Synthesis of metastable phases and compounds in a plasma assisted chemical vapor deposition technique

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**SYNTHESIS OF METASTABLE PHASES AND
COMPOUNDS IN A PLASMA ASSISTED
CHEMICAL VAPOR DEPOSITION TECHNIQUE**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2014

**SYNTHESIS OF METASTABLE PHASES AND COMPOUNDS IN
A PLASMA ASSISTED CHEMICAL VAPOR DEPOSITION
TECHNIQUE**

**SYNTHESIS OF DIAMOND CRYSTALS IN A PLASMA ASSISTED
CHEMICAL VAPOR DEPOSITION TECHNIQUE**

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A thesis submitted to the Nanyang Technological University

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Abstract

Diamond is a wide band gap semiconductor of 5.5eV, and it has high carrier mobility, mechanical hardness, optical transparency, highest atom density, largest room temperature thermal conductivity and smallest thermal expansion. Pure diamond has low conductivity; but when intentionally doped with impurities (doping level from 10^{18} cm^{-3} to 10^{20} cm^{-3}), diamond will be converted to n-type or p-type semiconductors. The surpassing properties of diamond and doped diamond crystals broadened its applications to protective and anti-corrosion coatings, electronic and optoelectronic device, electrochemistry and so on. Traditionally, diamond is synthesized in thermal quasi-equilibrium conditions provided by high temperature high pressure (HTHP, 3000°C, 150Kbar). Recently, many methods at low temperature low pressure have been developed to deposit diamond crystals; especially plasma enhanced chemical vapor deposition (PECVD) that plasma provides the non-equilibrium conditions for diamond growth.

In this report, microwave discharge system is used to generate the plasma. A Microwave Plasma enhanced Chemical Vapor Deposition (MPCVD) system is designed in the laboratory to synthesize diamond crystals. It has a horizontal quartz tube reactor inside the microwave generator and a furnace wrapped out of the reaction chamber, to provide required temperature gradient as well as plasma intensity distribution. SEM, XRD, XPS and Raman spectroscopy are used to study the morphology, microstructure and quality of as-grown diamond crystals.

Diamond crystals are successfully deposited on Silicon substrate in our self-designed equipment. The sizes of as-grown diamond individual crystals vary from 10 μm to about 100 μm . The growth rate of diamond crystal is about 2-3 $\mu\text{m}/\text{h}$. Compared with

the smooth (100) plane of as-grown CVD diamond, the (111) plane is rough and has some excrescences on the surface due to different growth mechanism.

The influence of experiment conditions on diamond quality is studied. It is proved that experiment conditions, especially temperature, pressure and C/H ratio, are crucial to diamond growth. The best deposition conditions are found to be at 800°C, 30Torr. At other conditions, low quality diamond or even non-diamond carbon materials are formed, such as cauliflower-like carbon, carbon fiber and carbon nanowall.

The influence of various substrate pretreatment, such as scratching, covering with diamond like carbon film, and coating with platinum interlayer, have been tried to deposit large area diamond films. These methods have effectively enhanced the diamond nucleation. By combining some of the methods, large area continuous diamond films have been deposited on the silicon substrate, with a significant fraction of sp^3 bonded carbon.

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Chapter 1 Introduction

1.1 Background

Diamond is a metastable form of carbon at normal conditions. Traditionally, diamond is synthesized in thermal dynamic quasi-equilibrium conditions, at very high temperature (3000°C) and pressure (150Kbar). Great breakthrough occurs in 1970s when Aisenberg and Chabot[1] first deposit diamond like carbon thin films using low pressure methods in laboratory. Till now, quite a lot of methods both physical vapor deposition and chemical vapor deposition have been reported to successfully deposited diamond and doped diamond films, such as ion beam deposition, sputtering, cathodic arc, pulsed laser deposition and plasma enhanced chemical vapor deposition (PECVD). PECVD is the most popular deposition methods in laboratory as it is easy to control and able to fabricate high quality films on a large scale on various kinds of substrate materials. The deposition methods and mechanism of diamond is well understood.

Diamond is constructed by tetrahedrally bonded carbon atoms. Compared with other forms of Carbon allotropes, such as graphite and amorphous carbon, diamond has many surpassing properties[2] derived from its strong sp^3 bonds. It is a wide band gap semiconductor of 5.5eV, and it has low conductivity, high mechanical hardness, optical transparency, highest atom density, largest room temperature thermal conductivity and smallest thermal expansion. Thus it can be used as protective coatings against corrosion for mechanical cutting-tool parts, and used for heat removal and thermal management of electronics[3]. In natural diamond, Hall mobility of holes is 1800 cm^2/Vs , and of electrons it is 2000 cm^2/Vs [4]. While Isberg et al.[5] has reported Hall mobility of holes 3800 cm^2/Vs and electrons 4500 cm^2/Vs measured in high purity CVD single crystal diamond.

When intentionally doped with impurities during deposition, the conductivity of diamond is significantly increased besides its intrinsic extreme properties. Ekimov et al.[6] has reported superconductivity in diamond below superconducting transition temperature $T_c \approx 4\text{K}$. And it survives in a magnetic field $H_{c2}(0) \geq 3.5\text{T}$. Diamond can be doped to n-type semiconductor by doping with P, S, N, and p-doped with B[7]. The doping level will significantly affect its surface and properties. The most common type and most studied is Boron doped diamond (BDD) which can be found in nature. It has wonderful electrochemical properties including low cost, wide potential window and electrocatalytic active for a variety of redox reaction, while much more chemical inert than graphite.[7, 8]

1.2 Motivation of the project

The motivation of this project is to obtain materials metastable in ambient conditions, to study the physical behavior of new phases and design functional materials with useful properties for microelectronics. In this project the crystal structure of diamond assure the proper band gap and the doping will control the proper charge transport into the semiconductor. This in turn will make us better understand the properties, the doping effect and its applications by tuning its synthesis conditions. Diamond crystals are synthesized in plasma assisted system under a required temperature gradient and plasma intensity distributions. Structural characterization and quality of the single crystals will be conducted with equipment such as Optical Microscopy, SEM, Confocal Raman, XPS and XRD. Additionally, physical properties such as electrical conductivity, thermal properties, Hall effect or even superconductivity will be measured and analyzed.

1.3 Research Objectives and Scope

This project focuses on growth and characterization of microwave plasma enhanced chemical vapor deposited diamond crystals, and the influence of introducing dopants and defects into diamond crystals on its properties. It aims to clarify the deposition mechanism and find out the best deposition conditions for growing good quality single crystal diamond. The detailed scope is listed below.

- I. Design and set up of the MPCVD system in laboratory
- II. Growth of diamond crystals and doped diamond crystals from MPCVD system
- III. Measurement of the crystals structure and physical properties
- IV. Detection of impurities distribution and doping level in the crystals.

Chapter 2 Literature Survey

2.1 Physical property of Diamond

Diamond is a metastable form of carbon. The diamond lattice is a variation of face centered cubic structure, and it is constructed by tetrahedrally bonded carbon atoms. Diamond has many surpassing properties[2] derived from its strong sp^3 bonds. It has a wide band gap of 5.5eV, and it has low conductivity, high mechanical hardness, optical transparency, highest atom density, largest room temperature thermal conductivity and smallest thermal expansion. Isberg et al.[5] has reported Hall mobility of holes 3800 cm^2/Vs and electrons 4500 cm^2/Vs measured in high purity CVD single crystal diamond.

Mostly, diamond is used as protective coatings against corrosion for mechanical cutting-tool parts, and used for heat removal and thermal management of electronics[3] because of its mechanical and thermal properties.

Under room temperature, diamond is less stable than graphite thus it will convert to graphite with a very small conversion rate (Figure 1).The chemical bonds of diamond are weaker than the sp^2 bonds of graphite. But the interaction between the sheets of graphite is Van der Waals force, making the overall structure weak.[9]

Figure 1: Berman-Simon phase diagram of carbon [10]

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2.2 Plasma assisted Synthesis of Diamond crystals

Ever since Aisenberg and Chabot[1] first deposit diamond like carbon thin films using ion beam deposition, quite a few low pressure methods have been proved success in deposition diamond in laboratory. According to the reaction occurred during the deposition, these methods can be divided into physical vapor deposition and chemical vapor deposition methods. Physical Vapor Deposition methods have been reviewed by Robertson J.[10]. It is suitable for depositing diamond-like carbon films, and includes ion beam deposition, sputtering, cathodic arc deposition, pulsed laser deposition and so on. Of which, sputtering is the most common method in industrial deposition of protective coatings. Here we will only discuss about Plasma Enhanced Chemical Vapor Deposition which is more common in laboratory to deposit large area high quality diamond crystals on various substrate materials.

2.2.1 Synthesis mechanism

In chemical vapor deposition of diamond crystals, the precursor gas is normally a mixture of hydrocarbon gas and hydrogen with hydrocarbon gases no more than 5%, such as most conventional CH_4/H_2 system. The plasma provides a non-equilibrium conditions for the growth of metastable diamond[11], in which the electron temperature is high and gas temperature relatively low. Precursor gas is dissociated and activated into hydrogen atoms, carbon atoms, methyl radicals (CH_3), acetylene (C_2H_2), which play an important role in diamond deposition[12].

Table 1: Typical gas phase composition in non-equilibrium discharge system of CH_4/H_2 for diamond deposition [13]

Component	Molar fraction, %	Component	Molar fraction, %
H	2.44	C_2H	0.00413
CH_3	0.48	C_2H_6	0.000173
C_2H_2	2.93	C_2H_4	0.0146
CH_2	0.0135	C_2H_5	0.000516
CH_2 (singlet)	0.00133	C_2H_3	0.0023
CH	0.00105	CH_4	1.01
C	0.00108	H_2	93.1

H_2 plays a very important role in the nucleation and growth of diamond crystals. Atomic hydrogen can convert hydrocarbon into radicals which are necessary for diamond formation. Similarly, atomic hydrogen can abstract hydrogen from hydrocarbons absorbed on substrate and provide active sites for diamond growth.[14] Furthermore, atomic hydrogen and ionic hydrogen are able to remove non-diamond

species, as it etches sp^2 bonded carbon much more faster than sp^3 carbon.[15] Finally, hydrogen termination stabilize the diamond surface.[16]

Diamond nucleation and growth on non-diamond substrate is proposed to start with the formation of an intermediate layer on the substrate, like Diamond like Carbon, graphite or metal carbides[17]. This intermediate layer is formed at the substrate surface due to the reaction of ionized gas species and substrate materials. The mechanism of this nucleation mode can be shown in Figure 2. Firstly, carbon clusters are formed on the substrate and sp^1 bonded carbon converts to sp^2 bonded carbon. Then the sp^2 bonded carbon converted to more stable sp^3 bonded carbon while less stable sp^1 and sp^2 carbon is etched by H plasma at the same time.

Figure 2: Nucleation mechanism of CVD diamond: (a) formation of carbon cluster on the substrate; (b) crystallization of amorphous phase; (c) growth of diamond crystal with growth species in gas phase; (d) faceting of diamond crystal

The next step is the crystallization of disordered sp^3 bonded carbon to diamond crystals, which act as the nucleation sites on substrate.

The crystalized surface has functional groups C-H that react with hydrogen atom in gas phase and form hydrogen molecule as in equation (1). The free carbon bond is active for diamond growth.[13] And this process can be balanced by the reverse reaction as in Equation (2), which covers the open carbon bond at surface without growth of the film. Subsequently, aforementioned CH₃ and C₂H₂ radicals react with the crystalized sites[18] and attached to the surface as reaction (3) and (4). Thus a new layer of diamond lattice is created and subsequent growth takes place at this region.

2.2.2 Precursor gases

In 1982, Matsumoto et al.[19] first succeed in depositing diamond films onto non-diamond substrate with plasma enhanced chemical vapor deposition system. Now it is the most popular deposition method of diamond in laboratory. The growth rate of CVD diamond is quite low, only about several micrometers per hour, but it is excellent for growing uniform high quality diamond films. And its ability to deposit large area diamond on various substrates expands the potential applications of diamond. Normally, a mixture of a hydrocarbon gas, hydrogen and sometimes argon is chosen as the precursor. There are three main energy sources to activate the gas phase and produce the plasma, radio frequency power, hot filament and microwave discharge. Plasma will generate on top of the substrate under low system pressure.

Figure 3: Bachmann triangle [20]

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Because the deposition is conducted under different conditions, with different kinds of gas precursor and various substrate materials, the diamond deposition rate, purity and quality varies significantly. Bachmann et al. [20] reviews over 30 years CVD diamond research and more than 80 experiments, developed a common C-H-O phase diagram corresponding to deposition of non-diamond films, diamond films, or no deposition at all due to domination of etching (Figure 3).

Figure 4: Growth rate Vs ionization potential of varies of precursor gases [10]

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Robertson J.[10] has reviewed the deposition rate and ionization potentials of several hydrocarbon species that has been used for diamond deposition (Figure 4). Acetylene looks like a promising carbon source gas with its relatively low ionization potential and high deposition rate, but it is not available in high purity forms that will introduce impurities into the crystals. So mostly, people still choose methane to study diamond crystals in spite of its low growth rate and high content of hydrogen termination introduced.

2.2.3 Diamond Nucleation

A lot of materials have been tried to use as the Substrate for diamond film depositions, such as Pt, W, Ti, p-type Si, Ta, Mo, Nb etc. The substrate is divided into 3 groups

according to the interactions between carbon and the substrate material as summarized in Table 2.

Table 2: Substrate materials for diamond deposition [21]

Little or no solubility or reaction	Diamond, Graphite, Cu, Ag, Au, Sn, Pb
C-diffusion only	Pt, Pd, Rh
Carbide formation	
metallic	Mo, W, Fe, Co, Ni, Ti, Zr, V, Nb, Ta, Cr
covalent	B, Si
ionic	Al, Y

Substrate materials will affect the nucleation rate of diamond on the surface. For instant, carbide forming substrate has a higher nucleation rate than non-reaction substrate. Sometimes, the substrate was pretreated to increase the nucleation rate, such as mechanically scratching and seeding with diamond powder, coating with an intermediate layer and so on. By scratching the surface, defects are introduced and some small diamond crystals are embedded into the substrate, these serve as the initial diamond nucleation sites.

In order to realize the applications of CVD diamond crystals, it is essential to study how to deposit large scale uniform doped diamond films on the substrate. Substrate pretreatment is necessary to enhance the diamond nucleation.[4] Table 3 summarizes nucleation enhancement of different pretreatment methods.

Table 3: Surface nucleation densities of diamond after substrate pretreatment [17]

Pretreatment Method	Nucleation density (cm ⁻²)
No pretreatment	10 ³ -10 ⁵
Scratching	10 ⁶ -10 ¹⁰
Ultrasonic Scratching	10 ⁷ -10 ¹¹
Seeding	10 ⁶ -10 ¹⁰
Biasing	10 ⁸ -10 ¹¹
Covering/Coating with	
Fe film	4.84 x 10 ⁵
Graphite film	10 ⁶
Amorphous carbon film	3 x 10 ¹⁰
As ⁺ ion implantation	10 ⁵ -10 ⁶

2.2.4 Different discharge systems for diamond deposition

I. Microwave discharges

Microwave plasma enhanced chemical vapor deposition system is conventional for synthesizing diamond films from hydrocarbon gases and it is advantageous for the purity of produced diamond.[22] A magnetron resonator is attached to the system to generate microwave, and sometimes waveguide is used to guide the microwave into reaction chamber. The microwave discharge chambers are built either in magnetron or microwave waveguide. The chamber is usually made of stainless steel. The Fraunhofer Institute[23] has designed an ellipsoidal reaction chamber as shown in Figure5 to better concentrate the microwave and increase deposition rates. Diamond deposition is

performed at a pressure of 20-130Torr in a mixture of hydrogen, hydrocarbon and sometimes argon.

Figure 5: A commercialized MPCVD reaction system designed by Fraunhofer Institute [23]

II. RF discharges

Radio Frequency plasma enhanced chemical vapor deposition is popular in laboratory for depositing diamond. And the deposition rate can be quite high, up to $30\mu\text{m/h}$. The reactor consisted of two electrodes of different area. Substrate is mounted on the smaller electrode, where the RF power is coupled; the other electrode, including the chamber wall, is grounded. RF plasma can be dispersed into a relatively larger area than microwave plasma, but the quality of as grown diamond is not as good as MPCVD diamond. Thus it is more suitable for deposition of diamond like carbon films as reviewed by Roberson, J.[10] .

Figure 6: Schematic diagrams of the RF plasma beam source[10]

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III. Thermal discharges

The first CVD grown diamond and the highest deposition rate of CVD diamond (1 mm/h) is achieved in Hot filament chemical vapor deposition[4]. In HFCVD system, a refractory filament is heated up to more than 2000°C. When H₂ gas flows by the hot filament, it is activated to hydrogen atoms and ions, resulting in a thermal and close to quasi-equilibrium condition. If the precursor gas is oxygen-containing, the deposition temperature will be broadened. But the uniformity of deposited diamond films is not as good as previous systems.

Figure 7: Schematic diagrams of Hot Filament CVD system using W filament[24]

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2.3 Doping and defects in Diamond

Pure diamond is a wide band gap semiconductor and it is transparent and colorless as we can observe from most of the natural diamond. So it is not easy to introduce impurities into diamond's rigid lattice, but some elements such as small amount of Boron, Nitrogen and Hydrogen can be found in natural diamonds. These impurities and lattice defects result in the beautiful colors of diamond. For example, Nitrogen and Boron is responsible for the yellow and blue colors, respectively; irradiation by alpha particles is responsible for green color; while plastic deformation of the lattice of diamond crystal may cause some pink, brown or red diamond. While can be explained by the band gap theory, different colors correspond to the changes in the band gap. Similar with Silicon, the defects and impurities in the lattice affects the resistance of diamond significantly. Ekimov[6] has reported bulk boron doped diamond to be type-

II superconductor. The synthesis and characterization of doped diamond of different conduction type and doping level have been studied. Boron is the most widely used and studied dopant to form p-typed diamond. Other elements such as N, P and S have also been introduced into diamond lattice to get n-typed diamond.[25, 26] Different doping level also has an effect on the property and application of diamond.[27]

P-type diamond is achieved by doping with Boron which already exists in nature. Boron is relatively easy to be incorporated into diamond lattice due to its small radius. Boron Doped Diamond (BDD) is well studied, and the doping level is controllable from lightly doped (10^{18} cm^{-3}) to highly doped (10^{20} cm^{-3}). Ekimov[6] have reported highly doped diamond synthesized by reacting B_4C and graphitic carbon under high pressure high temperature conditions. Success on controlling doping by boron ion-implantation is also reported. However, ion-implantation may cause the metastable diamond bond transfer to more stable graphite bonding.[28] Thus either a low dose high energy B implantation deeply, or a high dose low energy B implantation followed by etching of graphite is used to solve this problem. While CVD technique is widely introduced to synthesis diamond in laboratory, Boron is also added into the CVD precursor to grow doped semiconducting diamond.

Surface conduction of CVD hydrogen terminated diamond film without doping has been observed by Landstrass et al.[29] and the conduction type has been confirmed as p-type by Maki et al.[30]. Scanning tunneling currents have been observed in air [31, 32] and in ultrahigh vacuum [33] to clarify the mechanism of semiconductivity on hydrogenated diamond surface. It is reported that limited surface area of hydrogenated diamond is semiconductive, while after surface oxygenation, this semiconductivity will be changed back to insulating diamond.

N-type diamond can be achieved by doping with substitutional atoms such as P, N, S, or with interstitial defects such as Li, Na. The doping method is same with p-type diamond doping, donor elements are added into the CVD system to be incorporated into diamond lattice. Clear donor activities have been reported in phosphorus doped diamond.[28]

Doping level of diamond films will modify the surface terminations from hydrogen terminated toward oxygen terminated bonds.[34] It can be well controlled especially when doping Boron by adding in different B/C concentrations. The introduction of dopants will obviously increase the defects in the diamond film, more sp^2 bonds at grain boundaries and surface oxidations. Thus, highly doped diamond will have a more hydrophilic character. Besides, highly doped diamond have a more reversible respond to redox couples, and the surface active states that mediate in charge transfer increases[27], compared to lightly doped diamond.

2.4 Application of diamond and doped diamond crystals

Diamond crystals have so many fascinating physical and chemical properties that expended its application into lots of areas. Diamond can be used as cutting tools due to its hardness and low coefficient of friction. It can also be coated onto various of substrate for protection[35], such as magnetic disks. Thermal conductivity of diamond is about 2000 W mK^{-1} at room temperature[3] that it can be used to remove heat in electronics. Eden[36] have reported to use thick diamond films as integrated circuits (IC) packaging or multichip module (MCM) substrate materials.

Diamond is ideal for electronic applications due to its wide band gap, high thermal conductivity and high carrier mobility. Satoshi Koizumi et al.[37] have reported ultraviolet emission at 235 nm under forward bias of 20 V, from a diamond pn

junction, formed by a Boron doped p-type diamond layer and a Phosphorous n-type diamond layer on single crystal diamond. M. W. Geis et al.[38] have studied the function of surface treatment and internal doping on field emission from diamond, and reported a very small electric field $< 0.2 \text{ V } \mu\text{m}^{-1}$ which occurs in N-doped and Cs treated diamond in air. Gildenblat et al.[39] and Zeisse et al.[40] have fabricated metal semiconductor field effect transistors (MESFET) and metal insulator field effect transistors (MISFET) devices, respectively. However, the devices are not yet good enough for practical application. The quality of the deposited diamond film and the fabrication methods of device should be improved upon further research.

Boron doped diamond electrode has already been applied to practical electrochemistry because of its low cost, wide potential window, electrocatalytic activity, and chemical inertness. Oxygen evolution potential on BDD electrode in 0.5 M H_2SO_4 solution is 2.3 V.[41] The wide potential window of diamond indicates its high current efficiency in electrochemical oxidation. Particularly, boron doped diamond electrode has been reported to be active for degradations of various pollutants, such as phenol, dyes and herbicides [42-44].

Chapter 3 Apparatus and characterization

3.1 Equipment Design

Normally, the CVD system is composed of microwave generator, wave guide, reaction chamber, heater, gas flow and vacuum system. The tuner on the wave guide is designed to adjust the intensity and wavelength of the output microwave. The heating element is mounted under the sample holder in the chamber, thus it directly heats up and monitors the temperature of the substrate. The chamber is pumped to quite low pressure with a flow of carbon source gas and other gases. The plasma ball will generate just above the substrate with the effect of microwave. A typical microwave plasma enhanced chemical vapor deposition system is shown as below (Figure 8).

Figure 8: A design drawing of Microwave plasma Chemical Vapor Deposition system

Previous experiment is conducted in such a vertical system. But sample position is hard to handle that we have only got diamond like carbon materials instead of high

quality diamond crystals. So our idea here for designing the MPCVD system is similar with the traditional one. Each part is quite essential in the deposition procedures providing required temperature gradient and plasma distribution. While in order to study the effect of plasma, the reaction chamber is designed as a horizontal system instead of the traditionally vertical one. So we can put in several samples at the same time and study films deposited at different position, and find the best experiment conditions for diamond-like carbon coatings.

Figure 9: Schematic diagram of self-designed MPCVD system

Figure 9 is the drawing of our equipment designed for diamond deposition using Microwave Plasma Enhanced Chemical Vapor Deposition. The gas precursor we chose is a mixture of hydrogen, argon and vaporized methyl formate. A bubbler is designed to bring out the carbon source. When argon goes through the bubbler, it will bring out vaporized methyl formate molecules. The amount of methyl formate can be calculated by counting how many bubbles per minute. Hydrogen is produced from hydrogen generator and desiccated by going through a gas purifier.

The quartz tube which acts as the reaction chamber is put in the middle of the magnetron, where the output power is focused. Thus the plasma is generated there. The furnace is wrapped electric heater strips on a piece of quartz tube with larger diameter, and it is covered with thermal insulation cotton and alumina foil in order to shield the thermal and electrical influence of the microwave plasma. In this case, the heater can also heat up a large area. And it can be put into the magnetron by being wrapped with a half-terete shaped copper foil to shield the electrical influence of the microwave plasma. Besides, a metal mesh is designed outside of the whole system to prevent microwave leakage.

Figure 10: A design drawing of metal mesh cover of the MPCVD system

Figure 10 is the design of the metal mesh cover. It is a big cage which is constructed with porous metal plate. A door is designed in the front of the cage to access the reaction chamber. The thermal and electrical parts, such as the microwave oven, quartz

tube and furnace, are put inside this cage to shield the possible microwave leakage. And through the holes on the plate, we are able to observe the plasma. The bubblers and the gas flow are mounted on the side wall of the cage. So the flow meters are put together that the flow rate of all gases can be adjusted and monitored.

3.2 Deposition of diamond crystals

The diamond crystals deposited in our laboratory were grown using microwave plasma-assisted chemical vapor deposition on *p-type* Si (111) substrates. Precursor gas is a mixture of H₂ generated from hydrogen generator (TH-300), Argon (ultrahigh purity 99.999%), and vaporized methyl formate (Sigma-Aldrich).

At first, the gas flow is closed and the system is pumped to pressure below 10⁻²Torr for half hour. After stabilized, hydrogen flow, argon flow, magnetron power and heater is turned on in sequence to generate plasma and achieve required temperature. The C/H ratio in the precursor gases is controlled by the adjustment of the flow rate of hydrogen and argon. The deposition is conducted for several hours. Diamond crystals are successfully deposited under 800°C and 30Torr.

In the end, to stop the deposition, Argon flow is closed at first, so there is only Hydrogen flow in the system. The samples are exposed to Hydrogen plasma for several minutes. This post growth treatment in atomic hydrogen etches away non-diamond carbon impurity[45], and terminate the as deposited diamond crystals with hydrogen atoms which stabilized the diamond film. Then the heater and the microwave power are turned off in sequence. And the system is cooled down to room temperature under the protection of Hydrogen flow. At last, the pump and the Hydrogen flow is closed, the system pressure recovers to atmospheric pressure slowly.

3.3 Characterization of diamond crystals

3.3.1 Thin film X-ray Diffraction (XRD)

The X-ray diffraction (XRD) data were obtained with a Shimadzu XRD-6000 diffractometer (CuK α =1.5406Å radiation at 50kV, 40mA). The divergence, anti-scatter and receiving slits were fixed at 1°. The range is from 10° to 150° with a scan speed of 4°/min.

3.3.2 Scanning Electron Microscope (SEM)

The surface morphology of the sample was observed by using scanning electron microscope (JEOL 6340, 5.0kV).

3.3.3 Confocal Raman spectroscopy

The film microstructure was investigated by Raman spectroscopy. Spectra were acquired at room temperature, using a Confocal Raman Spectroscopy (WITec, Witec alpha300 SR).

3.3.4 X-ray photoelectron spectroscopy (XPS)

The composition, and chemical state information of the surface was obtained by using X-ray photoelectron spectroscopy by a Kratos-Axis spectrometer with monochromatic Al K α (1486.71 eV)X-ray radiation (15 kV and 10 mA) and a hemispherical electron energy analyzer.

Chapter 4 Parametric studies on diamond crystal deposition

In chemical vapor deposition, many factors would affect the quality of deposited crystals, such as the flow rate of the gas, C/H ratio in the precursor, microwave power, substrate temperature, and system pressure and so on. Under different experimental conditions, we have successfully deposited some kinds of carbon materials with quite different morphologies such as diamond, cauliflower-like carbon, carbon fiber and carbon nanowall. In this chapter, we will mainly discuss about the effect of experimental parameters on the deposition and the characterization of as grown diamond crystals.

4.1 Effect of pressure in chamber

The pressure in the reaction chamber can be adjusted by the control of gas flow rate and the exhaust regulating valve of the pump. Change of the pressure in chamber will affect the plasma distribution most effectively. According to the literature and the preliminary experiment results, we know that the deposition occurs mainly at the two edges of the plasma ball. So the adjustment of the pressure in order to optimize the plasma distribution and diamond deposition is very important.

Under high vacuum, the plasma gets very strong and it will fill up the area of entire reaction chamber. As the pressure increases in the system, the plasma ball gets weaker and smaller, and the plasma region narrows down in the quartz tube. In our system, if the pressure ramp up to more than 50 Torr, the plasma ball will disappear or become very unstable in the system. If the pressure is too low, say less than 1 Torr, the energy

of the plasma will be too high, thus the main reactions happened on the substrate is etching and we got no depositions on substrate. Finally, the best deposition pressure is found to be around 20-30 Torr, that we can achieve the best temperature gradient and plasma distribution, thus have deposition of diamond crystals or some other kinds of carbon materials.

4.2 Effect of C/H ratio in precursor gas

The precursor gases are a mixture of argon, vaporized methyl formate and hydrogen. The carbon source is liquid, which is put inside a bubbler. As the argon gas flows through, it carries vaporized methyl formate gas into the system. Thus the C/H ratio in the precursor gas is adjusted by the flow rate of the argon gas and the hydrogen gas.

As explained before, H plays a very important role in the deposition of diamond. With high hydrogen flow rate and relatively low carbon flow rate, diamond crystal is deposited slowly on the substrate at the edge of the plasma ball, while hydrogen plasma etches away the sp^2 allotropy of deposited carbon. Only for C/H ratio less than 5% has been reported successfully deposited diamond crystals. If the C ratio is too high in the precursor gas, the deposition rate is relatively high and one allotropy of sp^2 bonded carbon, cauliflower like carbon, will be formed preferentially in the plasma enhanced CVD system.

Figure 11: SEM image of (a) cauliflower like carbon; (b) and (c) etched surface morphology; (d) carbon nanowalls

Figure 11(a) shows the morphology of so called ‘cauliflower like carbon’. If cauliflower like carbon has been deposited on the substrate, which followed by low C/H deposition, the effect of hydrogen plasma becomes dominating. The sp^2 bonded carbon will be etched away by the Hydrogen plasma. Gradually, the cauliflower like carbon will be etched into small pieces and finally a uniform film will be formed on the substrate. The morphology of such deposited carbon film can be observed as in Figure 11(d), which is defined as carbon nanowall.

4.3 Effect of deposition temperature

Temperature is a very important factor in the process of diamond deposition. Herein, we mainly discuss about the influence of temperature on the quality of diamond crystals.

Figure 12 is the SEM image of diamond crystals deposited at different temperature and reaction time. At 450°C, very few diamond crystals are deposited on the substrate. From the morphology of the crystal, we know that many lattice defects and imperfection are formed inside. This can be explained by the mechanism of diamond nucleation that the CH₃ radical density in gas phase is reduced and the surface reactions are slowing down at relatively low temperature. When the substrate is heated up to 800°C, more crystals with better crystallinity are formed. The size of individual crystal can reach 100μm, which indicates that the growth rate is also increased at higher temperature. As the reaction time gets longer, even more nucleation sites and crystals can be found on silicon substrate, while the size of the crystal does not increase significantly. This is because of the Hydrogen terminated surface and the secondary nucleation on the substrate.

Figure 12: SEM image (Left) and First Order Raman spectrum (Right) of diamond crystal: (a) deposited at 450°C for 24 hours; (b) deposited at 800°C for 8 hours; (c) deposited at 800°C for 24 hours.

Table 4: Raman bands of some functional groups of Carbon [46]

Functional Group/Vibration	Regions
$\nu(\text{sp}^3 \text{ C-C})$	1332 cm^{-1}

$\delta(\text{CH}_3)$	1380 cm^{-1}
$\delta(\text{CH}_2)$	1400 - 1470 cm^{-1}
$\nu(\text{C}=\text{C})$	1500 - 1900 cm^{-1}
$\nu(\text{C}=\text{O})$	1680 - 1820 cm^{-1}
$\nu(\text{C}-\text{H})$	2800 - 3000 cm^{-1}
$\nu(=\text{C}-\text{H})$	3000 - 3100 cm^{-1}

Raman spectrum of all the samples is taken using 488 nm laser excitation wavelength. The first order active mode of sp^3 carbon atom in diamond is at wave number 1332 cm^{-1} . The features present in the spectrum gives us some feelings about the diamond quality. A high quality diamond crystal should have a strong and narrow peak at 1332 cm^{-1} , and do not have other non-diamond peaks. Table 4 is the Raman bands of some functional groups that may present in CVD diamond. 1332 cm^{-1} is first order diamond peak, as described before. Graphite G band, which is the in plane vibration of sp^2 carbon, is at 1480 cm^{-1} ; while 1350 cm^{-1} and 1620 cm^{-1} are D band and D' band, respectively. The D band is caused by disordered structure of sp^2 -hybridized carbon systems, and the D' band is because of some randomly distributed impurities or surface charges.

We can deposit diamond-like carbon with significant fractions of sp^3 bonds at a relatively low temperature, 450°C. As the temperature and reaction time increases, the non-diamond species disappear and we are able to grow high quality diamond with a narrow and strong peak at 1332 cm^{-1} .

4.4 Deposition of diamond crystals

By adjusting the experimental parameters, including temperature, pressure, C/H ratio, we can deposit diamond crystals at 800°C, 30Torr in a $\text{H}_2/\text{Ar}/\text{C}_2\text{H}_4\text{O}_2$ system. The size of the diamond crystal varies from 10 μm to 100 μm and the deposition rate of as-grown diamond crystal is about 2-3 $\mu\text{m}/\text{h}$.

A representative diamond crystal is shown in Figure 10 (a). Because the growth rate of (110) plane is the highest among the low index planes in CVD diamond, it normally appears with rectangle (100) facets and hexagonal (111) facets. From the SEM images, we observed that the morphology of diamond (100) and (111) planes is different. The (100) plane is very smooth, while the (111) plane is rough with pyramidal excrescences on the surface.

Figure 13: SEM images of: (a) as-grown diamond crystal; (b) pyramidal nucleation site on silicon substrate

The morphology differences are generated due to different deposition mechanisms. On (100) plane, the main growth species are CH_3 radicals, which can diffuse to the edge of a growth spiral when absorbed on the surface. Thus the surface will grow

continuously. Moreover, defects and imperfections in the lattice can also diffuse to the edge to form a smooth plane.

Growth of (111) plane mainly depends on C_2H_2 , which needs more energy to be incorporated into the lattice. And the diffusion of C_2H_2 and lattice defects is difficult because of relatively larger inter atom spacing and tensile stress. As a result, the quality of (111) plane is not as good as (100).

The pyramidal excrescences on the (111) surface is the secondary nucleation site. Similar structure could be found on the silicon substrate as shown in Figure 10 (b).

Figure 14: XRD patterns of diamond crystals

The as grown crystals are scanned with X-ray diffractometers using CuK α I radiation from 10° to 150° . Profile fitting yields satisfactory results with five cubic diamond reflections, (111), (220), (311), (400) and (331).

Chapter 5 Diamond nucleation and film morphology

Although high purity diamond crystals have been proved to be deposited on silicon substrate, the nucleation rate of samples as discussed before is too low, that we can only get individual diamond crystals instead of uniform diamond films. In order to deposit large area diamond film on the substrate, some kinds of substrate pretreatment have been tried to increase the nucleation sites, such as scratching, seeding, covering or coating with an intermediate layer and so on. Herein, we will mainly discuss about the influence of these substrate pretreatment on the film formation and the morphology of as deposited films.

5.1 Growth on scratched Si substrate

Considering the preliminary experiments with deposition of individual crystals, the diamond crystals are more frequently found at the broken edge of the silicon wafer. Thus we assume that diamond prefer to nucleate at sites with more defects. To prove this hypothesis, silicon wafer is scratched with glass cutter, which introduces defects and embedded small diamond seeds. After several hours' deposition, diamond crystals are found to be deposited along the scratch. And the nucleation rate is much higher in the scratch than on the untreated flat surface. Therefore, substrate is pretreated which introduces a lot of defects on the surface, surface morphology after scratching shown in Figure 15.

Figure 15: SEM image of (a) untreated Silicon substrate; (b) scratched substrate surface

Figure 16 compares two samples deposited under same temperature, pressure and C/H concentration conditions. Sample (a) is deposited on untreated Si substrate, while sample (b) is deposited on substrate scratched with sand paper. It can be seen from the SEM images of the samples that on pretreated substrate, the nucleation rate is higher than untreated substrate, and the nucleation sites distribute more evenly on the surface. This proves that scratching defects act as the initial nucleation sites, and this pretreatment is able to enhance the diamond nucleation and be beneficial to the formation of diamond films.

Figure 16: SEM image of diamond crystals deposited at 800°C, 30Torr for 24 hours on (a) untreated Silicon substrate; (b) scratched Silicon substrate

5.2 Growth on Diamond like carbon film

According to the deposition mechanism of the diamond formation, carbon clusters are firstly deposited on the substrate. Then at some sites, the sp^2 bonded carbon crystalized to sp^3 bonded carbon, which acts as the nucleation site of the diamond growth. Thus the nucleation density on an amorphous carbon film is higher than on some other substrates.

In our system, the experiment is conducted by two stages. The first stage is the deposition of a diamond like carbon film under 30Torr, 400°C of the $H_2/Ar/C_2H_4O_2$ system. Then it is followed by the deposition of diamond crystals by ramping up the temperature to up to 800°C. The SEM image of the as deposited film is shown in Figure 17.

Figure 17: SEM image of diamond crystals deposited on a diamond like carbon film

As a diamond like carbon film has been deposited on to the substrate in the first stage under a relatively low temperature, the sp^3 species in the diamond like carbon film serve as the nucleation sites for the second stage diamond growth. By this pretreatment

of the silicon wafer to be covered with a diamond like carbon intermediate layer, the diamond nucleation is enhanced on the surface and the nucleation density is increased.

5.3 Growth on Platinum interlayer

Diamond is also tried to be deposited on Platinum intermediate layers on the substrate. The platinum interlayer is sputtered onto the substrate. The thickness is about 50 nm. The platinum acts as the catalyst and intensifies the plasma. Thus a layer of uniform amorphous carbon is formed on the Platinum, as shown in Figure 18(a). On the top, diamond crystals are nucleated and growing at some active sites.

Figure 18: SEM image of (a) amorphous carbon array on Platinum coated substrate; (b) diamond crystal deposited on the amorphous carbon film

Figure 19: (a) Optical microscopy image of as grown continuous diamond film; (b) SEM image of diamond film with rectangle (100) facets

The platinum catalyst accelerates the formation of amorphous carbon layer and increases the active nucleation sites. Thus the deposition rate is increased and a large area uniform diamond film is formed on the silicon substrate. The as-grown diamond film exposes its rectangle (100) facets (Figure 19).

5.4 Film formation

Figure 20: SEM image of the deposited diamond film: (a) front view; (b) cross section view

As discussed before, some methods of substrate pretreatment have been tried to increase the nucleation density and grow large area diamond films, such as the scratching, covering with diamond like carbon film and coating with platinum interlayer. These methods have been proved to successfully increase the nucleation density on the substrate.

And by combining these methods, which is firstly sputtering with platinum layer and then immersing into adamantane which can be easily absorbed by platinum to form a carbon layer on the surface, diamond films are successfully deposited as shown in Figure 20(a). And the cross section SEM of the film shows that the film thickness is about 30 μm after 24 h's deposition. The growth rate is about 1-2 $\mu\text{m}/\text{h}$.

Figure 21: C1s spectra of the X-ray photoelectron spectroscopy of diamond film

The X-ray photoelectron spectroscopy is used by a Kratos-Axis spectrometer with monochromatic Al K α (1486.71 eV)X-ray radiation (15 kV and 10 mA) and a hemispherical electron energy analyzer. The composition, elemental and chemical state information of the surface was obtained from the C1s spectra. Considering the C1s spectra, it was divided into peaks of sp³ C-C bonds and sp² C=C bonds which arises from the grain boundaries. The surface study with XPS also shows the successful deposition of continuous diamond films with a large sp³ carbon bonding fractions.

Chapter 6 Conclusion

In this report, a self-designed Microwave Plasma enhanced Chemical Vapor Deposition (MPCVD) system is used to synthesize diamond crystals. The deposition equipment is designed with a horizontal quartz tube reactor inside the microwave generator and a furnace wrapped out of the reaction chamber, to provide required temperature gradient as well as plasma intensity distribution.

With the self-designed MPCVD system, carbon materials with different morphologies have been deposited under various experimental conditions, such as cauliflower-like carbon, carbon fiber and carbon nanowall. By adjusting the parameters, diamond crystals are successfully deposited on Silicon substrate. The sizes of as-grown diamond individual crystals vary from 10 μm to about 100 μm . The deposition rate of diamond crystal is about 2-3 $\mu\text{m}/\text{h}$. Compared with the smooth (100) plane of as-grown CVD diamond, the (111) plane is rough and has some excrescences on the surface due to different growth mechanism.

In order to deposit large area diamond films, different methods of substrate pretreatment have been tried, such as scratching, covering with diamond like carbon film, and coating with platinum interlayer. These methods have been proved to successfully enhance the diamond nucleation. Scratching introduces defects and embedded some small diamond crystals to the substrate, where the nucleation and deposition preferentially occurs. While covering with an interlayer of diamond like carbon film, also increases the nucleation density. By combining some of the methods, large area diamond films have been deposited on the silicon substrate, with a significant fraction of sp^3 carbon.

Chapter 7 Recommendation for Future work

7.1 Synthesis and Characterization of doped diamond films

When the large scale uniform diamond films could be deposited on substrate, it is possible to start introducing dopants into diamond.[47-50] Take boron doped diamond into consideration, the boron source is added into the precursor of CVD system either in the form of BH_3 gas or B_2O_3 dissolved in methanol. The doping level can be controlled from lightly doped (10^{18} cm^{-3}) to high doped (10^{20} cm^{-3}).

SEM, XRD and Raman spectroscopy could be used to study the morphology, microstructure and film quality of doped diamond films. The doping level will make changes to the microstructures of the film (Figure 22) and thus may affect the properties of doped diamond films.

Figure 22: Raman spectrum of boron doped diamond [51]

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Some physical properties will also be measured such as the Hall effect to determine accurate carrier density, electrical resistivity, and the mobility of carriers in semiconductors. Kalish R.[28] has measured the Hall effect of 600 ppm Phosphorous doped diamond films. The temperature dependence of Hall coefficient is negative, proving its n-type conductivity. As shown in Figure 23 which is deduced from Hall effect measurement, activation energy of 0.46eV, electron concentration at 600°C of $3 \times 10^{17} \text{ cm}^{-3}$ and electron mobility $\leq 30 \text{ cm}^2/\text{V/s}$ is obtained.

Figure 23: Hall effect measurement: temperature VS electron concentration and mobility [28]

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Preliminary work has been done in order to deposit boron doped diamond films. B_2O_3 is dissolved in methanol, and then added to methyl formate. The argon flows through the liquid and carries out the carbon source and boron source. After the deposition in the MPCVD system, continuous diamond film and boric acid film has been deposited separately instead of boron doped diamond films, which is confirmed by the characterization of both confocal Raman and XRD. Thus, more effort should be done to find the best conditions for introducing dopant.

7.2 Potential application of doped diamond films

Boron doped diamond films are promising electrode materials for electrochemical degradations of pollutant in the environment. Its low cost, and surpassing chemical properties like wide potential window, electrocatalytic activity, and chemical inertness attracts much attention. Santana et al.[52] has reported an increase of working potential window during anodic switching potential investigation because of an etching effect of amorphous sp^2 on the surface (Figure24). Swain et al has also studied the electrochemical properties of BDD electrode in electrochemical systems[49], and the direct electrochemistry of Cytochrome c at the BDD surface[8].

Figure 24: Cyclic Voltammetry of BDD electrode (---) and treated BDD electrode (—); 3.0 M H₂SO₄, 25°C, scan rate of 100 mV s⁻¹[52]

(Reprinted from *Electrochimica Acta*, 50(10), Santana, M.H.P., L.A. De Faria, and J.F.C. Boodts, Electrochemical characterization and oxygen evolution at a heavily boron doped diamond electrode, 2017-2027, Copyright (2005), with permission from Elsevier)

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