. Therefore, it is desirable that the diamond deposition temperature be less than the strain temperature of the glass substrate.

Diamond films that adhere to quartz and fused silica substrates have been widely reported for plasma-assisted and hot-filament assisted CVD processes. The strain point temperature of fused silica (99.9% SiO₂) is 956 C, which is compatible with the deposition temperature range of typical diamond deposition reports^[96]. Its thermal expansion coefficient is 0.55×10^{-6} , which is somewhat less than that of diamond^[97]. For more commonly used commercial silica-based glasses, the problems of strain can be appreciable

because they have strain point temperatures that are significantly lower than fused silica. They also have thermal expansion coefficients that are significantly higher than fused silica. For example the strain point temperature of common window glass, which is approximately 72.6% SiO_2 , is 473 C and its thermal expansion coefficient is 9.2×10^{-6} [98]. Diamond deposition has been reported at temperatures less than the strain point of soda-lime glass; however, the deposition rates are generally quite low.

Borosilicate glasses are a family of glass types that are commonly used commercially for chemical and electrical applications, including substrates for liquid crystal displays. They have a strain temperature well above 500 C, thus they are candidates for low-temperature diamond deposition. A possible application for borosilicate glass as a diamond film substrate is as a back-plate for a field-emission, flat-panel display.

6.2.2 Methods for Improving Film Adhesion to Optical Substrates

Three techniques that have been reported to improve diamond film adhesion on thermally mismatched substrates are (1) bonding a free standing film to the optical substrate, (2) use of inter-layers and (3) mechanically altering the interface. They are summarized in the next three sections.

6.2.2.1 Applying Optical Coatings to IR windows by Optical Brazing

A process called “optical brazing” has been used by William D. Parlow et. al. to thermal bond diamond to infrared-transmitting windows of ZnSe and ZnS [84]. Bonding diamond to these substrates is necessary because atomic hydrogen etches these materials. It has been shown that this process does provide good adhesion. With this technique, the

diamond film is first grown to the desired thickness on a silicon substrate. Then the diamond coated substrate is placed in a stack where a bonding glass preform is placed between the diamond film and the infrared window material. Then the stack is heated to the appropriate bonding temperature and pressure is applied. Most of the preform is squeezed out, leaving a thin film between the window and the diamond. The final step is to etch away the silicon to expose the smooth nucleation side of the diamond film. The measured transmission for a bonded sample is 71% at wave numbers between 1000 cm^{-1} and 4000 cm^{-1} .

6.2.2.2 Improved Adhesion Provided by Inter-layers

A second method of attaching diamond films to ZnSe and ZnS that also yields good adhesion is deposition of diamond on an optically transparent inter-layer. Of course this is the end result of the “optical brazing”. It has been shown by Costello et. al. that diamond can deposited on IR windows that are etched by atomic hydrogen if a inert inter-layer is deposited on the substrate first^[91]. The result is transmission of at least 60% for wave numbers between 1000 cm^{-1} and 4000 cm^{-1} .

6.2.2.3 Interfaces Engineered to Improve Diamond Adhesion

The use of a three dimensional (3D) graded interface is another method of improving adhesion of thin films that are thermally mismatched with the deposition substrate. It has been shown by Singh et. al. that an engineered 3D interface dramatically improves adhesion of diamond films to steel and tungsten-carbide^[92]. Engineering the interface means that the smooth surface of the substrate is modified into a surface with peaks and

valleys. Singh uses a multi-pulse laser to create this surface. The deposited film covers the entire substrate and fills in the valleys creating a interlock between the materials. In the case where the substrate compresses the deposited film, the materials are locked together as the substrate pinches the portion of the film in the interlock valleys.

This technique has been applied by Parlow to further enhance the adhesion of diamond to the inter-layer between the film and the IR window. The results were that adhesion improved and transmission at high wave numbers was reduced due to scattering at the engineered interface. At 4000 cm^{-1} wave number, the transmission went from near 60% for the smooth inter-layer to less than 20% for the engineered inter-layer.

6.3 Results for Diamond Deposition on Glass Substrates

A total of 69 low-temperature diamond deposition experiments were conducted with 1.1 mm thick, Corning 7059 glass substrates, which had diameters of 2, 3 and 4 inches. For the majority of these experiments, diamond films were deposited on the 2 inch diameter 7059 substrates. The results of 56 experiments, which deposited diamond films on the 2 inch substrates, are listed in Appendix E. Appendix F and Appendix G list the data for the experiments where diamond films were deposited on 3 inch and 4 inch 7059 substrates respectively. Additionally, there were 5 experiments where diamond films were deposited on Corning 7050 substrates, which had a diameter of 2 inches. The results of these experiments are listed in Appendix H.

The objective of the experiments during which diamond films were deposited on glass substrates was to investigate processes that yield smooth, high quality films that adhere to glass substrates. Hence, there was not an emphasis on duplicating all of the data

that was presented in Chapter 5 for comparison. Instead, what were deemed to be the most promising process parameters in Chapter 5 were applied to glass substrates. The next four subsections present an overview of some of the observations regarding the glass substrate deposition experiments. First, there is a comparison of the temperature dependence of diamond deposition on glass substrates to that of silicon substrates. Included in the discussion is a comparison to the Harris-Goodwin model. Second, results are reported for pilot experiments where diamond films were deposited on glass substrates with MCPR-C8, which had a heated substrate receptor. Third, observations of film uniformity are presented. In the final section, visual observations are noted regarding the optical transmission of diamond films that were deposited on glass substrates that were pretreated with the photoresist method and scratch seeding method.

6.3.1 Comparison to the Harris-Goodwin Growth Model

In section [5.2.1], an analysis was presented that compared the predicted weight gains of a diamond growth model, w_{gHG} , which was published by Harris and Goodwin, to measured weight gains from diamond films that were deposited on silicon substrates. Measured, experimental weight gains were presented from experiments that had varying substrate temperatures. It was shown in figure 5.1 that there was a good correlation between the experimental weight gains and those predicted by the model.

Consequently, it is interesting to compare the analysis of diamond deposition rates that were observed from silicon substrates with those that were acquired from diamond films that were deposited on Corning 7059 substrates. Figure 6.1 shows a replot of the graph in figure 5.1 with the addition of two measured weight gains from 2 inch diameter

glass substrates, which were G7-2 and G7-3. The significance of these two substrates is that diamond films were deposited on them under near identical conditions as were recorded for the silicon substrates in section [5.2.1]. The circles and the x's in the figure are the measured weight gains from the silicon substrates from figure 5.1 and from the glass substrates respectively. The solid line is the model's predicted weight gain, w_{HG} , which was shown in figure 5.1. The graph in the figure shows that the measured weight gains from the glass substrates correlates well to the model's predicted weight gain and the measured weight gains from silicon substrates in Chapter 5. Hence, it appears the deposition rate on glass substrates is the same as it was for silicon ones.

The two glass experiments, G7-2 and G7-3, were conducted with MCPR-C2, at a gas pressure of 7 torr. The incident microwave power was approximately 350 Watts, the gas chemistry was 200 sccm of H_2 , 8 sccm of CO_2 and 3 sccm of CH_4 , the deposition durations were 40 hours and the substrates were seeded prior to deposition with photoresist diamond powder seeding.

A measurement of the Raman spectrum was recorded for the diamond film on G7-2 and is shown in figure 6.2. The corresponding, calculated FWHM for the Raman is 14.1 which is somewhat higher than that of the film's on the silicon substrate that were discussed in section [5.2.1.1]. De-convolution of the spectrum showed that there was virtually no graphite in the film; however amorphous carbon was present.

6.3.2 Deposition with a Substrate Heater - MCPR-C8

It was observed from early deposition experiments that substrates that were processed below the floor of the brass cavity had diamond films with non-uniform thickness.



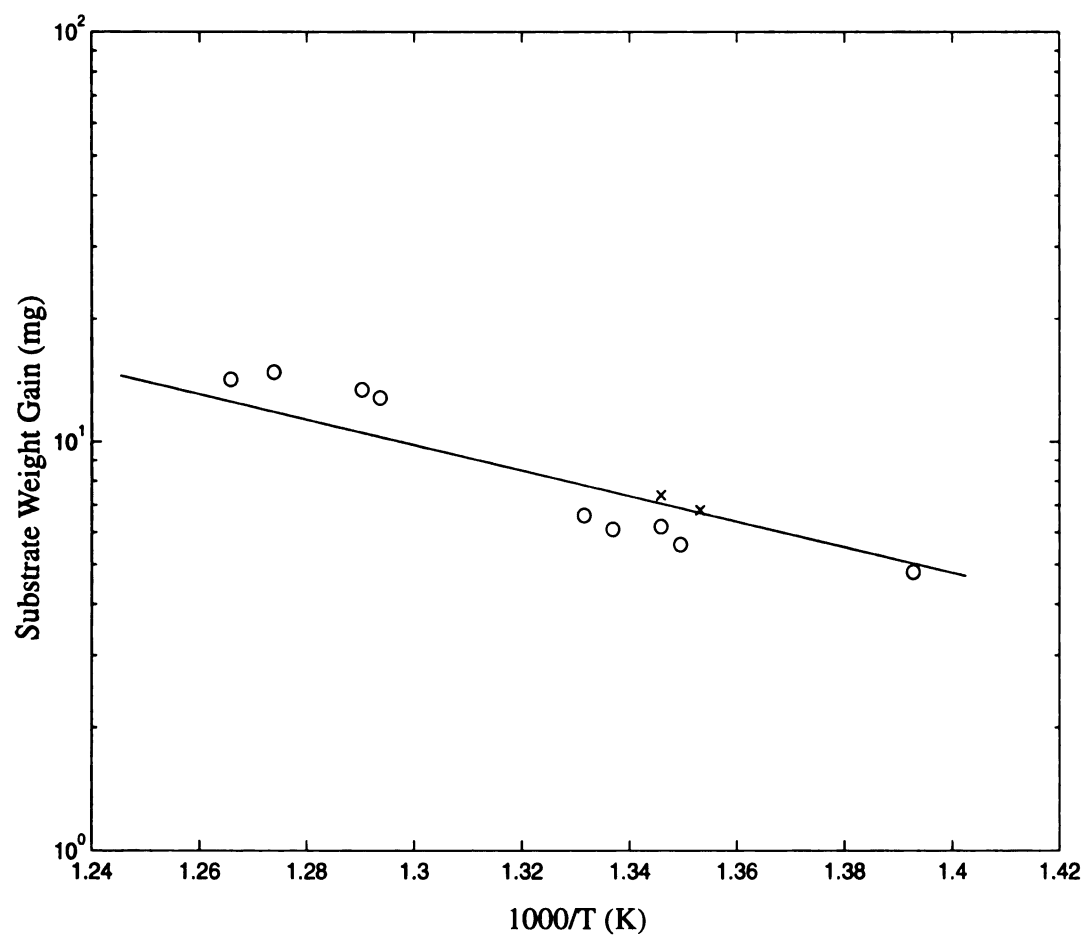


Figure 6.1 Comparison of experimental weight gains to the H-G model.

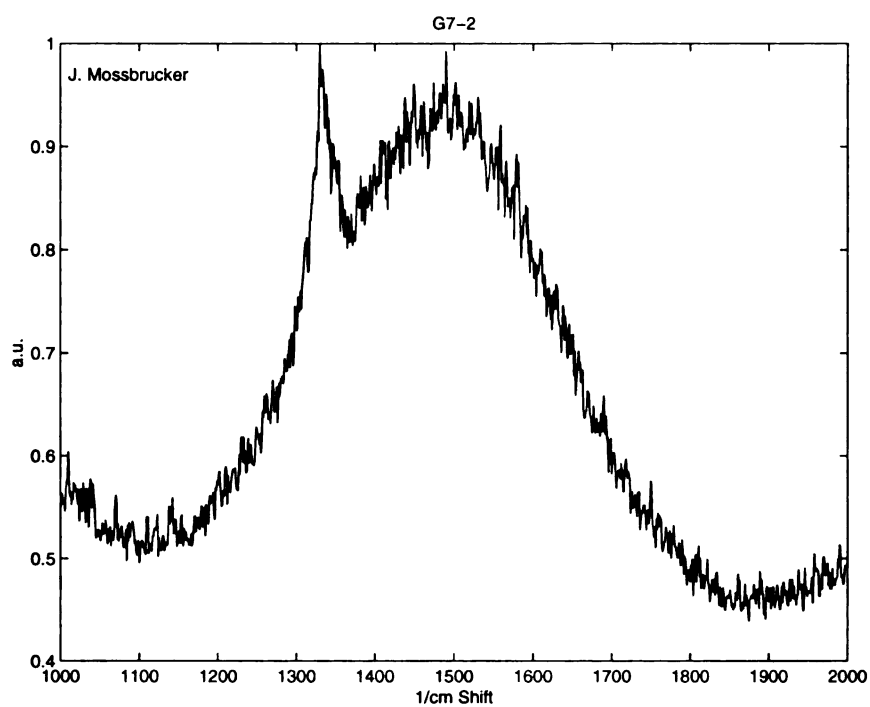


Figure 6.2 The Raman B spectrum recorded from substrate G7-2.

This concern was later resolved by moving the substrate to a location where it was level with the floor of the brass cavity (refer to section [5.6.3] and section [6.3.3]). Prior to this however, an alternate technique for improving the thickness uniformity was investigated -- one that used a substrate heater. The rationale for this was that a heater allows operation at lower gas pressures, which in the MCPR corresponds to larger plasma volumes for a given CW microwave power magnitude.

Comparisons of deposition results with an application of the Harris-Goodwin model, which were presented in section [5.2.1], showed that the deposition rate in the operating regime of this dissertation is highly dependent on the substrate's temperature. From this one might conclude that non-uniform deposition is a result of a non-uniform temperature profile across the substrate. Two things that can cause a non-uniform substrate temperature profile are non-uniform heating and cooling. For substrates that have poor thermal conductivity, such as glass, thermal gradients can be created internally. To preclude this, it is necessary to maintain a uniform environment adjacent to the substrate.

During diamond deposition in the MCPR, the substrate is normally heated by hydrogen recombination on its surface. Calculations of heat flow in section [4.7.1.1] showed that very little heat flows through substrate receptor assemblies that sit atop quartz tubes. Hence, in the steady-state, heat flows from the substrate radiatively and conductively through the neutral gas to the quartz bell-jar. If either of these heating or cooling processes is non-uniform, it is likely that the temperature profile of a poorly conducting material would also be non-uniform.

It was observed by visual inspection of the plasma during early deposition experiments that the intensity of the light radiating from the plasma in the region above the sub-

strate was not uniform. From this, it seemed likely that the flux of chemical species transported to the surface of the substrate was not uniform. Hence, this might have explained why the thickness of the deposited films was non-uniform. It was hypothesized that if the distribution of the plasma in the region above the substrate caused the non-uniform growth and not conductive and radiative cooling, perhaps reducing the gas pressure or relocating the substrate might improve deposition uniformity. The latter technique later proved to be an adequate solution, the former was not.

MCPR configuration 8, which had a substrate heater, was designed for two types of deposition uniformity experiments. One application for this configuration was as a downstream substrate receptor. The idea was that moving the substrate towards the discharge chamber floor might improve the distribution of chemical species transported to the substrate surface through diffusion over longer distances. Hence, MCPR-C8 could be used for downstream diamond deposition. Second, MCPR-C8 could be used for low-pressure diamond deposition. Again, the distribution of chemical species transport the substrate surface might be improved through increased diffusion at lower pressures.

In the MCPR, lowering the gas pressure and moving the substrate to a downstream have been observed to dramatically reduce the substrate temperatures. Hence an electric heater was added the MCPR-C8 such that deposition rates would be proportional to other MCPR configurations (refer to section [4.7.1]).

In all, 23 diamond deposition experiments were conducted with MCPR-C8 and Corning 7059 glass substrates. The specific deposition results are listed in Appendix E for substrates G7-18 through G7-39 and G7-41. Generally, analysis of the diamond films that were deposited during these experiments showed that there was no improvement in the

deposition uniformity. By visual observation, the distribution of the plasma in the downstream configuration and at pressures in the range of 3 torr to 9 torr appeared to be unaffected by the MCPR configuration. Furthermore, it is likely that the highly conductive components, such as the stainless steel tube that replaced the traditional quartz tube in MCPR-C8, created non-uniform substrate cooling due to increased heat flow through the metallic substrate receptor.

Many of the deposition experiments that were conducted with MCPR-C8 did not deposit diamond films from the center to the edge of substrate. Table 6.1 summarizes five of the deposition experiments that were conducted with MCPR-C8. These 5 substrates were selected for comparison because they all had deposition from the center to the edge and they were all grown from the same gas chemistry. From the data in the table it is observed that the deposition rate, measured by weight gain in mg, increases with increasing gas pressure and heater voltage. These results are consistent with the MCPR characteristic of increasing substrate temperatures with increasing gas pressures and increasing applied heater voltages.

6.3.3 Observations of Diamond Film Uniformity

In section [5.6.3], it was noted that diamond films could be deposited to within 2 colors, which corresponds to a uniformity on the order of 100-nm, over areas as large as 3-inches in diameter. To achieve this uniformity, it was noted that the pressure should be 7 torr, and the top surface of the substrate should be located at between 0-mm and 3-mm above the floor of the brass cavity. For MCPR-C7, this substrate placement was achieved with a quartz tube height of $d_1=58\text{mm}$.

Substrate	Chemistry H_2 - CO_2 - CH_4 (sccm)	Gas Pressure (Torr)	Applied Heater Voltage 50 Vac	Applied Heater Voltage 60 Vac	Thermocouple Temperature ($^{\circ}F$)	Thermocouple Temperature ($^{\circ}F$)	Substrate Weight Gain (mg)
G7-29	200-8-3	7	X		616		3.2
G7-26	200-8-3	9	X			463	3.3
G7-32	200-8-3	5		X	640		3.8
G7-30	200-8-3	7		X	459		5.2
G7-27	200-8-3	9		X			6.7

Table 6.1: Summary of Deposition Results with MCPR-C8.

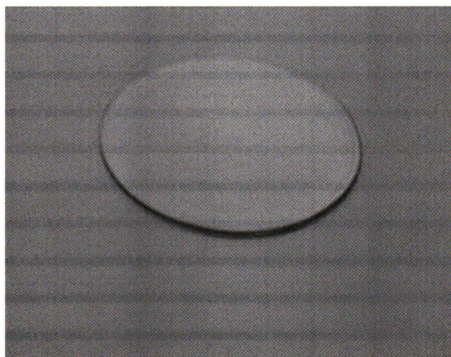


Figure 6.3 Photo of the diamond film on substrate G7-60.

For films that were deposited on glass substrates, similar uniformity results were observed. For gas pressures in the ranging from 5 torr to 9 torr, films with observed uniformity to within two colors were routinely deposited on 2-inch diameter substrates. Photos of two such films are shown in figure 6.3 and figure 6.4. The photo in figure 6.3 was taken of the diamond film on substrate G7-60, which had a diameter of 2-inches. This film was deposited at 9 torr with MCPR-C7 ($d_1=58\text{mm}$) and hydrogen and methane gas flows of 200 sccm and 5 sccm respectively. Its thickness as determined by its optical transmission spectrum was 775-nm. The photo in figure 6.4 was taken of the diamond film on substrate G7-66, which also had a diameter of 2-inches and was deposited under the same conditions as G7-60. The diamond film on G7-66 had a thickness as determined by its optical transmission spectrum of 1840-nm. Even though the film on G7-66 was considerably thicker than the one on G7-60 its uniformity was still observed to be within two colors, or approximately 100-nm. For comparison, a photo of a very non-uniform film, G7-30, which had more than 20 color changes over its 2-inch diameter, is shown in figure 6.5. The difference between G7-30 and the uniform films was that this film was deposited at a position in the MCPR discharge chamber that was 2-cm lower than the others.

6.3.4 Observations of the Effects of Seeding Method

In section [5.6.2] it was observed that substrates that were pre-treated with the photo-resist seeding method had a significantly higher measured rms surface roughness than those that were pre-treated with the diamond powder scratching method. Photos that were taken of two diamond coated glass substrates are shown in figure 6.6 and figure 6.7. The film on the left in the photos was pre-treated with the photo-resist method, the film on

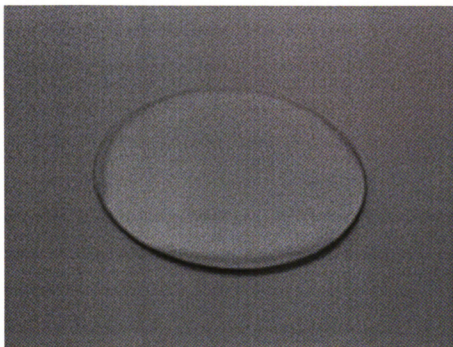


Figure 6.4 Photo of the diamond film on substrate G7-66.

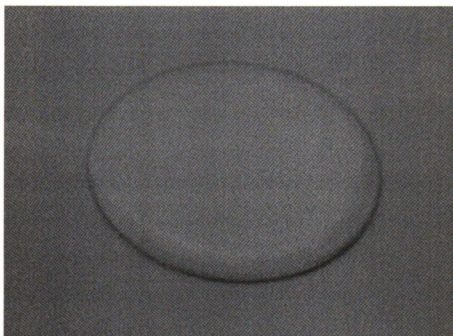


Figure 6.5 Photo of the diamond film on substrate G7-30.

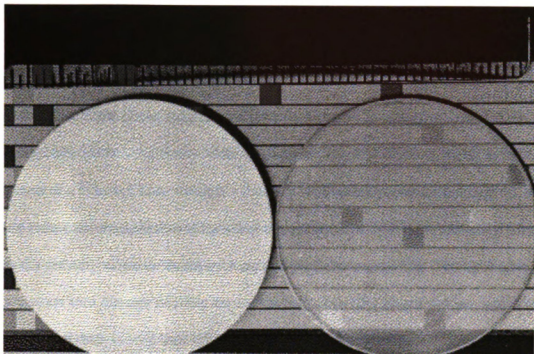


Figure 6.6 Photo of diamond coated glass substrates sitting on a color plate.

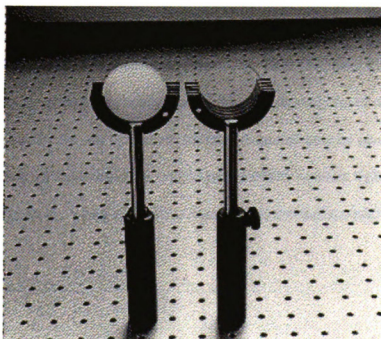


Figure 6.7 Photo of diamond coated glass substrates on an optical table.

the right was pre-treated with the diamond powder scratch-seeding method. In both instances, the diamond particles used had a diameter of 0.25µm and less. The thickness of the two films, as determined by weight gain, was approximately 1µm. From the photos, it is observed the apparent optical transmission of the scratch-seeded diamond film is much better than that of the photo-resist seeded diamond film. In fact the photo-resist seeded film seen in the photo has a frosty white appearance. This is an indication that the surface roughness of a diamond film, which is a function of substrate pre-treatment method, can greatly reduce the transmission of light. For comparison, the light-table mounting holes in figure 6.7 are only viewable through the scratch-seeded diamond film. The light-table holes that are seen through this film are several feet behind the glass substrate, which is an indication that there is very little diffusion of light through this film.

6.4 Optical Transmission of Diamond Films Grown on Glass Substrates

6.4.1 Theoretical Optical Transmission Through a Thin Diamond Film

For the ideal case of an optically smooth, planar diamond film of uniform thickness, d , on a glass substrate, the optical transmission is limited only by specular reflection. The classic relation for the intensity of transmitted, normally incident light through a thin film from air to glass, T_c , which is shown in figure 6.8, is defined in equation [6.1]^[85].

$$T = \frac{(1 - (r_{01})^2)(1 - (r_{12})^2)}{1 + (r_{01})^2(r_{12})^2 + 2r_{01}r_{12}\cos\left(\frac{4\pi n_1 d}{\lambda}\right)} \quad \text{eq (6.1)}$$

The terms r_{mn} are fresnel reflection coefficients. The indices 0, 1 and 2 correspond to air,

diamond and glass respectively. Hence, the term n_1 is the refractive index of the diamond film. The term λ is the wavelength of the incident light in free space. In equation [6.1], optical absorption is assumed to not be present in the thin diamond film. Absorption due to C-C bond vibrations in the far infrared and electronic transitions across the band gap in the ultra violet are phenomenon that occur outside the wavelength range considered here. Furthermore, absorption due to defect states in the diamond film are also considered to be negligible.

Equation [6.1] can be modified for light that originates in glass and transmits to air, T, which is shown in figure 6.8. The result is shown in equation [6.2].

$$T = \frac{(1 - (r_{12})^2)(1 - (r_{10})^2)}{1 + (r_{21})^2(r_{10})^2 + 2r_{21}r_{10}\cos\left(\frac{4\pi n_1 d}{\lambda}\right)} \quad \text{eq (6.2)}$$

The diamond to air fresnel reflection coefficient r_{10} is defined as

$$r_{10} = \frac{(n_1 - n_0)}{(n_0 + n_1)} \quad \text{eq (6.3)}$$

and the glass to diamond fresnel reflection coefficient r_{21} is defined as

$$r_{21} = \frac{(n_2 - n_1)}{(n_1 + n_2)} \quad \text{eq (6.4)}$$

where n_0, n_1 , and n_2 are the refractive index for air, glass and diamond respectively.

Since the light in equation [6.2] originates in the glass, the effects of light traveling from air into the glass and multiple reflections in the glass must be added, T_{obs} , which is

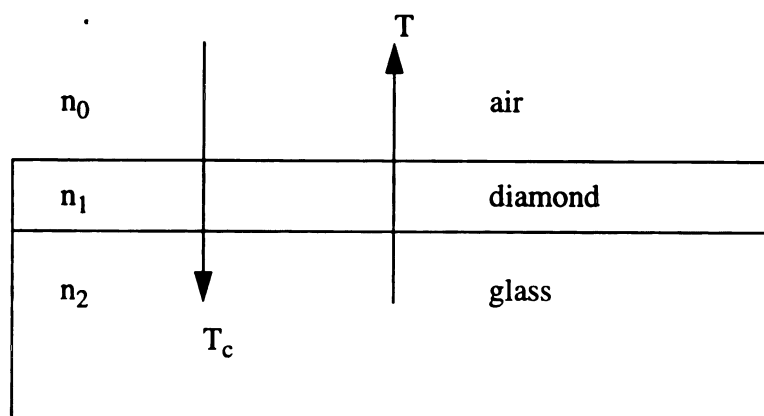


Figure 6.8 Graphical description of T and T_c .

shown in figure 6.9. Coherent interference in the glass is not included since the glass is optically thick. The observed transmission, T_{obs} , through the glass and diamond from air and back to air is shown in equation [6.5]^[86].

$$T_{obs} = T(1 - R_{20})(1 + R_{20}(1 - T) + [R_{20}(1 - T)]^2 + \text{higher orders}) \quad \text{eq (6.5)}$$

The term R_{20} is the power reflection coefficient at the glass/air interface and is equal to $(r_{20})^2$. The Fresnel reflection coefficient r_{20} is similar to those in equation [6.3] and equation [6.4]. The higher order terms in equation [6.5] contribute on the order of 0.1% and are ignored in this treatment.

The ideal transmission resulting from a 1 μm thick diamond film on a glass substrate as predicted by equation [6.5] is shown in figure 6.10. The refractive index values for air, glass, and diamond were chosen to be 1, 1.5, and 2.4 respectively. Also shown in figure 6.10, for comparison purposes, is the transmission for a free standing, 1 μm thick diamond film. Note that the glass acts as an anti-reflection layer, improving the average transmission.

6.4.1.1 Sellmeier Equation

For light with wavelengths ranging from 0.225 μm through the infrared, the refractive index n_1 of diamond is described by the Sellmeier Equation^[93]

$$n_1^2 - 1 = \frac{4.3356\lambda^2}{\lambda^2 - (0.1060)^2} + \frac{0.3306\lambda^2}{\lambda^2 - (0.1750)^2} \quad \text{eq (6.6)}$$

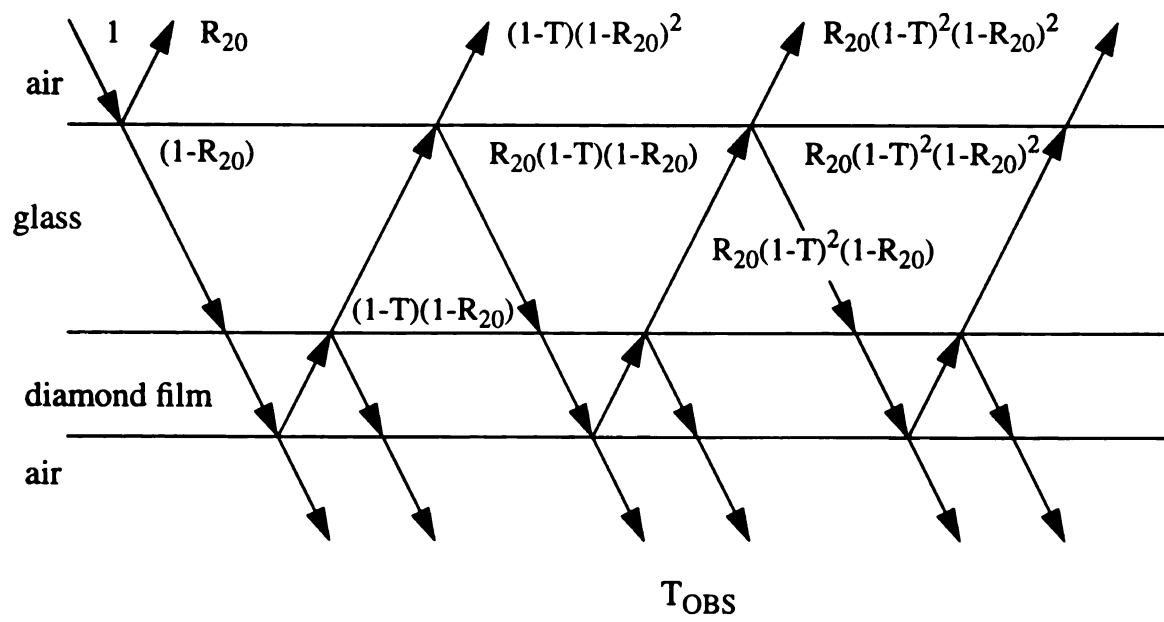


Figure 6.9 Graphical description of T_{obs} .

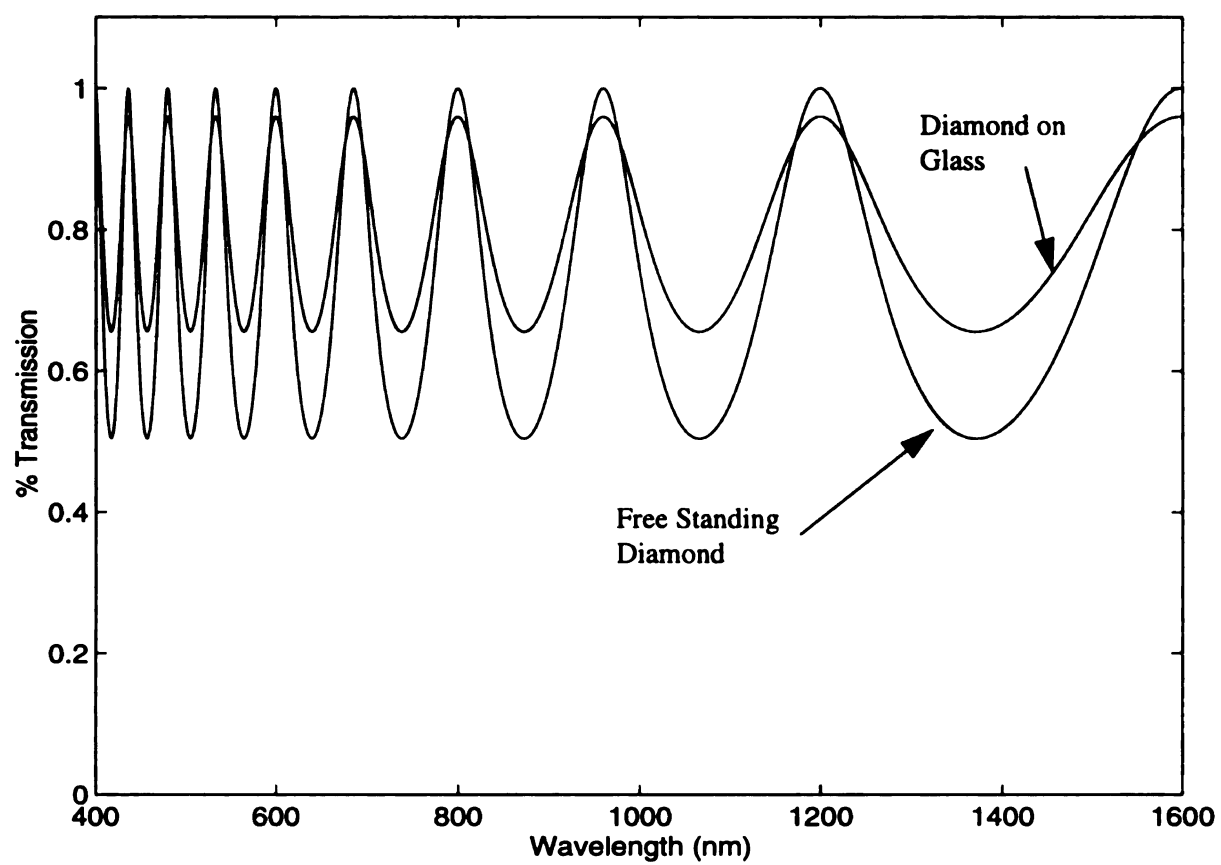


Figure 6.10 Theoretical optical transmission of diamond films.

The wavelength λ in equation [6.6] is in micrometers. A plot of n_1 as described by equation [6.6] is shown in figure 6.11 for wavelengths from 400 nm to 1600 nm.

6.4.1.2 Inclusion of Scattering at the Diamond-Air Interface

Actual CVD diamond films on glass differ from the ideal case in that the growth of diamond nuclei leads to polycrystalline films with rough surfaces. These surface irregularities cause phase differences in light as it transmits through the rough interface, from the diamond film to air. Such phase differences result in interference that can significantly reduce the amount of light transmitted through a thin diamond film.

Following Filinski^[87], a correction factor for power transmission, S_T , may be included in equation [6.2] to compensate for the rough surface of the thin film.

$$S_T = \exp\left[-\left(\frac{2\pi\sigma(n_0 - n_1)^2}{\lambda}\right)^2\right] \quad \text{eq (6.7)}$$

Here, σ is the root-mean-square of the surface roughness, assuming a Gaussian distribution. The free-space wavelength of light is λ . The power transmission through the rough diamond surface from diamond to air is defined as T_{10} .

$$T_{10} = (1 - r_{10}^2)S_T \quad \text{eq (6.8)}$$

The thin film's rough surface also effects the interference terms due to multiple reflections within the diamond film. The power reflection at a rough surface is multiplied by a correction term S_R .

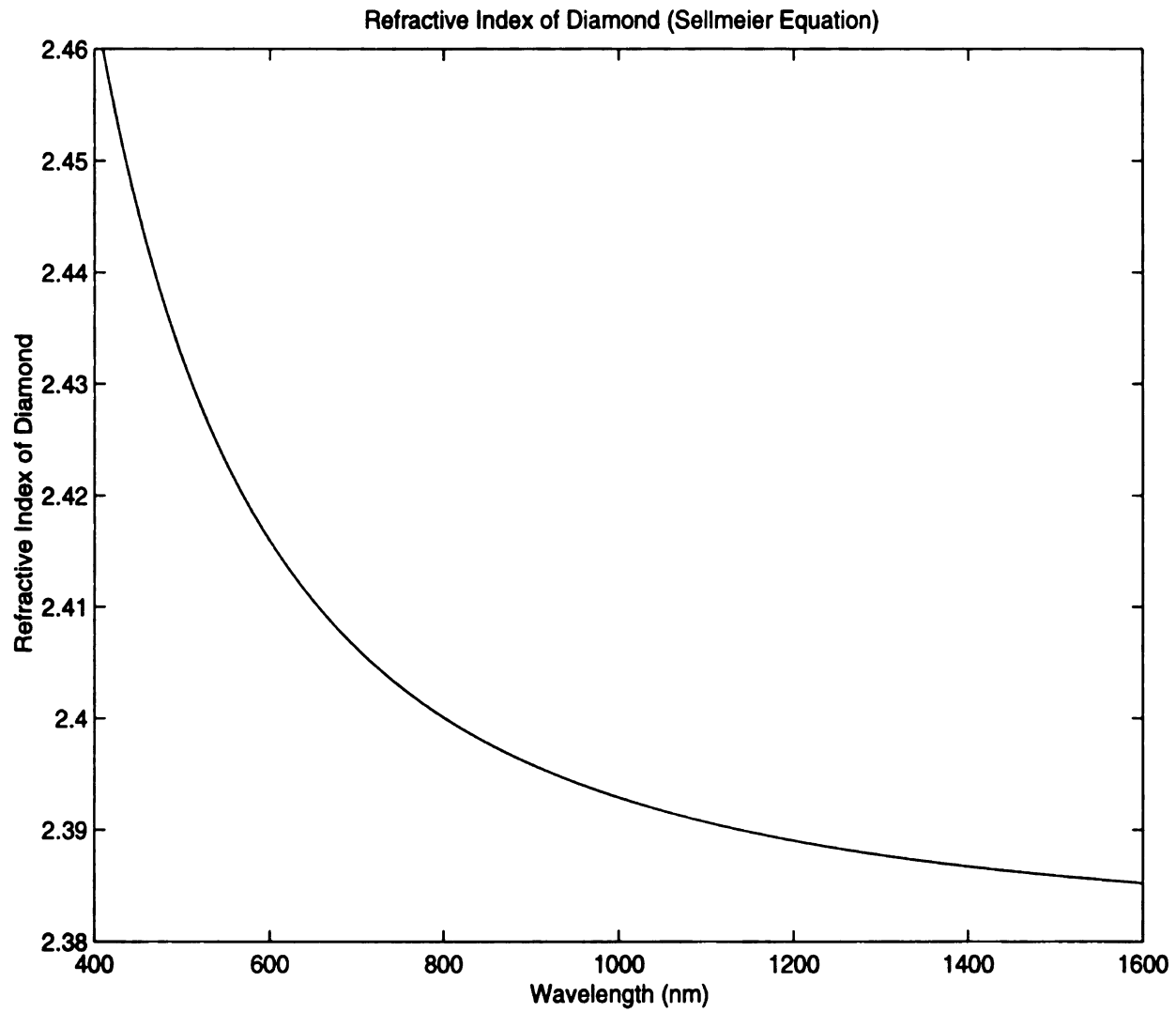


Figure 6.11 A plot of n_1 as described by the Sellmeier Equation.

$$S_R = \exp\left[-\left(\frac{4\pi\sigma n_1}{\lambda}\right)^2\right] \quad \text{eq (6.9)}$$

The refractive index n_1 is the medium in which the light is traveling, in this case diamond.

If one also assumes that the field amplitude reflection coefficient is corrected by a factor $(S_R)^{1/2}$, then the expression for T in equation [6.2] is modified to account for the rough surface with the terms in eq. [6.7], eq. [6.8] and eq. [6.9] to become $T_R^{[88][89][90]}$.

$$T_R = \frac{(1 - r_{21}^2)(1 - r_{10}^2)S_T}{1 + (r_{21})^2(r_{10})^2S_R + 2r_{21}r_{10}\sqrt{S_R}\cos\left(\frac{4\pi n_1 d}{\lambda}\right)} \quad \text{eq (6.10)}$$

The observed transmission T_{OBS} from air to air through the glass and the diamond film is redefined in equation [6.11] as $(T_{obs})_R$, for the case of a diamond film with a rough surface.

$$(T_{obs})_R = T_R(1 - R_{20})(1 + R_{20}(1 - T_R) + [R_{20}(1 - T_R)]^2 + \text{higher orders}) \quad \text{eq (6.11)}$$

Figure 6.12 shows graphs of the theoretical transmission of thin diamond films that have surface roughness ranging from 0 nm to 100 nm. These graphs were created with equation [6.11], which assumes that absorption in the diamond is negligible. The films in the figure are also assumed to be adhering to thick glass substrates. It is observed from the graphs in the figure that at wavelengths of 400 nm the transmission is reduced from near 90% to near 0%. This reduction in transmission is due to the increase in rms surface roughness from 0 nm to 100 nm respectively. For applications that require transmission of at least 60% at wavelengths near 400 nm, the data in the figure indicates that the rms film

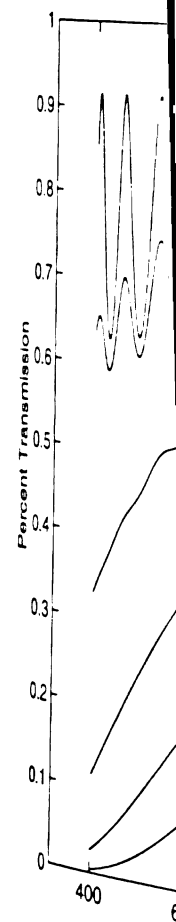


Figure 6.12

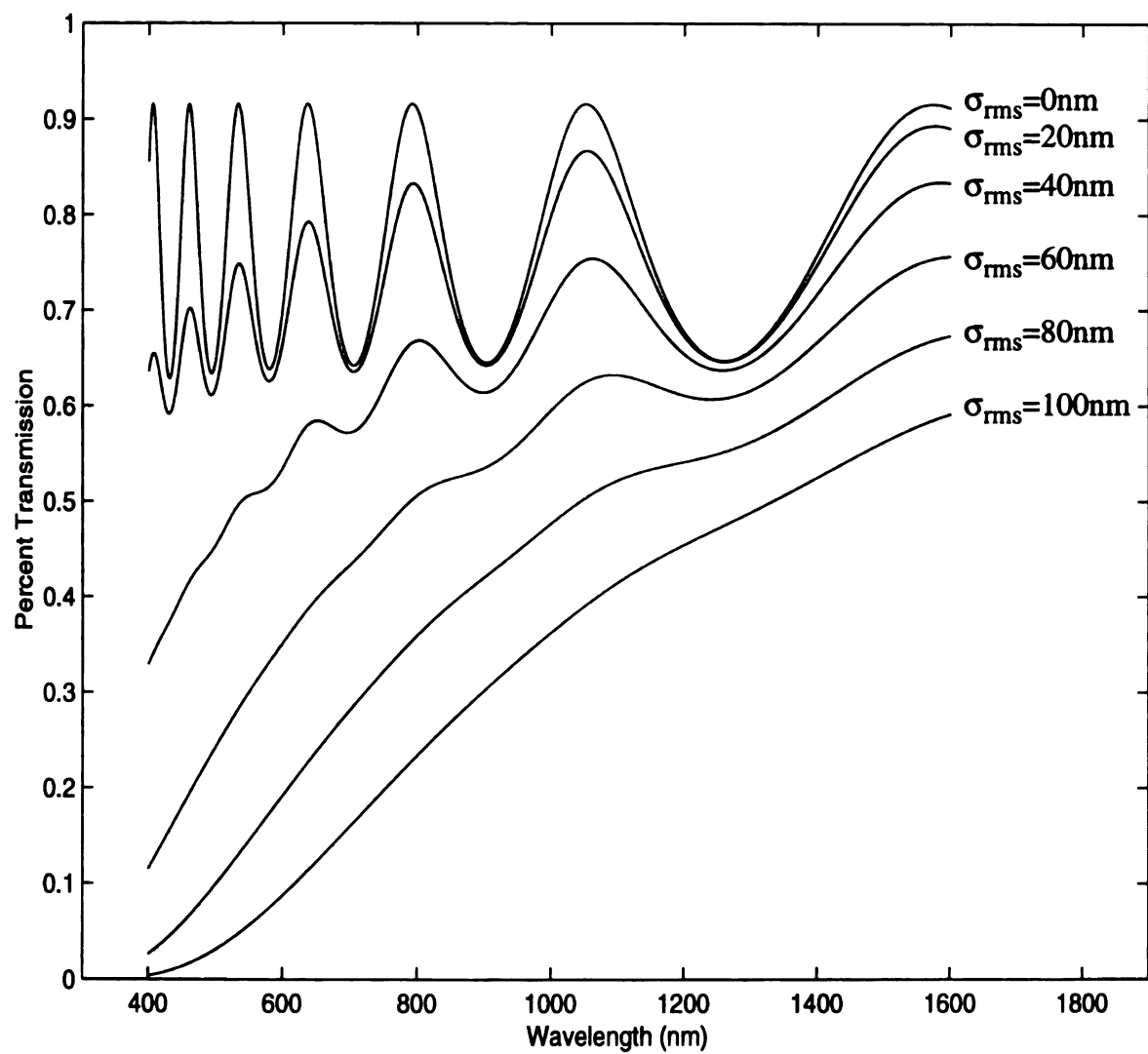


Figure 6.12 Theoretical optical transmission of rough diamond films.

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6.4.2 Measurements of Optical Transmission Through a Thin Diamond Film

During the development of the optical transmission equation for thin diamond films on glass substrates, equation [6.11], it was shown that the surface roughness of the film, at the diamond-air interface, can significantly reduce optical transmission. These transmission losses that result from the film's surface roughness have a wavelength dependence and are first noticeable at the blue end of the visible spectrum.

In section [5.6.2], it was noted that the substrate pretreatment method, i.e. seeding method, and the deposition chemistry significantly affect the surface roughness of diamond films that are deposited in the MCPR operating regime of this dissertation. Diamond films that were deposited on substrates, which were pretreated with diamond powder scratching, had measured rms surface roughness, σ_{rms} , that were lower than equivalent films that were grown on photo-resist seeded substrates. This presumption that photo-resist seeding could not yield transparent films was confirmed in section [6.3.4]. It was observed by visual inspection that photo-resist seeding and scratch seeding resulted in noticeably different amounts of light scattering and optical transmission. When comparing the rms surface roughness of films that were deposited with varying chemistries, it was also observed in section [5.6.2] that the lowest measured surface roughness resulted from gas flows of 200 sccm of H_2 , 8 sccm of CO_2 and 8 sccm of CH_4 .

To further investigate these effects, optical transmission measurements were taken from films that were grown under different conditions. For these measurements, diamond films were grown on 2-inch diameter Corning 7059 glass substrates that had a thickness of

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1.1mm. Prior to deposition, the glass substrates were pre-treated with one of the above mentioned methods. In all cases the H_2 flow rate was 200 sccm. The CO_2 and CH_4 flow rates were varied between 0 sccm and 20 sccm. The specific process conditions for each deposition experiment are listed in Appendix E.

Optical transmission measurements were taken near the center of each film for light ranging from 400-nm to 1600-nm in increments of 20-nm by the method that was presented in section [3.4.3], *Film Thickness Measurements*. Afterwards, the theoretical optical transmission, which is described by equation [6.11], was fitted to the measured optical transmission by adjusting the theoretical film thickness, d , and rms surface roughness, σ_{rms} . The resulting measured and theoretical optical transmission spectra for the diamond films on substrates G7-2, G7-27, G7-30, G7-52, G7-60, G7-63, G7-66 and G7-67 are shown in figure 6.13 through figure 6.20.

The optically measured thickness in the center of these films was determined to be in the range of approximately 600-nm to near $2\mu m$. For comparison, the film thickness was also determined from the substrate weight gains as was outlined in section [3.4.3.1], and the surface roughness of some of the films was measured by Dektak. Table 6.2 lists the measured and theoretical values for the thickness, d , and rms surface roughness, σ_{rms} , for the films in figure 6.13 through figure 6.20. From the transmission spectra and the data in table several observations were made.

First, the measured values of surface roughness from the Dektak were substantially less than the fitted surface roughness from the figures. In the future, these measurements should be re-investigated with a scanning force microscope. An atomic force microscope requires cutting or breaking small sections from the substrates. Which for the 1.1-mm

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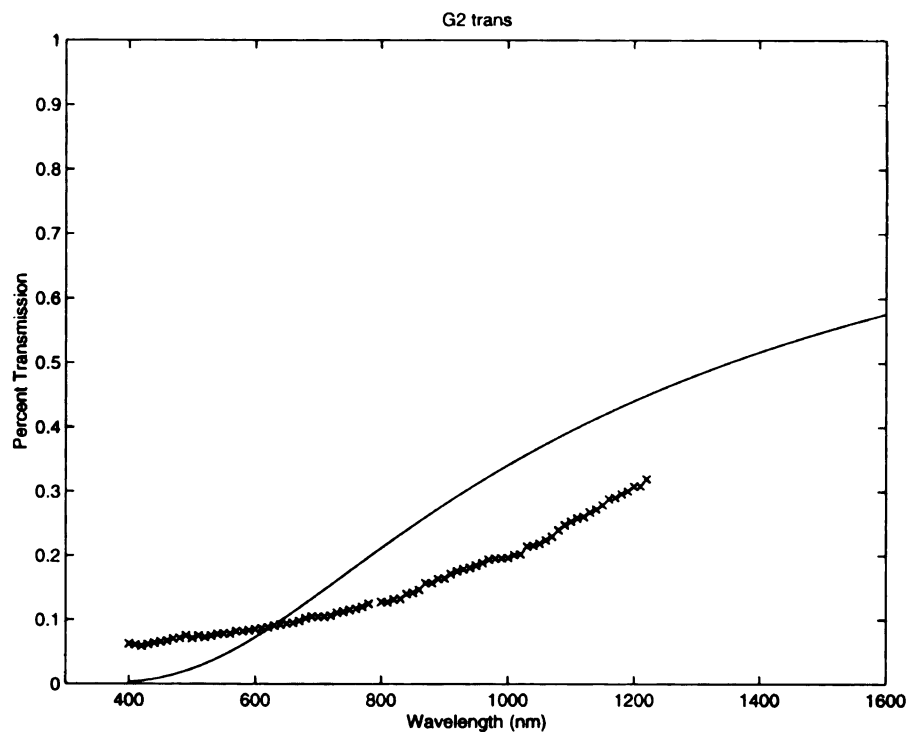


Figure 6.13 Optical transmission of G7-2.

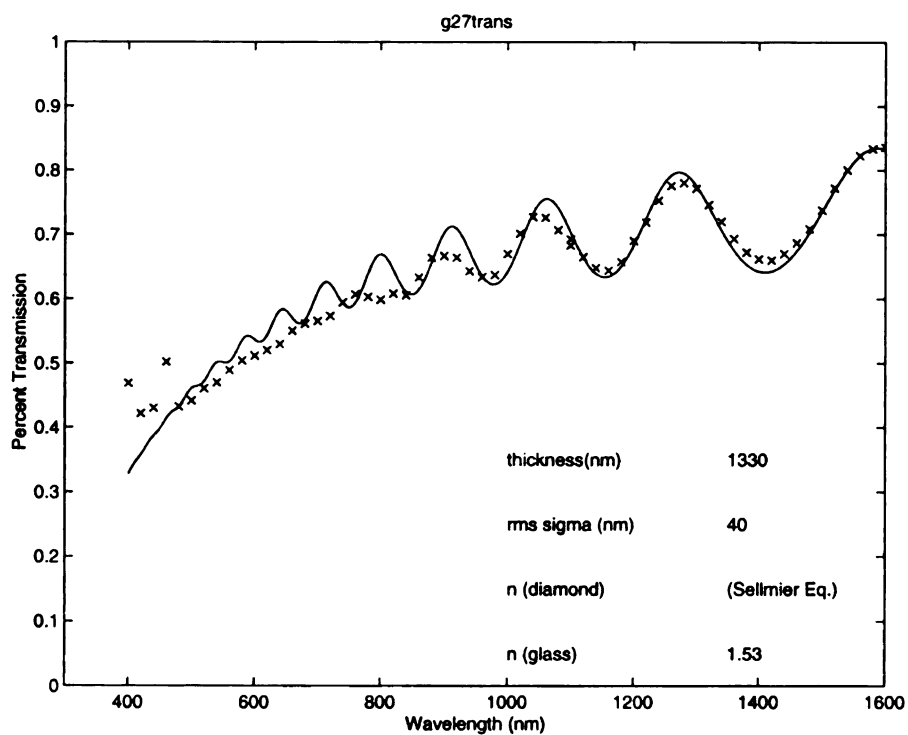


Figure 6.14 Optical transmission of G7-27.

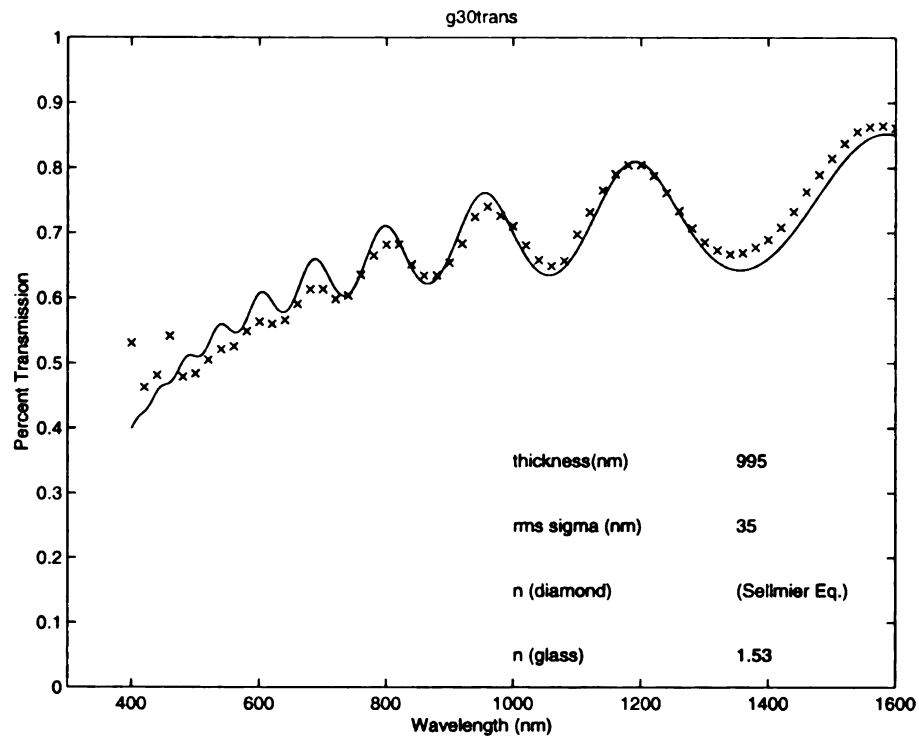


Figure 6.15 Optical transmission of G7-30.

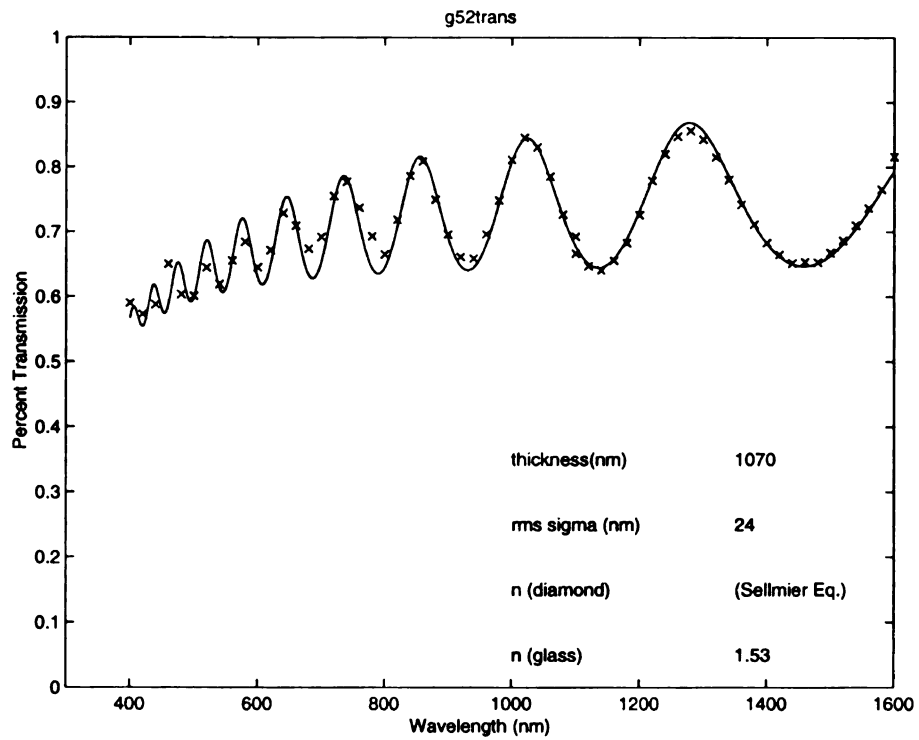


Figure 6.16 Optical transmission of G7-52.

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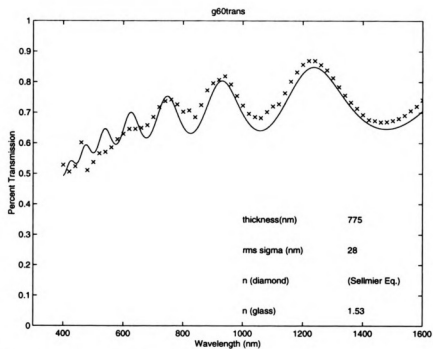


Figure 6.17 Optical transmission of G7-60.

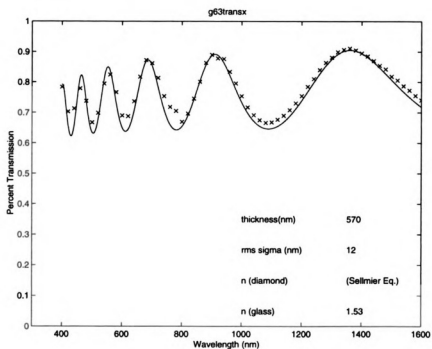


Figure 6.18 Optical transmission of G7-63.

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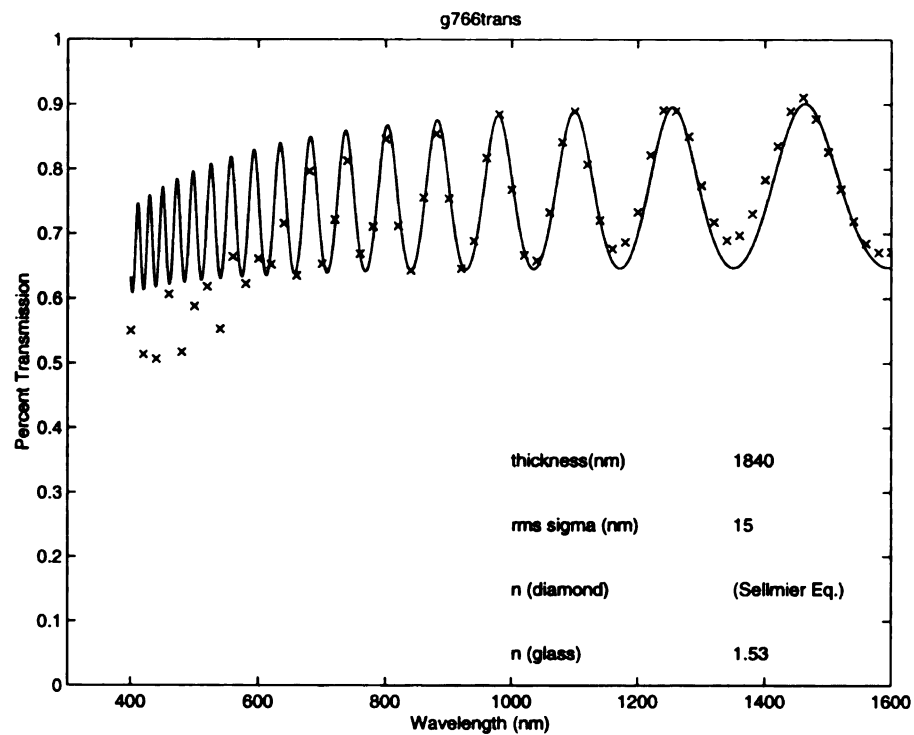


Figure 6.19 Optical transmission of G7-66.

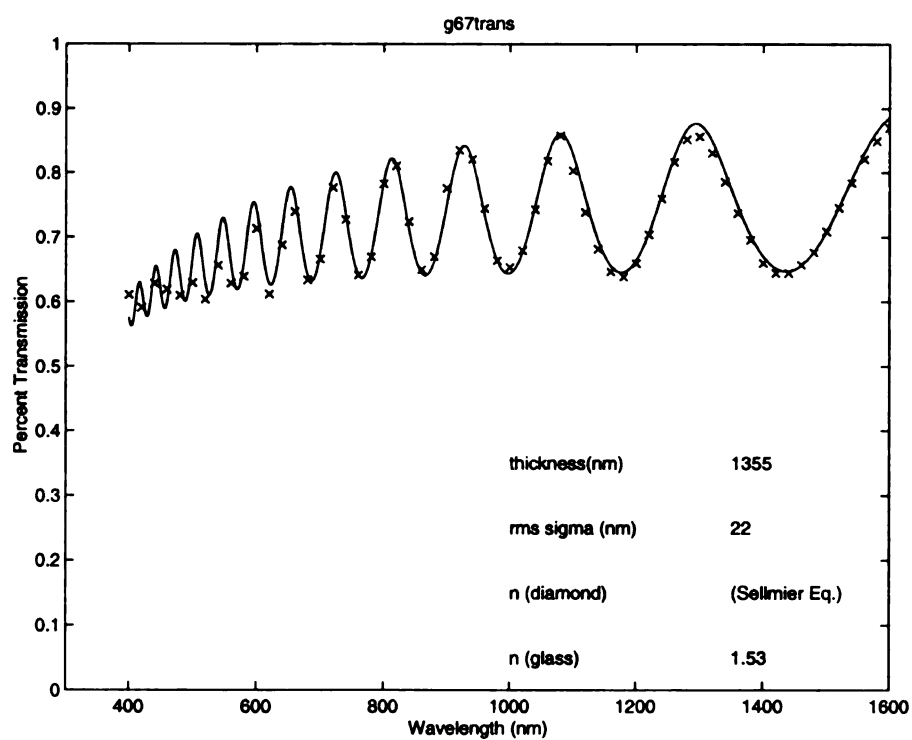


Figure 6.20 Optical transmission of G7-67

Substrate	
G7-2	2
G7-27	2
G7-30	2
G7-52	2
G7-60	2
G7-63	200
G7-66	20
G7-67	200

Table 6.2

Substrate	Deposition Chemistry $\text{H}_2\text{-CO}_2\text{-CH}_4$ (sccm)	Measured Weight Gain (mg)	Film Thickness, d Determined by Weight Gain (nm)	Film Thickness, d Determined by Optical Transmission (nm)	Surface Roughness, σ_{rms} Measured by Dektak (nm)	Surface Roughness, σ_{rms} Determined by Optical Transmission (nm)	Raman FWHM
G7-2	200-8-3	7.4	1040	N/A	104	N/A	14.1
G7-27	200-8-3	6.7	940	1330	20	40	15.0
G7-30	200-8-3	5.2	730	990	15	36	13.8
G7-52	200-0-5	8.5	1190	1070		24	
G7-60	200-0-5	6.0	840	775		28	13.7
G7-63	200-0-20/5	4.3	600	570		12	14.3
G7-66	200-8-8	12.0	1680	1840		15	14.1
G7-67	200-0-20/5	10.3	1450	1355		22	

Table 6.2: Experimental Data for Diamond Films on 7059 Glass Substrates

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thick glass substrates randomly caused the films to peel from such substrates. For the remainder of the discussion in this section only the optically determined surface roughness will be included.

Second, the film with the highest measured and theoretical σ_{rms} and the lowest transmission at 400-nm was G7-2. It was the only one of the eight films in the figures that was deposited with photo-resist seeding. This confirms the fact that photo-resist seeded films that do not have a highly oriented texture have a significant amount of scattering and very low optical transmission in the spectrum from 400-nm to 1600-nm. This film had a frosty-white appearance and no brown or grey shades. Hence, its transmission losses are due to scattering not absorption. The theoretical optical transmission of equation [6.11] could not be matched to the measured optical transmission of G7-2. Perhaps the surface roughness of the film did not have a Gaussian distribution and a value $\ll \lambda$ as was assumed during the development of equation [6.11].

The other diamond films, G7-27 through G7-67, were deposited with scratch seeding and one of four deposition chemistries. G7-27 and G7-30 were deposited with gas flows of 200 sccm of H_2 , 8 sccm of CO_2 and 3 sccm of CH_4 . G7-52 and G7-60 were deposited with gas flows of 200 sccm of H_2 and 5 sccm of CH_4 . G7-63 and G7-67 were unique in that they were deposited with a two step process. For the first 30 minutes, the gas flows were 200 sccm of H_2 and 20 sccm of CH_4 . Afterwards, the CH_4 flow rate was reduced to 5 sccm. It was reported by Wu and Rai that a high concentration of methane at the beginning of deposition results in an order of magnitude increase in nucleation density on scratch seeded silicon wafers^[77]. Hence, this process was included in this work. G7-66 was deposited with gas flows of 200 sccm of H_2 , 8 sccm of CO_2 and 8 sccm of CH_4 .

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As was postulated in earlier sections, these chemistries produced films with a range of measured optical transmission and optically determined surface roughness. There was no chemistry that provided the lowest surface roughness and the best optical transmission throughout the range of 400-nm to 1600-nm. The chemistry that yielded the lowest optically determined σ_{rms} was that of G7-66; however, this film exhibited a λ dependent absorption in visible range. From the optical transmission spectrum in figure 6.19 it is apparent that it has a λ dependent absorption in the wavelength range from 400-nm to approximately 600-nm. This film has a slight brownish color, which indicates that it has some absorption in it. So while its low σ_{rms} resulted in a nearly ideal transmission in the near infrared, its absorption negated the achievement throughout most of the visible range. The chemistry with the best transmission in the visible range was the 2-step process that was used on G7-63 and G7-67. Although they did not have a σ_{rms} as low as G7-66, they were free of detectable absorption.

An evaluation of the films that did not exhibit detectable absorption is summarized as follows. The films with the lowest transmission at 400-nm were G7-27 and G7-30, which correlates well with the results of section [5.6.2], *Measurements of Film Surface Roughness*. They had optical transmissions at 400-nm in the range of 40% to 50% and σ_{rms} near 40-nm. The next best range of optical transmission at 400-nm and lowest σ_{rms} were measured from G7-52 and G7-60. They had optical transmissions at 400-nm in the range of 50% to 60% and their σ_{rms} were in the range of 24-nm to 28-nm. The films highest range of optical transmission at 400-nm were G7-63 and G7-67. They had optical transmissions at 400-nm in the range of 60% to >70% and their σ_{rms} were in the range of 12-nm to 22-nm. Again what was unique about G7-63 and G7-67 was that they were

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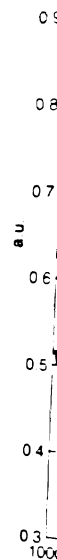
grown with a two-step process. The film G7-63 was so clear that it was nearly undetectable until the substrate's weight gain and optical transmission were documented.

The film on G7-66 was the thickest one that was measured. It was also the only film that exhibited obvious absorption. A further investigation of this is required to determine if this absorption is unique to this deposition chemistry. Possible sources for absorption in this film are a high percentage of sp^2 bonds and inclusion of nitrogen. The latter is reported to produce yellow to brown looking diamond. Data from Chrenko and Strong shows that nitrogen content in diamond can shift the absorption edge from 230-nm to near 600-nm.^[99]

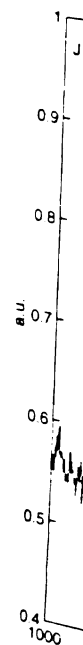
While there were vast differences in the optical transmission properties of the diamond films presented here, there was very little difference in that Raman spectrum. All the films had a diamond peak near 1332 cm^{-1} . Their spectra, which de-convolved into peaks near 1440-cm^{-1} and 1520-cm^{-1} , also indicated that amorphous carbon was present. The FWHM are listed in table 6.2. The individual Raman spectra are shown in figure 6.21 through figure 6.26.

6.5 Observations of the Adhesion of the Diamond Films on Glass Substrates

CVD diamond film delamination is often reported to be problematic, and was the primary motivation for maintaining low substrate temperatures during deposition on glass substrates for this dissertation. More than 100 diamond films were deposited on silicon substrates and only one of them showed any signs of delamination. Conversely however, many of the diamond films that were deposited on glass substrates did eventually delaminate. Delamination of the diamond films from the glass substrates had a high occurrence



Figure



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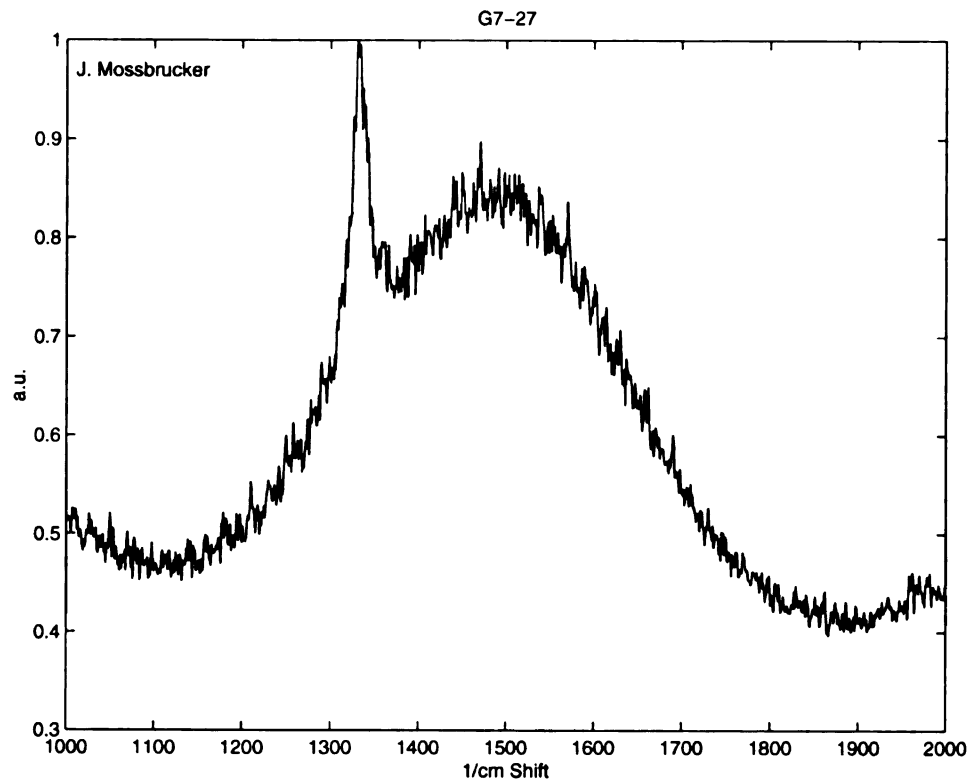


Figure 6.21 The Raman B spectrum recorded from substrate G7-27.

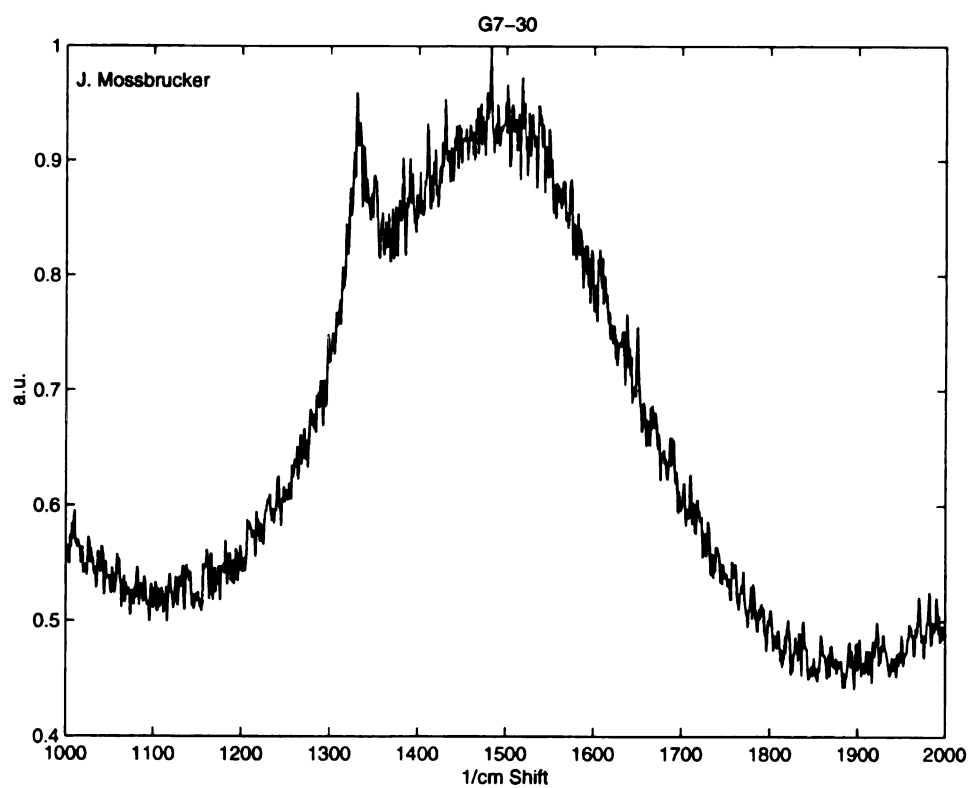


Figure 6.22 The Raman B spectrum recorded from substrate G7-30.

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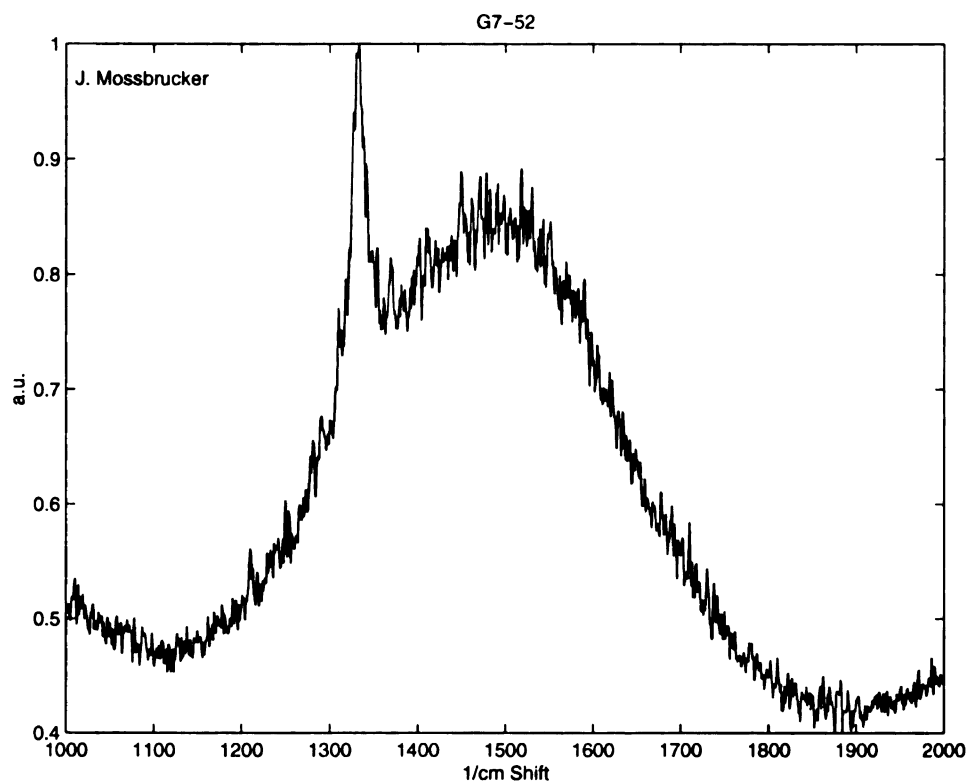


Figure 6.23 The Raman B spectrum recorded from substrate G7-52.

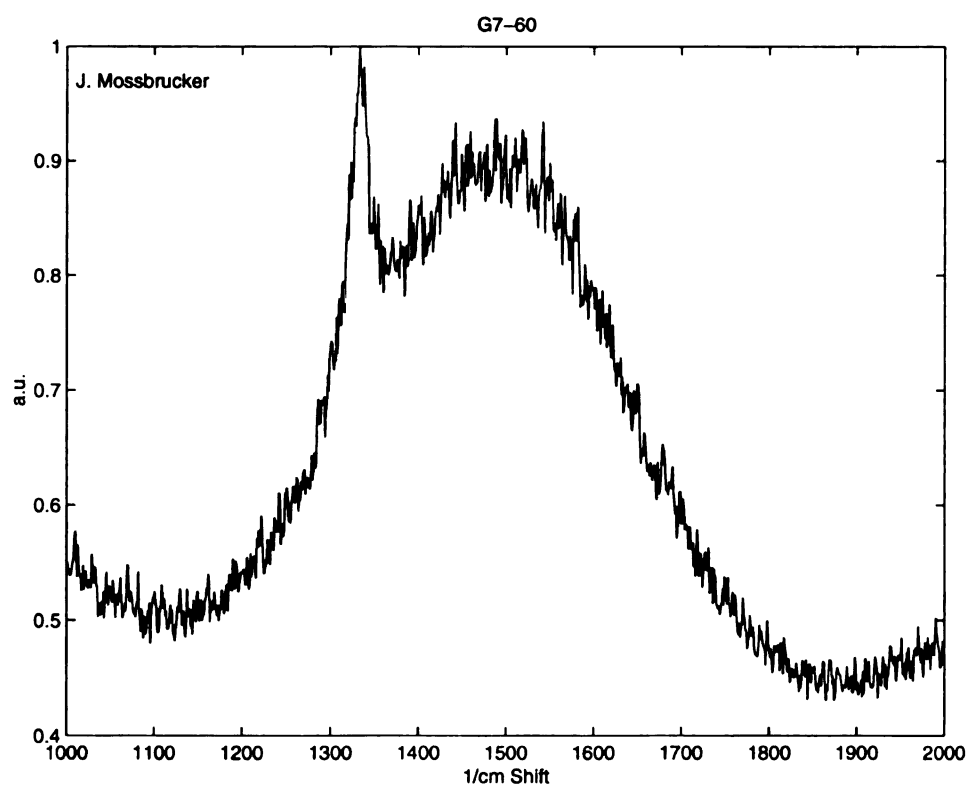


Figure 6.24 The Raman B spectrum recorded from substrate G7-60.

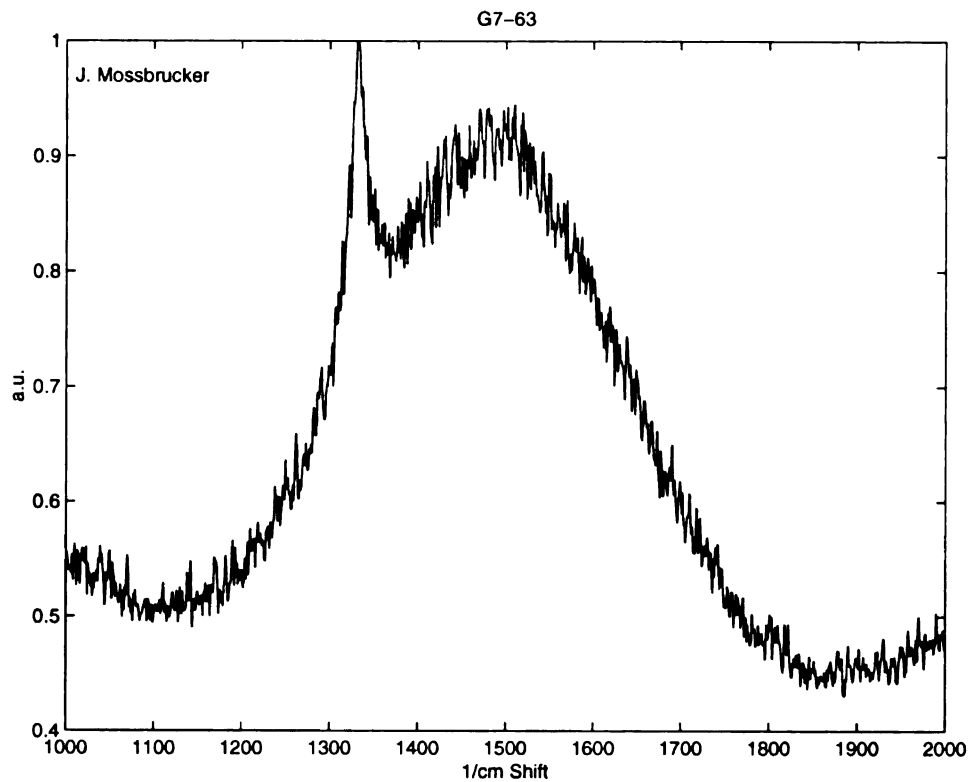


Figure 6.25 The Raman B spectrum recorded from substrate G7-63.

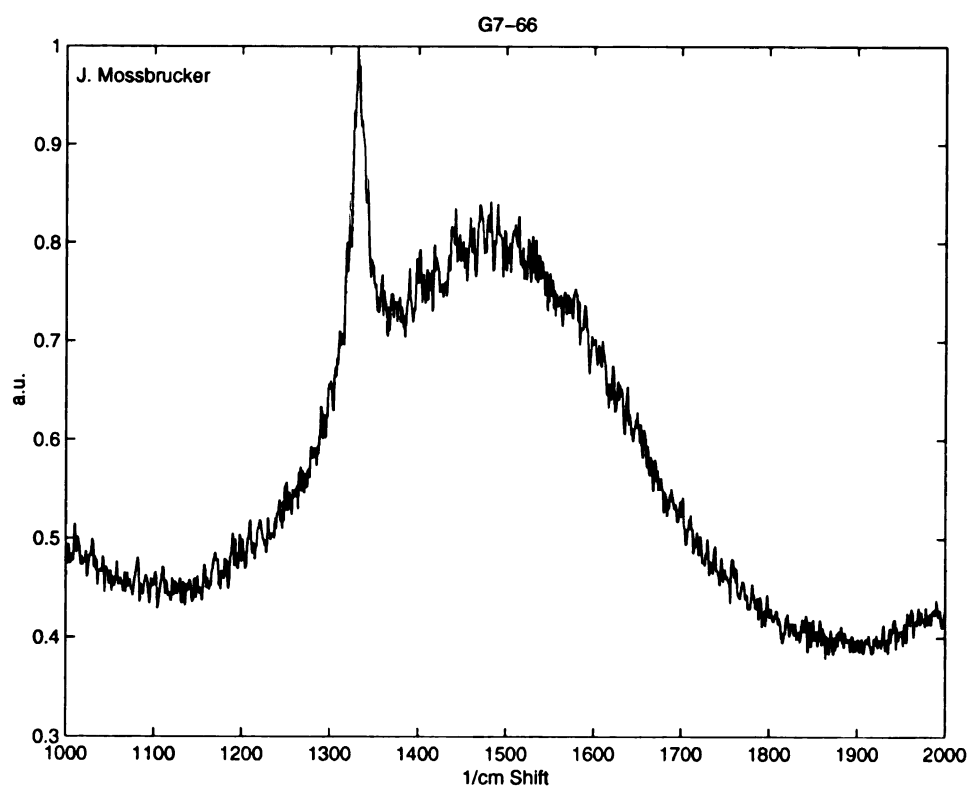


Figure 6.26 The Raman B spectrum recorded from substrate G7-66.

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as either partial or complete delamination. A total of 35 polycrystalline diamond films with a weight gain of 5 mg or more were deposited on 2-inch diameter Corning 7059 substrates during a period of approximately 5 years. In the time since these films were grown, more than half of them have peeled to some extent.

6.5.1 Intrinsic and Thermal Strain in Diamond Films

The difference between the occurrence of delamination from the silicon and the glass may be related to the amount of strain that is present at the interface of the film for these two substrates. Strain at the diamond-substrate interface is created two ways, by internal strain in the film and by thermal strain at the interface between the film and the substrate. It is unlikely that there was a large difference in the film's internal strain with regards to substrate material used for this dissertation; however, the thermal strain is much larger for the borosilicate glass substrates that were used during this dissertation than it is for silicon substrates. Hence, one would expect a higher occurrence of delamination from the glass substrates.

A report by Windischmann and Epps showed that the internal strain in diamond films that are deposited by microwave plasma CVD is a function of gas composition and deposition temperature.^[100] It was reported that the film's internal strain is tensile when the deposition temperature is in the range of 550 C to 900 C. The magnitude of this intrinsic strain was noted to decrease with decreasing substrate temperature and increasing methane concentration. Its origin was explained in terms of a grain boundary relaxation model due to a fine-grained porous micro-structure. The inverse relationship between the intrinsic strain and the methane concentration was attributed to impurities such as sp^2 car-

bon and hydrogen.

For diamond films that are deposited on glass substrates, a significant amount of thermal strain is created at the film-substrate interface. The thermal strain for two isotropic materials that have differing thermal expansion coefficients (CTE) is shown in equation [6.12].^[101]

$$\varepsilon = (\alpha_f - \alpha_s)_i \Delta T_i \quad \text{eq (6.12)}$$

The term ε is the thermal strain at the interface and is not necessarily the strain in the bulk material. The terms α_f , α_s and ΔT are the CTE of diamond, the CTE of the substrate and temperature range for the *i*th interval respectively. For the thin diamond films that were grown during this dissertation, the stress throughout the diamond can be described by Hooke's Law of thin planar strain, which is shown in equation [6.13].

$$\sigma_f = \frac{E_f}{(1 - \nu_f)} \quad \text{eq (6.13)}$$

The assumption is that the film is very thin and that the strain in the film is uniform throughout. The term $E_f/(1-\nu_f)$ in equation [6.13] is the biaxial Young's modulus of the diamond film, which can be approximated to be that of bulk diamond 1345 GPa^[102]. From equation [6.13] and the CTE of diamond^[103] and Corning 7059 glass^[104], the calculated thermal stress in a diamond film on a Corning 7059 glass substrate is approximately 1.7 GPa compressive for a temperature change from 475 C to 25 C, using 100 C intervals.

6.5.2 Observations of Film Adhesion to Corning 7059 Substrates

Observations of film adhesion to glass substrates were variable over the years. From the early experiments with photo-resist seeding it was observed that adhesion was directly related to the film thickness and deposition temperature. In more recent experiments with scratch seeding however, there have been inconsistencies in relating adhesion to the film thickness. Another variable in adhesion observations was the time required for a film to peel, which ranged from as little as a few minutes to as much as several months. In some cases, samples that were grown under presumably identical conditions had varying degrees of adhesion. What was consistent, was the manner in which the films peeled, which was independent of the time it took for the film to peel. The delamination began with film bubbling along narrow lines that look like small mountain ranges, such as the ones that are shown in figure 6.28. Eventually, large areas of the film would peel off as is shown in figure 6.27.

Another interesting characteristic was that the pieces of that film that peeled all had a potato-chip shape. They all appeared to bend down towards the glass side of the film, which indicates that the intrinsic strain in the film was more compressive on the substrate side than on the deposition side.

The early observations of adhesion were of films that were grown on substrates that were seeded by the photo-resist method. A summary of these observation is listed in table 6.3 for films that were grown on Corning 7050 substrates and table 6.4 for films that were grown on Corning 7059 Substrates.

All the films that are listed in table 6.3 were grown under identical conditions as are listed in Appendix H, and their temperatures were all near 450 C. From the data in the

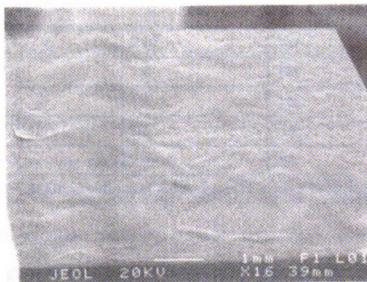


Figure 6.27 An SEM photo of a film peeling from a 7059 substrate.

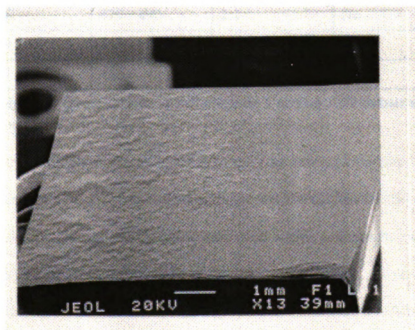


Figure 6.28 An SEM photo of leading edge of the peel region.

Substrate	Film Thickness (μm)	Long Term Adhesion?
GP-1	0.67	Yes
GP-4	1.0	Yes
GP-2	1.7	Yes
GP-3	2.5	No
GP-5	2.5	No

Table 6.3: Observations of Adhesion on Corning 7050 Substrates

Substrate	Substrate Temperature ($^{\circ}\text{C}$)	Film Thickness (μm)	Long Term Adhesion
G7-5	506 - 511	2.3	No
G7-6	479 - 490	2.1	No
G7-9	445 - 455	1.1	Yes
G7-7	450	1.0	Yes

Table 6.4: Observations of Adhesion on Corning 7059 Substrates

table its clear that the adhesion of films that were grown under these conditions has a thickness dependence. The films with a thickness under 2 μ m showed long term adhesion and those with a thickness over 2 μ m did not.

The films listed in table 6.4 were grown with identical chemistries and varying gas pressures, as are noted in Appendix B. Those that were grown at higher pressures had higher substrate temperatures and were thicker. Here again, the films under 2 μ m showed long term adhesion and those thicker than 2 μ m did not.

Observations of more recent films are listed in table 6.5. These films differ from those in table 6.3 and table 6.4 in two ways. They were grown on substrates that were scratch seeded with diamond powder and they had varying gas chemistries. These films were all grown at 9 torr and had similar substrate temperatures in the range of 465 C. The data lists three films that exhibited partial or complete delamination, which had a thickness that was less than 2- μ m. The inconsistency is that the two thickest films, G7-66 and G7-67, did not peel.

6.6 Summary

It has been demonstrated in this chapter that transparent polycrystalline diamond films can be deposited on Corning 7059 substrates with current MCPR technology. The growth rate of these films is relatively low, on the order of 50-nm/hr to 80-nm/hr; however these rates are consistent with the deposition rates on silicon substrates that were reported in chapter 5. The uniformity of these films was also equal to that of the films that were deposited on silicon substrates. Single color films with 10% and better uniformity were routinely deposited on Corning 7059 glass substrates with diameters of 2-inches. Pilot

Substrate	Chemistry $\text{H}_2\text{-CO}_2\text{-CH}_4$ (sccm)	Pressure (torr)	Thickness Determined by Weigh Gain (mm)	Long Term Adhesion	Partial Delamination	Complete Delamination
G7-52	200-0-5	9	1.2		X	
G7-60	200-0-5	9	0.84	X		
G7-61	200-0-20/5	9	1.1			X
G7-62	200-0-20/5	9	1.0			X
G7-63	200-0-20/5	9	0.6	X		
G7-66	200-8-8	9	1.7	X		
G7-67	200-0-20/5	9	1.7	X		

Table 6.5: Observation of Adhesion of Scratch Seeded Films

experiments with a substrate heater indicated that MCPR-C8, which had a substrate heater, offered no distinguishable advantage in deposition uniformity over the other MCPR configurations.

Observations and measurements of the optical transmission of diamond films that were adhering to Corning 7059 substrates demonstrated that transmission was a function of substrate pre-treatment method and deposition chemistry. It was shown that scratch seeded films have a higher transmission than photo-resist seeded films throughout the wavelength range of 400-nm to 1600-nm. The optical transmission of films that were grown with varying chemistries had mixed results. The chemistry with the lowest optically fit surface roughness was the mixture of 200 sccm of H_2 , 8 sccm of CO_2 and 8 sccm of CH_4 . In the near IR from approximately 800-nm to 1600-nm this mixture also had the best optical transmission. In the visible region though, from 400-nm to 600-nm, the film grown with this mixture exhibited absorption, which notably reduced its transmission in this range. The best optical transmissions in the wavelength range of 400-nm to 800-nm were the films that were grown with a two-step process. The two-step process had a high methane flow of 10% CH_4 for the first 30 minutes of the deposition and a CH_4 flow of 2.5% for the remainder. Films grown with this process had a slightly higher optically fit surface roughness than those grown with the mixture of 200-8-8; however, they did not exhibit any detectable absorption. Hence, the two-step process had the best optical transmission in the wavelength range of approximately 400-nm to 800-nm.

Observations of film adhesion were that many of the films that were deposited on Corning 7059 and 7050 borosilicate glass substrates exhibited some amount of delamination. For the films that were deposited with photo-resist seeded with a single chemistry,

adhesion appeared to be a function of film thickness and deposition temperature. Films that were thicker than 2- μm tended to peel and those with a thickness of 2- μm and less tended to adhere. The relationship between deposition chemistry and adhesion was not clear. Pilot experiments with varying chemistries resulted in some films delaminating even though thicker films that were deposited with the same chemistry did not.

Chapter 7

Summary and Conclusions

7.1 Contributions of this Dissertation

The primary contribution of this thesis was the development and investigation of a large-area, low-temperature diamond deposition process that produces adherent, optically transparent films on temperature-sensitive substrates. As a result of this work, it has been shown that current MCPR technology can be used to uniformly deposit thin diamond films on silicon and glass substrates. It has been demonstrated that in the low-pressure regime of the MCPR, below 15 torr, diamond films can be deposited over areas as large as 80 cm^2 with a uniformity of near $\pm 10\%$ over an area as large as 46-cm^2 . Furthermore, films with optical transmissions in the range of 60% to 70% at a wavelength of 400-nm have been deposited on boro-silicate glass substrates with this process.

7.2 Summary of Results

7.2.1 MCPR Configurations

Over the last two decades, several models of the Microwave Cavity Plasma Reactor (MCPR) have been developed at Michigan State University for plasma processing. Recently, industrial applications for MCPR technology such as plasma etching and plasma

chemical vapor deposition (CVD) have been investigated. Specifically, microwave plasma CVD of poly-crystalline diamond films has resulted in the development of two distinct MCPR designs, one with a 4-inch quartz bell-jar and one with a 5-inch quartz bell-jar. At the beginning of this work it was not known which of these designs would yield the better low-temperature diamond deposition process, so the two most recent 2.45 GHz reactors were both included in this investigations. Additionally, there were several configurations of these reactors that had the potential to provide a high quality low-temperature diamond deposition process. A portion of this dissertation was dedicated to investigating several of the numerous possible MCPR configurations.

A total of nine MCPR configurations were developed for low-temperature diamond deposition during this dissertation. Data was presented that showed that all but one of these, configuration 4, could be used for diamond deposition at substrate temperatures below 550 °C. The other eight configurations could generate plasmas and diamond deposition environments such that circular disk shaped substrates could be evenly coated. In some configurations diameters up to 4-inches could be processed.

Table 7.1 summarizes the deposition processing areas, and the availability of a dc biased or thermally controllable substrate receptor assembly for MCPR configurations 1 - 9. In configurations 1, 2 and 3, which were the thermally and electrically insulated configurations of the 4-inch MCPR, the diameter of the substrate processing area was limited to 2-inches by the characteristics of the reactor. No diamond films were successfully deposited with configuration 4, which had a dc biased substrate receptor. The diameter of the processing area of configuration 6, which was a dc biased configuration in the 5-inch MCPR, was also limited to 2-inches by design. The thermally insulated and thermally

MCPR Configuration	2" Substrates	3" Substrates	4" Substrates	Variable dc bias	Variable Thermal Conductance	Variable Substrate Heating
1	< 1.5"					
2	X					
3	X					
4	X			X		
5	X	X	X			
6	X			X		
7	X	X	X			
8	X	X				X
9	X	X			X	

Table 7.1: Summary of MCPR Configurations.

adjustable configurations of the 5-inch MCPR, which were named configurations 5, 7, 8 and 9, could all process substrates with diameters up to 3-inches. Diamond deposition on 4-inch diameter substrates could only be achieved with modified versions of configurations 5 and 7, neither of which had a bias or any thermal adjustments.

In seven of the MCPR configurations the substrate was placed in a receptor that was seated on top of a quartz tube. The quartz tube was a critical component in these assemblies for two reasons. First its transparency to microwaves precluded it from altering the resonant electromagnetic fields in the MCPR cavity. Second, its extremely low thermal conductivity created a large thermal resistance between the substrate receptor and the MCPR's water cooled base plate. If the material used had a higher thermal conductivity than that of quartz, the temperature of the substrate might have been reduced below that necessary for diamond deposition.

In addition to the seven thermally insulated configurations with quartz tubes supporting the substrate receptor, there were two thermally adjustable ones. MCPR configuration 8 had a heated substrate receptor assembly where a BN heater was used to provide heat to the substrate in addition to that provided by the plasma. This configuration was designed with the intent of achieving the ability to maintain a constant substrate temperature over a range of pressures. It allowed the temperature of the substrate to be controllable independent of the pressure, a feature not available in the seven thermally insulated configurations.

MCPR configuration 9 had a closed-loop, liquid cooled substrate receptor assembly that could vary the conductive heat flux from the substrate to the MCPR base-plate. It was created so that diamond films could be deposited on temperature sensitive substrates,

e.g. Corning 7059 glass, at pressures above 20 torr -- a condition where the substrate would overheat in configurations 1 through 8.

For low temperature diamond deposition with MCPR configurations 1 through 9, the plasma was excited by tuning the microwave power in the cavity to one of two TM_{01n} modes, the TM_{011} mode in the 4-inch MCPR and the TM_{013} mode in the 5-inch MCPR. The measured tuning points for the TM_{011} mode where the reflected power is minimized while a plasma is present were generally 7-cm for the cavity height h and 2-cm for the coupling probe insertion length l . At 15 torr the reflected power for this mode was typically 5 percent or less. For the TM_{013} mode the measured MCPR tuning points were approximately 16.0-cm indicated (22.3-cm actual) for the cavity height h , and 3.2-cm for the probe insertion length l . For the non-thermally adjustable configurations in the 5-inch MCPR, which were operated at 15 torr and less, the reflected power of the TM_{013} mode was 30 percent or less. For the heated substrate receptor configuration however, the reflected power was as high as 50 percent. The best tuning match for the TM_{013} mode in the 5-inch MCPR was achieved with the liquid cooled configuration -- the reflected power was generally less than 10 percent. The variations of load matching of the TM_{013} mode are characteristic of how the 5-inch MCPR reacts to changes in pressure. At lower pressures the reflected power is always higher than at higher pressures. Since the heated substrate receptor assembly was operated at pressures substantially lower than that of the cooled or thermally insulating ones the load matching was worst.

7.2.2 Benchmark Diamond Deposition on Silicon Substrates

Traditionally, CVD diamond-deposition-process development with MCPR and other plasma sources is carried out with silicon wafer substrates. Likewise, benchmarking for this dissertation was conducted with silicon substrates. Afterwards, useful deposition processes were applied to temperature sensitive substrates, which were typically Corning 7059 boro-silicate glass.

It has been shown that the MSU developed MCPR technology is capable of producing continuous, thin diamond films on silicon substrates at temperatures in the range of 400 C to 550 C. Furthermore, it has been shown that the low-temperature MCPR diamond deposition process, which was developed during this dissertation, is capable of depositing diamond films on disk shaped substrates with diameters up to 4-inches. Deposition rates, which are highly dependent on the substrate's temperature and the gas chemistry, were in the range of 10 nm/hr to 100 nm/hr.

Comparisons between actual experimental deposition results and the predictions of two growth models were presented. The first model was the one that was developed by Harris and Goodwin. The model predicts changes in diamond film deposition rates that occur due to variations in the substrate temperature and the methyl radical concentration. An adaptation of this model was presented that includes gas flows, gas pressure and substrate temperature, which are MCPR variables. The second model was the Bachmann C-H-O gas phase diagram. This model is generic in that it predicts the trends of the deposition rate and the film quality independent of the CVD process and the input gas chemistry.

It was found that the experimental, diamond-film deposition-rate correlated in part with our adaptation of the Harris-Goodwin growth model. For deposition at varying sub-

strate temperatures, experimental results correlated well with the model; however, when gas pressure and methane flow rate were examined as independent process variables the data did not always match our adaptation of the model. The model's prediction of increased diamond film deposition rate, w_{HG} , with increasing substrate temperature was matched very well by the experimental results.

When the gas pressure is singled out as a process variable, our adaptation of the model predicts an increase in deposition rate, w_{HG} , with increasing pressure; however, experimental data did not show an increase in growth rate with increasing pressure. It remained essentially the same for pressures in the range of 7 torr to 15 torr. One possible explanation for the difference between the model and experimental results for varying gas pressures was that increasing the gas pressure in the MPCR may reduce the distribution of electron temperatures, T_e . A reduction in the distribution of T_e would in-turn cause a reduction in the dissociation rate of CH_4 . It was assumed in the application of Harris-Goodwin model to this range of operation of the MCPR, that increasing the gas pressure produces higher concentrations of methyl radicals, $[\text{CH}_m]$.

When the methane flow rate was singled out as a process variable, the results were mixed. The applied model predicts that if the methane dissociation rate remains the same while the methane concentration is increased, that the deposition rate, w_{HG} , will increase with increasing methane concentration. At methane flow rates equal to and less than 2.5% of the flow rate of hydrogen, the experimental results showed that there was an increase in the deposition rate, which correlated well with the model. For methane flow rates in the range of 2.5% to 5% of the flow rate of hydrogen however, the experimental deposition rate saturated and no additional increase was observed. While the saturation at flow rates

higher than 2.5% is not predicted by our adaptation of the model, it is similar to the results that were reported by Zhang^[36].

A comparison of experimental deposition results with the predicted trends of the Bachmann C-H-O gas phase diagram was also included in this chapter. Included in this discussion were experiments where diamond films were deposited from mixtures of hydrogen, methane, and carbon dioxide. The qualitative predictions of the Bachmann model correlated well with the experimental results. The model's prediction that growth rates diminish with decreasing $X_{C/\Sigma}$ matched the results of deposition experiments. Furthermore, a pilot experiment that used only CH_4 and CO_2 had agreement with the model's prediction that diamond can be grown from a CVD process without the use of H_2 .

Data from investigations of three methods for improving the deposition rate in the plasma CVD process was also presented in this chapter. In the first case, a dc bias was added to the substrate to investigate how it might affect diamond deposition at low substrate temperatures in the MPCR. The result was that the growth rate and film quality were essentially unaffected by the addition of the dc bias. Second, a thermally-adjustable substrate cooler was investigated to determine if deposition rate would increase at higher pressures, which were in the range of 15 torr to 30 torr, while the substrate's temperature was maintained below 550 C. Here the cooler was necessary to control the flow of heat from the substrate. At pressures of 15 torr and above, the substrate's temperature would exceed the 550 C point without the aide of the cooler. The results from the cooler experiments were that there seemed to be no clear improvement to the deposition rate. The deposition rate at 25 torr and 500 C was the same as that below 10 torr. Third, deposition with pulsed microwave power was investigated for improvements to the deposition rate. Again,

no clear advantage was observed. In fact the deposition rates for experiments with pulsed microwave power were less than those with CW microwave power.

Lastly, data was presented for experiments that investigated the photo-resist seeding method, measurements of surface roughness, deposition on large area substrates, and deposition on silicon ICs. The investigation of the photo-resist seeding method was initiated because the procedure that was outlined by Masood did not yield a high enough nucleation density to produce a continuous diamond film with a thickness of 1.0 μm or less. The result was that continuous diamond films were deposited by the Masood method with only one change to the process. It was determined that increasing the diamond powder quantity to 16 times that of the Masood recipe was sufficient to produce continuous diamond films. The measurement data for diamond film surface roughness revealed three interesting facts. First, the surface roughness of diamond films that were deposited on substrates, which were pretreated with the photo-resist method, is on the order of 100 nm and greater. This is predicted to be too high for optical applications at wavelengths below 1600 nm. Second, the surface roughness of diamond films that were deposited on substrates, which were pretreated with the diamond powder scratching method, were as low as 10 nm. This low surface roughness is predicted to meet the needs of optical applications at wavelengths above 400 nm. Third, the low surface roughness of 10 nm was dependent on two variables, the substrate pretreatment method and the deposition gas chemistry. It was learned that when the flow rates of CH_4 and CO_2 were equal, a very smooth, fine-grained film was deposited. The data that was presented from the large area deposition experiments showed that the deposition area at low temperatures with the MCPD was sufficient to coat substrates with diameters as large as 4 inches. Furthermore, the deposition of 1 μm

and 2 μm films with a uniformity to within 100nm was achieved to a diameter as large as 3 inches. Finally, data was presented for a pilot experiment where a diamond film was deposited on a 2 inch silicon IC, which contained components made of aluminum. Micro photos were presented that showed that the aluminum components suffered no damage during the diamond deposition process. This indicates that diamond films can be deposited on temperature sensitive substrates with the low-temperature diamond deposition process that was developed during this dissertation with the current MCPR technology.

7.2.3 Deposition and Characterization of Diamond Films on Glass Substrates

It has been demonstrated that transparent polycrystalline diamond films can be deposited on Corning 7059 substrates with current MCPR technology. The growth rate of these films is relatively low, on the order of 50-nm/hr to 80-nm/hr; however these rates are consistent with the deposition rates on silicon substrates that were reported in chapter 5. The uniformity of these films was also equal to that of the films that were deposited on silicon substrates. Single color films with $\pm 10\%$ and greater uniformity were routinely deposited on Corning 7059 glass substrates with diameters of 2-inches. Pilot experiments with a substrate heater indicated that MCPR-C8, which had a substrate heater, offered no distinguishable advantage in deposition uniformity over the other MCPR configurations.

Observations and measurements of the optical transmission of diamond films that were adhering to Corning 7059 substrates demonstrated that transmission was a function of substrate pre-treatment method and deposition chemistry. It was shown that scratch seeded films have a higher transmission than photo-resist seeded film throughout the wavelength range of 400-nm to 1600-nm. The optical transmission of films that were grown

with varying chemistries had mixed results. The chemistry with the lowest optically fit surface roughness was the mixture of 200 sccm of H_2 , 8 sccm of CO_2 and 8 sccm of CH_4 . In the near IR from approximately 800-nm to 1600-nm this mixture also had the best optical transmission. In the visible region though, from 400-nm to 600-nm, the film grown with this mixture exhibited absorption, which notably reduced its transmission in this range. The best optical transmissions in the wavelength range of 400-nm to 800-nm were the films that were grown with a two-step process. The two-step process had a high methane flow of 10% CH_4 for the first 30 minutes of the deposition and a CH_4 flow of 2.5% for the remainder. Films grown with this process had a slightly higher optically fit surface roughness than those grown with the mixture of 200-8-8; however, they did not exhibit any detectable absorption. Hence, the two-step process had the best optical transmission in the wavelength range of approximately 400-nm to 800-nm.

Observations of film adhesion were that many of the films that were deposited on Corning 7059 and 7050 borosilicate glass substrates exhibited some amount of delamination. For the films that were deposited with photo-resist seeded with a single chemistry, adhesion appeared to be a function of film thickness and deposition temperature. Films that were thicker than 2- μm tended to peel and those with a thickness of 2- μm and less tended to adhere. The relationship between deposition chemistry and adhesion was not clear. Pilot experiments with scratch seeding and varying chemistries resulted in some films delaminating even though thicker films that were deposited with the same chemistry did not.

7.3 Recommendations for Future Research

7.3.1 Improving Deposition Rates

At temperatures below 500 C in the MCPR, diamond deposition rates have been reported to be in the range of 10-nm/hr to 80-nm/hr, which are quite low as compared to most high temperature diamond deposition processes. Pilot experiments that were geared toward improving the deposition rate at temperatures below 500 C with a substrate cooler and pulsed microwave power did not produce the desired results. In both instances however, there were regions of operation at higher microwave power levels that could not be investigated with the current experimental set-up. The current configuration uses coaxial waveguides with a maximum rating of 1KW to transport microwave power into the MCPR. In the future, deposition rate improvements could be investigated with higher power levels if the MCPR and the waveguide system were upgraded for higher CW power levels.

7.3.2 Improving Deposition Uniformity

The investigation of deposition uniformity that was conducted with MCPR-C7 was limited in that the microwave power was consistently at 1KW. During this work it was observed that there are “hot spots” in the plasma. These region were observed to emit somewhat more visible light than the rest of the plasma, and they disappear at lower power levels. At reduced power levels the plasma’s volume decreases which reduces the deposition uniformity. Perhaps there exists an optimum CW microwave power level that reduces the intensity of the “hot spots”, minimizes the size reduction of the plasma and increases

the region of uniform deposition. Future investigations of deposition uniformity with reduces power levels and varying gas pressures and substrate heights should be conducted to confirm this.

7.3.3 Improving Optical Transmission

It was shown in Chapter 6 that the substrate pretreatment method and deposition chemistry significantly affect the optical transmission of diamond films that are deposited at low-temperatures on glass substrates with the MCPR. Measurements of the optical transmission of eight films that were grown on scratch seeded substrates with various mixtures of H_2 , CO_2 and CH_4 had optical transmissions at 400-nm ranging from 30% to >70%. It was noted that scattering from film surface roughness and film bulk absorption contributed reductions in transmission. These loss types have an inverse λ relationship and are not always trivial to separate. Separation of scattering and absorption effects and the determination of their dependencies on process variables is desirable. A great deal of future work is necessary to investigate optical transmission of diamond films that could be grown from the endless combination of process gases available today.

7.3.4 Improving Film to Glass Adhesion

Delamination of diamond films from boro-silicate glass substrates was noted be to related to film thickness. It was likely caused by thermal strain at the film-substrate interface and intrinsic strain in the film. Future investigations of film adhesion should target a reduction in the film's internal strain, which is related deposition variables such as gas

composition and substrate temperature. Additionally, adhesion improvements might be realized by using a glass with a CTE that more closely matches that of diamond.

APPENDICES

Appendix A

A Matlab Program to Plot Optical Transmission

This appendix contains of the Matlab “.m” files that were used to generate all of the plots of theoretical and measured transmission of thin diamond films on glass substrates in Chapter 6. As was stated in section [3.4.3.3] the following assumptions are made for each theoretical transmission graph (1) the diamond films can be considered thin films, (2) the glass substrates are thick so that coherent interference average out, (3) there is negligible absorption in the diamond film for the wavelengths of light under consideration, and (4) the refractive index of the diamond film is determined by the Sellmeier equation.

The below listed “.m” files are designed to generate three windows. The primary window is created first by executing the ct.m file in matlab. The ct.m file is the only file that the user must invoke. All the other files are called by functions in the ct.m file and its subordinate files. In primary window, the user can adjust the following variables, the film thickness, the rms surface roughness of the film, and the refractive index of the glass substrate. These variables can be typed in or adjusted by slide bars (thk_slider.m and sig_slider.m files). To input the measured transmission data for a particular diamond film, the user can enter the file name for a data file that contains the data. The data must be column format with the first column containing the wavelength of light in nm, and the second containing the measured transmission (normalized to between 0 and 1.0). Besides the variable fields, there are three buttons in the primary program window. One button is labeled “plot” and when pressed invokes the code of the files ct_PlotOpt6.m and ct_optics6.m. These files open a second window, the plot display window, and display in

Appendix A

it the theoretical and measured transmission data as determined from the parameters of the first window. The second button invokes the file `ct_print.m`, which opens a third window and displays a preview of how the plot data of the plot display window will be printed. In the print preview window there are two more buttons. One is labeled “print” this button invokes the file `ct_printfig.m` which closes the print preview window and prints the plot to the file `optic.ps`. The other button in the print preview window is labeled “cancel”. This button invokes the file `deleteprintfig.m` which just closes the print preview window. The third button in the primary window is labeled “done”. This button invokes the file `closefig.m`. The `closefig.m` file closes the primary program window, closes the plot display window if it has been generated, and terminates program execution. The following paragraphs are a listing of the above mentioned files.

Appendix A

Source Code for the ct.m file

```

fd=0;
figure;
clf;
H=gcf;
set(H,'color',[0.6,0.6,0.6]);
set(H,'Position',[200,650,260,450]);
h1=uicontrol('Style','Pushbutton','Position',[140 10 100 30],'Callback','close-
fig','String','Done');
h2=uicontrol('Style','Pushbutton','Position',[20 10 100 70],'Call-
back','ct_PlotOpt6','String','Plot Data');
% file name
h3=uicontrol('Style','edit','Position',[140 90 100 50],'String','');
% film thickness
h4=uicontrol('Style','edit','Position',[140 180 100 50],'String','660');
% Surface roughness (rms)
h5=uicontrol('Style','edit','Position',[140 270 100 50],'String','30');
% n(glass)
h6=uicontrol('Style','edit','Position',[140 330 100 50],'String','1.53');
% n(diamond)
h7=uicontrol('Style','edit','Position',[140 390 100 50],'String','2.4');
% sig rms slider
h8=uicontrol('Style','Slider','Position',[20 240 220
20],'Value',30,'Min',0,'Max',200,'Callback','sig_slider');
% thickness slider
h9=uicontrol('Style','Slider','Position',[20 150 220
20],'Value',660,'Min',100,'Max',3000,'Callback','thk_slider');

```

Appendix A

% print command

```
h2=uicontrol('Style','Pushbutton','Position',[140 50 100 30],'Call-
back','ct_print','String','Print');
set(h3,'BackgroundColor',[1.0,1.0,1.0]);
set(h3,'ForegroundColor',[0.0,0.0,0.0]);
set(h4,'BackgroundColor',[1.0,1.0,1.0]);
set(h4,'ForegroundColor',[0.0,0.0,1.0]);
set(h5,'BackgroundColor',[1.0,1.0,1.0]);
set(h5,'ForegroundColor',[1.0,0.0,0.0]);
set(h6,'BackgroundColor',[1.0,1.0,1.0]);
set(h6,'ForegroundColor',[0.0,0.8,0.0]);
set(h7,'BackgroundColor',[1.0,1.0,1.0]);
set(h7,'ForegroundColor',[0.0,0.8,0.0]);
h3l=uicontrol('Style','edit','Position',[20 90 100 50],'String','data file name');
h4l=uicontrol('Style','edit','Position',[20 180 100 50],'String','thickness (nm)');
h5l=uicontrol('Style','edit','Position',[20 270 100 50],'String','sigma (rms)');
h6l=uicontrol('Style','edit','Position',[20 330 100 50],'String','n (glass)');
h7l=uicontrol('Style','edit','Position',[20 390 100 50],'String','n (diamond)');
%text(120,225,'Data File Name');
```


Appendix A

Source Code for the ct_PlotOpt6.m file

```
if(fd==0)
    figure;
    hp1=gcf;
end
figure(hp1);
clf;
fd=1;
set(hp1,'Position',[100 100 550 400]);
set(hp1,'color',[0.5,0.5,0.5]);
file=get(h3,'String');
temp=get(h4,'String');
t=str2num(temp);
temp=get(h5,'String');
sig=str2num(temp);
temp=get(h6,'String');
ng=str2num(temp);
temp=get(h7,'String');
nd=str2num(temp);
ct_optics6;
set(gca,'color',[0.8,0.8,0.8]);
```

Appendix A

Source Code for the ct_optics6.m file

```
%
% File Name 'matlab/research/Transmission_Data/optics6.m
%
% A program to plot Measured and Predicted Light Transmission through
% glass that is coated with a thin homogenous film of diamond.
% The theoretical transmission equation used in this program
% is eq. 3.14.2 in vasicek's book "OPTICS OF THIN FILMS"
% The direction of light propogation in this program is:
% from air to glass to diamond to air. The diamond air interface
% is concidered to be the only rough surface in the scattering effected
% transmission solutions.
%
% variable definitions:
%      T: Transmission of light from glass through the diamond
%      film into air. Scattering is not concidered. The
%      first air glass interface is ignored so a correct
%      is added later.
%      Ts: The same as T only scattering from the diamond air
%      interface is included (per filinski's paper).
%      TSC:The intensity of light that is transmitted through
%      all layers (air-glass-diamond-air). This variable
%      is Ts multiplied by a correction factor for the
%      air-glass interface.

% read the measured transmission data from a file
```

Appendix A

```

if ~isempty(file) %~= ''
    wavelength=[];
    transmission=[];
    load (file);
    a=(eval(file));
    Mwavelength=a(:,1); % measurement wavelengths
    Mtransmission=a(:,2); % measured transmission at the above lambda
end

% initialize variables for Predicted Transmission
wavelength=400:1:1600; % lambda for theoretical data (more points)
%t=660; % film thickness (nm)
%sig=30; % film surface roughness (Ra) rms value

na=1.0; % refractive index for air
%nd=2.38; % refractive index for diamond
%ng=1.53; % refractive index for glass

lamda=0.400:0.001:1.600;
lamda2=lamda.^2;
term1=(4.3356*lamda2)./(lamda2-(0.1060.^2));
term2=(0.3306.*lamda2)./(lamda2-(0.1750.^2));
nd=sqrt(1+term1+term2);

S=2.*3.14.*sig;

% glass diamond air interface
% amplitude ratios for reflected light (normal incidence)

```

Appendix A

$r_{01} = (n_d - n_g) / (n_d + n_g)$; % vasicek eq. 2.6.11

$r_{12} = (n_a - n_d) / (n_a + n_d)$; % vasicek eq. 2.6.12

% intensity of transmitted light

$t_{01} = (1 - r_{01}^2)$; %

$t_{12} = (1 - r_{12}^2)$;

% phase difference of the light rays of the film

$x = 4 \cdot \pi \cdot n_d \cdot t / \text{wavelength}$;

% predicted transmission neglecting scattering (normal incidence)

% vasicek eq 3.15.2

$\text{num} = t_{01} \cdot t_{12}$;

$\text{denom} = 1 + r_{01}^2 \cdot r_{12}^2 + 2 \cdot r_{01} \cdot r_{12} \cdot \cos(x)$;

$T = \text{num} / \text{denom}$;

% predicted transmission considering scattering (normal incidence)

$\text{nums} = t_{01} \cdot t_{12} \cdot \exp(-(S / \text{wavelength})^2 \cdot (n_d - n_a)^2)$;

$e_1 = \exp(-4 \cdot (S / \text{wavelength})^2 \cdot n_d^2)$;

$e_2 = \exp(-2 \cdot (S / \text{wavelength})^2 \cdot n_d^2)$;

$\text{denoms} = 1 + r_{01}^2 \cdot r_{12}^2 \cdot e_1 + 2 \cdot r_{01} \cdot r_{12} \cdot e_2 \cdot \cos(x)$;

$T_s = \text{nums} / \text{denoms}$;

%-----

Appendix A

```
% Correction for first interface (air to glass)

Rg=((ng-na)./(na+ng)).^2; % reflection at air-glass interface
Tg=1-Rg;                % transmission at air-glass interface
Rs=1-Ts;                % reflection at glass-diamond interface
cf=Tg.*(1+(Rs.*Rg)+(Rs.^2.*Rg.^2)); % correction factor
Tsc=Ts.*cf;

if ~isempty(file) %~= ''
    plot(wavelength,Tsc,'b',Mwavelength,Mtransmission,'rx');
else
    plot(wavelength,Tsc,'b');
end

axis([300,1600,0,1]);
xlabel 'Wavelength (nm)';
ylabel 'Percent Transmission';
```

Appendix A

Source Code for the thk_slider.m file

```
tempn=get(h9,'Value');  
numstr=num2str(tempn);  
set(h4,'String',numstr);  
if(fd==1)  
    PlotOpt6;  
end
```

Appendix A

Source Code for the sig_slider.m file

```
tempn=get(h8,'Value');  
numstr=num2str(tempn);  
set(h5,'String',numstr);  
if(fd==1)  
    PlotOpt6;  
end
```

Appendix A

Source Code for the ct_print.m file

```

pd=1;
figure;
pf1=gcf;
set(pf1,'Position',[480,650,550,400]);
ct_optics6;
temp=get(h3,'String');
title(temp);
% thickness
temp=get(h4,'String');
text(1000,0.35,'thickness(nm)');
text(1350,0.35,temp);
% rms sigma (nm)
temp=get(h5,'String');
text(1000,0.25,'rms sigma (nm)');
text(1350,0.25,temp);
% n diamond
temp=get(h7,'String');
text(1000,0.15,'n (diamond)');
text(1350,0.15,'(Sellmier Eq.)');
% n glass
temp=get(h6,'String');
text(1000,0.05,'n (glass)');
text(1350,0.05,temp);
h1=uicontrol('Style','Pushbutton','Position',[80 60 60 30],'Callback','deleteprint-
fig','String','Cancel');
h2=uicontrol('Style','Pushbutton','Position',[150 60 40 30],'Call-
```


Appendix A

```
back', 'ct_printfig_2', 'String', 'Print');
```

Appendix A

Source Code for the ct_printfig_2.m file

```

delete(pf1);
figure;
pf2=gcf;
set(pf2,'Position',[490,650,550,400]);
ct_optics6;
temp=get(h3,'String');
title(temp);
% thickness
temp=get(h4,'String');
text(1000,0.35,'thickness(nm)');
text(1350,0.35,temp);
% rms sigma (nm)
temp=get(h5,'String');
text(1000,0.25,'rms sigma (nm)');
text(1350,0.25,temp);
% n diamond
temp=get(h7,'String');
text(1000,0.15,'n (diamond)');
text(1350,0.15,'(Sellmier Eq.)');
% n glass
temp=get(h6,'String');
text(1000,0.05,'n (glass)');
text(1350,0.05,temp);
%print -deps ct.ps;
print -deps plain_film.ps;

```

Appendix A

```
delete(pf2);
```

Appendix A

Source Code for the deleteprintfig.m file

```
delete(pf1);
```

Appendix A

Source Code for the closefig.m file

```
ch=gcf;  
delete(ch);  
  
if(fd==1)  
    delete(hp1);  
end
```

Appendix B

Deposition Experiments on 2" Silicon and IC Substrates

This Appendix contains tabular data that was recorded from diamond deposition experiments with polished 2" silicon wafers and 2" processed silicon ICs. This data is presented as a reference for discussions in earlier chapters regarding diamond deposition on these substrates. The tables include all the measurable data that was recorded, including experiments that were not included in earlier discussions.

There are vast differences between many of the experiments that are listed here, as was noted in chapters 4 - 6. The data in the tables includes measurable experimental parameters such as measured weight gains and measured substrate temperatures; however, they do not reflect the quality of the deposited film or the coverage area. There were many experiments where problems occurred such as an unexpected shift in the position of the plasma or the substrate. These random occurrences were caused by things like cracked quartz tubes and coating on the quartz bell jar etc. Hence, in addition to making comparisons of the data in the tables it is necessary to characterize each specific film, as was done prior to the development of the discussions that were presented in earlier chapters.

Appendix B

Date Exp. Began	11/15/93	11/18/93	11/20/93	11/22/93	11/26/93
Sample	S1	S2	S3	S4	S5
Duration (hours)	50	50	50	50	45
Initial Weight (g)	1.2852	1.2939	1.2880		1.2915
Resistivity					
Seeding Lot					
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₄ (sccm)	3	4	5	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	7 torr	7 torr	7 torr	7 torr	7 torr
Input Power (watts)	399	399	295	294	364
Bias Voltage					

Results

Final Weight (g)	1.3068		1.2955		1.2974
Weight Gain (mg)	21.6		11.5		5.9
Bias Current					
Temperature (°C)	465	461			460-470
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.1 Deposition Results of Substrates S1 - S5

Appendix B

Date Exp. Began	11/29/93	12/1/93	12/3/93		12/5/93
Sample	S6	S7	S8		S10
Duration (hours)	30	40	40		40
Initial Weight (g)	1.2934				1.2990
Resistivity					
Seeding Lot					
H ₂ (sccm)	200	200	200		200
CO ₂ (sccm)	8	8	8		8
CH ₄ (sccm)	2	4	5		3
O ₂ (sccm)	0	0	0		0
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	7 torr	7 torr	7 torr		7 torr
Input Power (watts)	364	306	299		352
Bias Voltage					

Results

Final Weight (g)	1.2972				1.3100
Weight Gain (mg)	3.8				11.0
Bias Current					
Temperature (°C)		481	482		488
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.2 Deposition Results of Substrates S6 - S10

Appendix B

Date Exp. Began	12/7/93	12/9/93	12/11/93	12/13/93	12/15/93
Sample	S11	S12	S13	S14	S15
Duration (hours)	40	40	40	40	40
Initial Weight (g)		1.2955	1.3162		
Resistivity					
Seeding Lot					
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₄ (sccm)	3	3	3	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	7 torr	7 torr	7 torr	7 torr	7 torr
Input Power (watts)	352	352	352	352	352
Bias Voltage					

Results

Final Weight (g)		1.3097	1.3300		
Weight Gain (mg)		14.2	14.8	12.8	13.4
Bias Current					
Temperature (°C)		517	512	500	502
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.3 Deposition Results of Substrates S11 - S15

Appendix B

Date Exp. Began	12/18/93	12/20/93	12/22/93		1/5/94
Sample	S16	S17	S18		S20
Duration (hours)	40	40	40		40
Initial Weight (g)					
Resistivity					
Seeding Lot					
H ₂ (sccm)	200	200	200		200
CO ₂ (sccm)	8	8	8		8
CH ₄ (sccm)	3	3	3		3
O ₂ (sccm)	0	0	0		0
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	7 torr	7 torr	7 torr		7 torr
Input Power (watts)	306	306	306		306
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)	6.2		6.1		5.6
Bias Current					
Temperature (°C)	470	468-496	470-480		468
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.4 Deposition Results of Substrates S16 - S20

Appendix B

Date Exp. Began			1/7/94	1/10/94	
Sample			S23	S24	
Duration (hours)			40	40	
Initial Weight (g)					
Resistivity					
Seeding Lot					
H ₂ (sccm)			200	200	
CO ₂ (sccm)			8	8	
CH ₄ (sccm)			3	3	
O ₂ (sccm)			0	0	
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure			7 torr	7 torr	
Input Power (watts)			306	306	
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)			8.2		
Bias Current					
Temperature (°C)			475-481	465-470	
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.5 Deposition Results of Substrates S23 - S24

Appendix B

Date Exp. Began			1/19/94		1/26/94
Sample			S28		S30
Duration (hours)			40		40
Initial Weight (g)					
Resistivity					
Seeding Lot					
H ₂ (sccm)			200		200
CO ₂ (sccm)			10		6
CH ₄ (sccm)			3		3
O ₂ (sccm)			0		0
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure			7 torr		7 torr
Input Power (watts)			352		352
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)			7.8		8.0
Bias Current					
Temperature (°C)			440-505		470-480
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.6 Deposition Results of Substrates S28 - S30

Appendix B

Date Exp. Began	1/29/94			2/2/94	3/6/94
Sample	S31			S34	S35
Duration (hours)	40			40	4
Initial Weight (g)					
Resistivity					
Seeding Lot					
H ₂ (sccm)	200			200	200
CO ₂ (sccm)	8			8	8
CH ₄ (sccm)	3			3	3
O ₂ (sccm)	0			0	0
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	7 torr			7 torr	7 torr
Input Power (watts)	352			352	918.2
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)	6.6			6.1	1.3
Bias Current					
Temperature (°C)	470-480			470-480	
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.7 Deposition Results of Substrates S31 - S35

Appendix B

Date Exp. Began	3/7/94	3/19/94	3/8/94	3/20/94	
Sample	S36	S37	S38	S39	
Duration (hours)	40	4	40	40	
Initial Weight (g)					
Resistivity					
Seeding Lot					
H ₂ (sccm)	200	200	200	200	
CO ₂ (sccm)	8	8	8	8	
CH ₄ (sccm)	3	3	3	3	
O ₂ (sccm)	0	0	0	0	
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	7 torr	9 torr	7 torr	9 torr	
Input Power (watts)	918.2	918.2	918.2	918.2	
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)	2.2	2.1	1.3	2.5	
Bias Current					
Temperature (°C)			445		
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.8 Deposition Results of Substrates S36 - S39

Appendix B

Date Exp. Began	3/24/94				4/2/94
Sample	S41				S45
Duration (hours)	40				40
Initial Weight (g)					
Resistivity					none
Seeding Lot					
H₂ (sccm)	200				200
CO₂ (sccm)	8				8
CH₄ (sccm)	3				3
O₂ (sccm)	0				0
Cavity Conf					8
Susceptor A.					MEC4
Upper Quartz					20mm
Lower Quartz					24mm
Pressure	9 torr				15 torr
Input Power (watts)	918.2				3.0mW
Bias Voltage					+100V _{dc}

Results

Final Weight (g)					
Weight Gain (mg)	5.2				N/A
Bias Current					8.54mA
Temperature (°C)	460-470				500-518
Film Deposited					Not Dia.
Film Type					continuous
Film Thickness					N/A
Growth Rate (nm/hr)					N/A

Table B.9 Deposition Results of Substrates S41 - S45

Appendix B

Date Exp. Began	4/8/94	4/8/94	4/10/94	4/15/94	4/17/94
Sample	S46	S47	S48	S49	S50
Duration (hours)	40	40	40	40	40
Initial Weight (g)	1.2882	1.2865	1.2929	1.2758	1.3033
Resistivity					
Seeding Lot		10.1	10.1	10.1	10.1
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₄ (sccm)	3	3	3	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	8	8	8	8	8
Susceptor A.	MEC4	MEC4	MEC4	MEC4	MEC4
Upper Quartz	20mm	20mm	20mm	20mm	20mm
Lower Quartz	24mm	24mm	24mm	24mm	24mm
Pressure	15 torr	15 torr	15 torr	15 torr	15 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	+100V _{dc}	+100V _{dc}	Open	+100V _{dc}	open

Results

Final Weight (g)	N/A	1.2979	1.3074	1.2888	1.3172
Weight Gain (mg)	N/A	11.4	14.5	13.0	13.9
Bias Current	N/A	1.51mA	-0.19mA	1.62mA	none
Temperature (°C)	N/A	513-520	501-518	512-524	501-504
Film Deposited	N/A	Diamond	Diamond	Diamond	Diamond
Film Type	not cont.	continuous	continuous	continuous	continuous
Film Thickness	N/A	1.6μm	2.035μm	1.82μm	1.95μm
Growth Rate (nm/hr)	N/A	40.00	50.88	45.62	48.78

Table B.10 Deposition Results of Substrates S46 - S50

Appendix B

Date Exp. Began	4/19/94	4/22/94	5/13/94	6/26/94	7/2/94
Sample	S51	S52	S53	S54	S55
Duration (hours)		40	40	40	40
Initial Weight (g)	1.2814	1.2540	1.2600	1.3132	1.2600
Resistivity					
Seeding Lot	10.1	10.1	10.1	10.1	10.1
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₄ (sccm)	3	3	3	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	8	8	8	9	9
Susceptor A.	MEC4	MEC4	MEC4	MEC5.2	MEC5.2
Upper Quartz	20mm	20mm	20mm	22mm	22mm
Lower Quartz	24mm	24mm	24mm	24mm	24mm
Pressure	15 torr	15 torr	9 torr	7 torr	9 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	-100Vdc	+100Vdc	none	none	none

Results

Final Weight (g)	1.2923	1.2687	1.2654	1.3270	1.2710
Weight Gain (mg)	10.9	14.7	5.4	13.8	11.0
Bias Current	none	none	none	none	none
Temperature (°C)			457 - 464	460 - 465	456 - 466
Film Deposited	Diamond	Diamond	Diamond		
Film Type	Peeled	Continuous	Not Contin.		
Film Thickness	1.5μm	2.063μm	0.758μm	1.937μm	1.544μm
Growth Rate (nm/hr)	N/A	51.58	18.95	48.43	38.6

Table B.11 Deposition Results of Substrates S51 - S55

Appendix B

Date Exp. Began	8/12/94	8/13/94	8/15/94	8/18/94	8/21/94
Sample	S56	S57	S58	S59	S60
Duration (hours)	40	40	40	40	40
Initial Weight (g)	1.2943	1.1929	1.2282	1.0989	1.1896
Resistivity					
Seeding Lot	10.2	10.2	10.2	10.2	10.2
H ₂ (sccm)	200	200	200	200	0
CO ₂ (sccm)	8	8	16	0	15
CH ₄ (sccm)	3	3	3	3	15
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	9	9
Susceptor A.	MEC5.2	MEC5.2	MEC5.2	MEC5.2	MEC5.2
Upper Quartz	22mm	22mm	22mm	22mm	22mm
Lower Quartz	24mm	24mm	24mm	24mm	24mm
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	3.0mW	3.0mw	3.0mw	3.0mw	3.0mw
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	1.2944	1.1980	1.2293	1.1083	1.2135
Weight Gain (mg)	0.1	5.1	1.1	9.4	24.1
Bias Current	none	none	none	none	none
Temperature (°C)	?	438 - 442	440 - 446	462 - 471	470 - 473
Film Deposited		Diamond	Diamond	Diamond	Not Dia.
Film Type		Not Cont.	Not Cont.	Not Cont.	Not Cont.
Film Thickness	N/A				
Growth Rate (nm/hr)	N/A				

Table B.12 Deposition Results of Substrates S56 - S60

Appendix B

Date Exp. Began	8/23/94	8/25/94	8/25/94	8/26/94	8/26/94
Sample	S61	S62	S63	S64	S65
Duration (hours)	40	10	10	10	10
Initial Weight (g)	1.1302	2.1525	2.1481	2.1204	2.1331
Resistivity					
Seeding Lot	10.2	10.2	12.1	13.1	12.1
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	0	0	0	0	0
CH ₄ (sccm)	5	5	5	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	9	9
Susceptor A.	MEC5.2	MEC5.2	MEC5.2	MEC5.2	MEC5.2
Upper Quartz	22mm	22mm	22mm	22mm	22mm
Lower Quartz	24mm	24mm	24mm	24mm	24mm
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	1.1417	2.1535	2.1501	2.1218	2.1341
Weight Gain (mg)	11.5	1.0	2.0	1.4	1.0
Bias Current	none	none	none	none	none
Temperature (°C)	465 - 468	468 - 473	465 - 467	460 - 463	463 - 468
Film Deposited	Diamond	Diamond	Diamond	Diamond	Diamond
Film Type	Not Cont.	Not Cont.	Not Cont.	Not Cont.	Not Cont.
Film Thickness					
Growth Rate (nm/hr)					

Table B.13 Deposition Results of Substrates S61 - S65

Appendix B

Date Exp. Began	8/28/94	8/29/94	8/30/94	8/31/94	9/1/94
Sample	S66	S67	S68	S69	S70
Duration (hours)	10	10	10	10	10
Initial Weight (g)	2.1558	2.1490	2.1449	2.1266	2.1382
Resistivity					
Seeding Lot	14.1	13.1	15.1	14.1	16.1
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	0	0	0	0	0
CH ₄ (sccm)	5	5	5	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	9	9
Susceptor A.	MEC5.2	MEC5.2	MEC5.2	MEC5.2	MEC5.2
Upper Quartz	22mm	22mm	22mm	22mm	22mm
Lower Quartz	24mm	24mm	24mm	24mm	24mm
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	2.1568	2.1498	2.1466	2.1278	2.1403
Weight Gain (mg)	1.0	0.8	1.7	1.2	2.1
Bias Current	none	none	none	none	none
Temperature (°C)	463 - 468	448 - 453	455 - 460	459 - 463	458 - 468
Film Deposited	Diamond	Diamond	Diamond	Diamond	Diamond
Film Type	Not Cont.	Not Cont.	Not Cont.		
Film Thickness					
Growth Rate (nm/hr)					

Table B.14 Deposition Results of Substrates S66 - S70

Appendix B

Date Exp. Began	9/6/94	9/7/94	9/8/94	9/13/94	9/13/94
Sample	S71	S72	S73	S74	S75
Duration (hours)	10	10	40	10	40
Initial Weight (g)	2.1751	2.1619	2..1324	2.1111	2.1559
Resistivity					
Seeding Lot	17.1	18.1	17.1	19.1	19.1
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	0	0	0	0	0
CH ₄ (sccm)	5	5	5	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	9	9
Susceptor A.	MEC5.2	MEC5.2	MEC5.2	MEC5.2	MEC5.2
Upper Quartz	22mm	22mm	22mm	22mm	22mm
Lower Quartz	24mm	24mm	24mm	24mm	24mm
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	2.1783	2.1673	2.1465	2.1141	2.1708
Weight Gain (mg)	3.2	5.4	14.1	3.0	14.9
Bias Current	none	none	none	none	none
Temperature (°C)	463 - 468	468 - 472	468 - 473	468 - 473	470 - 475
Film Deposited	Diamond	Diamond	Diamond	Diamond	
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.15 Deposition Results of Substrates S71 - S75

Appendix B

Date Exp. Began	9/15/94	9/17/94	9/19/94		
Sample	S76	S77	S78		
Duration (hours)	40	40	40		
Initial Weight (g)	2.1675	1.9554	1.6255		
Resistivity					
Seeding Lot	20.1	20.1	20.2		
H ₂ (sccm)	200	200	200		
CO ₂ (sccm)	0	0	0		
CH ₄ (sccm)	5	5	10		
O ₂ (sccm)	0	0	0		
Cavity Conf	9	9	9		
Susceptor A.	MEC5.2	MEC5.2	MEC5.2		
Upper Quartz	22mm	22mm	22mm		
Lower Quartz	24mm	24mm	24mm		
Pressure	9 torr	9 torr	9 torr		
Input Power	3.0mW	3.0mW	3.0mW		
Bias Voltage	none	none	none		

Results

Final Weight (g)	2.1769	1.9718	1.6428		
Weight Gain (mg)	9.4	16.4	17.3		
Bias Current	none	none	none		
Temperature (°C)	468 - 473	468 - 474	471 - 473		
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.16 Deposition Results of Substrates S76 - S78

Appendix B

Date Exp. Began			10/5/94	10/11/94	12/18/94
Sample			S83	S84	S85
Duration (hours)			40	40	15
Initial Weight (g)			1.9356	2.0416	2.1466
Resistivity					
Seeding Lot			21.2	21.2	SC-9
H ₂ (sccm)			200	200	200
CO ₂ (sccm)			0	0	0
CH ₄ (sccm)			5	8	5
O ₂ (sccm)			0	0	0
Cavity Conf			9	9	9
Susceptor A.			MEC5.2	MEC5.2	MEC5.2
Upper Quartz			22mm	22mm	22
Lower Quartz			24mm	24mm	24
Pressure			9 torr	9 torr	9 torr
Input Power			3.0mW	3.0mW	3.0mW
Bias Voltage			none	none	none

Results

Final Weight (g)			1.9525	2.0594	2.1513
Weight Gain (mg)			16.9	17.8	4.7
Bias Current			none	none	none
Temperature (°C)			468 - 471	468 - 470	467 - 472
Film Deposited					Diamond
Film Type					Continuous
Film Thickness					0.660μm
Growth Rate (nm/hr)					44

Table B.17 Deposition Results of Substrates S83 - S85

Appendix B

Date Exp. Began	12/28/94	1/1/95	1/3/95	1/10/95	1/13/95
Sample	S86	S87	S88	S89	S90
Duration (hours)	25	25	25	25	25
Initial Weight (g)	2.2663	1.9874	1.6360	1.6079	2.0453
Resistivity					
Seeding Lot	SC-11	SC-12	SC-13	SC-14	SC-15
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₄ (sccm)	3	3	3	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	9	9
Susceptor A.	MEC5.2	MEC5.2	MEC5.2	MEC5.2	MEC5.2
Upper Quartz	22	22	22	22	22
Lower Quartz	24	24	24	24	24
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	2.2688	1.9907	1.6378	1.6137	2.0461
Weight Gain (mg)	2.5	3.3	1.8	5.8	0.8
Bias Current	none	none	none	none	none
Temperature (°C)	468 - 473	471 - 473	463 - 468	470 - 476	465 - 472
Film Deposited	Diamond	Diamond	Diamond	Diamond	Diamond
Film Type					
Film Thickness	0.351μm	0.463μm	0.253μm	0.814μm	0.112μm
Growth Rate (nm/hr)	14.04	18.52	10.12	32.56	4.48

Table B.18 Deposition Results of Substrates S86 - S90

Appendix B

Date Exp. Began	1/15/95	1/29/95	1/31/95	2/2/95	2/8/95
Sample	S91	S92	S93	S94	S95
Duration (hours)	15	25	15	15	15
Initial Weight (g)	1.6134	1.9925	2.0253	2.0337	2.2514
Resistivity					
Seeding Lot	SC-16	SC-18	SC-19	SC-20	SC-21
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	0	8	0	0	0
CH ₄ (sccm)	5	5	5	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	9	9
Susceptor A.	MEC5.2	MEC5.2	MEC5.1	MEC5.3	MEC5.1
Upper Quartz	22	22	22	22	18
Lower Quartz	24	24	24	24	28
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	1.6189	1.9991	2.0295	2.0387	2.2570
Weight Gain (mg)	5.5	6.5	4.2	5.0	5.6
Bias Current	none	none	none	none	none
Temperature (°C)	448 - 454 $\epsilon=0.65$	470 $\epsilon=0.65$	460 $\epsilon=0.65$	466 - 471 $\epsilon=0.65$	494 - 500 $\epsilon=0.65$
Film Deposited		Diamond		Diamond	Diamond
Film Type		Continuous		Continuous	Continuous
Film Thickness	0.772 μ m	0.912 μ m	0.590 μ m	0.702 μ m	0.786 μ m
Growth Rate (nm/hr)	51.47	36.48	39.33	46.80	52.40

Table B.19 Deposition Results of Substrates S91 - S95

Appendix B

Date Exp. Began	3/4/95	3/5/95		4/8/95	2/11/95
Sample	S96	S97	S98	S99	S100
Duration (hours)	15	30	15	15	25
Initial Weight (g)	2.2484	2.2056	1.9226	2.1363	2.0442
Resistivity					
Seeding Lot	SC-21	SC-21	SC-21	SC-21	SC-22
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	16	16	8	8	8
CH ₄ (sccm)	5	5	8	8	8
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	10	9
Susceptor A.	MEC5.2	MEC5.2	MEC5.2	HA1.2	MEC5.2
Upper Quartz	18	18	18	3.8 cm	22
Lower Quartz	28	28	28		24
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	3.0mW	3.0mW	3.0mW	2.5mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	2.2496	2.2092	1.9276	2.1391	2.0526
Weight Gain (mg)	1.2	3.6	5.0	2.8	8.4
Bias Current	none	none	none	none	none
Temperature (°C)	N/A	484 - 485	484 - 488	N/D	
Film Deposited		Diamond	Diamond		Diamond
Film Type		Not. Cont.	Continuous		Continuous
Film Thickness	0.168μm	0.505μm	0.702μm	0.393μm	47.16 μm
Growth Rate (nm/hr)	11.20	16.83	46.80	26.20	47.16

Table B.20 Deposition Results of Substrates S96 - S100

Appendix B

Date Exp. Began		7/1/95	12/27/95	1/3/96	
Sample	S101	S102	S103	S104	S105
Duration (hours)		20	15	15	
Initial Weight (g)		2.1220			
Resistivity					
Seeding Lot	SC-21	PR-19	SC	SC	
H ₂ (sccm)		200	200	200	
CO ₂ (sccm)		0	0	0	
CH ₄ (sccm)		5	10	5	
O ₂ (sccm)		0	0	0	
Cavity Conf		9			
Susceptor A.		MEC5.2	CS	CS	
Upper Quartz		22			
Lower Quartz		24			
Pressure		9 torr	30	30	
Input Power		3.0mW	3.4mW	3.4mW	
Bias Voltage		none			

Results

Final Weight (g)		2.1250			
Weight Gain (mg)		3.0			
Bias Current		none			
Temperature (°C)		480 - 488	470 $\epsilon=0.35$	467 $\epsilon=0.65$	
Film Deposited		Diamond			
Film Type		Not Cont.			
Film Thickness		42.11 μm			
Growth Rate (nm/hr)					

Table B.21 Deposition Results of Substrates S101 - S105

Appendix B

Date Exp. Began	1/4/96	1/8/96	1/9/96	1/17/96	
Sample	S106	S107	S108	S109	S110
Duration (hours)	15	15	15/25	15	15
Initial Weight (g)	2.3335	2.1935	2.3141		
Resistivity					
Seeding Lot	SC	SC	SC		
H ₂ (sccm)	200	200		200	200
CO ₂ (sccm)	0	0		0	0
CH ₄ (sccm)	5	10		5	5
O ₂ (sccm)	0	0		0	0
Cavity Conf					
Susceptor A.	CS	CS	CS	CS	CS
Upper Quartz					
Lower Quartz					
Pressure	25 torr	25 torr	25 torr	25 torr	25 torr
Input Power	3.4mW	3.4mW	3.4mW	3.4mW	3.4mW
Bias Voltage	45°C	45°C	45°C	45°C	45°C

Results

Final Weight (g)	2.3378	2.1979	2.3174/ 2.3258		
Weight Gain (mg)	4.3	4.4	3.3/11.7		
Bias Current					
Temperature (°C)	439 $\epsilon=0.65$	451 $\epsilon=0.65$	453 $\epsilon=0.65$	441 $\epsilon=0.44$	
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.22 Deposition Results of Substrates S106 - S110

Appendix B

Date Exp. Began	1/21/96	1/23/96	1/24/96	1/25/96	1/26/96
Sample	S111	S112	S113	S114	S115a
Duration (hours)	15	15	15	15	15
Initial Weight (g)		2.2553	2.2847	1.9725	2.2189
Resistivity					
Seeding Lot					
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	0	0	0	0	0
CH ₄ (sccm)	5	5	5	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf					
Susceptor A.	CS	CS	CS	CS	CS
Upper Quartz					
Lower Quartz					
Pressure	25 torr	25 torr	25 torr	25 torr	25 torr
Input Power	3.4mW	3.4mW	3.4mW	3.4mW	3.4mW
Bias Voltage	45 °C	45 °C	45 °C	45 °C	45°C

Results

Final Weight (g)		2.2621	2.2940	1.9778	2.2294
Weight Gain (mg)		6.8	9.3	5.3	10.2
Bias Current					
Temperature (°C)	467 $\epsilon=0.65$	511 $\epsilon=0.65$	502 $\epsilon=0.65$	491 $\epsilon=0.65$	550 $\epsilon=0.65$
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.23 Deposition Results of Substrates S111 - S115a

Appendix B

Date Exp. Began	2/5/96	2/9/96	2/14/96	2/16/96	2/21/96
Sample	S115b	S115c	S115d	S115e	S115f
Duration (hours)	15	15	15	15	15
Initial Weight (g)	2.2294	2.2411	2.5551	2.2685	2.2830
Resistivity					
Seeding Lot					
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	0	0	0	0	0
CH ₄ (sccm)	5	5	5	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf					
Susceptor A.	CS	CS	CS	CS	CS
Upper Quartz					
Lower Quartz					
Pressure	25 torr	25 torr	25 torr	25 torr	25 torr
Input Power	3.4mW	3.4mW	3.4mW	3.4mW	3.4mW
Bias Voltage	45°C	45°C	45°C	45°C	45°C

Results

Final Weight (g)	2.2411	2.5551	2.2685	2.2830	2.2970
Weight Gain (mg)	11.7	14.0	13.4	14.5	14.0
Bias Current					
Temperature (°C)	547 $\epsilon=0.65$	546 $\epsilon=0.65$	545 $\epsilon=0.65$	545 $\epsilon=0.65$	536 $\epsilon=0.65$
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.24 Deposition Results of Substrates S115b - S115f

Appendix B

Date Exp. Began	6/11/96				
Sample	S116	S117	S118	S119	
Duration (hours)	15	15	25	25	
Initial Weight (g)	2.1517				
Resistivity					
Seeding Lot	SC	SC	SC	SC	
H₂ (sccm)	40	40	200	200	
CO₂ (sccm)	0	0	3	0	
CH₄ (sccm)	1	1	3	3	
O₂ (sccm)	0	0	0	0	
Cavity Conf	9	9	9		
Susceptor A.	MEC5.2	MEC5.2	MEC5.2		
Upper Quartz	22 mm	22 mm			
Lower Quartz	24 mm	24 mm			
Pressure	9 torr	9 torr		9 torr	
Input Power	3.0mW	3.0mW		3.0mW	
Bias Voltage	none	none			

Results

Final Weight (g)					
Weight Gain (mg)					
Bias Current					
Temperature (°C)					
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.25 Deposition Results of Substrates S116 - S119

Appendix B

Date Exp. Began					
Sample	S121	S122	S123	S124	S125
Duration (hours)	25	25	15	15	15
Initial Weight (g)					
Resistivity					
Seeding Lot	SC	SC			
H ₂ (sccm)	200	0	200	200	200
CO ₂ (sccm)	0	60	0	0	0
CH ₄ (sccm)	3	30	3	3	3
O ₂ (sccm)					
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	7 torr	7 torr	7 torr	7 torr	7 torr
Input Power		1kW	1kW	1kW	1kW
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)					
Bias Current					
Temperature (°C)					
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.26 Deposition Results of Substrates S121 - S125

Appendix B

Date Exp. Began					2/6/98
Sample					S130
Duration (hours)					40
Initial Weight (g)					
Resistivity					
Seeding Lot					
H₂ (sccm)					200
CO₂ (sccm)					0
CH₄ (sccm)					7
O₂ (sccm)					0
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure					9 torr
Input Power					3.0mW
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)					
Bias Current					
Temperature (°C)					
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table B.27 Deposition Results of Substrate S130

Appendix B

Date Exp. Began		7/5/94		1/24/95	
Sample	IC-1	IC-2		IC-4	
Duration (hours)		40		25	
Initial Weight (g)		1.3822		1.4047	
Resistivity					
Seeding Lot		Spin		SC-17	
H ₂ (sccm)	200	200		200	
CO ₂ (sccm)	8	8		8	
CH ₄ (sccm)	3	3		3	
O ₂ (sccm)	0	0		0	
Cavity Conf		9		9	
Susceptor A.		MEC5.2		MEC5.2	
Upper Quartz		22		22	
Lower Quartz		24		24	
Pressure		9 torr		8 torr	
Input Power		3.0mW		3.0mW	
Bias Voltage	none	none		none	

Results

Final Weight (g)		1.3870		1.4089	
Weight Gain (mg)		4.8		4.2	
Bias Current	none	none		none	
Temperature (°C)		460 - 465			
Film Deposited		Diamond		Diamond	
Film Type		Continuous		Continuous	
Film Thickness					
Growth Rate (nm/hr)					

Table B.28 Deposition Results of Substrates IC-1 - IC-4

Appendix C

Deposition Experiments on 3" Silicon Substrates

This Appendix contains tabular data that was recorded from diamond deposition experiments with polished 3" silicon wafers. This data is presented as a reference for discussions in earlier chapters regarding diamond deposition on these substrates. The tables include all the measurable data that was recorded, including experiments that were not included in earlier discussions.

There are vast differences between many of the experiments that are listed here, as was noted in chapters 4 - 6. The data in the tables includes measurable experimental parameters such as measured weight gains and measured substrate temperatures; however, they do not reflect the quality of the deposited film or the coverage area. There were many experiments where problems occurred such as an unexpected shift in the position of the plasma or the substrate. These random occurrences were caused by things like cracked quartz tubes and coating on the quartz bell jar etc. Hence, in addition to making comparisons of the data in the tables it is necessary to characterize each specific film, as was done prior to the development of the discussions that were presented in earlier chapters.

Appendix C

Date Exp. Began	2/16/94	2/25/94	3/12/94	3/17/94	3/18/94
Sample	S3-1	S3-2	S3-3	S3-4	S3-5
Duration (hours)	40		40	24	30
Initial Weight (g)		4.1486	3.6183	3.9600	3.6606
Resistivity					
Seeding Lot					
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₄ (sccm)	3	3	3	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	6	6	6	6	6
Susceptor A.	MB2	MB2	MB2	MB2	MB2
Upper Quartz	none	none	none	none	none
Lower Quartz	4.5cm	4.5cm	4.5cm	4.5cm	4.5cm
Pressure	7 torr	7 torr	7 torr	7 torr	7 torr
Input Power	3.0mW	3.0mW	3.2mW	3.25mW	3.2mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)		4.1566		3.9644	3.6645
Weight Gain (mg)		8.0		4.4	3.9
Bias Current	none	none	none	none	none
Temperature (°C)	475 - 485	445 - 450	465 - 475	470 - 480	460 - 465
Film Deposited	Diamond	Diamond	Diamond	Diamond	Diamond
Film Type					
Film Thickness		0.5μm		0.275μm	0.244μm
Growth Rate (nm/hr)					

Table C.1 Deposition Results of Substrates S3-1 - S3-5

Appendix C

Date Exp. Began					7/10/94
Sample					S3-10
Duration (hours)					40
Initial Weight (g)					
Resistivity					
Seeding Lot					
H₂ (sccm)					200
CO₂ (sccm)					8
CH₄ (sccm)					3
O₂ (sccm)					0
Cavity Conf					9
Susceptor A.					MEC5.2
Upper Quartz					22mm
Lower Quartz					24mm
Pressure					8 torr
Input Power					3.0mW
Bias Voltage					none

Results

Final Weight (g)					
Weight Gain (mg)					
Bias Current					none
Temperature (°C)					447 - 453
Film Deposited					Diamond
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table C.2 Deposition Results of Substrate S3-10

Appendix C

Date Exp. Began	8/1/94	9/21/94	9/23/94		
Sample	S3-11	S3-12	S3-13	S3-14	
Duration (hours)	40	40	40	10	
Initial Weight (g)		3.9876	4.1678	3.6987	
Resistivity					
Seeding Lot		20.2	20.2	20.2	
H ₂ (sccm)	200	200	200	200	
CO ₂ (sccm)	8	0	0	0	
CH ₄ (sccm)	3	5	5	5	
O ₂ (sccm)	0	0	0	0	
Cavity Conf	7	9	9	9	
Susceptor A.	MEC5.2	MEC5.2	MEC5.3	MB2	
Upper Quartz	22mm	22mm	22mm	none	
Lower Quartz	24mm	24mm	24mm	5.3cm	
Pressure	9 torr	9 torr	9 torr		
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	
Bias Voltage	none	none	none	none	

Results

Final Weight (g)		4.0170	4.1903	3.7018	
Weight Gain (mg)		29.4	22.5	9.1	
Bias Current	none	none	none	none	
Temperature (°C)	438 - 447	468 - 473	468 - 473		
Film Deposited	Diamond	Diamond	Diamond	Diamond	
Film Type		Continuous	Continuous	Not Cont.	
Film Thickness		1.83 μm	1.41 μm	0.57 μm	
Growth Rate (nm/hr)		45.75	35.25	57.00	

Table C.3 Deposition Results of Substrates S3-11 - S3-14

Appendix C

Date Exp. Began		10/1/94	10/4/94	11/26/94	11/27/94
Sample		S3-17	S3-18	S3-19	S3-20
Duration (hours)		40	40	22	22
Initial Weight (g)		4.1467	4.1226	3.9861	3.6569
Resistivity					
Seeding Lot		21.2	21.2	SC-1	SC-2
H ₂ (sccm)		200	200	200	200
CO ₂ (sccm)		0	0	0	0
CH ₄ (sccm)		5	5	5	5
O ₂ (sccm)		0	0	0	0
Cavity Conf		9	9	9	9
Susceptor A.		MEC5.2	MEC5.3	MEC5.2	MEC5.2
Upper Quartz		22mm	22mm	22	26
Lower Quartz		24mm	24mm	24	24
Pressure		9 torr	9 torr	9 torr	9 torr
Input Power		3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage		none	none	none	none

Results

Final Weight (g)		4.1824	4.1491	3.9957	3.6713
Weight Gain (mg)		35.7	26.5	9.6	14.4
Bias Current		none	none	none	none
Temperature (°C)		468 - 473	468 - 472	467-473 ε=0.65	490-505 ε=0.65
Film Deposited		Diamond	Diamond	Diamond	Diamond
Film Type		Continuous	Continuous		
Film Thickness		2.23 μm	1.66 μm	0.6μm	0.9μm
Growth Rate (nm/hr)		55.75	41.50	27.27	40.91

Table C.4 Deposition Results of Substrates S3-17 - S3-20

Appendix C

Date Exp. Began	11/29/94	21/1/94	12/7/94		
Sample	S3-21	S3-22	S3-23		
Duration (hours)	40	22	40		
Initial Weight (g)	4.1770	3.9471	4.0734		
Resistivity					
Seeding Lot	SC-3	SC-4	SC-5		
H ₂ (sccm)	200	200	200		
CO ₂ (sccm)	0	0	0		
CH ₄ (sccm)	5	5	5		
O ₂ (sccm)	0	0	0		
Cavity Conf	9	9	9		
Susceptor A.	MEC5.2	MEC5.2	MEC5.2		
Upper Quartz	22	30	26		
Lower Quartz	24	24	24		
Pressure	9 torr	9 torr	7 torr		
Input Power	3.0mW	3.0mW	3.0mW		
Bias Voltage	none	none	none		

Results

Final Weight (g)	4.2076	3.9621	4.1002		
Weight Gain (mg)	30.6	15.0	26.8		
Bias Current	none	none	none		
Temperature (°C)	468-472 e=0.65	470-478 e=0.90	468-470 e=0.65		
Film Deposited	Diamond	Diamond	Diamond		
Film Type					
Film Thickness	1.91μm	0.94μm	1.675μm		
Growth Rate (nm/hr)	47.75	42.72	41.86		

Table C.5 Deposition Results of Substrates S3-21 - S3-23

Appendix C

Date Exp. Began	2/15/98				
Sample	pulse-15				
Duration (hours)	15				
Initial Weight (g)					
Resistivity					
Seeding Lot					
H₂ (sccm)	100				
CO₂ (sccm)	0				
CH₄ (sccm)	1.5				
O₂ (sccm)					
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	15 torr				
Input Power	1kW				
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)	11.2				
Bias Current					
Temperature (°C)	520				
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table C.6 Deposition Results of Substrate pulse-15

Appendix D

Deposition Experiments on 4" Silicon Substrates

This Appendix contains tabular data that was recorded from diamond deposition experiments with polished 4" silicon wafers. This data is presented as a reference for discussions in earlier chapters regarding diamond deposition on these substrates. The tables include all the measurable data that was recorded, including experiments that were not included in earlier discussions.

There are vast differences between many of the experiments that are listed here, as was noted in chapters 4 - 6. The data in the tables includes measurable experimental parameters such as measured weight gains and measured substrate temperatures; however, they do not reflect the quality of the deposited film or the coverage area. There were many experiments where problems occurred such as an unexpected shift in the position of the plasma or the substrate. These random occurrences were caused by things like cracked quartz tubes and coating on the quartz bell jar etc. Hence, in addition to making comparisons of the data in the tables it is necessary to characterize each specific film, as was done prior to the development of the discussions that were presented in earlier chapters.

Appendix D

Date Exp. Began	2/27/94	3/2/94	4/4/94	4/5/94	10/9/94
Sample	S4-1	S4-2	S4-3	S4-4	S4-5
Duration (hours)	40	40	24	40	40
Initial Weight (g)	6.6184	6.6008			9.1174
Resistivity					
Seeding Lot			Sondes		21.2
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	0
CH ₄ (sccm)	3	3	3	3	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	6	6	6	6	9
Susceptor A.	MB1	MB1	MB1	MB1	MEC6
Upper Quartz	none	none	none	none	22mm
Lower Quartz	4.8 cm	4.8 cm	5.3cm	5.3cm	24mm
Pressure	7 torr	7 torr	6 torr	7torr	9 torr
Input Power	3.1mW	3.2mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	6.8070	6.7943			9.1614
Weight Gain (mg)	18.86	19.35			44.00
Bias Current	none	none	none	none	none
Temperature (°C)	465 - 470	460 - 470	490 - 500	500 - 510	470 - 476
Film Deposited	Diamond	Diamond	Diamond	Diamond	Diamond
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table D.1 Deposition Results of Substrates S4-1 - S4-5

Appendix D

Date Exp. Began	10/24/94				
Sample	S4-6				
Duration (hours)	40				
Initial Weight (g)	9.0938				
Resistivity					
Seeding Lot	21.3				
H₂ (sccm)	200				
CO₂ (sccm)	0				
CH₄ (sccm)	5				
O₂ (sccm)	0				
Cavity Conf	9				
Susceptor A.	MEC6				
Upper Quartz	22mm				
Lower Quartz	24mm				
Pressure	8 torr				
Input Power	3.0mw				
Bias Voltage	none				

Results

Final Weight (g)	9.1312				
Weight Gain (mg)	37.4				
Bias Current	none				
Temperature (°C)	463 - 469				
Film Deposited	Diamond				
Film Type					
Film Thickness	1.3μm				
Growth Rate (nm/hr)					

Table D.2 Deposition Results of Substrate S4-6

Appendix E

Deposition Experiments on 2" Corning 7059 Substrates

This Appendix contains tabular data that was recorded from diamond deposition experiments with 2" Corning 7059 substrates. This data is presented as a reference for discussions in earlier chapters regarding diamond deposition on these substrates. The tables include all the measurable data that was recorded, including experiments that were not included in earlier discussions.

There are vast differences between many of the experiments that are listed here, as was noted in chapters 4 - 6. The data in the tables includes measurable experimental parameters such as measured weight gains and measured substrate temperatures; however, they do not reflect the quality of the deposited film or the coverage area. There were many experiments where problems occurred such as an unexpected shift in the position of the plasma or the substrate. These random occurrences were caused by things like cracked quartz tubes and coating on the quartz bell jar etc. Hence, in addition to making comparisons of the data in the tables it is necessary to characterize each specific film, as was done prior to the development of the discussions that were presented in earlier chapters.

Appendix E

Date Exp. Began	1/21/94	1/24/94	2/7/94	3/4/94	4/24/94
Sample	G7-1	G7-2	G7-3	G7-4	G7-5
Duration (hours)	30	40	38	40	40
Initial Weight (g)		6.1718	6.0790		6.1783
Seeding Lot	0	0	0	0	100
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₄ (sccm)	3	3	3	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	4	4	4	4	7
Susceptor A.	MEC1.1	MEC1.1	MEC1.1	MEC1.1	MEC4
Upper Quartz					20mm
Lower Quartz					24mm
Pressure	7 torr	7 torr	7 torr	7 torr	15 torr
Input Power	1.0mW	1.15mW	1.15mW	1.1 mW	3.0mW
Heater Voltage	none	none	none	none	none

Results

Final Weight (g)	6.1499	6.1792	6.0858		6.1948
Weight Gain (mg)		7.4	6.8		16.5
Heater Current	none	none	none	none	none
Temperature (°C)		470	466		506-511
Film Deposited					Diamond
Film Type					Peeled
Film Thickness (w.g.)		1.04μm	0.95μm		N/A
Film Thickness (x-mission)					
Growth Rate (nm/hr)		25.97	25.9		N/A

Table E.1 Deposition Results of Substrates G7-1 - G7-5

Appendix E

Date Exp. Began	4/26/94	4/29/94	5/1/94	5/5/94	
Sample	G7-6	G7-7	G7-8	G7-9	
Duration (hours)	40	38	40	40	
Initial Weight (g)	6.0895	6.1648	6.1264	6.1014	
Seeding Lot	100	100	100	100	
H ₂ (sccm)	200	200	200	200	
CO ₂ (sccm)	8	8	8	8	
CH ₄ (sccm)	3	3	3	3	
O ₂ (sccm)	0	0	0	0	
Cavity Conf	7	7	7	7	
Susceptor A.	MEC4	MEC4	MEC4	MEC4	
Upper Quartz	20mm	20mm	20mm	20mm	
Lower Quartz	24mm	24mm	24mm	24mm	
Pressure	13 torr	9 torr	11 torr	11 torr	
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	
Heater Voltage	none	none	none	none	

Results

Final Weight (g)	6.1043	6.1722	6.1380		
Weight Gain (mg)	14.8	7.4	11.6	7.8	
Heater Current	none	none	none	none	
Temperature (°C)	479-490	450	455-470		
Film Deposited	Diamond	Diamond	Diamond	Diamond	
Film Type	Peeled	Continuous	Process Error	Continuous	
Film Thickness (w.g.)	N/A	1.179μm	N/A	N/A	
Film Thickness (x-mission)					
Growth Rate (nm/hr)	N/A	29.48	N/A		

Table E.2 Deposition Results of Substrates G7-6 - G7-9

Appendix E

Date Exp. Began			10/19/94	12-11/94	12/15/94
Sample			G7-13	G7-14	G7-15
Duration (hours)			100	50	15
Initial Weight (g)			6.0723	6.1025	6.1246
Seeding Lot			100	SC-6	SC-7
H ₂ (sccm)			200	200	200
CO ₂ (sccm)			0	0	0
CH ₄ (sccm)			5	5	5
O ₂ (sccm)			0	0	0
Cavity Conf			9	9	9
Susceptor A.			MEC5.2	MEC5.2	MEC5.2
Upper Quartz			22mm	22	22
Lower Quartz			24mm	24	24
Pressure			9 torr	9 torr	9 torr
Input Power			3.0mW	3.0mW	3.0mW
Heater Voltage			none	none	none

Results

Final Weight (g)				6.1335	6.1330
Weight Gain (mg)				31.0	8.4
Heater Current			none	none	none
Temperature (°C)			468 - 470	465-470	468-472
Film Deposited			Diamond	Diamond	Diamond
Film Type			Peeled	Continuous	Continuous
Film Thickness (w.g.)				4.35μm	1.18μm
Film Thickness (x-mission)					1.68μm
Growth Rate (nm/hr)				87.02	78.6, 112.0

Table E.3 Deposition Results of Substrates G7-13 - G7-15

Appendix E

Date Exp. Began	12/17/94	12/20/94	4/9/95	4/12/95	4/14/95
Sample	G7-16	G7-17	G7-18	G7-19	G7-20
Duration (hours)	25	25	40	15	15
Initial Weight (g)	6.1715	6.1554	6.1235	6.1383	6.1328
Seeding Lot	SC-8	SC-17	SC-23	SC-23	SC-23
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	0	8	8	8	8
CH ₄ (sccm)	5	3	8	8	8
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	10	10	10
Susceptor A.	MEC5.2	MEC5.2	HA1.2	HA1.2	HA1.2
Upper Quartz	22	22	3.4	3.4	3.4
Lower Quartz	24	24			
Pressure	9 torr	9 torr	7 torr	7 torr	7 torr
Input Power	3.0mW	3.0mW	2.5mW	2.5mW	2.5mW
Heater Voltage	none	none	none	70 Vac	60 Vac

Results

Final Weight (g)	6.1844	6.1499	6.1249	6.1452	6.1380
Weight Gain (mg)	12.9	5.5	1.4	6.9	5.2
Heater Current	none	none	none	3.02	2.51
Temperature (°C)	448 - 454 $\epsilon=0.65$	455 - 457 $\epsilon=0.65$	N/A	452 - 464 $\epsilon=0.65$	437 - 443 $\epsilon=0.65$
Temocouple (°F)				675	630
Film Deposited	Diamond	Diamond			
Film Type	Continuous			Peeled	Peeled Late
Film Thickness	1.81 μ m	0.772 μ m	0.196 μ m	0.968 μ m	0.730 μ m
Growth Rate (nm/hr)	72.43	30.88	N/A	64.53	48.67

Table E.4 Deposition Results of Substrates G7-16 - G7-20

Appendix E

Date Exp. Began	4/15/95	4/16/95	4/16/95	4/17/95	4/18/95
Sample	G7-21	G7-22	G7-23	G7-24	G7-25
Duration (hours)	15	25	15	15	15
Initial Weight (g)	6.1579	6.1523		6.1436	6.1662
Seeding Lot	SC-24	SC-24	SC-24	SC-25	SC-25
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	0	0
CH ₃ (sccm)	8	8	8	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	10	10	10	10	10
Susceptor A.	HA1.3	HA1.2	HA1.2	HA1.2	HA1.2
Upper Quartz	3.4	3.4	3.4	3.4	3.4
Lower Quartz					
Pressure	7 torr	7 torr	4 torr	4 torr	4 torr
Input Power	2.5mW	2.5mW	2.5mW	2.5mW	2.5mW
Heater Voltage	60 Vac	60 Vac	60 Vac	52 Vac	60 Vac

Results

Final Weight (g)	6.1579	6.1543	6.1153	6.1454	6.1685
Weight Gain (mg)	4.9	2.0	3.4	1.8	2.3
Heater Current (A)	2.52	2.50	2.50	2.06	2.42
Temperature (°C)	428 - 434 e=0.65	N/A	N/A	N/A	428 e=0.65
Temocouple (°F)	638	633	614	583	626
Film Deposited					
Film Type	Peeled Late		Peeled Late		
Film Thickness	0.688μm	0.281	0.477	0.253	0.323
Growth Rate (nm/hr)	45.87	N/A	31.80	16.87	21.53

Table E.5 Deposition Results of Substrates G7-21 - G7-25

Appendix E

Date Exp. Began	4/23/95	4/25/95	4/30/95	5/19/95	5/31/95
Sample	G7-26	G7-27	G7-28	G7-29	G7-30
Duration (hours)	25	25	25	25	25
Initial Weight (g)	N/A	6.1290	6.1730	6.1612	6.1066
Seeding Lot	SC-25	SC-25			
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₃ (sccm)	3	3	3	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	10	10	10	10	10
Susceptor A.	HA2.2	HA2.2	HA2.2	HA2.2	HA2.2
Upper Quartz	3.4	3.4	3.4	3.4	3.4
Lower Quartz					
Pressure	9 torr	9 torr	9 torr	7 torr	7 torr
Input Power	2.5mW	2.5mW	2.5mW	2.5mW	2.5mW
Heater Voltage	50 Vac	60 Vac	none	50 Vac	60 Vac measured

Results

Final Weight (g)	6.1521	6.1357	6.0727	6.1644	6.1118
Weight Gain (mg)	3.3	6.7	-0.3	3.2	5.2
Heater Current(A)	2.03	2.53	none	2.04	2.60
Temperature (°C)	463 $\epsilon=0.65$	N/A	N/A	N/A	N/A
Temocouple (°F)	N/A	N/A	451	616	459
Film Deposited	Diamond	Diamond	Diamond	Diamond	
Film Type	Continuous	Continuous	Not Cont.		
Film Thickness	0.463	0.940 μ m	---	0.449 μ m	0.730 μ m
Growth Rate (nm/hr)	18.52			17.96	

Table E.6 Deposition Results of Substrates G7-26 - G7-30

Appendix E

Date Exp. Began		6/8/95	6/10/95	6/12/95	6/20/95
Sample	G7-31	G7-32	G7-33	G7-34	G7-35
Duration (hours)		25	25	25	25
Initial Weight (g)		6.0500	6.0376	6.0404	6.0519
Seeding Lot					
H ₂ (sccm)		200	200	200	200
CO ₂ (sccm)		8	8	8	8
CH ₃ (sccm)		3	3	3	3
O ₂ (sccm)		0	0	0	0
Cavity Conf		10	10	10	10
Susceptor A.		HA2.2	HA2.2	HA2.2	HA2.2
Upper Quartz		3.4	3.4	3.4	3.4
Lower Quartz					
Pressure		5 torr	3 torr	4 torr	9 torr
Input Power		2.5mW	2.5mW	2.5mW	2.5mW
Heater Voltage		60 Vac measured	60 Vac measured	60 Vac measured	50 Vac measured

Results

Final Weight (g)		6.0538	---	6.0418	---
Weight Gain (mg)		3.8	---	1.4	---
Heater Current(A)		2.58	2.56	2.57	2.11
Temperature (°C)		N/A	N/A		
Thermocouple (°F)		640	668	636	674
Film Deposited		Diamond	No Film	Diamond	No Film
Film Type		continuous	---	No Film near Edge	
Film Thickness		0.533μm	---	0.197μm	
Growth Rate (nm/hr)				7.88	

Table E.7 Deposition Results of Substrates G7-31 - G7-35

Appendix E

Date Exp. Began	6/25/95	6/26/95	6/28/95	6/29/95	7/5/95
Sample	G7-36	G7-37	G7-38	G7-39	G7-40
Duration (hours)	25	25	25	25	20
Initial Weight (g)	6.0800	6.0258	6.0160	5.9979	6.0521
Seeding Lot					
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	0
CH ₃ (sccm)	3	3	3	3	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	10	10	10	10	9
Susceptor A.	HA2.2	HA2.2	HA2.2	HA2.2	MEC5.2
Upper Quartz	3.4	3.4	3.4	3.4	
Lower Quartz					
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	2.5mW	2.5mW	2.5mW	2.5mW	3.0mW
Heater Voltage	50 Vac measured	50 Vac measured	50 Vac measured	50 Vac measured	none

Results

Final Weight (g)	6.0804	6.0276	---	---	6.0588
Weight Gain (mg)	0.4	1.8	---	---	6.7
Heater Current(A)	2.10	2.14	2.15	2.10	N/A
Temperature (°C)					
Thermocouple (°F)	570	550 - 556	425	552	
Film Deposited	No Film	Diamond in Center	No Film	Diamond in Center	Diamond Peeled later
Film Type					
Film Thickness		0.253μm			0.94μm
Growth Rate (nm/hr)		10.12			47.00

Table E.8 Deposition Results of Substrates G7-36 - G7-40

Appendix E

Date Exp. Began	7/7/95	8/27/95	9/7/95	9/8/95	9/10/95
Sample	G7-41	G7-42	G7-43	G7-44	G7-45
Duration (hours)	25	25	10	15	15
Initial Weight (g)	6.0908		6.0318		6.0256
Seeding Lot			95-200-SC-1	95-201-SC-1	95-202-SC-1
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	0	0	0
CH ₃ (sccm)	3	3	5	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	10	10	9	9	9
Susceptor A.	HA2.2	MEC5.2	MEC5.2	MEC5.2	MEC5.2
Upper Quartz	3.4				
Lower Quartz					
Pressure	9 torr	7 torr	7 torr	7 torr	7 torr
Input Power	2.5mW	3.0mW	3.0mW	3.0mW	3.0mW
Heater Voltage	50 Vac measured	none	none	none	none

Results

Final Weight (g)	6.0913		6.0345	6.0343	6.0284
Weight Gain (mg)	0.5	none	2.8	3.2	2.8
Heater Current(A)		N/A	N/A	N/A	N/A
Temperature (°C)					
Thermocouple (°F)					
Film Deposited	No Film	No Film	Diamond	Diamond	
Film Type			Cont.	Off Center	
Film Thickness			0.393μm	0.463μm	0.393μm
Growth Rate (nm/hr)			39.3	30.87	26.20

Table E.9 Deposition Results of Substrates G7-41 - G7-45

Appendix E

Date Exp. Began	9/23/95				
Sample	G7-46	G7-47			
Duration (hours)	10				
Initial Weight (g)	6.0342	6.0552			
Seeding Lot					
H₂ (sccm)	200				
CO₂ (sccm)	0				
CH₃ (sccm)	8				
O₂ (sccm)	0				
Cavity Conf	9				
Susceptor A.	MEC5.2				
Upper Quartz	2.2				
Lower Quartz	2.4				
Pressure	7 torr				
Input Power	3.0mW				
Heater Voltage	none				

Results

Final Weight (g)	6.0345	6.0581			
Weight Gain (mg)	2.3	2.9			
Heater Current(A)					
Temperature (°C)					
Thermocouple (°F)					
Film Deposited	Diamond				
Film Type					
Film Thickness	0.323μm				
Growth Rate (nm/hr)	32.30				

Table E.10 Deposition Results of Substrates G7-46 - G7-47

Appendix E

Date Exp. Began				10/10/96	11/10/96
Sample	G7-51	G7-52	G7-53	G7-54	G7-55
Duration (hours)	15	15	15	15	30
Initial Weight (g)	6.0400	6.0344			2.0109
Seeding Lot					
H ₂ (sccm)	200	200		200	200
CO ₂ (sccm)	0	0	60	0	0
CH ₃ (sccm)	5	5	30	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf				12	12
Susceptor A.	MEC7.2	MEC7.2	MEC7.2	MEC7.2	MEC7.2
Upper Quartz	58 mm	58 mm	58 mm	58 mm	58 mm
Lower Quartz					
Pressure	7 torr	9 torr	3 torr	5 torr	5 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Heater Voltage				none	none

Results

Final Weight (g)	6.0451	6.0424			
Weight Gain (mg)	5.1	8.5		2.9	6.2
Heater Current(A)					
Temperature (°C)		517			
Thermocouple (°F)					
Film Deposited	Diamond	Diamond	Not Diamond		
Film Type					
Film Thickness (w.g.)	0.72μm	1.19μm		0.407μm	0.87μm
Film Thickness (x-mission)		1.07μm			
Growth Rate (nm/hr)	48.0	79.3		27	29

Table E.11 Deposition Results of Substrates G7-51 - G7-55

Appendix E

Date Exp. Began					
Sample					G72-60
Duration (hours)					15
Initial Weight (g)					
Seeding Lot					
H₂ (sccm)					200
CO₂ (sccm)					0
CH₄ (sccm)					5
O₂ (sccm)					
Cavity Conf					MEC7
Susceptor A.					
Upper Quartz					58mm
Lower Quartz					
Pressure					9 torr
Input Power					1kW
Heater Voltage					

Results

Final Weight (g)					
Weight Gain (mg)					6.0
Heater Current					none
Temperature (°C)					463
Film Deposited					Diamond
Film Type					cont.
Film Thickness (w.g.)					0.84μm
Film Thickness (x-mission)					0.78μm
Growth Rate (nm/hr)					56.0

Table E.12 Deposition Results of Substrate G72-60

Appendix E

Date Exp. Began	2/15/98	2/15/98	2/15/98	2/15/98	2/16/98
Sample	G72-61	G72-62	G72-63	G72-64	G72-65
Duration (hours)	0.5/15.0	0.5/14.5	0.5/9.5	15	20
Initial Weight (g)					
Seeding Lot					
H ₂ (sccm)	200/200	200/200	200/200	200	200
CO ₂ (sccm)	0/0	0/0	0/0	8	8
CH ₄ (sccm)	20/5	20/5	20/5	8	8
O ₂ (sccm)					
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure	9 torr	9 torr	9 torr	9 torr	9 torr
Input Power	1kW	1kW	1kW	1kW	1kW
Heater Voltage					

Results

Final Weight (g)					
Weight Gain (mg)	7.7	7.4	4.3	3.2	
Heater Current					
Temperature (°C)	463	463	463	481 $\epsilon=0.65$	
Film Deposited	Diamond	Diamond	Diamond	No CO ₂	No CO ₂
Film Type	Peeled	Peeled	cont.	Not Diamond	Not Diamond
Film Thickness (w.g.)	1.1 μ m	1.0 μ m	0.6 μ m		
Film Thickness (x-mission)			0.6 μ m		
Growth Rate (nm/hr)	71.0	69.3	60.0		

Table E.13 Deposition Results of Substrates G72-61 - G72-65

Appendix E

Date Exp. Began	2/15/98	4/11/98			
Sample	G72-66	G72-67			
Duration (hours)	25	0.5/24.5			
Initial Weight (g)	6.1871	6.2216			
Seeding Lot					
H₂ (sccm)	200	200			
CO₂ (sccm)	8	0			
CH₄ (sccm)	8	20/5			
O₂ (sccm)	0	0			
Cavity Conf	MEC7.2	MEC7.2			
Susceptor A.					
Upper Quartz	58 mm	58 mm			
Lower Quartz					
Pressure	9 torr	9 torr			
Input Power	1kW	1kW			
Heater Voltage					

Results

Final Weight (g)	6.1991	6.2319			
Weight Gain (mg)	12.0	10.3			
Heater Current	none	none			
Temperature (°C)	475	522			
Film Deposited	Diamond	Diamond			
Film Type	cont.	continuous			
Film Thickness (w.g.)	1.68 μm	1.45 μm			
Film Thickness (x-mission)	1.84 μm	1.35 μm			
Growth Rate (nm/hr)	67.2	58.0			

Table E.14 Deposition Results of Substrates G72-66 - G72-67

Appendix F

Deposition Experiments on 3" Corning 7059 Substrates

This Appendix contains tabular data that was recorded from diamond deposition experiments with 3" Corning 7059 substrates. This data is presented as a reference for discussions in earlier chapters regarding diamond deposition on these substrates. The tables include all the measurable data that was recorded, including experiments that were not included in earlier discussions.

There are vast differences between many of the experiments that are listed here, as was noted in chapters 4 - 6. The data in the tables includes measurable experimental parameters such as measured weight gains and measured substrate temperatures; however, they do not reflect the quality of the deposited film or the coverage area. There were many experiments where problems occurred such as an unexpected shift in the position of the plasma or the substrate. These random occurrences were caused by things like cracked quartz tubes and coating on the quartz bell jar etc. Hence, in addition to making comparisons of the data in the tables it is necessary to characterize each specific film, as was done prior to the development of the discussions that were presented in earlier chapters.

Appendix F

Date Exp. Began	6/2/94	6/11/94	9/29/94	10/7/94	10/13/94
Sample	G73-11	G73-12	G73-13	G73-14	G73-15
Duration (hours)	40	80	30	50	50
Initial Weight (g)	13.8521		13.8170	13.7441	13.8081
Seeding Lot			21.1	21.1	21.1
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	0	8	0
CH ₄ (sccm)	3	3	5	3	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	9	9
Susceptor A.	MEC5.2	MEC5.2	MEC5.2	MEC5.2	MEC5.2
Upper Quartz	20	20	22	22	22
Lower Quartz	26	26	24	24	24
Pressure	10 torr	8 torr	9 torr	9 torr	9 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	13.8701		13.8491	13.7707	13.8533
Weight Gain (mg)	18.0	28.0	32.1	26.6	45.2
Bias Current	none	none	none	none	none
Temperature (°C)	455 -465	436 - 440	468 - 473	465 - 470	496 - 473
Film Deposited	Diamond	Diamond	Diamond	Diamond	Diamond
Film Type			Continuous	peeled	Continuous
Film Thickness		1.75 μm	2.01 μm	1.66 μm	2.83 μm
Growth Rate (nm/hr)		21.86	67.00	33.20	56.6

Table F.1 Deposition Results of Substrates G73-11 - G73-15

Appendix F

Date Exp. Began	10/17/94				
Sample	G73-16				
Duration (hours)	50				
Initial Weight (g)	13.9142				
Seeding Lot	21.1				
H₂ (sccm)	200				
CO₂ (sccm)	8				
CH₄ (sccm)	3				
O₂ (sccm)	0				
Cavity Conf	9				
Susceptor A.	MEC5.2				
Upper Quartz	22				
Lower Quartz	24				
Pressure	9 torr				
Input Power	3.0mW				
Bias Voltage	none				

Results

Final Weight (g)	13.9421				
Weight Gain (mg)	27.9				
Bias Current	none				
Temperature (°C)	468 - 470				
Film Deposited	Diamond				
Film Type	Continuous				
Film Thickness	1.74 μm				
Growth Rate (nm/hr)	34.8				

Table F.2 Deposition Results of Substrate G73-16

Appendix F

Date Exp. Began	10/14/96	10/18/96			
Sample	LBL-1	LBL-2			
Duration (hours)	30	20			
Initial Weight (g)	13.6366	13.6681			
Seeding Lot	101196.1.1	101196.1.1			
H₂ (sccm)	200	200			
CO₂ (sccm)	8	8			
CH₄ (sccm)	3	3			
O₂ (sccm)	0	0			
Cavity Conf	12	12			
Susceptor A.	MEC7.2	MEC7.2			
Upper Quartz	58 mm	58 mm			
Lower Quartz					
Pressure	6 torr	6 torr			
Input Power	3.0mW	3.0mW			
Bias Voltage	none	none			

Results

Final Weight (g)	13.6496	13.6750			
Weight Gain (mg)	13.0	6.9			
Bias Current	none	none			
Temperature (°C)	---	---			
Film Deposited	Diamond	Diamond			
Film Type	Transparent (rough)	Transparent (smooth)			
Film Thickness	0.813μm	0.431μm			
Growth Rate (nm/hr)	27.10	21.55			

Table F.3 Deposition Results of Substrates LBL-1 - LBL-2

Appendix G

Deposition Experiments on 4" Corning 7059 Substrates

This Appendix contains tabular data that was recorded from diamond deposition experiments with 4" Corning 7059 Substrates. This data is presented as a reference for discussions in earlier chapters regarding diamond deposition on these substrates. The tables include all the measurable data that was recorded, including experiments that were not included in earlier discussions.

There are vast differences between many of the experiments that are listed here, as was noted in chapters 4 - 6. The data in the tables includes measurable experimental parameters such as measured weight gains and measured substrate temperatures; however, they do not reflect the quality of the deposited film or the coverage area. There were many experiments where problems occurred such as an unexpected shift in the position of the plasma or the substrate. These random occurrences were caused by things like cracked quartz tubes and coating on the quartz bell jar etc. Hence, in addition to making comparisons of the data in the tables it is necessary to characterize each specific film, as was done prior to the development of the discussions that were presented in earlier chapters.

Appendix G

Date Exp. Began	10/26/94	10/28/94	11/1/94	11/8/94	11/11/94
Sample	G74-1	G74-2	G74-3	G74-4	G74-5
Duration (hours)	50	80	80	4	50
Initial Weight (g)	25.0084	25.0471	25.0808		25.0781
Seeding Lot	21.3	21.3	21.3	none	
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	0	0	0	0	0
CH ₄ (sccm)	5	5	5	5	5
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	9	9	9	9	9
Susceptor A.	MEC6	MEC6	MEC6.2	MEC6.2	MEC6.2
Upper Quartz	none	none	none	none	none
Lower Quartz	24	24			
Pressure	8 torr	7 torr	7 torr	9 torr	8 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)		25.1168			25.1003
Weight Gain (mg)	50.0	69.7	67.7	N/A	22.2
Bias Current	none	none	none	none	none
Temperature (°C)	455 - 460	446 - 448	444 - 448	468 - 477	451 - 453
Film Deposited					
Film Type					
Film Thickness					0.78mm
Growth Rate (nm/hr)					

Table G.1 Deposition Results of Substrates G74-1 - G74-5

Appendix H

Deposition Experiments on 2" Pyrex Substrates

This Appendix contains tabular data that was recorded from diamond deposition experiments with 2" Corning 7050 substrates. This data is presented as a reference for discussions in earlier chapters regarding diamond deposition on these substrates. The tables include all the measurable data that was recorded, including experiments that were not included in earlier discussions.

There are vast differences between many of the experiments that are listed here, as was noted in chapters 4 - 6. The data in the tables includes measurable experimental parameters such as measured weight gains and measured substrate temperatures; however, they do not reflect the quality of the deposited film or the coverage area. There were many experiments where problems occurred such as an unexpected shift in the position of the plasma or the substrate. These random occurrences were caused by things like cracked quartz tubes and coating on the quartz bell jar etc. Hence, in addition to making comparisons of the data in the tables it is necessary to characterize each specific film, as was done prior to the development of the discussions that were presented in earlier chapters.

Appendix H

Date Exp. Began	5/8/94	5/10/94	5/15/94	5/21/94	5/29/94
Sample	GP-1	GP-2	GP-3	GP-4	GP-5
Duration (hours)	40	60	80	40	80
Initial Weight (g)	8.6421	8.8328	8.4799	8.5032	8.1770
Seeding Lot	101	101	101	101	101
H ₂ (sccm)	200	200	200	200	200
CO ₂ (sccm)	8	8	8	8	8
CH ₄ (sccm)	3	3	3	3	3
O ₂ (sccm)	0	0	0	0	0
Cavity Conf	7	7	7	7	7
Susceptor A.	MEC4	MEC4	MEC4	MEC4	MEC4
Upper Quartz	20mm	20mm	20mm	20mm	20mm
Lower Quartz	24mm	24mm	24mm	24mm	24mm
Pressure	9 torr	9 torr	9 torr	9 torr	10 torr
Input Power	3.0mW	3.0mW	3.0mW	3.0mW	3.0mW
Bias Voltage	none	none	none	none	none

Results

Final Weight (g)	8.6469	8.8451	8.4978	8.5101	8.1952
Weight Gain (mg)	4.8mg	12.3mg	17.9mg	6.9mg	18.2mg
Bias Current	none	none	none	none	none
Temperature (°C)		440 -452	435-445		
Film Deposited	Diamond	Diamond	Diamond	Diamond	Diamond
Film Type	Not Contin.	Continuous	Continuous	Not Contin.	Continuous
Film Thickness	0.67μm	1.73μm	2.51μm		2.55μm
Growth Rate (nm/hr)	16.8	28.77	31.38		31.92

Table H.1 Deposition Results of Substrates GP-1 - GP-5

Appendix H

Date Exp. Began					
Sample	GP-6				
Duration (hours)					
Initial Weight (g)	8.4914				
Seeding Lot					
H₂ (sccm)					
CO₂ (sccm)					
CH₄ (sccm)					
O₂ (sccm)					
Cavity Conf					
Susceptor A.					
Upper Quartz					
Lower Quartz					
Pressure					
Input Power					
Bias Voltage					

Results

Final Weight (g)					
Weight Gain (mg)					
Bias Current					
Temperature (°C)					
Film Deposited					
Film Type					
Film Thickness					
Growth Rate (nm/hr)					

Table H.2 Deposition Results of Substrate GP-6

Appendix I

Operating Procedures for the Gerling Microwave Power Supply

Figure I.1 shows the controls and tell-tail lights as they appear on the front of the Gerling's control module. This control panel governs entirely the generation of microwave energy from the Gerling. The next three sections outline the specific details regarding the warm-up, shut-down, and operating procedures for the Gerling.

I.1 Warm-Up Procedure

Figure I.2 contains a listing of the steps in the start-up of the Gerling Model GL119 as taken from the Gerling's users manual. At the completion of these steps the Gerling will be in a stand-by mode where it is ready to generate microwave energy. At this point the plasma.exe software may enable the output of the microwave power supply as was stated in section [3.2.2]. The buttons and tell-tail lights in the list are shown in figure I.2.

I.2 Adjusting the Output Microwave Level

To adjust the amount of microwave power that is generated by the Gerling Model GL119 during CW operation one must simply vary the position of the knob labeled *Set Microwave Power* in the *Control Mode* group (refer to figure I.1). The amount of incident CW microwave power increases linearly with this adjustment.

I.3 Shut-Down Procedure

Figure I.3 is a listing of the steps necessary for shutting down the Gerling Model GL119 microwave power supply. The Gerling's manual recommends that before beginning these steps the power supply be allowed to cool down. Therefore, one should allow a

Appendix I

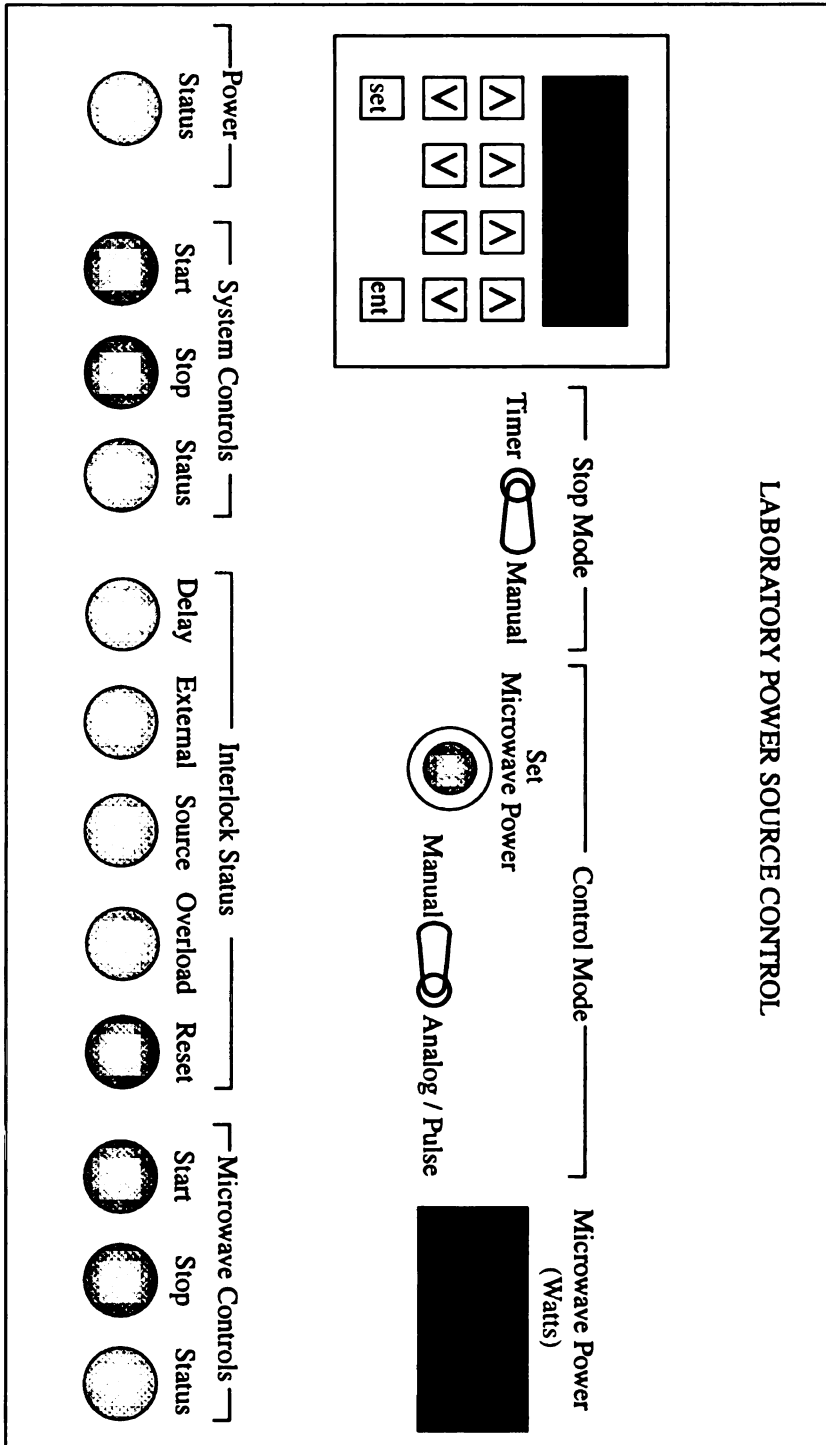


Figure 1.1 **The Controls of the Gerling Model GL119**

Appendix I

- 1) Set the switch on the back of the Laboratory Power Source Control to computer mode. Do this only when there is no power applied to the Gerling.
 - 2) Set the three circuit breakers on the Gerling's magnetron unit to the up position. The *amber power-status light* will illuminate.
 - 3) Turn on the flow of the water cooling for the waveguide loads and circulators.
 - 4) Press the *green start button* in the *systems controls* group. The *amber external and source lights in the interlock status* group will illuminate.
 - 5) Turn on the neslab liquid cooling unit. Set the temperature to 20 C. Verify that the pressure in the neslab unit is below 75 psi.
 - 6) Wait three minutes for the *amber delay light in the interlock status* group to illuminate.
 - 7) Set the *microwave power* adjustment knob in the *control mode* group to 0.0.
 - 8) The Gerling is now ready to generate microwave energy.
- Figure I.2*

Figure I.2 Warm-up procedure for the Gerling Model GL119.

Appendix I

minimum cool down period of 30 minutes after the Gerling stops generating microwave energy. During this cool down period, all of the liquid cooling systems should be left on.

Appendix I

- 9) Return the *microwave power* adjustment knob in the *control mode* group to 0.0.
- 10) Turn on the neslab liquid cooling unit.
- 11) Press the *red stop button* in the *systems controls* group. The *amber delay, external and source lights in the interlock status* group will turn off
- 12) Turn off the flow of the water cooling for the waveguide loads and circulators.
- 13) Set the three circuit breakers on the Gerling's magnitron unit to the down position. The *amber power-status light* will turn off.

Figure I.3 Shut down procedure for the Gerling Model GL119.

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