Diamond thin films grown by microwave plasma
assisted chemical vapor deposition

by

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Major: Solid State Physics

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Ames, Iowa
1991
DEDICATION

To my wife and children:
Lilis, Christopher, and Felicia
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ABSTRACT

Undoped and boron doped diamond thin films have been successfully grown by microwave plasma chemical vapor deposition from CH₄, H₂, and B₂H₆. The films were characterized using x-ray diffraction techniques, Raman and infrared spectroscopies, scanning electron microscopy, secondary ion mass spectrometry, and various electrical measurements. The deposition rates of the diamond films were found to increase with the CH₄ concentration, substrate temperature, and/or pressure, and at 1.0% methane, 900 °C, and 35 Torr, the value was measured to be 0.87 µm/hour. The deposition rate for boron doped diamond films, however, decreases as the diborane concentration increases. The morphologies of the undoped diamond films are strongly related to the deposition parameters. As the temperature increases from 840 to 925 °C, the film morphology changes from cubo-octahedron to cubic structures, while as the CH₄ concentration increases from 0.5 to 1.0%, the morphology changes from triangular (111) faces with a weak preferred orientation to square (100) faces. Furthermore, at 2.0% CH₄ or higher the films become microcrystalline with cauliflower structures. Scanning electron microscopy analyses also demonstrate that selective deposition of undoped diamond films has been successfully achieved using a lift-off process with a resolution of at least 2 µm. The x-ray diffraction and Raman spectra demonstrate that high quality diamond films have been achieved. The concentration of the nondiamond phases in the films grown at 1.0% CH₄ can be estimated from the Raman spectra to be less than 0.2% and increases with the CH₄ concentration. The Raman spectra of the boron doped diamond films also indicate that the presence of boron tends to suppress the nondiamond phases in the films. Infrared spectra of the undoped diamond films show very weak CH stretch peaks which suggest that the hydrogen concentration is very low. Infrared measurements on the boron doped diamond films provide a rapid way to detect the presence of boron in the films with a lower limit of less
than $5.2 \times 10^{19}$ cm$^{-3}$. Secondary ion mass spectrometry analyses and various electrical measurements demonstrate that p type semiconducting diamond films have been successfully deposited. The boron concentration in the films depends strongly upon the boron concentration in the gas phase. The resistivity of the films and its activation energy were found to decrease as the boron concentration in the films increases. As the doping level increases from $3.0 \times 10^{19}$ to $42.0 \times 10^{19}$ cm$^{-3}$, the resistivity decreases from 43.57 to 0.08 Ω cm. The activation energy of the films was measured to be from 0.013 to 0.158 eV depending upon the doping level. Blue-green electroluminescence has been observed from the undoped diamond films deposited using a step etching process. The mechanism can be explained by donor-acceptor pair recombination. The donor and the acceptor are believed to be N and B, respectively.
I. INTRODUCTION

A. Historical Background

Diamond is one of the most technologically and scientifically valuable crystalline solids found in nature, as it has a unique combination of excellent mechanical, physical, and chemical properties. Because of its unusual properties and commercial value, its synthetic production has long been a goal of numerous organizations and researchers around the world. Initially, high pressure methods were used simply because diamond is the densest carbon phase. As understanding of chemical thermodynamics developed throughout the 20th century, the pressure-temperature (P-T) range of diamond stability was explored. These efforts culminated in the announcement in 1955 of a process for diamond synthesis with a molten transition metal solvent catalyst at pressures where diamond is the thermodynamically stable phase. Figure 1 illustrates the thermodynamically stable regions for diamond and graphite. The P-T curves

Figure 1. Stability region of diamond and graphite
for several diamond-liquid metal eutectics, which define the minimum P-T conditions for high pressure diamond synthesis by the solvent catalyst method, are also plotted in the figure.

A parallel effort directed toward the growth of diamond at low pressures where it is the metastable form of solid carbon has also been explored for several decades. The experimental beginnings of the low pressure diamond synthesis have been traced as far back as 1911 when von Bolton claimed to have achieved growth on diamond seed crystals from the decomposition of illuminating gas (C_2H_2) in the presence of Hg vapor at 100 °C. The first successful attempt of diamond growth at low pressures was reported by William G. Eversole at the Union Carbide Corporation who initiated the work in 1949 and achieved growth on diamond seed crystals at the end of 1952. Eversole's work was very extensive and included much sophisticated experimentation. The diamond was deposited on diamond seeds from the decomposition of a carbon-containing gas such as methane or CO-CO_2 mixtures at temperatures of 600 - 1600 °C and pressures of 0.1 - 1.0 mm Hg.

Angus and co-workers at Case Western University were the first to confirm Eversole's results. They studied the rates of diamond and graphite growth in a CH_4-H_2 gas mixture and in ethylene and were the first to report on the preferential etching of graphite compared to diamond by atomic hydrogen. They also demonstrated that the vapor deposited product could be doped with boron to produce p-type semiconducting diamond. The next confirmation of Eversole's work was obtained by Derjaguin's group at the Institute of Physical Chemistry in Moscow which started research on diamond synthesis in 1956. In this work, pure methane at pressures from 0.1 to 0.3 Torr and temperatures from 950 to 1050 °C were used for deposition on seed crystals. Derjaguin's group has taken many approaches to metastable diamond growth including vapor-liquid-solid (VLS) processes, vapor transport methods, as well as chemical vapor deposition from hydrocarbon gas mixtures. The synthesis of diamond using the decomposition of CBr_4 or CCl_4, for example, was described and marked
the beginning of a steady output on vapor phase synthesis of diamond by thermal decomposition of hydrocarbons. They also performed theoretical investigations of the relative nucleation rates of diamond and graphite.

The role of hydrogen in permitting metastable diamond growth was recognized throughout the early work. The low energy electron diffraction (LEED) study of Lander and Morrison is the most significant. They showed that a (111) diamond surface saturated with hydrogen gave an unreconstructed (1x1) LEED pattern. The unsatisfied dangling bonds normal to the surface are terminated with hydrogen atoms, which maintain the integrity of the lattice to the outermost surface layer of atoms. When hydrogen is absent, the surface reconstructs into more complex structures.

By the mid-1970s diamond growth at low pressures had been achieved by several groups, but the most significant initiative in recent years has been a large program in metastable diamond growth started in 1974 by N. Setaka, S. Matsumoto, M. Kamo, and Y. Sato at the National Institute for Research in Inorganic Materials (NIRIM) in Japan. In a series of remarkable papers starting in 1982, they described techniques for synthesizing diamond at rates of several µm per hour from microwave or DC discharges, or from gases decomposed by a hot filament. These processes produced individual faceted crystals without the use of a diamond seed crystal.

The growth rates for low pressure diamond synthesis are typically low. Many researchers have attempted several methods in order to increase the deposition rates and lower the deposition temperature. Polycrystalline diamond film synthesis from an oxyacetylene flame has been reported to achieve high growth rates up to 200 µm per hour. Patterson and coworkers at Rice University claimed to have achieved growth of thin diamond films by passing a halogen-methane gas mixture over substrates heated to as low as 300 °C. However, no other group has ever confirmed the report.
Chemical vapor deposition of diamond from hydrocarbon containing gas has been the most successful method of metastable diamond growth. However, numerous other methods have been attempted, such as the ion beam method and ion implantation. In 1971 Aisenberg and Chabot\(^\text{35}\) reported that thin carbon films with properties remarkably like some of those of diamond could be deposited from an accelerated ion beam at room temperature. The films were called "diamondlike" carbon because definitive diffraction identification was not possible. Spencer and coworkers also claimed in 1976 that the formation of finely divided polycrystalline diamond could be achieved using a beam of carbon ions with energies in the range of 50 to 100 eV.\(^\text{36}\) Diamond growth by ion implantation has also been reported by Freeman and coworkers.\(^\text{37–38}\) The latest development regarding metastable diamond growth was reported by J. Narayan, V. P. Godbole, and C. W. White\(^\text{39}\), who claimed to have achieved growth of single crystal diamond films using a combination of carbon ion implantation and laser melting.

B. Metastable Diamond Deposition Technology

Metastable phases can form from precursors with high energy if the activation barriers to more stable phases are sufficiently high. As the precursors fall in energy, they can be trapped in a metastable configuration. Formation of a metastable phase depends on selecting conditions where rates of competing processes to undesired products are very low.\(^\text{40}\) In this case the spontaneous graphitization of the diamond surface and growth of the graphitic phase are the two processes competing with diamond growth.

Diamond thin films have been successfully grown at low pressures by a large variety of energetically assisted chemical vapor deposition processes. These may be conveniently divided into two broad categories:
1. Thermally assisted chemical vapor deposition (CVD), for example: hot filament assisted CVD\textsuperscript{24,41-43}

2. Plasma assisted CVD (PACVD), for example: microwave PACVD, radio frequency PACVD, and DC PACVD\textsuperscript{25,44-48}

In all processes, a carbon-containing gas such as CH\textsubscript{4} or C\textsubscript{2}H\textsubscript{2} is energetically activated to decompose the source gas molecules. The methods differ mainly in the means used to decompose the source gas. The CVD process conditions for diamond growth are given in Table 1.

Table 1. The CVD process conditions for diamond growth

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature (°C)</td>
<td>450 – 1100</td>
<td>950</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>0 – 760</td>
<td>35</td>
</tr>
<tr>
<td>Hydrocarbon source</td>
<td>CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, CO</td>
<td>CH\textsubscript{4}</td>
</tr>
<tr>
<td>Hydrocarbon (%)</td>
<td>0 – 3.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>remainder</td>
<td>99.0</td>
</tr>
<tr>
<td>Flow rate (sccm)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Substrate</td>
<td>Si, Mo, W,</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>Cu, Ni</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2 shows the schematic diagram of a hot filament assisted CVD system.\textsuperscript{24,41} A filament such as W, Ta, Mo, or Re is heated at 1700 to 2500 °C to dissociate the gas mixture.
containing from 0.2 to 2 % CH₄ in H₂, typically at about 40 Torr. The substrate is located about 1 cm below the filament to minimize thermalization and recombination of radicals. However, radiation heating can produce excessive substrate temperatures and lead to nonuniformity and even graphitic deposits. One approach to the problem of excessive radiation heating has been to withdraw the filament slightly and bias it negatively to provide an electron current to the substrate. It is represented by the dashed line in Figure 2. The major disadvantage of the hot filament CVD is that filament contamination is present to more than 10¹⁵ cm⁻³ in the films.

Schematic diagrams of a DC plasma assisted CVD and DC plasma jet are shown in Figures 3 – 4. A stabilized DC plasma assisted CVD produced growth rates up to 20 µm per hour at the anode. However, only graphitic deposits form on the cathode. The DC plasma

Figure 2. Schematic diagram of a hot filament assisted CVD system. Also shown as a dashed line is the change required to operate the system in the electron assisted mode (EACVD)
Figure 3. Schematic diagram of a DC plasma-assisted CVD system

Figure 4. Schematic diagram of a DC Plasma Jet system
jet has been reported to produce diamond at high growth rates of up to 80 µm per hour.\textsuperscript{45} The typical applied voltage and current density in the DC plasma assisted CVD techniques are 1 kV and 4 A/cm\textsuperscript{2}, respectively.

The deposition technique that currently has the best potential for obtaining electronic grade diamond films is the microwave plasma assisted CVD (MPACVD). There are two different versions of MPACVD systems. Figure 5 shows a schematic diagram of a microwave tube reactor\textsuperscript{25}, in which the heating occurs in the substrate by immersion in the plasma. This type of reactor is currently adequate to deposit high quality polycrystalline diamond films at about 1µm/hour. The primary difficulty with this type of reactor is that the substrate temperature is a function of the input microwave power. This problem has been solved in the bell jar reactor\textsuperscript{49} as shown in Figure 6. In this system the microwave power is applied over a large area, up to 8 cm in diameter, through the use of a rectangular to circular converter.

Figure 5. Schematic diagram of a microwave tube reactor
The substrate is heated by conduction from the induction heated susceptor on which it resides. Diamonds have also been grown in microwave discharges in a magnetic field (magneto-microwave plasma), in which the discharge area is 7 - 8 cm in diameter. Another method that yields high deposition rates of up to 180 µm/hour has been the growth from an atmospheric pressure oxyacetylene torch. The schematic diagram of an oxyacetylene plasma torch is illustrated in Figure 7. The substrate temperature is controlled by mounting the substrate on a water-cooled stainless steel or copper block. Tzeng et al. reported to have achieved growth of high quality diamond films from an oxyacetylene flame using an O₂:C₂H₂ volume ratio of 0.98.

C. Mechanism of Metastable Diamond Growth

The basic molecular mechanisms involved in both nucleation and growth of diamond are still a subject of current research. Angus et al. proposed that the molecular processes that
occur during low pressure diamond growth are initiated by the dissociation of the molecular hydrogen. Because the H–H bond energy is greater than the C–H bond energy, atomic hydrogen will add to vacant surface sites, S·, and abstract hydrogen from filled sites, S–H, and from other hydrocarbon molecules, R–H.

\[
\begin{align*}
H_2 & \rightarrow 2 \text{H·} \quad (1) \\
S· + \text{H·} & \rightarrow S\cdot\text{–H} \quad (2) \\
S\cdot\text{–H} + \text{H·} & \rightarrow S· + \text{H}_2 \quad (3) \\
R\cdot\text{–H} + \text{H·} & \rightarrow R· + \text{H}_2 \quad (4)
\end{align*}
\]

Reactions (2) and (3) provide a steady state concentration of free radical surface sites which can undergo reaction with carbon containing species, R·, produced by reaction (4):

\[
S· + R· \rightarrow S\cdot\text{–R} \quad (5)
\]

Steady state kinetic analysis of reaction networks implied by reactions (1) through (5) show that the diamond growth rate will be proportional to the product of the concentrations of atomic hydrogen and free radical surface sites.

**Figure 7.** Schematic diagram of an oxy-acetylene plasma torch system
hydrogen and the hydrocarbon species R–H.\textsuperscript{50}

The growth species, R\textsubscript{z}, responsible for the extension of the diamond crystal, has attracted much interest. Tsuda et al.\textsuperscript{51-52} have proposed the methyl radical as the dominant growth species, while Frenklach and Spear\textsuperscript{53} suggested that acetylene molecules are more favorable. In situ optical emission and mass spectroscopy have been used by Celii et al.\textsuperscript{54} and Harris et al.\textsuperscript{55} to show that C\textsubscript{2}H\textsubscript{2}, CH\textsubscript{3}, and CH\textsubscript{4} are the most likely species available for extending the diamond lattice during the hot filament synthesis.

Although the mechanism of synthesis of the chemical vapor deposited diamond is not completely understood, there is general agreement that atomic hydrogen plays several very important roles in the process. These include:

1. Stabilization of diamond surface
2. Generation of vacant surface sites as previously discussed
3. Preferential etching of graphite

Figure 8 illustrates the reconstruction of the diamond surface in the absence of atomic hydrogen, while Figure 9 depicts the stabilization of the diamond surface by atomic hydrogen.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{diamond_surface}
\caption{Reconstruction of diamond surface in the absence of atomic hydrogen}
\end{figure}
hydrogen. Experiments show that atomic hydrogen etches graphite much more rapidly than diamond in the temperature range of the CVD diamond growth. Figure 10 shows the relative etching rates of diamond and graphite by atomic hydrogen.

\[ \text{H} = \text{Hydrogen} \]
\[ \bullet = \text{Carbon} \]

Figure 9. The stabilization of diamond surface by atomic hydrogen

(a) Only CH\(_4\)  
(b) Only H\(^0\)  
(c) CH\(_4\) + H\(^0\)

Growth only  
Etching only  
Combined growth and etching

Figure 10. Relative growth and etching rates of diamond and graphite in the presence of CH\(_4\) and atomic hydrogen. (a) Both diamond and graphite grow together in the CH\(_4\) pyrolysis, (b) in the presence of atomic H, etching of graphite is dominant, and (c) in the presence of CH\(_4\) and atomic H, under certain conditions of pressure and temperature growth of diamond is significant, and graphite is etched.
D. Properties and Potential Applications of Diamond

Diamond exhibits several remarkable properties that make it a highly desirable material for many applications. Diamond stands alone as the strongest, and hardest known material. Table 2 shows the hardness of diamond compared to several other hard materials.\(^{58}\)

Table 2. Microhardness of several hard materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Microhardness (kg/mm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>diamond</td>
<td>9,000</td>
</tr>
<tr>
<td>BN</td>
<td>5,000</td>
</tr>
<tr>
<td>a-C:H</td>
<td>4,000</td>
</tr>
<tr>
<td>SiC</td>
<td>2,500</td>
</tr>
</tbody>
</table>

Figure 11. Thermal conductivity of diamond, silver, and copper
The thermal conductivity of diamond at room temperature is the highest among the materials used for heat sinks. It is about five times that of copper (Figure 11). Diamond also has a high refractive index (about 2.4) and wide spectral transparency from 250 nm in the ultraviolet to the infrared region. Furthermore, its electrical properties are excellent. When doped, it is a high band gap semiconductor (5.45 eV). The breakdown voltage is $1.0 \times 10^7$ Vcm$^{-1}$, and the saturated electron velocity is $2.7 \times 10^7$ cm/s; these are the highest for any known semiconductor.\textsuperscript{59}

Table 3. illustrates some electronic properties of Si, GaAs, and diamond.\textsuperscript{60} From Table 3, it is clear that diamond based electronic devices offer many significant advantages as compared with Si and GaAs based devices, including higher breakdown voltages, superior power handling capabilities, and the potential for very high temperature operation.

Table 3. Some electronic properties of Si, GaAs, and diamond at room temperature

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Si</th>
<th>GaAs</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap (eV)</td>
<td>1.12</td>
<td>1.43</td>
<td>5.45</td>
</tr>
<tr>
<td>Relative dielectric constant</td>
<td>11.70</td>
<td>13.80</td>
<td>5.50</td>
</tr>
<tr>
<td>Electron mobility (cm$^2$/eV-s)</td>
<td>1500</td>
<td>8800</td>
<td>1900</td>
</tr>
<tr>
<td>Hole mobility (cm$^2$/eV-s)</td>
<td>480</td>
<td>400</td>
<td>1600</td>
</tr>
<tr>
<td>Breakdown electric field (V/cm)</td>
<td>$3.0 \times 10^5$</td>
<td>$3.5 \times 10^5$</td>
<td>$1.0 \times 10^7$</td>
</tr>
<tr>
<td>Maximum electron velocity (cm/s)</td>
<td>$1.0 \times 10^7$</td>
<td>$2.5 \times 10^7$</td>
<td>$2.7 \times 10^7$</td>
</tr>
<tr>
<td>Maximum operating temperature (°C)</td>
<td>225</td>
<td>470</td>
<td>1900</td>
</tr>
</tbody>
</table>
Potential applications of diamond include abrasives, bearings and wear resistant surfaces, tool coatings, heat sinks or heat spreaders, optical coatings, optical windows, and as active electronic device elements. Current applications, actually in the market place, are relatively few and include instrument windows and high frequency speaker diaphragms. The use of vapor grown diamond as an active electronic component requires the growth of heteroepitaxial diamond films, which at this time has not been achieved.

E. Scope of the Research

Since there were very few reports on the growth and characterization of chemical vapor deposited diamond films as this research was started, the original goal of this work was to demonstrate that diamond thin films could be grown using microwave plasma assisted chemical vapor deposition. To accomplish this initial goal, a simple microwave plasma assisted CVD system was then built using a minimum resource of equipment that already existed in the laboratory. As the progress continued, the goal was expanded and an attempt to deposit p type semiconducting diamond films was carried out to study whether doping of the diamond films could be performed and controlled by the amount of the dopant gas introduced into the deposition chamber. Furthermore, measurements on the electroluminescence of undoped diamond films were also carried out to investigate the possibility of diamond electroluminescence devices.

In this project, both undoped and boron doped diamond thin films have been grown by microwave plasma assisted chemical vapor deposition and characterized using optical and scanning electron microscopes, Read and x-ray diffraction techniques, Raman and infrared spectroscopy, secondary ion mass spectroscopy, and several electrical measurements.
II. SAMPLE PREPARATION

A. Deposition System

All of the samples reported in this thesis were prepared by a microwave plasma assisted chemical deposition technique. A schematic diagram of the deposition system is shown in Figure 12. The microwaves from a 2.45 GHz power supply were guided via a rectangular waveguide through a power monitor, a wave guide transition (WR 340 to WR 284), and a three-stub tuner to a 38 mm outer diameter, 610 mm long quartz tube reactor that intersected the waveguide applicator. The microwave generator and the power monitor were manufactured by Varian Industrial Microwave Systems (Model PPS-2.5A), while the waveguide applicator and the three-stub tuner were designed and assembled by the author in the Ames Laboratory. An adjustable short (plunger) was built inside the wave guide applicator and was used together with the three-stub tuner to adjust the position of the plasma and to minimize the reflected microwave power. The substrate (1.3 cm by 1.3 cm) was placed in the center of the quartz tube on a graphite susceptor that was supported by a 6 mm quartz rod. The ends of the quartz tube were connected to a pumping system and to a reactant gas feed line with compression fittings (Cajon 1.5" Ultra-torr Fittings) that used viton O-ring seals. For the gas source, hydrogen (Air Products, 99.997%) and a mixture of 5% volume methane and hydrogen (Air Products, certified) were used. Both H₂ and CH₄/H₂ flow rates were controlled and monitored by Matheson NRS valves, Hastings flow meters (Model ST), and a Hastings flow monitor (Model PR-4) with full scales of 100 sccm. For boron-doped diamond films, a mixture of diborane (B₂H₆) and hydrogen was added to the gas lines. The diborane concentrations that have been used are 1000 ppm and 12 ppm. The flow rate of B₂H₆/H₂ was controlled by a mass flow controller (Tylan, MFC-260) with a full scale of 100 sccm.
Figure 12. Schematic diagram of microwave plasma assisted CVD
Since the diborane gas is extremely toxic, and methane and hydrogen are flammable, a check valve and an excess flow valve (Nupro) were installed in each gas feed line for safety precautions. The deposition chamber was routinely evacuated using a turbomolecular pump (Balzer TPU-050) backed by a rotary pump (Balzer DUO 1.5A) to a base pressure of about $5 \times 10^{-5}$ Torr prior to each film deposition. The base pressure was measured using a Veeco APC-1000 ionization gauge controller with an Elcon BMW-100 vacuum gauge, while the pressure during deposition was measured with a 100 Torr full scale Leybold–Heraeus vacuum gauge. The gas pressure in the reactor was varied by first fully closing the main valve and adjusting the butterfly valve in the bypass line (see Figure 12). The bypass line is very important so that the desired pressure can be obtained at a high reactant gas flow rate. In addition to the high purity gases used in the diamond deposition, argon gas (Air Products, 99.9%) was used to purge and to open the tube after each deposition.

B. Preparation of Undoped and Boron-doped Diamond Films

The diamond films were deposited on 13x13 mm$^2$ n or p type Si wafers with (100) orientation. If commercially available mirror polished Si wafers are used for the substrate, only diamond particles are grown. However, it is well known that the diamond nucleation is greatly enhanced if the Si wafer was scratched with diamond powder before deposition. As a result, uniform polycrystalline diamond films are deposited. In the experiments, the following substrate pretreatment was carried out in order to grow uniform diamond films. Prior to growth, the Si wafers were polished with 0.25 µm diamond paste (Buehler Metadi diamond paste) for about 20 minutes and followed by ultrasonic cleaning in deionized water, acetone, and methanol. Finally, the wafers were dried with nitrogen gas. Besides the above
pretreatment, several other methods such as scratching the Si wafer with SiC, alumina powder, or with a sharp stainless steel tweezer, roughening the Si surface by chemical or reactive ion etching, and creating craters on the Si surface using an Ar ion beam have been attempted.

In this work, although silicon wafers have been used as the main substrate material, experiments on depositing diamond films using several different substrates have also been carried out. The substrates include: molybdenum, copper, nickel, stainless steel, amorphous silicon and germanium thin films, and quartz. The purpose of these experiments was to investigate whether diamond could be synthesized on those substrate materials and whether films could form without scratching the surface with the diamond paste.

The start up procedure of the deposition is as follows: After the base pressure is reduced to about 5x10^{-5} Torr, the pump is put on "stand by" mode, and the main valve is completely closed. The reactant gas was then introduced into the tube reactor, and the microwave radiation was supplied to turn on the plasma. Since it is easier to turn on the plasma at lower pressure (< 25 Torr), the microwave radiation is usually applied when the pressure reaches about 20 Torr. Then, the gas pressure is finally set by adjusting the butterfly valve. It requires more microwave power to turn on the plasma at pressures higher than 25 Torr. The desired substrate temperature was set by adjusting the microwave power. To measure the substrate temperature, an optical pyrometer manufactured by Leeds and Northrup Co. was used. Since the emissivity of the substrate during the synthesis is not known, black body radiation was assumed for the temperature measurements, and no correction was made for the absorption due to the quartz tube wall. While not an accurate determination of the temperature, the precision was sufficient to allow reproducible deposition from run to run. The position of the plasma was adjusted by sliding the plunger so that the substrate was entirely immersed in the plasma. Finally, the reflected power was minimized using the three-stub
tuner. Typical parameters used in the deposition of undoped diamond films are summarized in Table 4.

One of the advantages of diamond film growth by the chemical vapor deposition technique is that doping of the film can be performed simply by mixing the dopant gases in the reactant gas. In this work p type semiconducting diamond films were synthesized by introducing diborane in the microwave reactor. Since there was very limited information in the literature about the diborane concentration as the doping work was started, the boron doping of diamond films was first attempted using a mixture of 1000 ppm diborane in hydrogen. After several trials, it was found that a lower diborane concentration was needed, and a mixture of 12 ppm B$_2$H$_6$/H$_2$ was later used. Polycrystalline boron-doped diamond films were deposited on n or p type Si wafers with (100) orientation at 1.0% methane concentration, 900 $^\circ$C, 35 Torr, and several different diborane concentration. When the 1000 ppm B$_2$H$_6$/H$_2$ gas was used, its flow rate was varied from 0.5 to 2.0 sccm, while with the 12 ppm concentration, its flow rates range from 4 to 64 sccm which correspond approximately to B$_2$H$_6$/CH$_4$ ratios of about 50 to 800 ppm.

Table 4. Typical parameters for undoped diamond film deposition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
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<tr>
<td>CH$_4$/H$_2$ (%)</td>
<td>0.5 – 5.0</td>
</tr>
<tr>
<td>Total flow rate (sccm)</td>
<td>100</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>18 – 70</td>
</tr>
<tr>
<td>Substrate temperature ($^\circ$C)</td>
<td>840 – 925</td>
</tr>
<tr>
<td>Microwave power (watt)</td>
<td>200 – 400</td>
</tr>
</tbody>
</table>
C. Preparation of Selectively Deposited Diamond Films

In order to facilitate application of diamond films for semiconductor devices, a technique to selectively nucleate and grow the films is highly desirable. Such patterning of the diamond films is essential for fabricating microstructures. There have been several attempts to selectively grow diamond films. Hirabayashi et al.\textsuperscript{62} reported selective nucleation of diamond by using Ar ion beam etching on a pretreated substrate which was patterned with resist, while Ma et al.\textsuperscript{63} claimed to have more accurate selectivity using oblique irradiation of an Ar ion beam. Leksono and Shank\textsuperscript{64} reported that the selective growth of microwave plasma deposited diamond films could be performed by a lift-off process. The idea of using a lift-off process was based on the previous experimental results that diamond grew very poorly on top of amorphous silicon thin films, but the nucleation was greatly increased on a Si wafer that had been polished with diamond paste. Figures 13 (a)–(c) show schematically the lift-off process on a polished Si wafer:

- A clean n-type Si (100) wafer was polished using 0.25 µm diamond paste, followed by ultrasonic cleaning in deionized water, acetone and methanol. This is the usual pretreatment to increase the diamond nucleation.
- A ZnO thin film was deposited on the pretreated wafer and then patterned by standard photolithography. A 5 % HCl solution was used to etch the ZnO.
- An amorphous silicon (a-Si:H) thin film was deposited on the patterned wafer using a glow discharge system. Finally, the ZnO layer was lifted-off using the HCl solution to produce a patterned crystalline Si (x-Si)/amorphous Si wafer that was ready for the selective growth of diamond films.

Diamond films were selectively deposited under the following conditions: methane content: 1 – 2%, total flow rate: 100 sccm, pressure: 18 – 50 Torr, and substrate temperature: 840 – 925 °C.
Figure 13. Schematics of the lift-off process on a polished Si wafer for the selectively deposited diamond films. (a) A Si wafer was polished with 0.25µm diamond paste. (b) A ZnO thin film was deposited on the wafer and patterned by a standard photolithography. (c) Deposition of an a–Si:H thin film followed by the ZnO lift-off process using HCl solution (after Leksono and Shanks).
III. SAMPLE CHARACTERIZATION

A. Thickness Measurements

The thickness and the surface roughness of the diamond films was mechanically measured using a Sloan Dektak Stylus profilometer (accuracy ± 1000 A). A step of the same height as the film thickness was intentionally formed by masking part of a Si substrate with another smaller piece of Si wafer. The height of the step was then measured after the deposition with the Dektak stylus profilometer.

Scanning electron microscopy (SEM) has also been utilized to measure the film thickness. Prior to the measurements the film was cleaved and coated with a thin layer of gold, and its cross section was then viewed in the electron microscope.

B. X-ray Diffraction Measurements

Read camera and x-ray diffractometer techniques have been used to measure the x-ray diffraction spectra of both undoped and boron-doped diamond films. The Read camera has proved to be more sensitive for obtaining the x-ray pattern of a very thin layer of diamond film, even if no uniform film was deposited. The experimental geometry of the Read camera is shown in Figure 15.65. The x-ray diffraction patterns are obtained from a monochromatic x-ray beam (Cu K\(\alpha\), for example) impinging at a glancing angle of 6 to 14 degrees to the sample surface. The beam is collimated through two pinholes, and the patterns at all angles are recorded simultaneously on film placed on a 5 cm radius from the sample center. The exposure time is usually about 12 hours depending upon the film thickness and uniformity.

For the powder x-ray diffraction (XRD) spectra measurements, the sample was mounted vertically on a microscope slide using a small amount of vaseline. The XRD spectra
were measured using a microcomputer-controlled Rigaku diffractometer equipped with copper target and diffracted beam graphite monochromator for Cu $K_{\alpha}$ radiation with a step scan rate of 0.01 degree/second over the 2$\theta$ angular range of 20 to 95 degrees.

The basis for x-ray diffraction is the Bragg equation which describes the condition for constructive interference for x-rays scattering from atomic planes of a crystal. The condition for constructive interference is\(^{66}\)

$$2d \sin \theta = n \lambda \tag{6}$$

where $\lambda$ : the wavelength of the incident radiation

$d$ : the interplanar spacing of the crystal

$\theta$ : the diffraction angle

$n$ : the diffraction order.

For the Cu $K_{\alpha}$ line, $\lambda$ is 1.541838 Å.\(^{67}\)
C. Raman Measurements

Raman spectroscopy is a well known and widely utilized, nondestructive technique for the characterization of materials. It offers the advantage of sensitivity not only to crystalline material, but also to the various possible noncrystalline phases. In the case of diamond films, the Raman technique is sensitive in detecting the presence of the nondiamond phases such as graphite and amorphous carbon. Well crystallized diamond produces only a single first–order Raman peak at 1332 cm$^{-1}$ which corresponds to 4-fold coordinated sp$^3$ type bonding,\textsuperscript{68} while graphite exhibits a peak at 1581 cm$^{-1}$.\textsuperscript{69–70} Glassy carbon and pyrolitic graphite, which consist of amorphous sp$^2$ structures, produce two broad bands at 1360 and 1590 cm$^{-1}$.\textsuperscript{71}

![Figure 15. Schematic diagram of a Raman micro–probe spectrometer](image-url)
Furthermore, an asymmetric broad band at around 1530 cm\(^{-1}\) is usually observed in diamondlike amorphous carbon (a-C) films.\(^{72}\) In analyzing the Raman spectra of diamond films, the difference in Raman scattering efficiency of graphite and diamond (more than 50:1) must be taken into consideration.\(^{73-74}\)

Raman spectra of diamond films were measured at room temperature with a 530.9 nm line of a krypton ion laser at relatively low power of about 50 mW on the samples. The Raman spectra were recorded using a Spex model 1877D Raman micro–probe spectrometer. The laser beam is focused on the sample with a spot size of approximately 10 \(\mu\)m. Figure 15 schematically illustrates the experimental set up of a Raman micro–probe spectrometer.

D. Surface Morphology Characterization

Both optical and Scanning Electron Microscopes (SEM) have been used to evaluate the uniformity and the surface morphology of the diamond films. The optical microscope (Olympus Vanox or Nikon AFX–IIA) was mainly used to get quick information on the film uniformity and a rough idea about the surface morphology right after the film was removed from the reactor. The Scanning Electron Microscope (Cambridge Stereoscan 200) was extensively utilized to examine the surface morphology and the uniformity of the diamond films. In general, high quality diamond films exhibit well faceted crystal structures with (100) or (111) planes, depending upon the deposition parameters. Figure 16 illustrates the change from cubic to octahedral diamond.\(^{75}\) Note that in most cases, the scanning electron microscopy was performed following the deposition without any cleaning or coating after removal from the reactor. To obtain the cross sectional view of the films, the samples were mounted vertically using a silver paste on an aluminum sample holder and coated with a thin layer of gold.
E. Infrared Measurements

Infrared (IR) measurements can be used to provide several types of information about the film such as the bonding configuration of the atoms in the film and hydrogen concentration. Infrared spectra also provide a complementary determination of the film thickness and index of refraction of the film. Diamond films used in the IR measurements were those deposited on doubled sided polished Si wafers. The infrared spectra of both free standing diamond films and films on Si substrates were measured from 400 to 3400 cm\(^{-1}\) using a single beam Digilab FTS–50 Fourier Transform Infrared (FTIR) spectrometer. To get a free standing film, the Si substrate was etched away with a mixture of HNO\(_3\) and HF solution with 3:1 concentration.

![Polyhedrals of diamond](image)

Figure 16. Polyhedrals of diamond
F. Electrical Measurements

Electrical measurements were mainly carried out to characterize the boron doped diamond films. There are several characterization techniques that have been used to provide information about the conductivity type, sheet or surface resistance, current/voltage (I/V) characteristics, and activation energy of the semiconducting diamond films. Electrical measurements were done on free standing films and on films that were still attached to the substrate. For I/V characteristics and activation energy measurements, electrical contacts to the samples were made by depositing a Ti/Au thin layer or using silver epoxy. Ti or silver epoxy have been reported to make good ohmic contact with diamond films,61, 76–77 while Schottky contacts are usually made of Al or gold.78–79

1. Conductivity Type and Sheet Resistance Measurements

A thermoelectric or hot probe technique was used to perform a quick check of the conductivity type of the doped diamond films. In the thermoelectric probe method the conductivity type is determined by the sign of the thermal emf or Seebeck voltage generated by a temperature gradient. Figure 17 (a) illustrates the experimental diagram of the thermoelectric probe method. Two probes, one hot and the other cold, are in contact with the sample surface, and thermal gradients produce currents in the sample. The currents due to the majority carriers for n– and p–type semiconductor materials are80

\[ J_n = -qn \mu_n \pi_n dT/dx \] (7)

\[ J_p = -qp \mu_p \pi_p dT/dx \] (8)

where \( \pi_n < 0 \) and \( \pi_p > 0 \) are the differential thermoelectric power for n and p type materials, respectively.
Figure 17. Basic schematic diagrams of a thermoelectric and a four point probe techniques: (a) thermoelectric probe, and (b) four point probe.
The four point probe technique has been used to measure the sheet resistance of the boron doped diamond films. The schematic diagram of the four point probe is depicted in Figure 17 (b) in which the current flows into probe 1, out of probe 4, and the voltage is sensed across probes 2 and 3. The general expression of the sheet resistance $\rho_s$ (in units of ohm per square) is given by:

$\rho_s = \frac{F_1 V}{I}$

where $F_1$ is the correction factor that depends on the size of the sample and the probe spacing. For rectangular samples the correction factor $F_2$ is plotted in Figure 18. The size of the samples used in the measurements is $13 \times 13 \text{ mm}^2$, and the probe spacing is $1.02 \text{ mm}$. Therefore, $d/s$ is equal 12.80, and $F_2$ is approximately determined to be 4.32 (see Figure 18). Note that $d$ is the sample width, and $s$ is the probe spacing.

![Figure 18. Sample size correction factors as a function of normalized wafer width for rectangular samples. $d$ is the sample width, and $s$ is the probe spacing.](image-url)
2. **Current/Voltage and Activation Energy Measurements**

The I/V characteristics were measured using a computerized Hewlett Packard 4145B Semiconductor Parameter Analyser, while the activation energy \( (E_a) \) was determined by measuring the electrical conductivity of the diamond films over the temperature range of 300 to 450 K using the experimental set up as shown in Figure 19. The activation energy for the conduction was obtained from a plot of electrical conduction or current vs. reciprocal of the temperature.

![Experimental diagram to measure the electrical conductivity at different temperatures](image-url)
3. Electroluminescence Measurements

To investigate the electroluminescence of the microwave plasma deposited diamond films, a simple diamond thin film electroluminescence device (ELD) was fabricated by depositing an In$_2$O$_3$ thin film that was used as a transparent electrode on an undoped diamond film and by using a silver epoxy as the other electrode. The electroluminescence spectrum and its relative intensity were measured using the experimental set up as shown in Figure 20. The diamond ELD was driven by a 60 Hz AC power supply, and the emitted light passed through the chopper and an Oriel monochromator (M) to a photomultiplier tube (PMT). The spectrum was then measured by a lock-in amplifier.

![Experimental set up to measure the luminescence of the diamond ELD](image-url)
G. Boron Concentration Measurements

Secondary Ion Mass Spectrometry (SIMS) has been performed to determine the boron concentration of the p type semiconducting diamond films. The technique relies on removal of material from a solid by sputtering and mass spectroscopy of the sputtered ionized species. Therefore, SIMS determines the total impurity concentration, but not the concentration of the electrically active impurity. To get semiquantitative SIMS results, two undoped diamond films were prepared for boron ion implantation. The boron was implanted into the undoped diamond films with the maximum or peak concentration of $5 \times 10^{18}$ cm$^{-3}$ and $2 \times 10^{19}$ cm$^{-3}$. The films resulting from the ion implantation were used as standards in the boron concentration calculations. SIMS measurements were performed using Perkin Elmer model 6300 SIMS system with an oxygen gun.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chip No.</th>
<th>Substrate Impurity</th>
<th>Pressure (Torr)</th>
<th>Deposition (nm)</th>
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<td>ML30</td>
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<td>ML101</td>
<td>1.0</td>
<td>922</td>
<td>18</td>
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<td>ML102</td>
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<td>770</td>
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<td>900</td>
<td>18</td>
<td>3.5</td>
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</table>

The table above shows the deposition parameters for the semiconducting diamond films.
IV. RESULTS AND DISCUSSION

Both undoped and boron doped diamond films have been deposited using microwave plasma chemical vapor deposition. In this work, several series of diamond films were prepared at various deposition parameters. These parameters include methane concentration, substrate temperature, diborane concentration (for boron doped diamond films), and total gas pressure in the deposition chamber. Table 5 shows the deposition parameters used for the selectively grown diamond films, while Tables 6 and 7 summarize the deposition parameters used for undoped and boron doped diamond, respectively.

Table 5. Deposition parameters for the selectively deposited diamond films. The total gas flow rate is 100 sccm for all of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH4/H2 ( % )</th>
<th>Substrate temperature ( °C )</th>
<th>Pressure ( Torr )</th>
<th>Deposition time ( hours )</th>
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<td>840</td>
<td>35</td>
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<td>ML166</td>
<td>1.0</td>
<td>870</td>
<td>35</td>
<td>3.5</td>
</tr>
<tr>
<td>ML169</td>
<td>1.0</td>
<td>900</td>
<td>18</td>
<td>3.5</td>
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</table>
Table 6. Deposition parameters for various undoped diamond films. The total gas flow rate is 100 sccm for all of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH$_4$/H$_2$ ( % )</th>
<th>Temperature ( C )</th>
<th>Pressure ( torr )</th>
<th>Time ( hours )</th>
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</tr>
<tr>
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<tr>
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<td>a-Si/rough Si</td>
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<td>ML166</td>
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<tr>
<td>ML169</td>
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Table 6. Continued

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<td>ML255</td>
<td>900</td>
<td>900</td>
<td>8</td>
<td>Mo, Cu, stainless steel</td>
</tr>
<tr>
<td>ML256</td>
<td>900</td>
<td>900</td>
<td>8</td>
<td>Mo, Cu, stainless steel</td>
</tr>
<tr>
<td>ML269</td>
<td>900</td>
<td>900</td>
<td>8</td>
<td>Mo, Cu, stainless steel</td>
</tr>
</tbody>
</table>

Table 7. Deposition parameters for the boron doped diamond films. All samples were grown on Si(100) with 1.0 % methane, 900 °C, 35 Torr, and 100 sccm total flow rate

<table>
<thead>
<tr>
<th>Sample</th>
<th>B₂H₆/H₂ flow rate (sccm)</th>
<th>Cylinder type</th>
<th>Deposition time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML209</td>
<td>0.5</td>
<td>I</td>
<td>6</td>
</tr>
<tr>
<td>ML210</td>
<td>1.0</td>
<td>I</td>
<td>6</td>
</tr>
<tr>
<td>ML215</td>
<td>1.5</td>
<td>I</td>
<td>8</td>
</tr>
<tr>
<td>ML250</td>
<td>4.0</td>
<td>II</td>
<td>8</td>
</tr>
<tr>
<td>ML249</td>
<td>8.0</td>
<td>II</td>
<td>8</td>
</tr>
<tr>
<td>ML255</td>
<td>16.0</td>
<td>II</td>
<td>8</td>
</tr>
<tr>
<td>ML256</td>
<td>32.0</td>
<td>II</td>
<td>8</td>
</tr>
<tr>
<td>ML269</td>
<td>64.0</td>
<td>II</td>
<td>8</td>
</tr>
</tbody>
</table>

aI and II stand for the cylinders that contain the B₂H₆/H₂ mixture of 1000 and 12 ppm, respectively.
A. Deposition Rate

The deposition rates of the microwave plasma deposited diamond films were studied at various methane concentrations, pressures, and substrate temperatures. The deposition rate was calculated by dividing the measured thickness by the deposition time. Figure 21 plots the deposition rate as a function of methane concentration. As expected, the deposition rate increases with increasing methane concentration. It is also shown that the deposition rate appears to increase linearly, within experimental error, with the methane concentration. The straight line in the figure represents the least square fit for the data. It should be noted that the deposition rate is very low at low methane concentration so that it generally requires longer deposition time in order to get uniform films.

Figure 21. Deposition rate of undoped diamond films as a function of methane concentration. The films were deposited on Si (100) substrates at 900 °C and 35 Torr.
The effect of the pressure on the deposition rate was investigated by varying the gas pressure in the reactor from 18 to 70 torr at a constant substrate temperature of 900°C and with a methane concentration of 1.0%. As shown in Figure 22, the deposition rate increases slowly with pressure of up to 30 torr and then increases more rapidly from 30 to 40 torr. At pressures higher than 40 torr, the deposition rate tends to saturate. This behavior is possibly due to the plasma density and uniformity around the substrate. At lower pressures, the plasma becomes less dense and tends to spread out, while at higher pressures the plasma shrinks and causes nonuniformity around the substrate region. Figure 22 indicates that there is an optimum pressure for the deposition rate between 35 to 45 torr.

![Figure 22](image)

Figure 22. The deposition rate of undoped diamond films as a function of total gas pressure in the reactor. The films were synthesized with 1.0% methane and 900°C.
Figure 23 illustrates the deposition rate as a function of substrate temperature. Within the temperature range studied in this work, the deposition rate increases with substrate temperature. This is very obvious because at a fixed pressure, the substrate temperature depends strongly on the microwave power. So far, the lowest temperature at which the diamond can be deposited is about 840 °C. An attempt was made to grow a diamond film at 800 °C, but it was not successful. This is primarily due to the very low microwave power which produces a very weak plasma around the substrate, and only diamond particles are deposited.

Figure 24 depicts the film thickness as a function of the deposition time. It should be noted that after 2 hours growth, only diamond particles and clusters were formed. Therefore, in this case the film thickness is represented by the average height of the diamond particles. As shown in the figure, the thickness of the diamond films increases linearly, within experimental error, with the deposition time. The growth rate can be calculated from the slope of the curve. For the microwave plasma deposition used in this work, the growth rate is found to be 0.87 µm per hour. This value is very typical for the diamond films grown by the microwave plasma assisted chemical vapor deposition technique.

The effect of the diborane concentration on the deposition rate was investigated by depositing boron doped diamond films at several different flow rates of B₂H₆/H₂. A problem was encountered when a mixture of 1000 ppm B₂H₆/H₂ was used as the dopant source because boron was very easily deposited on the quartz tube. The microwave power was mostly absorbed by the deposit on the tube, and this caused plasma distortion around the substrate even after about 30 minutes of deposition. It was noticed that after about 1 hour, the deposit on the tube wall became thicker, and the deposition had to be terminated because no plasma was observed around the substrate. When a mixture of 12 ppm B₂H₆/H₂ was used as
Figure 23. The deposition rate of undoped diamond films as a function of substrate temperature. The films were grown with 1.0% methane and at 35 Torr.

Figure 24. The thickness of the undoped diamond films vs. deposition time. The films were deposited at 1.0% methane concentration, 900 °C, and 35 Torr.
a dopant source, the problem with the boron deposition on the quartz tube was minimized, and the deposition of boron doped diamond films could continue for 8 hours. Nevertheless, at B\textsubscript{2}H\textsubscript{6}/H\textsubscript{2} flow rates of 32 and 64 sccm the quartz tube had to be replaced because of the thin dark brown deposit on it. The samples used to produce the data in Figure 25 were those deposited using a diborane mixture of 12 ppm. The flow rates of the B\textsubscript{2}H\textsubscript{6}/H\textsubscript{2} were varied from 4 to 64 sccm. As shown in Figure 25, the growth rate of the boron doped diamond films decreases as the diborane concentration increases. At flow rates higher than 32 sccm, the growth rate appears to saturate. This is probably caused by the boron deposit on the tube wall that absorbed most of the incoming microwave power. Once the deposit on the tube was formed, the growth of the diamond films were dramatically suppressed.

Figure 25. The effect of the boron doping on the deposition rate of semiconducting diamond films. The films were grown on Si (100) substrates at 1.0% methane, 900 °C, and 35 Torr
B. X-ray Diffraction Spectra

X-ray diffraction measurements were carried out for the undoped and boron doped diamond films using both Read camera and x-ray diffractometer (XRD) techniques. Figure 26 shows the Read pattern of the undoped diamond films deposited at 1.0 % methane, 925 °C, and 35 torr. The pattern exhibits very strong lines corresponding to the reflections due to the (111) and (220) planes of diamond, while the reflections due to the (311) and (400) planes are weak and very weak, respectively. Note that the spots on the background are the patterns due to the silicon substrate. Figure 27 displays the XRD spectrum of the same film whose Read pattern is shown in Figure 26. The (111) diffraction is very strong and sharp with full width at half maximum (FWHM) of about 0.30 degree which indicates good crystallinity of the diamond film. However, unlike in the Read pattern, the (220) and (311) peaks are very small, and the (400) peak is not observed. Table 8 lists the observed results for the interplanar spacings for the undoped diamond film synthesized at 1.0 % methane, 925 °C, and 35 Torr. The interplanar spacings were calculated from the $2\theta_{\text{Cu}}$ using $\lambda_{\text{Cu}} = 1.541838$ Å. Table 8 demonstrates that the Read camera and XRD results agree reasonably well with the American Society for Testing Materials (ASTM) values.

Figure 28 depicts the Read pattern of an undoped diamond film deposited at 2.0% methane, 35 Torr, and 925 °C. For this film, the Read pattern shows that the diffraction lines, especially the (111) line, become broader and weaker, but no other diffraction lines corresponding to nondiamond or graphitic carbon are observed. However, it will be shown in the next section that the Raman spectrum of this film indicates the presence of some amorphous carbon. This fact suggests that the Read camera technique is probably not sensitive enough in detecting the small amount of nondiamond or graphitic carbon that might form in the film.
Figure 26. Read pattern of an undoped diamond film deposited at 1% methane, 925°C, and 35 torr.
Figure 27. XRD spectra of the same diamond film whose Read pattern is depicted in Figure 26.
Table 8. Interplanar spacings and the diffraction angles ($2\theta_{Cu}$) of the undoped diamond films deposited 1.0% methane, 925 °C, 35 Torr.

<table>
<thead>
<tr>
<th>hkl</th>
<th>d (Å)</th>
<th>2$\theta_{Cu}$ (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASTM</td>
<td>Read$^a$</td>
</tr>
<tr>
<td>111</td>
<td>2.0593</td>
<td>2.053 S</td>
</tr>
<tr>
<td>220</td>
<td>1.2610</td>
<td>1.256 S</td>
</tr>
<tr>
<td>311</td>
<td>1.0754</td>
<td>1.072 W</td>
</tr>
<tr>
<td>400</td>
<td>0.8917</td>
<td>0.890 VW</td>
</tr>
<tr>
<td>331</td>
<td>0.8182</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$S, M, W, and VW stand for relative intensities: S strong, M medium, W weak, and VW very weak.

The Read pattern of an undoped diamond film grown at 0.5% methane, 35 Torr, and 925 °C is depicted in Figure 29. As the methane concentration was reduced to 0.5%, there is a slight nonuniformity in the intensity of the (111) diffraction line. It is more intense around the center, but weaker otherwise. This indicates that the film might have a preferred orientation as will be shown later from the scanning electron micrograph. An attempt was made to confirm the orientation using XRD by rotating the sample around the $\omega$ axis, but the result only shows a weak preferred orientation in the film structure. Figure 30 shows the XRD spectrum of the same film whose Read pattern is shown in Figure 29, while Figure 31 shows the x-ray profile for the (111) reflection where the $\omega$ scan was carried out from $\theta = 16$ to 29 degrees. Note that $\omega$ angle is identical to $\theta$ in an $\omega$ scan, but $2\theta$ is fixed.
Figure 28. Read pattern of an undoped diamond film grown at 2.0% methane, 925 OC, and 35 Torr.
Figure 29. Read pattern of an undoped diamond film grown at 0.5% methane, 925 °C, and 35 Torr.
Figure 30. XRD spectrum of the same undoped diamond film whose Read pattern is shown in Figure 29.
The XRD spectrum of the undoped diamond film synthesized at 0.5% methane shows a similar pattern as in Figure 27. It exhibits a very sharp and strong peak due to the (111) reflection, and small peaks corresponding to the (220) and (311) reflections. The ratios of the intensities of the (111) to (220) and (311) reflections suggest that the film is randomly oriented. However, the broad peak of the x-ray profile in Figure 31 really indicates that there is a weak preferred orientation in the film with a width of about 10 degrees. The x-ray diffraction
spectra of the undoped diamond films synthesized at different methane concentrations are shown in Figure 32. At low methane concentrations, the (111) diffraction peak is very sharp and strong. As the methane concentration increases, the intensity of the (111) peak decreases and becomes broader, whereas the intensity of the (220) and (311) lines remains almost the same. This is probably due to decrease of the diamond component in the films as the methane concentration in the deposition chamber increases. As it will be shown in the next section, the Raman spectra of the films deposited at higher methane concentrations show that more nondiamond phases are present in the films as the methane concentration increases. The fact that no other peaks corresponding to nondiamond phases were observed in the XRD spectra clearly demonstrates that the x-ray diffraction technique is not sensitive enough to detect any small components of amorphous and graphitic carbon in the films.

Figure 33 depicts the XRD spectra of undoped diamond films deposited on Si (100) substrates at 1.0% methane concentration and 900°C, but at different gas pressures, ranging from 18 to 70 Torr. As the gas pressure increases, the diamond (111) peak does not change nor it is shifted to a different position. Figure 33 demonstrates that within the range of pressures considered, the x-ray diffraction spectra are not affected by the gas pressure during the deposition.

The XRD spectra of undoped diamond films deposited on Si wafers at different substrate temperatures are illustrated in Figure 34. It is obvious from the figure that the x-ray diffraction spectra do not change as the temperature increases from 840 to 925°C.

X-ray diffraction spectra have also been measured for the boron doped diamond films to study whether the boron doping has any effect on the structures of the diamond films. As shown in Figure 35, the XRD spectra of the boron doped diamond films look essentially the
Figure 32. XRD spectra of undoped diamond films deposited on Si (100) substrates at different methane concentrations: (a) 0.5%, (b) 1.0%, (c) 1.5%, (d) 2.0%, and (e) 3.0%
same as the spectra of undoped films. In general, they exhibit a strong peak due to the reflection by the (111) planes, and small and broad peaks due to diamond (220) and (311) planes. Furthermore, the x-ray spectra do not change as the boron concentration increases. Therefore, the effect of the boron doping is not observed in the x-ray diffraction spectra.

Figure 33. XRD spectra of undoped diamond films grown at different gas pressures: (a) 18 Torr, (b) 35 Torr, (c) 50 Torr, and (d) 70 Torr
Figure 34. XRD spectra of undoped diamond films deposited at several different substrate temperatures: (a) 840°C, (b) 870°C, (c) 900°C, and (d) 925°C
Figure 35. XRD spectra of boron doped diamond films synthesized at 1.0% methane, 900 °C, 35 Torr, and using different flow rates of B₂H₆/H₂: (a) 4 sccm, (b) 8 sccm, (c) 16 sccm, (d) 32 sccm, and (e) 64 sccm
C. Raman Spectroscopy

The Raman spectra measurements have been performed for several undoped diamond films deposited at different methane concentrations, temperatures, and pressures to identify whether nondiamond phases such as graphite and amorphous carbon are present in the film. Figure 36 shows the Raman spectra of the undoped diamond film deposited on a Si substrate at 1.0% methane concentration, 35 torr, and 925°C. Figure 36 also displays the spectrum of natural diamond measured using the same Raman spectrometer that was used as reference. A sharp peak at 1332 cm\(^{-1}\) is indicative of crystalline diamond, and an asymmetric broad band centered at about 1500 cm\(^{-1}\) is observed due to the amorphous carbon phase that is present in the film. The full width at half maximum (FWHM) of the diamond peak is determined approximately to be 6.5 cm\(^{-1}\) which indicates good crystallinity of the film. As was mentioned in the previous chapter, the Raman sensitivity for graphite is more than 50 times higher than for diamond. Therefore, Figure 36 indicates that there is a very little amount of amorphous carbon in the film. By comparing the intensity of the diamond peak to the amorphous carbon peak and taking into account the Raman sensitivity, the concentration of the nondiamond phases in the film is found to be less than 0.2%.

The Raman spectra of undoped diamond films grown on Si wafers at different methane concentrations are shown in Figure 37. As the methane concentration increases, the diamond peak at 1332 cm\(^{-1}\) decreases and becomes broader, while the intensity of the 1500 cm\(^{-1}\) band increases. Furthermore, the Raman spectra of diamond films prepared with a methane concentrations of 2.0% or higher are dominated by the bands of amorphous and graphitic carbons. This demonstrates that the concentration of nondiamond phases or the sp\(^2\) type bonding in the film increases as the methane concentration increases. For films deposited at higher methane concentrations, it will be difficult from the Raman spectrum alone to prove that diamond is present in the films.
Figure 36. Raman spectrum of undoped diamond film deposited on a Si substrate at 1.0% methane, 35 Torr, and 925 °C. The Raman spectrum of natural diamond is also shown for reference.
Figure 37. Raman spectra of undoped diamond films deposited on Si wafers at different methane concentrations: (a) 0.5%, (b) 1.0%, (c) 1.5%, (d) 2.0%, and (e) 5.0%. The pressure and the temperatures were kept constant at 35 Torr and 925 °C, respectively.
Figure 38 illustrates the Raman spectra of undoped diamond films grown on Si substrates at different substrate temperatures. The methane concentration and the total gas pressure during the deposition were kept constant at 1.0% and 35 torr, respectively. As shown in Figure 38, the diamond 1332 cm\(^{-1}\) line decreases as the temperature decreases. The two films prepared at temperatures of 870 and 840 °C also show strong peaks at about 1500 cm\(^{-1}\) that corresponds to amorphous carbon. The reason for this behavior might be due to the grain size and the orientation of the crystals. It is also possible that at lower deposition temperatures more amorphous carbon is formed. This is in general agreement with the results of Liou et al.\(^83\) and Yarbrough et al.\(^84\), who reported the work on diamond deposition at low substrate temperatures. In this work, the best Raman spectra of the undoped diamond films were obtained from films grown at 925 °C.

The undoped diamond films have also been prepared with the same methane concentration of 1.0% and temperature of 900 °C, but at several different pressures ranges from 18 to 70 torr. Figure 39 depicts the Raman spectra of these undoped diamond films. As shown in the figure, the film deposited at 35 Torr exhibits the strongest diamond peak at 1332 cm\(^{-1}\). As the pressure decreases to 18 Torr, the diamond peak gets smaller and the amorphous carbon peak appears to dominate the spectrum. Even though the nondiamond carbon peak appears to be slightly higher than the diamond peak, this does not mean that the film contains more nondiamond carbon. It should be noted that the Raman data are much more sensitive (more than 50 times) to nondiamond carbon than to diamond. Similarly, the Raman spectra of the films deposited at 50 and 70 Torr also show the decrease of the diamond peak. The nature of this behavior is not fully understood. It might be due to the grain size or the surface roughness of the films. As will be shown in the next section, the surface morphology of the film grown at 18 torr appears to be rough and consists of different size crystal grains. Similarly, the surface of the films deposited at 50 and 70 torr also show several different grain
Figure 38. Raman spectra of undoped diamond films grown on Si wafers at different substrate temperatures: (a) 925 °C, (b) 900 °C, (c) 870 °C, and (d) 840 °C. The methane concentration and the pressure were kept constant at 1.0 % and 35 Torr, respectively.
Figure 39. Raman spectra of undoped diamond films deposited on Si substrates at the same methane concentration of 1.0% and temperature of 900 °C, but different pressures: (a) 18 Torr, (b) 35 Torr, (c) 50 Torr, and (d) 70 Torr.
sizes due to higher nucleation density. Tuinstra and coworkers\textsuperscript{69} have reported the grain size effect on the Raman spectra of various forms of graphite. They observed that the Raman intensity is inversely proportional to the crystallite size. This might also be true for diamond films. To illustrate the effect of the grain size on the Raman spectra of diamond films, measurements have been performed on different areas of a film that exhibit different grain size. Figures 40a – b depict the Raman spectra of two different areas from the same diamond film, with different grain sizes. Figure 40a corresponds to the area with large crystal grains, while Figure 40b to the smaller grains. Although the spectra were measured from the same film, the smaller grains (Figure 40b) exhibit a stronger and better diamond peak. The larger grains only show a small broad peak on top of a very high background level. To show the difference in the grain size, the SEM micrographs of the film are displayed in Figure 41a – b. Figure 41a – b represents the surface morphology of the films whose Raman spectra are shown in Figures 40a and 40b, respectively. These results clearly demonstrate the effect of the grain size on the Raman spectra of the diamond films.

Raman spectra measurements have been carried out for boron doped diamond films deposited at 1.0% methane, 35 Torr, and 900 °C, but at different diborane concentrations. The B\textsubscript{2}H\textsubscript{6}/H\textsubscript{2} gas was introduced into the chamber at flow rates of 4 to 64 sccm. The Raman spectra of boron doped diamond films with different boron concentrations are shown in Figures 42 – 43. With the addition of boron into the films, the diamond 1332 cm\textsuperscript{-1} peak becomes very sharp and the broad bands corresponding to the graphite and amorphous carbon are smaller. As the diborane concentration increases, the graphite and amorphous carbon peaks dramatically decrease. Several research groups\textsuperscript{85,86} have reported that the position of the diamond 1332 cm\textsuperscript{-1} peak does not change with the addition of boron into the films, but they do not report the suppression of the graphite and amorphous carbon peaks as the boron concentration increases. It is possible that the suppression of the nondiamond phases is caused
Figure 40. Raman spectra of different areas of a diamond film having different grain size: (a) large grains, and (b) smaller grains.
Figure 41. Scanning electron micrographs of the film surface whose Raman spectra are shown in Figures 40a and b: (a) large grain size, and (b) smaller grain size.
by the B-C bonding or it may be caused by the grain size and orientation of the films. As will be shown in the next section, the surface morphology of the boron doped film consists mostly of randomly oriented triangular (111) faces which makes the surface smoother. Measurements of the surface roughness using a profilometer reveal that boron doped diamond films exhibit smoother surfaces with a roughness of about 2500 Å. This value is about 50% less than the surface roughness of the film whose Raman spectra is shown in Figure 40a.

![Raman spectra of boron doped diamond films](image)

Figure 42. Raman spectra of boron doped diamond films prepared on a Si substrate with different diborane concentrations: (a) 0 sccm, (b) 4 sccm, and (c) 8 sccm. The films were deposited at 1.0% methane, 35 Torr, and 900 °C.
Figure 43. Raman spectra of boron doped diamond films prepared on a Si substrate with different diborane concentrations: (a) 16 sccm, (b) 32 sccm, and (c) 64 sccm. The films were deposited at 1.0% methane, 35 Torr, and 900 °C
D. Growth and Morphology

Optical and scanning electron microscopy have been extensively utilized to examine the nucleation, growth, and the surface morphology of the diamond films.

1. Substrate Materials and Surface Treatment

The purpose of this subsection is to investigate the nucleation and growth of diamond films on silicon wafers with several different pretreatment methods and on other substrate materials, such as Mo, Cu, Ni, stainless steel, amorphous silicon and germanium thin films, and quartz. In order to be consistent, the deposition parameters used in these studies were kept constant: methane concentration: 1.0%, total flow rate: 100 sccm, pressure: 35 Torr, and temperature of 925 °C.

Silicon wafers have been used as the main substrate material for the diamond deposition throughout the work reported in this thesis. Without any pretreatment, diamond grows very poorly on the silicon substrate, especially on the commercially polished surface. Figures 44a–b display the scanning electron micrographs of the diamond nucleation on a commercially polished silicon wafer and on the back (rough) surface of the wafer, respectively. It is clear that since only isolated diamond particles are deposited, the nucleation of diamond on those substrates is very poor.

Due to the very low nucleation density of diamond on the untreated silicon wafers, several different pretreatment methods have been attempted in order to enhance the nucleation. These pretreatments include:

- roughening the mirror-polished Si wafer by chemical etch
- patterning the Si wafer using reactive ion etching (RIE)
- creating a crater on the Si surface using an Ar ion beam
- scratching of the Si surface with alumina or SiC powder
- scratching of the back (rough) Si surface with a sharp stainless steel tweezer
- scratching of the rough Si surface with a sharp stainless steel tweezer and followed by partially etching the surface in an HF solution
- scratching of the rough Si surface with a sharp stainless steel tweezer and followed by etching the surface in an aqua regia solution
- scratching or polishing the Si surface using a 0.25 µm diamond paste as described in Chapter II.

Figure 44. Scanning electron micrographs of the diamond nucleation on a clean untreated Si wafers: (a) commercially polished Si wafer, and (b) the back (rough) surface
As shown in Figure 45, diamond nucleation is not increased by chemically etching the Si surface. The density of the diamond particles on this surface is very low. Figure 46a depicts the SEM of the diamond nucleation on an RIE patterned Si substrate which indicates that diamond grows very poorly under this pretreatment. Diamond particles are formed inside and outside the grooves without any selectivity. Note that there is no additional cleaning for this substrate; after the RIE process was completed, the substrate was placed inside the deposition chamber for the diamond growth. Another deposition was performed using the RIE patterned Si substrate, but prior to the deposition, the substrate was cleaned in boiled methanol and dried with N₂. As shown in Figure 46b, although a diamond film was not formed, the nucleation is increased. The diamond particles were deposited inside, outside, and on the wall of the grooves without much selectivity. However, there may be some enhancement along the step edges.

Figure 45. SEM micrograph of the diamond particles grown on a Si surface that has been roughened by chemical etch. The deposition time is 12 hours.
Figure 46. Diamond particles deposited on a Si substrate that has been patterned using RIE: (a) without any additional cleaning, and (b) with additional cleaning in boiled methanol
An attempt to grow diamond on the crater created on the Si surface by an Ar ion beam has also been performed with no success (Figure 47). There are only a few diamond particles around the crater region, and no diamond particles were deposited inside the crater even after 8 hours deposition.

Figures 48a – b show the scanning electron micrographs of the diamond nucleation on the silicon substrates that have been scratched with an alumina and SiC powder, respectively. Neither of these two pretreatment methods work to enhance the nucleation of diamond. Although scratches are created on the surface (Figure 48b), this does not seem to initiate the diamond nucleation.

Figure 47. Diamond nucleation around a crater created on the Si surface using Ar ion beam. The deposition time is 8 hours
Figure 48. SEM micrographs of the diamond particles grown on a Si substrates that have been scratched with alumina and SiC powder: (a) alumina powder, and (b) SiC powder.
During the examination of the diamond nucleation on the untreated Si substrate, it was noticed regularly that diamond islands were always grown in the corner of the substrate. As illustrated in Figure 49, the shape of the islands appeared to match the tweezer marks. Based on this observation and the author's curiosity, the rough Si surface was intentionally scratched with a sharp stainless steel tweezer prior to the deposition to see whether the nucleation could be enhanced. Figure 50 is the scanning electron micrograph of the uniform diamond film deposited for 12 hours on the rough Si surface that had been scratched with a tweezer. It is very clear that the nucleation is greatly enhanced under this pretreatment. The film exhibits well faceted cubic structures with a very rough surface. Although the nucleation is increased dramatically, the mechanism is not clear. It is possible that the tweezer creates structural or topological defects, and/or leaves some chemical impurity on the Si surface. To explore these possibilities, two different post–cleaning procedures were then performed. The first one was
to clean the Si substrate using an aqua regia solution to etch away all of the metal residues on the scratched surface, and the second one was etching partially the scratched Si surface in an HF solution. The result of the diamond nucleation on the Si surface that was cleaned in an aqua regia solution is shown in Figure 51. Under this pretreatment, the diamond nucleation is still increased, and this clearly shows that the enhancement is not caused by a chemical impurity on the scratched surface. Figures 52 displays the SEM micrograph of the scratched Si surface that has been etched in an HF solution, while Figure 53 shows the nucleation on the same substrate, but on the surface that was not etched with an HF solution. As seen in Figures 52 – 53, the diamond nucleation is enhanced even after the etching. These experiments clearly demonstrate that scratching the rough Si surface using a stainless tweezer does enhance the nucleation of diamond, and the enhancement is most probably caused by structural defects on the surface. Furthermore, these experiments also show that scratching the substrate using diamond powder is not the only method to greatly enhance the nucleation.

Figure 50. SEM of the uniform diamond film grown on a rough Si surface that has been scratched with a stainless steel tweezer.
Figure 51. Diamond nucleation on a rough Si surface that has been scratched with a tweezer and then cleaned in an aqua regia solution.

Figure 52. Diamond nucleation on a Si substrate that has been scratched with a tweezer and followed by HF etching.
Figure 53. Diamond nucleation on a Si substrate that has been scratched by a tweezer, but on the area that was not etched by HF solution

As described in Chapter II, it is well known that the diamond nucleation is greatly enhanced by scratching or polishing the Si wafers with the diamond paste. Figure 54 depicts the smooth uniform diamond film as a result of this pretreatment. The films shows highly faceted structure with (100) faces. Polishing the Si wafers with the diamond paste or diamond powder has proved to be the best pretreatment method to grow uniform diamond films.

Growth of diamond on several different substrate materials have also been attempted in this work. The substrate materials include: Mo, Cu, stainless steel, Ni, amorphous Si film, Ge thin film, and quartz. In general without any pretreatment, diamond grows very poorly on all of the above substrates. In comparison to the untreated Si wafers, Mo and Cu substrates provide higher nucleation density of diamond, while stainless steel substrates do provide a high nucleation density of black amorphous carbon (soot), and in several cases it was observed that a very small amount of diamond particles grow on the top of the uniform amorphous carbon film. Figure 55 depicts the diamond particles that were deposited on top of the black soot that
Figure 54. SEM micrograph of a uniform diamond film grown on a Si wafer that has been scratched with 0.25 µm diamond paste.

Figure 55. SEM micrograph of diamond particles grown on top of amorphous carbon film that was rapidly deposited on a stainless steel substrate.
Figure 56. Scanning electron micrograph of the diamond nucleation on a Mo substrate grew very rapidly on an stainless steel substrate. The nucleation of diamond on a clean Mo substrate is illustrated in Figure 56. The average size of the particles is about 12 µm which corresponds to the growth rate of approximately 2 µm/hour. As shown in the figure, the individual diamond crystal shows a well faceted cubic structure. The scanning electron micrograph of the diamond nucleation on a clean Cu substrate is depicted in Figure 57a. As in the case of the Mo substrate, Cu also provides a high nucleation density, and the diamond particles contain mostly well faceted (100) faces at 1.0 % methane concentration. However, the growth rate of diamond particles on Cu substrates appears to be higher than on Mo substrates. Figure 57b displays a diamond crystal deposited for 6 hours on a Cu substrate. The dimension of the crystal is 23.2 µm which corresponds to a growth rate of about 3.9 µm/hour. This is about 4 times higher than the growth rate of diamond particles on Si wafers. The particle exhibits a large (100) surface with some secondary nucleation on the other surfaces.
Figure 57. Scanning electron micrographs of the diamond nucleation on a Cu substrate: (a) diamond particles, and (b) a large individual diamond crystal with secondary nucleations on its surface.
Ni is an excellent choice that can be used as a substrate for diamond growth because it has a lattice constant that is very close to that of the diamond. Nevertheless, it was observed in this work that diamond also nucleated poorly on the Ni substrates. This is illustrated in Figure 58. Note that the light background surface (left region) is the Ni thin film on Si, while the darker background (right part) corresponds to the rough Si substrate. It is very clear that diamond nucleation is very low on the Ni film substrate. Several other researchers have also reported that heteroepitaxial growth of diamond film was not achieved using a Ni substrate.

Attempts to investigate the diamond nucleation on Ge and amorphous silicon thin films have also been carried out in this work, and the results indicate that diamond nucleates very poorly on these two substrates. Figures 59 and 60 show the nucleation of diamond on Ge and amorphous Si thin films, respectively. In Figure 59, the left part (light region) is the Ge thin film surface, while the right part (darker region) corresponds to the Si surface. The top part in Figure 60 corresponds to the a-Si:H surface that has been damaged at the high deposition temperature of diamond.

Figure 58. Diamond nucleation of a Ni substrate. The left (light) region is the Ni film surface, while the right (dark) region is the Si surface.
Figure 59. Diamond nucleation on a Ge thin film. The left (light) part is the Ge surface, while the right (dark) region corresponds to the Si surface.

Figure 60. Scanning electron micrograph of the diamond particles grown on a-Si:H film (upper part of the picture).
Figure 61. SEM micrograph of the diamond film grown on the corner of a quartz substrate.

The nucleation of diamond on quartz substrates has also been investigated in this research. Since it is very difficult to deposit diamond on untreated quartz substrates, prior to deposition the quartz substrates were scratched with 6 µm diamond paste to enhance the nucleation. Even under this pretreatment, the diamond appears to grow more along the edge or on corner of the substrate where there are more scratches. The center region of the substrate was mostly covered by an amorphous white deposit with only a few diamond particles. Figure 61 illustrates the diamond film deposited on the corner of a quartz substrate that has been scratched with diamond paste. It was observed that diamond film that was deposited on the corner of the quartz substrate also cracked very easily. In general, these results agree with the observation by Badzian et al. who reported that it is very hard to deposit diamond films even on a scratched quartz substrate, and in most cases only an amorphous white deposit was formed.
2. Surface Morphology

The surface morphology of the diamond films has been investigated by varying the deposition parameters. It was observed that the film morphology depends strongly on the methane concentration and the substrate temperature during the deposition. In this work, the methane concentration was varied from 0.5% to 5% with a constant pressure and temperature of 35 Torr and 900 °C, respectively. For methane concentration of 0.5 %, the surface morphology is dominated by the appearance of the triangular (111) faces (see Figure 62). Although most of the (111) faces are randomly oriented, in several regions of the film the (111) faces appear to be parallel to the film surface (Figure 63). This is the weak preferred orientation that was indicated by the x-ray Read pattern (Figure 29). Figure 64 shows the surface morphology of the uniform diamond film grown at 1.0% methane concentration.

Figure 62. SEM micrograph of a diamond film grown at 0.5% CH₄, 900 °C, and 35 Torr.
Figure 63. **Surface morphology of a diamond film grown at 0.5% methane that shows** some preferred orientation

Figure 64. **SEM micrograph of the diamond films grown at 1.0% CH₄, 900 °C, and 35 Torr**
In contrast to Figure 62, the film exhibits mostly highly faceted square (100) faces that are randomly oriented. The size of the (100) faces is of the order of 2 µm. Figures 65 (a) – (d) illustrate the film morphologies as the methane concentration was varied from 1.5 to 5.0%. As shown in Figure 65 (a), the (100) faces are still present as the methane concentration is increased to 1.5 %. The only difference is that the grain size is in general smaller than in the film deposited at 1.0 % methane. This is possibly caused by the high growth rate or nucleation rate that occurs at higher methane concentrations. As the methane concentration is increased to 2.0% or higher, the film surfaces become totally microcrystalline. At 3.0 and 5.0 % methane concentrations (Figures 65 (c) – (d), the crystallographic planes of diamond are not observed at all within the resolution of the SEM used. All of these films show the so called "cauliflower" structures as has been reported by a number of research groups. Such a cauliflower structure is believed to be caused by an increased amount of the sp² bonding, as confirmed by Raman spectra.

In order to study the effect of the temperature on the film morphology, several experiments have been conducted by varying the substrate temperature in the range of 840 to 925 °C at a pressure of 35 Torr, and 1.0% methane concentration. This can be easily done by changing the incident microwave power. Figure 66 is the scanning electron micrograph of a polycrystalline diamond film grown at 840 °C. The film surface looks rough and contains mostly cubo-octahedron structures. This may be caused by the decrease of the nucleation density at this low substrate temperature. From the cubo-octahedra the ratio of the growth rates in the [100] and [111] directions (v₁₀₀/v₁₁₁) can be determined by measuring the linear dimension of the (111) and the (100) faces, respectively. In this film v₁₀₀/v₁₁₁ is measured to be about 2.08. Upon increasing the substrate temperature to 870 °C, the films become denser and still show cubo-octahedron structures, but the size of the (100) faces clearly increases and becomes comparable to the (111) faces (Figure 67). As shown in Figures 64.
Figure 65. Surface Morphologies of the diamond films at grown at various methane concentration:

(a) 1.5 %, (b) 2.0 %, (c) 3.0 %, and (d) 5.0 %
Figure 66. Scanning electron micrograph of a diamond films synthesized at 840 °C, 1.0% methane, and 35 Torr

and 68, the morphologies of the diamond films grown at 900 and 925 °C are dominated by the square (100) faces. Thus, the area ratio of the {100} to {111} planes increases with the increasing substrate temperature. These observations are in good agreement with the results obtained by a number of research groups\textsuperscript{19,75,88} who reported that if the substrate temperature increases, the crystal habits change from the regular octahedron structure ($v_{100}/v_{111} > 3$) to cubic ($v_{100}/v_{111} < 1/\sqrt{3}$) via intermediate cubo-octahedron structures.

The effect of the gas pressure on the film morphology has been investigated by varying the gas pressure from 18 to 70 Torr, while the methane concentration and the substrate temperature were kept constant at 1.0% and 900 °C, respectively. Since under a constant microwave power the substrate temperature changes as the pressure changes, it is expected that the combined effect of the pressure and the amount of microwave power on the film morphology will be observed. Furthermore, the plasma uniformity surrounding the substrate
Figure 67. SEM micrograph of a diamond film grown at 870 °C, 1.0% CH₄, and 35 Torr

Figure 68. SEM micrograph of a diamond film grown at 925 °C, 1.0% CH₄, and 35 Torr
also changes with increasing pressure. At high pressures the plasma shrinks and causes a denser plasma in the center, while at low pressures the plasma tends to spread out so that the plasma density appears to be lower in the center region of the substrate. Figure 69 is the SEM micrograph of the film deposited at 18 Torr. Unlike the film grown at 35 Torr (Figure 64), the film is less dense and exhibits much smaller grains with some (100) faces. This is believed to be caused by the lower plasma density that covered the substrate during the deposition. The surface morphologies of the diamond films synthesized at 50 and 70 Torr are shown in Figures 70 and 71, respectively. The figures demonstrate that at higher pressures, the films look denser with more secondary nucleations that occur on the surface. Nevertheless, the films still exhibit well faceted cubic structures with smaller (100) faces than in the film grown at 35 Torr. This clearly shows that the higher plasma density increases the nucleation density, which also

![Figure 69. Scanning electron micrograph of the film morphology grown at 18 Torr, 900 °C, and 1.0% methane concentration](image-url)
Figure 70. Surface morphology of a diamond film deposited at 50 Torr, 1.0% CH$_4$, 900 °C

Figure 71. SEM micrograph of a diamond film grown at 70 Torr, 1.0% methane, and 900 °C
causes a decrease in the particle size. Note that in the early stages of the diamond growth, the individual particles grow to increase their size until they coalesce with other particles to form a uniform film. It is obvious that if the nucleation density is higher, a uniform film will form faster. When this occurs, the secondary nucleations will start to dominate, and the film will consist of smaller grains as shown in Figures 70 and 71. Based on the SEM results and the visual observation of the plasma uniformity during the diamond deposition, a pressure of 35 Torr seems to be the optimum deposition pressure for the system used in this work. This is why most of the diamond films reported in this thesis were deposited at 35 Torr. The fractured cross section of a dense uniform diamond film deposited for 3.5 hours at 70 Torr is shown in Figure 72. It is clearly seen that the film undergoes a columnar growth. Figure 73 illustrates another cross section of a dense uniform film grown for 6 hours at 1.0% methane, 35 torr, and 900 °C. The elongated individual grains can obviously be seen in the void free film. This
Figure 73. A cross sectional view of a uniform diamond film that clearly shows the elongation of the individual grains. The film was grown for 6 hours at 1.0% methane.

Figure 74. SEM micrograph of a particular region of the film where the nucleation density is low. It is clear that the individual particle grew bigger on this region.
figure demonstrates that the diamond undergoes a three dimensional growth. Initially, only individual diamond particles are formed on the substrate surface. The particles increased their sizes almost uniformly until they coalesce with other particles to form a film, and after a uniform film is formed, the secondary nucleation or growth will start to occur so that the film surface contains smaller grains. In the areas where the initial nucleation density is low, the crystals tend to grow bigger. This situation is illustrated in Figure 74.

The effect of the boron doping on the film morphology has been investigated by depositing the boron doped films at various diborane concentrations which are controlled by the flow rate of the B₂H₆/H₂ mixture. In order to be accurate, the surface morphology of the boron doped films is compared to the undoped film that was deposited one day before the series of the boron doped films were synthesized. This would provide roughly the same experimental environments, particularly in the concentration of the methane in the CH₄/H₂ gas cylinder. Figure 75 is the SEM of the undoped film that shows the typical well faceted (100) faces at 1.0 % methane concentration. The scanning electron micrograph of the boron doped films grown at 4.0 sccm B₂H₆/H₂ is depicted in Figure 76. It is clearly seen from the figure that the morphology of the film appears to be dominated by the triangular (111) faces. As the flow rate of B₂H₆/H₂ increases the film morphology does not show any appreciable change. Figure 77 and 78 show the boron doped diamond films grown at 16.0 and 64.0 sccm B₂H₆/H₂, respectively. Both of the films exhibit a mixture of highly faceted (100) and (111) faces with more (100) observed in the film with higher diborane concentration. Although the mechanism is not well understood, the introduction of boron seems to enhance the appearance of the (111) planes on the film morphology.

Twinning of the crystals across the (111) planes is very common in the polycrystalline diamond films. Figure 79 illustrates the 2-fold symmetry of the crystal twinning across
Figure 75. Surface morphology of a diamond film grown at 1.0% CH₄, 900 °C, and 35 Torr. This film was synthesized one day before the deposition of the boron doped films.

Figure 76. Surface morphology of the boron doped diamond film grown at 4 sccm B₂H₆/H₂.
Figure 77. Surface morphology of the boron doped diamond film grown at 16 sccm B₂H₆/H₂.

Figure 78. SEM micrograph of the boron doped diamond film grown at 64 sccm B₂H₆/H₂.
the (111) planes that occurs in the film deposited with 1.0% methane, 35 Torr, and 840 °C. Multiply twinned particles of diamond have also been observed during the scanning electron microscopy analysis. Figure 80 displays the multiply twinned particles that were deposited in the vicinity of a single crystal diamond particle. The particles were grown for 8 hours at 1.0% methane, 35 Torr, and 900 °C. Besides the various defect structures that occur in the films, diamond single crystals have also been grown in several locations on the substrate, particularly where the initial nucleation density is low. Figure 81 shows the single crystal diamond that exhibits high quality crystal habit.

Figure 79. SEM micrograph of crystal twinning across the (111) plane
Figure 80. Scanning electron micrograph of a multiply twinned diamond particle

Figure 81. SEM of a single crystal diamond particle that exhibits a high quality crystal habit
3. Selective Deposition

Selective deposition of diamond films has been successfully performed in this work using a lift-off process at several different deposition parameters. Figure 82 shows the scanning electron micrograph of the selectively deposited diamond films. The film was synthesized for 3.5 hours at 1.0% methane concentration, 35 Torr, and 840 °C. The figure demonstrates that the selectivity is very good. The diamond grows on the crystalline Si surface, but not on the amorphous silicon areas. The width and the spacings of the diamond lines is approximately 6 µm. At this low deposition temperature, the film is dominated by cubo–octahedron structures. Since the film was deposited for only 3.5 hours, it is expected that a smooth uniform film can be obtained by increasing the deposition time.

Figure 82. Scanning electron micrograph of a selectively deposited diamond film. The film was grown for 3.5 hours at 840 °C, 1.0% methane, and 35 Torr.
The scanning electron micrograph of a patterned polycrystalline diamond film grown for 3.5 hours at 870 °C, 1.0% methane, and 35 Torr is displayed in Figure 83. At this higher deposition temperature the selective nucleation of the diamond is still very good. The film exhibit smaller and denser grains, and it shows more faceting of (100) faces.

To investigate further the temperature effect on the selectivity, the diamond deposition was performed for 8 hours at 900 °C, 1.0% methane, and 35 Torr. Figure 84 shows well faceted individual crystals of diamond near the edge of the selectively deposited polycrystalline diamond film. The crystals grew in the pinholes that formed in the amorphous silicon areas which also means that they grew directly on top of the crystalline Si surface. Note that pinholes occur in the amorphous silicon as it is heated. The amorphous Si emits hydrogen and crystallizes even before reaching the diamond deposition temperature.

![Figure 83. SEM micrograph of a patterned diamond film grown at 870 °C, 1.0% methane, and 35 Torr. The film exhibits smaller and denser grains with (100) faces](image-url)
The selectivity of the diamond growth is also not affected by changing the methane concentration and/or pressure during the deposition. The SEM micrograph of the diamond films grown for 8 hours at 1.5% methane, 900 °C, and 35 Torr is shown in Figure 85. As seen in the figure, although the selectivity is still very good, it is clearly limited by the grain size and the sharpness of the photolithography. The diamond ball between the uniform film areas was again deposited in the pinhole of the amorphous silicon film. Figure 86 shows the edge of the selectively grown diamond film that was synthesized for 3.5 hours at 1.0% methane, 900 °C, and 18 Torr. This figure demonstrates that the selectivity depends very strongly on the grain size of the film. Although the amorphous silicon film crystallized before reaching the deposition temperature, no diamond nucleated on it. This clearly shows the importance of the polishing of the Si surface with the diamond paste for the nucleation.
Figure 85. SEM micrograph of selectively deposited diamond film grown at 900 °C, 1.5% methane, and 35 Torr.

Figure 86. SEM micrograph of the edge of selectively grown diamond film that clearly shows that the selectivity depends strongly on the grain size of the film.
E. Infrared Properties

The infrared absorption spectra measurements were carried out over the range from 400 to 3400 cm\(^{-1}\) for both undoped and boron doped diamond films. For undoped diamond thin films, infrared spectra have been mainly used to show the presence of hydrogen (C–H stretch) and silicon carbide (Si–C stretch). In the case of boron doped diamond films, in addition to the CH and SiC stretch, the infrared spectra also show B–C stretch mode which appears around 1280 cm\(^{-1}\). The absorption peaks due to sp\(^3\) C–H stretch modes appear between 2850 and 2950 cm\(^{-1}\), while the Si–C stretch mode is located at 800 cm\(^{-1}\). Figure 87 shows the infrared spectrum of an undoped diamond film deposited for 6 hours on a Si (100) substrate at 2.0% methane concentration, 900 °C, and 35 Torr. The absorption peak between 2850 to 2960 cm\(^{-1}\) is due to the CH and CH\(_2\) sp\(^3\) type bonding. The CH stretch peak is not very strong which indicates that hydrogen concentration in the film is quite low. It has been suggested by Matsumoto and coworkers\(^{92}\) that the hydrogen is chemisorbed only at the film surface and grain boundaries, but not contained in the diamond grains. It can be seen from Figure 87 that a SiC peak is not observed near 800 cm\(^{-1}\), which suggests that a SiC thin layer may not form during the initial growth of the diamond film. However, the formation of a SiC layer during the early stage of diamond synthesis has been reported by Meilunas and coworkers.\(^{93}\)

The infrared spectra of undoped diamond films synthesized at different methane concentrations are illustrated in Figure 88. The films were synthesized at 35 Torr, and 900 °C for 6 hours. As expected, the C–H stretch peak decreases as the methane concentration decreases. At 0.5% methane concentration, the absorption is not observed at all. Note that the interference patterns in the spectra demonstrate that the thickness of the films decreases with methane concentration. This confirms the results on the deposition rate presented in Section IV.A.
Figure 87. IR spectrum of an undoped diamond film grown for 6 hours at 2.0% methane, 900 °C, and 35 torr.

Figure 89 displays the infrared spectrum of the boron doped diamond film with the flow rate of B2H6/H2 of 8 sccm. The film was deposited at 1.0% methane, 35 Torr, and 900 °C. With boron incorporation, the film becomes more absorptive, and the interference pattern is very weak. The transmittance is greatly reduced due to free carrier absorption. The asymmetric absorption peak at about 1280 cm⁻¹ corresponds to the B–C stretch mode. From SIMS analyses, the boron concentration is determined to be 5.2 x 10¹⁹ cm⁻³. This indicates that IR measurements can be used to identify the presence of boron in the p type semiconducting diamond films. Due to a large difference in the value of the transmittance,
Figure 88. IR spectra of undoped diamond films deposited at different methane concentrations: (a) 2.0%, (b) 1.5%, (c) 1.0%, and (d) 0.5%
the infrared spectra of the boron doped diamond films grown with the flow rate of \( \text{B}_2\text{H}_6/\text{H}_2 \) from 16 to 64 sccm are illustrated separately in Figures 90 – 92. In general, as the diborane concentration increases, the absorption and the B–C stretch peak also increase. As the \( \text{B}_2\text{H}_6/\text{H}_2 \) flow rate increases from 8 to 64 sccm, the transmittance at about 3400 cm\(^{-1} \) is greatly reduced from 30 to almost 0%. For the \( \text{B}_2\text{H}_6/\text{H}_2 \) flow rate of 64 sccm, the B–C stretch peak appears very small due to the very high absorption. This is in general agreement with the results of Kobashi and coworkers.\textsuperscript{94} However, quantitative determination of the boron concentrations from the IR spectra was not attempted.

![Graph](image.png)

**Figure 89.** IR spectrum of boron doped diamond film deposited at 1.0% methane, 900 °C, 35 Torr, and the \( \text{B}_2\text{H}_6/\text{H}_2 \) flow rate of 8 sccm
Figure 90. IR spectrum of boron doped diamond film deposited at 1.0% methane, 900 °C, 35 Torr, and the B\textsubscript{2}H\textsubscript{6}/H\textsubscript{2} flow rate of 16 sccm

Figure 91. IR spectrum of boron doped diamond film deposited at 1.0% methane, 900 °C, 35 Torr, and the B\textsubscript{2}H\textsubscript{6}/H\textsubscript{2} flow rate of 32 sccm
Figure 92. IR Spectrum of boron doped diamond film deposited at 1.0% methane, 900 °C, 35 Torr, and the B₂H₆/H₂ flow rate of 64 sccm

F. Electrical Properties

1. Type of Conductivity and Sheet Resistance

The type of conductivity of boron doped diamond films was determined by the thermoelectric or hot probe method. The results are encouraging because in all cases it was confirmed that the boron doped diamond films have p type conductivity. Note that the measurements were performed on both free standing films and on films with substrates.

The sheet resistance of the boron doped diamond films was measured using a 4 point probe technique. The sheet resistance measurements were performed initially on films with
substrates to get a rough idea of the effect of the boron concentration. Although these measurements will not produce the absolute values of the sheet resistance, the relative values are useful to give qualitative results of the doping concentration. As expected the sheet resistance decreases as the diborane concentration in the films increases. The values range from 39.25 $\Omega$/square to 10.34 k$\Omega$/square depending upon the boron concentration in the films (Table 9). After the Si substrate was etched away, the measurements were repeated very carefully on the free standing films. It was found that regardless of whether n or p type Si wafers were used, the sheet resistance of the films was strongly affected by the substrate, particularly on the films with lower boron concentrations. As summarized in Table 9, the sheet resistance of the free standing films is lower than of the films with substrates. The values range from 234.79 $\Omega$/square to 92.65 k$\Omega$/square. This is not surprising because the resistivity of the Si substrates are in general lower than the semiconducting diamond films so that during the measurements more current flows through the Si substrate rather than the diamond film.

As the films becomes more conducting, the measured sheet resistance of the film before and after the substrate was etched away does not differ very much (Sample ML269). It should be noted that all discussions about the measurements of the sheet resistance on the free standing films only apply to samples that were deposited at B$_2$H$_6$/H$_2$ flow rate from 4 to 64 sccm.

The resistivity of the free standing diamond films can be obtained by multiplying the sheet resistance by the thickness of the films. The resistivity was determined to be 0.08 to 43.57 $\Omega$cm depending upon the boron concentration. Figure 93 shows the resistivity of the free standing boron doped diamond films as a function of the doping concentration. The figure shows that the resistivity decreases as the boron concentration increases. Assuming that the percentage of boron that is active in the films is constant with the concentration, the results clearly demonstrate that the boron really acts as a dopant in the diamond lattice.
Table 9. Boron doped diamond films and measured electrical properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>( N_B^\text{a} ) (x ( 10^{19} \text{ cm}^{-3} ))</th>
<th>( R_{sw}^\text{b} ) (( \Omega )/square)</th>
<th>( R_{sf}^\text{b} ) (( \Omega )/square)</th>
<th>( \rho^\text{c} ) (( \Omega )/cm)</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML209</td>
<td>57.0</td>
<td>103.29</td>
<td>N/A</td>
<td>---</td>
<td>0.013</td>
</tr>
<tr>
<td>ML210</td>
<td>78.0</td>
<td>82.51</td>
<td>N/A</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>ML215</td>
<td>150.0</td>
<td>72.66</td>
<td>N/A</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>ML250</td>
<td>3.0</td>
<td>10,360.00</td>
<td>92,650.00</td>
<td>43.57</td>
<td>0.158</td>
</tr>
<tr>
<td>ML249</td>
<td>5.2</td>
<td>7,384.00</td>
<td>39,130.00</td>
<td>19.37</td>
<td>0.129</td>
</tr>
<tr>
<td>ML255</td>
<td>8.2</td>
<td>1,288.00</td>
<td>5,557.00</td>
<td>3.21</td>
<td>0.111</td>
</tr>
<tr>
<td>ML256</td>
<td>19.0</td>
<td>205.30</td>
<td>2,503.00</td>
<td>0.88</td>
<td>0.049</td>
</tr>
<tr>
<td>ML269</td>
<td>42.0</td>
<td>60.50</td>
<td>235.00</td>
<td>0.08</td>
<td>0.027</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\) \( N_B \) stands for the boron concentration determined from SIMS measurements.

\(^{\text{b}}\) \( R_{sw} \) and \( R_{sf} \) stand for the sheet resistance before and after the substrate was etched away, respectively.

\(^{\text{c}}\) \( \rho \) stands for the resistivity.

2. I/V Characteristics and Activation Energy

I/V characteristic measurements have also been conducted for the semiconducting diamond films before and after the Si substrate was removed. The results confirm the resistivity measurements, i.e., the conductivity of the free standing films are lower than the films with substrates. To illustrate the substrate effect on the measurements, the I/V curve of Sample ML256 before and after the substrate was etched away is depicted in Figure 94.
As shown in the figure, the slope of the curve decreases after the substrate was removed. This can be easily explained because the substrate resistance is lower than that of the film, so that most of the electric current will flow through the substrate. Figure 95 shows the I/V curves of the free standing semiconducting diamond films deposited at different diborane concentrations. Note that the diborane concentrations are represented by the flow rates of the B₂H₆/H₂ gas mixture range from 4 to 64 sccm. As seen in the figure, as the diborane concentration in the deposition chamber increases, the slope of the curve decreases, which means that the conductivity of the films increases. This clearly demonstrates that the conductivity of the microwave plasma deposited diamond films can be controlled by the amount of the diborane introduced in the precursor gas mixtures.
Figure 94. I/V characteristics of the semiconducting diamond film before and after the substrate was etched away: (a) before etching, and (b) free standing film

The activation energy of the semiconducting diamond films was determined by measuring the conductivity at different temperatures range from room temperature to 190 °C. Although the measurements have been carried out on both free standing films and films with substrates, the results reported in this thesis are only those from the free standing films. In this case the values of the activation energy are not affected by the substrates. Figure 96 shows the plot of the logarithm of the conductivity vs. 1000/T for sample ML209. The curve appears to be very straight, and the activation energy is calculated to be 0.013 eV. This result is the same as the value obtained by Fujimori et al. who measured the activation energy of semiconducting diamond films grown on natural diamond substrates also using microwave plasma assisted chemical vapor deposition. Furthermore, they reported that the boron
concentration in the film was found to be in the order of $10^{20} \text{ cm}^{-3}$. This is also in good agreement with sample ML209 whose boron concentration was measured to be $5.7 \times 10^{20} \text{ cm}^{-3}$. Figure 97 displays the temperature dependence of the conductivity for the free standing diamond films deposited at $\text{B}_2\text{H}_6/\text{H}_2$ flow rate from 4 to 16 sccm. As shown in the figure, the curve looks very straight at higher temperatures ($100^\circ \text{C}$ and above), but at lower temperatures a slight deviation from a straight line is observed. This may be due to a surface moisture effect since the measurements were conducted in open air, or due to the inaccuracy in the temperature.
reading. Note that in the measurements, the free standing diamond films were placed on top of a microscope slide that was mounted very close to the thermocouple wire. It is likely that there is a temperature gradient between the film and the area probed by the thermocouple. The values of the activation energy of the various semiconducting diamond films are given in Table 9.

![Graph](image.png)

**Figure 96.** Logarithm of the electrical conductivity versus the inverse of the temperature for sample ML.209 whose boron concentration is $5.7 \times 10^{20}$ cm$^{-3}$

The activation energy appears to depend on the boron concentration. As the diborane concentration increases, the value of the activation energy decreases. The measured values of the activation energy are from 0.013 to 0.158 eV depending upon the diborane concentration. In general, these values are in good agreement with the results reported by several research groups. For example: Fujimori et al.\textsuperscript{61} reported the value of 0.013, Kamo et al.\textsuperscript{95} reported
values of 0.09 to 0.36 depending upon the boron concentration, and the value of 0.17 – 0.18 eV has also been reported for the high pressure experiments. Furthermore, Spitsyn et al. reported as the doping level is increased from 10^17 to 10^19 cm^-3, the activation energy decreased from 0.37 to about 0.10 eV.

![Graph](image.png)

**Figure 97.** Logarithm of the electrical conductivity plotted as a function of the inverse temperature of boron doped diamond films deposited at different B_2H_6/H_2 flow rates: (a) 4 sccm, (b) 8 sccm, and (c) 16 sccm

3. **Electroluminescence**

Electroluminescence (EL) measurements have been performed on both undoped and boron doped diamond films. However, EL has been observed only from the undoped diamond films that were deposited using a step etching process. Figure 98 shows the typical
EL spectrum of the diamond EL device and clearly indicates the blue-green broad band emission. The undoped diamond film which is about 15.2 µm thick was deposited at 1.0% methane, 900 °C, and 35 Torr for 20 hours. The broad band emission with a maximum at about 485 nm and called "band A" has also been observed by several authors. The mechanism of band A emission can be explained by the donor–acceptor (D–A) pair recombination. In this case, the donor is believed to be nitrogen because the nitrogen contamination can easily occur in the vacuum chamber that was evacuated to a base pressure of 5.0 x 10^-5 Torr.

![Figure 98. Luminescence spectrum of a diamond EL device](image)
Although the films used for the EL devices were not intentionally doped, the acceptor is believed to be boron. This was supported by the fact that the diamond EL device that showed the strongest emission was deposited after the deposition of a series of the boron doped diamond films was completed. Based on the D–A pair recombination theory, the energy of the emitted photon is inversely proportional to the D–A pair separation. Therefore, the broadness of the band is due to the large range of the separation between donors and acceptors. The nearest pairs contribute to the highest energy photons, while the distant pairs to the lowest energy photons. Figure 99a – b display the relative luminescence intensity and the current versus the applied voltage. It is clear that the luminescence intensity increases with applied voltage. The threshold voltage for the EL device is about 112 V peak to peak. Note that all of the EL measurements were performed at room temperature. However, electroluminescence at 77 K was also observed when the device was submerged in liquid nitrogen.

G. Doping Concentration

The SIMS analyses of the p type semiconducting diamond films show the presence of boron in the films. The doping concentration was measured using the standards of boron doped diamond films obtained by ion implantation. Table 10 summarizes the results of the SIMS analysis on the boron doped diamond films. The boron concentration in the films depends strongly on the diborane concentration in the starting gas mixtures as expected. As the flow rate of diborane (B₂H₆/H₂) increases, the boron concentration in the films also increases.
Figure 99. Relative luminescence intensity and the current plotted as a function of the applied voltage: (a) Relative intensity, and (b) Electric current
Table 10. SIMS results on the boron concentration in p type semiconducting diamond films

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{B}_2\text{H}_6/\text{H}_2$ flow rate (sccm)</th>
<th>Cylinder type$^a$</th>
<th>Boron concentration (atoms/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML209</td>
<td>0.5</td>
<td>I</td>
<td>$5.7 \times 10^{20}$</td>
</tr>
<tr>
<td>ML210</td>
<td>1.0</td>
<td>I</td>
<td>$7.8 \times 10^{20}$</td>
</tr>
<tr>
<td>ML215</td>
<td>1.5</td>
<td>I</td>
<td>$1.5 \times 10^{21}$</td>
</tr>
<tr>
<td>ML250</td>
<td>4.0</td>
<td>II</td>
<td>$3.0 \times 10^{19}$</td>
</tr>
<tr>
<td>ML249</td>
<td>8.0</td>
<td>II</td>
<td>$5.2 \times 10^{19}$</td>
</tr>
<tr>
<td>ML255</td>
<td>16.0</td>
<td>II</td>
<td>$8.2 \times 10^{19}$</td>
</tr>
<tr>
<td>ML256</td>
<td>32.0</td>
<td>II</td>
<td>$19.2 \times 10^{19}$</td>
</tr>
<tr>
<td>ML269</td>
<td>64.0</td>
<td>II</td>
<td>$42.0 \times 10^{19}$</td>
</tr>
</tbody>
</table>

$^a$I and II stand for the cylinders that contain the $\text{B}_2\text{H}_6/\text{H}_2$ mixture of 1000 and 12 ppm, respectively.

Figure 100 plots the boron concentration in the films as a function of the $\text{B}_2\text{H}_6/\text{H}_2$ flow rate. It appears that there is a linear relationship, within experimental error, between the amount of the diborane in the deposition chamber and the boron incorporated in the films. The straight line in the figure represents the least square fit for the data. Several authors$^{85,86,95}$ have reported that the boron concentration can be controlled by the boron in the gas phase, but very few quantitative results have been reported so far. By combining the results of the resistivity measurements with the semiquantitative SIMS analyses, it is believed that the boron is incorporated in the diamond films as an effective dopant.
Figure 100. Boron concentration as a function of the B$_2$H$_6$/H$_2$ flow rate
V. CONCLUSIONS

Both undoped and boron doped diamond films have been grown by microwave plasma assisted chemical vapor deposition from methane, hydrogen, and diborane gases. A complete study, including the effects of methane concentration, substrate temperature, and pressure on the structures and morphologies of the films, demonstrates that high quality diamond films have been successfully achieved. In all cases, the films have been analyzed using x-ray diffraction techniques, Raman and infrared spectroscopies, scanning electron spectroscopy, secondary ion mass spectrometry, and several different electrical measurements, including I/V characteristics, activation energy, and electroluminescence measurements.

The deposition rates of the diamond films have been investigated and found to be strongly dependent upon the deposition parameters. As the methane concentration, temperature, and/or pressure increase, the deposition rates also increase. This is as expected because as the methane partial pressure is increased, the amount of carbon source in the deposition chamber is also higher. It has been mentioned in the previous chapter that at a fixed pressure, the substrate temperature depends strongly on the microwave power. Therefore, higher temperatures require higher microwave power, and this means a more intense discharge in the deposition chamber. For boron doped diamond films, however, as the diborane concentration in the chamber increases, the deposition rate tends to decrease until it saturates due to the boron deposit on the tube wall that absorbed most of the incoming microwave power. The deposition rate for the undoped diamond films grown by microwave plasma assisted CVD system reported in this thesis is 0.87 µm/hour at 1.0% methane, 35 Torr, and 900 °C. This value is very typical for the microwave plasma assisted chemical vapor deposition systems, which commonly report values of about 1.0 µm/hour.
The structures of the diamond films have been analyzed using both Read camera and x-ray diffractometer (XRD) techniques. The Read and XRD spectra were found to be closely related to the methane concentration, but were not very much affected by substrate temperature, pressure, and/or diborane concentration. In most cases the films were determined to be polycrystalline with random orientations. Nevertheless, at low methane concentration (0.5 %), both Read and XRD spectra demonstrate a weak preferred orientation for the (111) reflection with a width of 10 degrees maximum.

Raman spectroscopy has been extensively used to identify the presence of nondiamond phases in the diamond films and proved to be sensitive in detecting a small amount of graphitic and amorphous carbon that was difficult to identify from the x-ray diffraction spectra. The diamond peak height at 1332 cm\(^{-1}\) depends strongly upon the deposition parameters, in particular, the methane concentration. At higher methane concentrations, the diamond peak decreases, while the broad amorphous carbon peak (about 1500 cm\(^{-1}\)) increases. This indicates that the diamond concentration (sp\(^3\) type bonding) in the films decreases with increasing methane concentration. The effect of the substrate temperature and the gas pressure during the deposition on the Raman spectra of the undoped diamond films has also been investigated. At lower temperatures and/or pressures, the diamond peak decreases, while the nondiamond peak increases. There are two possibilities that may explain this behavior. First, the diamond concentration in the films decreases, and secondly, the behavior may be related to the grain size and/or surface roughness of the films. It has been observed that the diamond surface which has smaller grains exhibits a stronger diamond peak than the surface having larger grains. The best Raman spectra of the undoped diamond films reported in this thesis were measured from films deposited at 925 °C, 35 Torr, and 1.0% methane concentration. The peak is very sharp with a full width at half maximum (FWHM) of about 6.5 cm\(^{-1}\). By comparing the peak intensity of the nondiamond phase to the diamond peak and taking into
account the Raman sensitivity factor, the amount of the nondiamond phases in the film is
determined to be less than 0.2%. The Raman spectra of boron doped diamond films show the
suppression of the of the nondiamond phases by the incorporation of boron in the films. As
the diborane concentration increases, the diamond peak at 1332 cm⁻¹ gets stronger, while the
amorphous carbon peak decreases. It is possible that this is caused by either the presence of
the B–C bonding or by the grain size and orientation of the films, or both. The SEM
micrographs of the boron doped diamond films show that the surfaces of the films contain
mostly small grains of randomly oriented (111) faces. Moreover, the surfaces of the boron
doped diamond films are also smooth, with roughness of about 2500 Å. More experiments
need to be conducted to confirm the mechanism, in particular, using a Raman microprobe with
a beam size of about 1 to 2 µm, so that the spectra of the individual crystals can be measured.

Both optical and scanning electron microscopy have been routinely utilized to analyze
the nucleation, growth, and surface morphology of the diamond films. Several attempts have
been carried out to investigate the nucleation and growth of diamond on several different
substrate materials, including the effect of surface pretreatments of the Si wafers. Among
several different pretreatment methods that have been tried, scratching the Si surface with
diamond paste or stainless steel tweezers are two methods that greatly enhance the diamond
nucleation. The nucleation enhancement caused by scratching the rough Si surface using
tweezers demonstrates that diamond paste is not the only solution to obtain uniform films.
Furthermore, several postcleaning procedures performed on the Si surface that has been
scratched with a tweezer, clearly suggest that the enhancement mechanism is caused by
structural defects on the surface. Diamond nucleation on several different substrate materials
such as Cu, Mo, and Ni has also been investigated in this work. Even though there is a lattice
match between diamond and Cu or Ni, it was observed that uniform diamond films could not
be successfully grown on either Cu or Ni. Note that the lattice constant of diamond is 3.567
Å, while those of Ni and Cu are 3.524 and 3.615 Å, respectively. As compared to Si, however, Mo and Cu provide higher nucleation density. The growth rate of diamond particles on Cu substrates is also approximately 4 times higher than on Si substrates. This result seems to contradict the observation by several authors who reported that carbide-forming substrates (Si, Mo, W) tend to have higher diamond nucleation densities than non carbide-forming substrates such as Cu and Au.

The surface morphologies of the diamond films have been analyzed and found to be strongly related to the deposition parameters. At low methane concentration (0.5 %), the film morphology is dominated by the appearance of the triangular (111) faces. As the methane concentration increases to 1.0 %, the morphology consists mostly of well faceted cubic (100) faces. The cubic (100) structures still show up in the films deposited at 1.5 % methane, but the grains are smaller than in films grown at 1.0 % methane. At methane concentrations of 2.0 % or higher, the films become totally microcrystalline with cauliflower structures. The cauliflower structure is believed to be caused by an increasing concentration of the sp² (graphitic) bonding, as confirmed by the Raman data.

The effect of substrate temperature and gas pressure during the deposition on the film morphology have also been investigated. At lower temperatures, the films contain mostly cubo-octahedron structures. Although CVD diamond films are known to have many defect structures, e.g., twinning, the films grown at lower temperatures tend to show more twinning, particularly across the (111) planes. Upon increasing the substrate temperature, the crystal habits change from cubo-octahedron to cubic structures. The gas pressure during the deposition appears to affect the grain size and the density of the films. At lower pressures, the films are less dense and exhibits smaller grains, while at higher pressures, the films look denser with smaller grains due to the more secondary nucleations.
The morphology of the boron doped diamond films has been analyzed by comparison with the undoped diamond films grown using the same deposition parameters. It was found that the presence of boron tends to cause the appearance of (111) faces.

SEM analyses have also confirmed that the selective deposition of polycrystalline undoped diamond films have been successfully achieved using a lift-off process on Si wafers that have been polished with diamond paste. The selectivity is very good with resolution of at least 2 µm and may be improved by further optimization of the lift-off process and the deposition parameters. Furthermore, the success of the selective deposition of the diamond films also demonstrates the importance of scratching the Si surface with diamond paste for diamond nucleation.

SIMS analyses on the p type semiconducting diamond films confirm the presence of boron in the films. As expected, the boron concentration in the films depends strongly on the diborane concentration in the starting gas mixtures.

The infrared spectra of the undoped diamond films show the absorption due to CH and CH₂ sp³ type bonding which increases with increasing methane concentration. It has been argued that the hydrogen is chemisorbed only at the film surface and grain boundaries. The results reported in this thesis seem to support the argument because the SEM micrographs of the films grown at higher methane concentrations contain mostly smaller grains.

Unlike the undoped films, the infrared spectra of the boron doped diamond films do not show any CH and CH₂ absorption peaks because the transmittance is dramatically decreased due to the free carrier absorption. However, the presence of boron can be detected clearly from the appearance of the asymmetric B–C peak at about 1280 cm⁻¹, even from the film with the lowest boron concentration of 5.2 x 10¹⁹ cm⁻³. This suggests that the lower limit of boron detection from the IR data should be lower than 5.2 x 10¹⁹ cm⁻³. Furthermore, for high boron concentrations, IR spectra provide a rapid way to determine the presence of boron in the films.
Various electrical measurements performed on the boron doped diamond films demonstrate that p type semiconducting diamond films have been successfully grown in this work. In all cases, the thermolectric probe analyses indicate that the films have p type conductivity. The resistivity and the I/V characteristics measurements on both free standing films and films on substrates consistently demonstrate that resistivity of the semiconducting diamond films depends strongly on the boron concentrations. As the boron concentration in the films increases, the resistivity decreases from 43.57 to 0.08 Ω-cm. Therefore, the results clearly show that boron is really incorporated in the films as an effective dopant. The temperature dependence of the conductivity of the films has been studied from room temperature to 190 °C. The activation energy of the acceptors has been determined, and the value ranges from 0.013 to 0.158 eV, depending upon the boron concentration.

Blue-green electroluminescence has been observed from the undoped diamond films deposited using a step etching process. The mechanism can be explained by the donor-acceptor (D-A) pair recombination. Even though the films were not intentionally doped, the donor and acceptor are believed to be nitrogen and boron, respectively. The mechanism of the electroluminescence can be explained qualitatively using the energy band diagram shown in Figure 101. Natural diamond is an indirect gap material with a band gap of about 5.45 eV. However, the band gap of 5.30 to 5.40 eV has been reported for vapor deposited diamond films.\textsuperscript{101} It is well known that in type Ib natural diamond (see Appendix), nitrogen behaves as a deep donor with an ionization energy of about 2.0 eV.\textsuperscript{102} On the other hand, in type Iib natural diamond and other synthetic p type semiconducting diamonds, boron is well known to act as an acceptor. The activation energy has been measured and determined to be 0.013 eV at 5.7 \times 10^{20} \text{cm}^{-3} doping concentration (this work) to 0.37 eV at a doping level of about $10^{17} \text{cm}^{-3}$. Both N donor and B acceptor levels are shown in Figure 101. The energy of the emitted radiation from the donor-acceptor recombination is given by\textsuperscript{80}
Using $E_g = 5.30 \text{ eV}$, $E_d = 2.0 \text{ eV}$, and $E_a = 0.37 \text{ eV}$, the energy of the emitted photon is calculated to be $2.93 \text{ eV}$. This value is $0.37 \text{ eV}$ off from the observed blue-green electroluminescence peak which is about $2.56 \text{ eV}$. The reason for this discrepancy is thought to be caused by the low N and B concentrations in the films. Since the diamond films used for the ELD were not intentionally doped, the N and B concentrations are very low. The values of the donor and acceptor ionization energy could be higher than 2.0 and 0.37 eV, respectively. Therefore, the blue-green electroluminescence reported in this thesis is concluded to be due to the donor-acceptor pair recombination.

Figure 101. Energy band diagram of the nitrogen donor and boron acceptor centers in diamond. $E_C$ = conduction band, $E_V$ = valence band, N = nitrogen donor level, and B = boron acceptor level.
VI. REFERENCES

67. ibid, p. 511.
VII. ACKNOWLEDGMENTS

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VIII. APPENDIX: TYPES OF NATURAL DIAMOND

Most natural diamonds have inclusions of various impurities that are incorporated in the diamond lattice. It is known that in some natural diamonds, nitrogen can be present up to 0.2% and boron up to 0.25 ppm. The presence of nitrogen has a pronounced influence on the optical absorption spectrum and the thermal conductivity. According to their optical, electrical properties, and their impurities, natural diamonds are classified into 4 types:

A. Type Ia

Type Ia is the most abundant type of natural diamond, about 98% of the total. These diamonds contain up to 0.1% of nitrogen in small aggregates, causing them to absorb ultraviolet light strongly. They are optically transparent at wavelengths > 320 nm. The nitrogen also induces infrared absorption and limits the thermal conductivity to 9 watts per cm K at room temperature. The electrical resistivity of type Ia diamond is higher than $10^{16} \Omega \text{ cm}$.

B. Type Ib

Type Ib natural diamonds are very rare (only 1% of natural diamonds). However, all synthetic diamonds are believed to belong to this class. These diamonds contain up to 0.2% paramagnetic nitrogen incorporated in the lattice. The optical, thermal, and electrical properties are very similar to type Ia diamonds.

C. Type IIa

This type of diamond is very rare and practically free of nitrogen. They are optically transparent to ultraviolet radiation above 225 nm. The thermal conductivity at room temperature is 26 watts per cm K. The electrical resistivity is in general similar to type Ia.
D. Type IIb

Type IIb diamonds are extremely rare in nature and virtually free of nitrogen (only about 20 ppm on average). These diamonds contain boron in small quantities which produce bluish color. They are p type semiconducting, and their electrical resistivity is only between 10 to 1000 $\Omega$ cm. Although it is difficult to control the amount of the boron impurity, type IIb diamonds have also been grown by high pressure synthesis.