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Synthesis of Thin and Thick Ultra-nanocrystalline Diamond

Films by Microwave Plasma CVD System

by

Dzung Tri Tran

A THESIS

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

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ABSTRACT

Synthesis of Thin, Thick Ultra-nanocrystalline Diamond Films by Microwave Plasma CVD System

By

Dzung Tri Tran

Ultrananocrystalline diamond (UNCD) films offer a number of valuable properties like high Young's modulus, chemical inertness, and low coefficient of friction. These properties combined with small crystal size and film smoothness result in UNCD being very promising for many applications such as surface acoustic wave (SAW) devices, coatings for AFM tips, and films for Micro-Electro-Mechanical System (MEMS) devices.

The process to grow a variety of thin, thick, or conductive UNCD films using a Microwave Plasma Assisted Chemical Vapor Deposition (MPACVD) System are investigated. UNCD films are deposited over a wide pressure range (60-180 Torr) and temperature range (400-800 $^{\circ}$ C). UNCD films were grown on Si (100), p-type boron doped, substrates with thicknesses ranging from 58 nm to greater than 70 µm. The highest growth rate of 1.12 µm/h was achieved at 180 Torr, with gas mixtures of H₂:Ar:CH₄ = 4:100:2 sccm and 3 kW microwave power. Film surface roughness, as low as 10 nm, was obtained as measured by AFM Microscope. The conductivity of UNCD diamond films varied with nitrogen flow rate. At 20 sccm flow rate of nitrogen in the gas mixture, the conductivity of UNCD films was found to be 10.3 (Ω .cm)⁻¹.

Dedicated to my loving parents,

Hai V Tran and Muon T Nguyen.

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"Images in this thesis are presented in color,"	

Chapter 01: Introduction

1.1 Introduction

Ultra-nano crystalline diamond (UNCD) thin films have many superior properties and are promising for many applications requiring smooth surfaces. There are various methods to grow nano-crystalline diamond film including hot filament chemical vapor deposition (HFCVD), plasma torch, microwave plasma assisted chemical vapor deposition (MPACVD), etc. The microwave plasma assisted CVD system has a number of advantages compared with other methods.

The MPCVD system can produce smooth thin films with large area and in a repeatable manner. Huang [Huang 2004] reported on the growth of nano-crystalline diamond across a wide range of pressure and power by microwave plasma assisted CVD with $Ar-H_2-CH_4$ gas mixtures. Those experimental results established the relationship between input variables and the resulting diamond thin films. In order to better understand the growth of nano-crystalline diamond thin films, more research needs to be conducted on the microwave plasma assisted CVD system.

1.2 Motivation

Synthesized nano-crystalline diamond films have drawn increased attention in recent years. The nano-crystalline diamond films, with very small crystals size and a smooth

surface, are preferred in many applications. The thickness of the diamond film is an critical application dependent parameter. Some applications require very thin diamond films, while others need thicker films. The development of processes to synthesis nano-crystalline diamond film with various thicknesses by microwave plasma assisted CVD is reported in this thesis. Three different gas mixtures including Ar-H₂-CH₄, He- H₂-CH₄ and Ar- N₂-CH₄ are used to grow nano-crystalline diamond in this investigation. The process of synthesizing thin and thick nano-crystalline diamond films using pressures from 60 to 180 Torr is also carried out in this investigation.

The nano-crystalline diamond film experiments are investigated with $Ar-H_2-CH_4$ and $He-H_2-CH_4$ gas mixtures. Argon and helium are both noble gas. Most of research reported in the literature used argon in the H₂-CH₄ gas mixture to grow nano-crystalline diamond. The synthetic process of nano-crystalline diamond using the noble gas helium still is open area of investigation. A part of this thesis will research on conducting nano-crystalline diamond film. By adding nitrogen into gas mixture, the characteristic of diamond films change to become electrically conducting.

The nano-crystalline diamond synthesis investigated in this thesis is directed toward three applications. First the potential application for diamond thin films as coatings atomic force microscope (AFM). The tips made by silicon or gold will be worn out very fast when working on a hard surface. With nano-crystalline coating, the tips will have a longer useful life.

A second potential application for thick nano-crystalline diamond films is surface acoustic wave (SAW) devices [Bi 2000]. Since the polishing of rough polycrystalline diamond surfaces is very difficult, nano-crystalline diamond film, with their very smooth surface, is more favorable material for the SAW device application.

A third potential application for conducting nano-crystalline diamond is for resonator devices. Resonators are a key component in micro electro mechanical structure (MEMS) devices. Resonators are actuated, usually electro statically, to oscillate at their natural resonant frequency. The nano-crystalline diamond films provide the highest resonance frequencies of any materials since it has a very high Young's modulus (E >800 GPa).

1.3 Research Objectives

The research objectives of this thesis included:

- Develop the process and methodology to synthesis nano-crystalline diamond thin films.
- (2) Develop the process and methodology to synthesis nano-crystalline diamond thick films.
- (3) Develop the process and methodology to synthesis nano-crystalline diamond conducting films.
- (4) Characterize the nano-crystalline diamond quality films deposited over a wide range of pressures and gas mixtures.

- (5) Establish the relationship of how the input variables (pressure, power, gas flow rate...) affect to the growth of nano-crystalline diamond films.
- (6) Establish the process to grow nano-crystalline diamond using the noble gas argon and helium.
- (7) Establish the reactor condition to deposit conducting nano-crystalline diamond with nitrogen gas.
- (8) Investigate the properties of grown nano-crystalline diamond films for three applications including (a) AFM tip coatings; (b) surface acoustic wave (SAW) devices and (c) ultra high frequency micromechanical (UHF-MEMS) resonators.

1.4 Thesis Outline

Chapter One is an introduction with general information and objectives of this thesis.

Chapter Two presents history, background and related literature of diamond films synthesis and nano-crystalline diamond films in particularly. The nucleation techniques, the methods to grow nano-crystalline diamond films at substrate low temperature, and methods to grow conducting nano-crystalline diamond films will be also introduced in this chapter.

Chapter Three describes the system operation and experimental methods. The microwave plasma assisted CVD system and procedures to grow nano-crystalline diamond are

introduced. The reactor's operating field map for three different gas mixtures ($Ar-H_2-CH_4$, $He-H_2-CH_4$ and $Ar-N_2-CH_4$) will also presented.

Chapter Four summarize the experiment results of this investigation. The surface morphology, growth rate, uniformity and conductivity of nano-crystalline diamond films are studied in this chapter.

Chapter Five presents the applications of nano-crystalline diamond including (a) surface acoustic wave devices, AFM tip coatings and ultra high frequency micromechanical resonator devices.

Chapter Six summarizes the thesis and present recommendations for further development of growth nano-crystalline diamond films using microwave plasma assisted CVD system.

Chapter 02: Background

2.1 General information

2.1.1 Historical

The natural diamond was found by the fourth century B.C in India. It is considered to be of the highest value among precious stones. Because diamond has many outstanding properties compared with others material, it also drew a lot of attention from scientists. Synthetic diamond was developed in the last forties year with various methods.

In the early 1950s, the process of high pressure high temperature (HPHT) synthetic diamond was invented by General Electric. In 1954, W. Eversole of Union Carbide Crop in the United State proved that diamond showed homoepitaxial growth from carbon-bearing gas under low pressure by the chemical vapor deposition (CVD) method [Eversole 1962].

In 1956, B.V. Deryagin and B.V. Spitsyn synthesized diamond by the CVD method in Russia. In these methods, the growth rate of diamond was extremely low, and graphite also grew simultaneously with diamond so that in each case the chemical reaction of the process had to be suspended [Spitsyn 1981].

In the early 1970s, atomic hydrogen was used during the growth phase in CVD method. In 1975, a high growth rate CVD process was announced by Deryagin's laboratory in Russia and also N. Setaka's group. This is a significant achievement as growth had only previously been possible on diamond substrates. In 1981, Matsumoto of NIRIM (National Institute for Research in Inorganic Materials), Japan, made a breakthrough in diamond synthesis by developing the hot filament CVD method, followed by development of a microwave CVD method by Kamo of NIRIM [Matsumoto 1982]. This method drew attention, as the experiment was reproducible and could produce crystals of good quality. Over the past two decades many researchers have worked to significantly advance the growth of diamond

As chips have shrunk over the years, engineers have struggled with ways of dissipating the heat they create. Because silicon, the main component of semiconductors, suffers electrical breaks down, some experts believe a new material will be need in the future. Diamonds might fit the bill. Diamond can withstand 500 $^{\circ}$ C; electrons and holes move through diamond with high mobility more easily at increased temperature of 100-200 $^{\circ}$ C.

Engineers could cram a lot more circuits onto a diamond-based microchip if they could perfect a way of making pure crystals cheaply. Chemical vapor deposition diamond technique became available in the form of extended thin films and free-standing plates or windows. With CVD-diamond a huge of new applications opened up.

2.1.2 Classifications

There are four known types of natural diamond (Ia, Ib, IIa, IIb), classified according to the presence of nitrogen in the crystal, and certain other properties.

Type I diamonds have nitrogen atoms as the main impurity. If the nitrogen is localized in clusters it does not affect the diamond's color (Type Ia). If it is dispersed throughout the crystal, it gives the stone a yellow tint (Type Ib). Typically a natural diamond crystal

contains both Type Ia and Type Ib material. Synthetic diamonds that contain nitrogen are Type Ib.

Type II diamonds have no nitrogen impurities. They contain either no or other impurities. Those containing no impurities are Type IIa and are colored clear pink, red or brown. The color arises by structural anomalies from plastic deformation. Type IIb are the natural blue diamonds which contain scattered boron within the crystal matrix.

Synthetic diamonds can also be categorized according to this scheme. However there can still be a wide variation in some properties between diamonds of the same type.

Almost all synthetics are of type Ib, having an even distribution of nitrogen atoms substituted for carbon atoms in the lattice (up to about 500ppm). It is believed that in the earlier stages of their history, all natural diamonds were type Ib

Most natural diamonds (~99.9%) are of type Ia, with a large amount of nitrogen concentrated in various aggregates in the crystal. The initially type Ib diamonds are considered to have changed to type Ia after many years in a HPHT (High pressure high temperature) environment, in which the nitrogen diffused and coalesced into aggregates.

Types IIa and IIb are very rare in nature but can be synthesized for industrial purposes. Natural diamonds consisting of several different types in one stone are sometimes seen. Diamonds occur in a variety of colors - steel, white, blue, yellow, orange, red, green, pink, brown and black. Colored diamonds contain impurities or defects that cause the coloration, whilst pure diamonds are always transparent and colorless. Diamond is an insulator, but due to the fact that it contains defects and impurities, it can behave like a semi-conductor, which makes it useful for several electronic applications.

2.1.3 Crystal Structure



Figure 2.1: Diamond Structure

Diamonds typically crystallize in the cubic crystal system and consist of tetrahedrally bonded carbon atoms. The diamond cubic crystal structure (Figure 2.1) consists of two interpenetrating face-center cubic (FCC) lattices, displaced from each other by one quarter of the body diagonal. Each carbon atom is tetrahedrally coordinated (using sp³ atomic orbital), creating strong, directed sigma bonds with its four neighboring carbon atoms. The bond length and lattice constant are 1.54 and 3.56 angstroms, respectively.

Graphite is the most common form of carbon. In graphite, each carbon atom is covalently bonded to three carbon atoms to give trigonal geometry. Bond angle in graphite is 120°. Each in-plane carbon atom combines with its three neighbors using hybrid sp² atomic orbits, with a covalent σ bond length of 1.42 angstroms. The repeating layers are pi bonds, perpendicular to the plans with a 3.35 angstrom lattice constant. Three out of four valence electrons of each carbon atom are used in bond formation with three other carbon atoms while the fourth electron is free to move in the structure of graphite (Figure 2.2).



Figure 2.2: Hexagonal Graphite

Diamond is carbon in its most concentrated form. Diamond is distinctly different from the common graphite which is also composed of carbon. Diamond's particular arrangement of carbon atoms, or its crystal structure, the feature that defines any fundamental properties.

2.1.4 Properties of diamond

Diamond has many superior properties compare with other materials such as extreme hardness, high thermal conductivity, high breakdown voltage, large band gap and high electrons and holes mobility (Table 2.1). Therefore diamond has many potential applications in industry and MEM device.

	Diamond	Si	Ga-As	CVD
Band Gap [eV]	5.45	1.12	1.43	5.5
Breakdown Field [V/cm]	107	3 x 10 ⁵	4 x 10 ⁵	10 ⁷
Resistivity [Ω cm]	$10^{13} - 10^{16}$	1.5 x 10 ⁵	10 ⁸	10 ⁸
Electron Mobility [cm2/V.s]	1900-2200	1350	8500	1350-1500
Hole Mobility [cm2/V.s]	1600	480	400	1000
Saturation Velocity [Km/s]	220	82	80	220
Mass Density [g/cm3]	3.51	2.33	5.23	3.51
Atomic charge [C]	6	14	31	6
Dialectric Constant	5.7	11.9	13.1	5.6
Optical Transparency	UV to	Visible to		
	microwave	mid-IR		
Thermal Conductivity [W/cm.K]	20-23	1.5	0.5	10-21
Thermal Expension Coeff				
[K ⁻¹]	0.8 x 10 ⁻⁶	2.6 x 10 ⁻⁶	5.8 x 10 ⁻⁶	2.0 x 10 ⁻⁶
Hardness [Kg/mm2]	10,000	1,000	600	10,000

Table 2.1: Characteristics of Diamond compares with Silicon and Ga-As

Ultra-Nanocrystalline Diamond (UNCD), a form of industrial diamond in which the grain size is in the range of several tens to hundreds of nanometers [Reinhard et al. 2004], captures many of the best properties of natural diamond in thin film form. UNCD has unique properties not found in any other carbon-based material. UNCD is currently being evaluated for a wide variety of applications including MEMS (RF & Optical-MEMS, BioMEMS), cold-cathode electron sources, chemical process pump seals, bioelectrochemical electrodes, and others.

2.2 Chemical Vapor Deposition of Diamond

2.2.1 Introduction

The complex chemical processes occurring in chemical vapor deposition of diamond are fascinating and have been studied by many scientists. How does one understand the process of growing diamond in chemical vapor deposition? This section describes a model for understanding the complex gas phase chemistry, environment, surface and bulk chemical in CVD process to growth diamond (Figure 2.3).

2.2.2 The gas-phase chemical environment

Many studies of the gas-phase chemistry, during diamond chemical vapor deposition, in the past two decades [Celii 1989], [Harris 1989], [Corat 1993], [McMaster 1995]. Most studies, both experimental and computational, discuss the CVD environment with respect to substrate temperature, atomic hydrogen concentration, hydrocarbon chemistry, deposition uniformity etc...



Figure 2.3: Schematic of processes occurring during growing CVD diamond [Butler 1993]

2.2.2.1 Substrate temperature

In hot filament and microwave system, the range of substrate temperature for diamond deposition is from 400-1100^oC with the more typical values being 700-1000^oC [Bachm 1991], [Zhu 1991], [Buttle 1998]. This range of substrate temperature allow various surface phenomena to occur including various adsorption, de-sorption and abstraction reactions to occur that lead to diamond growth [Grotjohn 2001]. If the substrate temperature becomes too high, the diamond will be converting to graphite. In microwave plasma systems, a heating or cooling device is sometime integrated within the substrate holders to ensure the proper substrate temperature. Substrate temperature plays an important role to improve the growth rate. Figure 2.4 shows the relation between growth rates versus substrate temperature. Film growth rates are seen to increase as the substrate temperature is increased.



Figure 2.4: Film growth rate versus substrate temperature

(CO₂/CH₄, 50/50%) [Pether 2002].

2.2.2.2 Atomic Hydrogen

Two types of radical are needed in the growth of CVD diamond including atomic hydrogen and carbon-containing growth species. First, atomic hydrogen is needed so that the surface is almost entirely covered with hydrogen to permit growth in the diamond phase of carbon and not the graphite phase [Grotjohn 2001]. Second appropriate carbon-containing growth species must be supplied to the growth surface. Atomic hydrogen is the most critical determinant of diamond film quality and growth rates.

In hot-filament systems, atomic hydrogen is produced heterogeneously by thermal decomposition of H_2 on the hot filament surface. The atomic hydrogen produced diffuses rapidly away from the filament, resulting in a concentration profile near the filament. As the hydrocarbon content of the gas is increase beyond a critical value, the H concentration drops because of graphite covers the filament [Celii 1989]. This critical hydrocarbon fraction corresponds closely to the solubility limit of carbon in hydrogen [Somm 1990].

In plasma-enhanced systems such as microwave, RF and DC arc jet reactors, H is produced homogeneously in the plasma. The external energy input couples directly to the free electrons in the plasma, which can dissociate the hydrogen via the reaction.

 $H_2 + e^ H + H + e^-$

This reaction often proceeds through successive vibration excitation of H_2 by electron impact, leading finally to dissociation. In general the new hydrogen is dissociated by

either electron impact or thermal dissociation. Typically, the lower pressure discharge (less than few tens of torr) has lower gas temperatures and the electron impact dissociation process dominates. The higher pressure (greater than few ten of torr) has higher gas temperatures (greater than 2000K) and thus thermal dissociation of hydrogen is the dominant dissociation process.

2.2.2.3 Hydrocarbon Chemistry

There are two dominant carbon-containing radicals important to diamond growth: CH_3 and C_2H_2 [Goodwin 1998]. The methyl radical CH_3 is generally acknowledges being the most important species for diamond growth. It is often obtained from the methane (CH_4) input feed gas. The CH_4 chemical reactions in the typical diamond deposition environment primarily occur as neutral-neutral chemistry rather than via electron collision process, which are more important for the hydrogen dissociation. In microwave plasma CVD reactor system, the hydrocarbon chemistry reactions occur on a time scale much shorter than the residence time of deposition gas in the discharge chamber. Hence, the hydrocarbon chemistry typically reaches an equilibrium condition for the discharge gas temperature and atomic hydrogen concentration found in the discharge.

The CH₃'s concentration depends on substrate temperature [McMaster 1994]. Below 1000 K the substrate temperature dependence of the CH₃ mole fraction can be described by activation energy of 3-4 kcal/mole. The explanation for this effect is recombination of CH₃ with H₂ to form CH₄ or CH₃ with another CH₃ to form C₂H₆, in the cool gas layer

near the substrate [Corat 1993]. In general the C_1 radicals are most often postulated to be important for polycrystalline diamond growth using H_2/CH_4 mixture. Alternately, the C_2 radical is the key growth species for nano-crystalline diamond growth using $Ar/H_2/CH_4$ mixtures [Grue 1995]. Species with three (C_3) or more carbon atoms are generally not important for diamond growth [Frenk 1989].

2.2.3 The growth species

The question of which carbon-bearing gas phase species is the dominate species for the growth of diamond film has been of great interest, both from academic and process optimisation standpoints. For the reactor designer, it is important to identify the "growth species" to maximize its concentration. The observation that MPCVD and HFCVD both deliver diamond films at similar growth rates indicates that the diamond growth precursor is likely to be a neutral species.

The modelling of gas phase reaction kinetics and consideration of measured diamond growth rates suggests that CH₃ and C₂H₂ are possible diamond precursor species [Harris 1988]. Table 2.2 shows the results of isotope labelling studies in which a 2:1 mixture of ¹³C methane and ¹²C acetylene was introduced into a HFCVD reactor in such a way as to minimise isotopic scrambling between the two species [D'Evelyn 1992]. The ¹³C mole fractions of the resulting (homoepitaxial and polycrystalline) films were determined by Raman spectroscopy and were found to be very similar to those of the input CH₄. It was assumed that CH₄ and CH₃ were in equilibrium; therefore CH₃ was concluded to be the

diamond precursor species. Similar results were obtained by Johnson [Johnson 1992] using a cavity plasma reactor, as shown in Table 2.2.

		¹³ C Mole Fraction (%)			
CVD Method	Film Type	Film	CH ₄	C ₂ H ₂	
Hot-filament	Polycrystalline	58.2 ± 3.6	61.6 ± 5.5	32.4 ± 5.6	
Hot-filament	Homoepitaxial	56.8 ± 1.2	58.6 ± 5.4	34.9 ± 5.3	
Microwave	Polycrystalline	77	83	29	

Table 2.2: Summary of results for C mole fraction (%) in the diamond film, CH_4 , and C_2H_2 for Hot-Filament [D'Evelyn 1992] and Microwave Plasma CVD [Johnson 1992].

Lee carried out a set of experiments in which jets of: (1) CH₃ and H₂; (2) CH₃ and H; (3) C_2H_2 and H; were directed at diamond seed crystals [Lee 1994]. Epitaxial diamond growth on these crystals was only observed for incident jets of CH₃ and H, whereas replacing CH₃ with C_2H_2 resulted in a largely graphitic deposit. This study and a number of others involving a wide variety of CVD diamond deposition methods [Celii 1992] have concluded that CH₃ is the major diamond precursor in low-pressure low-power diamond CVD reactors (*e.g.* HF, MPCVD and flame CVD). However, it should be noted that C₂, or C atoms may be the dominant growth species at higher powers (*i.e.* >5 kW) in, for example, a DC arc jet reactor [Yu 1994].

2.2.4 Diamond Surface Chemistry

One of the most important aspects of diamond surface chemistry is the reaction between atomic hydrogen and the diamond surface. During growth of diamond, the atomic hydrogen bombards the diamond surface continuously, so most of the diamond surface is hydrogenated, and therefore non-reactive with incoming hydrocarbon species. The fraction of surface sites which are not hydrogenated (the open site fraction f^*) is determined by a dynamic equilibrium between the two reactions

$$C_dH + H \longrightarrow C_d^* + H_2$$

And

 $C_d^* + H \longrightarrow C_d H$

Where C_dH represents a hydrogen-terminated surface site and C_d^* an equivalent site without hydrogen.

The nature of C-H bonding on hydrogenated diamond surface was studied by Thoms [Thoms 1995], Struck [Struck 1993] and McGonigal [McGo 1995]. These studied show that the (100), (110), and (111) surfaces are mainly covered by the monohydride (CH) species.

During diamond growth, the diamond surface is nearly fully saturated with hydrogen. This hydrogen coverage limits the availability of sites where hydrocarbon species may chemisorbs, and blocks migration sites once they are adsorbed. The temperature range between 600-1200 ⁰C is well above the temperatures at which physisorbed species desorbs [Zang 1988].

2.3 The ultra-nanocrystalline Diamond Synthesis

2.3.1 Carbon Dimer Growth Processes

Nanocrystalline diamond films (UNCD) posses very fine grains (with the crystal sizes on the order of nanometers) and a very smooth surface as compare to microcrystalline films. UNCD can be grown using Ar/CH₄ in a lower hydrogen concentration environment. Several research groups have employed spectroscopic techniques to measure the predominant species present during growth as a function of process parameters, especially under conditions of high argon concentration, typically Ar/H₂/CH₄ gas mixtures. Correlation between materials grown and species present in the growth environment is an important step in identifying the primary growth species.

As H_2 input is reduced and replaced by Ar, C_2 emission is greatly increased. This increase in C_2 emission is interpreted as being due to the increased C_2 ground state population [Gruen 1995]. This rise in C_2 population is correlated with the observed increase in growth rate, and thus supports that C_2 is a growth species for UNCD synthesis. Thus, dicarbon (C_2) is believed to be the key growth species [Gruen 1995] for nano-crystalline diamond growth instead of methyl (CH₃) and acetylene (C_2H_2), which are believed to be the important species in traditional CH₄/H₂ polycrystalline diamond growth.

The nano-crystalline diamond growth process is described as follows:

a) One C_2 adds to the reconstructed monohydride surface by inserting itself into first one C-H surface bond without abstraction of the terminating hydrogen bond (step l).

b) The C_2 molecule then rotates about the newly formed bond to insert its other carbon into the C-H bond across from it, thus forming a (100)-oriented surface dimmer row (step 2), producing an adsorbed ethylene-like structure.
c) A subsequent C₂ molecule then inserts itself into the adjacent surface C-H bond,

parallel to the newly inserted surface C_2 dimmer, to produce a surface with two adjacent ethylene-like (steps 3 and 4).

d) The original state of the (110) surface is finally recovered by the formation of a C-C single bond between adjacent ethylene-like groups (step 5) and thus producing a new layer on the diamond surface. This direct insertion growth mechanism for C_2 is unique in that it is not dependent on the abstraction of hydrogen atoms from the surface. Specially, the path for the formation of a C-C single bond between adsorbed, two-carbon moieties via step 5 does not involve any gas-phase atomic hydrogen.

In 1999, D.M. Gruen [Gruen 1999] reported: (1) the reaction of a singlet C_2 with the C=C double bond of the C₉H₁₂ cluster gives carbene structures, which lead to the formation of new diamond critical nuclei during growth, (2) on the other hand, the reaction of singlet C_2 with the HC-CH single bond or C-H bonds of the C_9H_{14} cluster results in a cyclobutene-like geometry, which leads to growth on the (100) surface in a series of steps, (3) the nucleation rates increase dramatically under conditions where small fractions of the reconstructed (100) surface are un-hydrided and C_2 concentrations in the plasma reach levels of 10^{12} cm⁻³, hydrogen and (4) low content plasma favor these conditions [Gruen 1999].

2.3.2 Ultra-Nanocrystalline Diamond Re-nucleation Growth Model

Ultra-nanocrystalline diamond films have potential advantages when compared with polycrystalline diamond CVD because the average surface roughness is lower on the order

of a few 10's of nanometers. Ultra-nanocrystalline diamond films usually are believed to grow by continuous re-nucleation.

A nano-crystalline growth model explains the structural evolution of the film based on a substrate seeded with diamond nuclei that grow isotropically [Huang 2001]. Very high heterogeneous re-nucleation rates (10¹⁰ cm⁻²sec⁻¹) ensure that growth occurs and results in the formation of smooth, phase-pure nano-crystalline diamond films. This high secondary nucleation rates allows the transition from microcrystalline to nanocrystalline diamond films.

2.4 Ultra-nano-crystalline Diamond Film Deposition Techniques

In general, nano-crystalline diamond film grows in high concentration of Ar (75-99%), 0.5-2% CH₄ and zero to a few percentage of H₂. The resulting crystal sizes are usually smaller than 50 nm and often are as small as 10 or less nm. There are some techniques which have been involved to synthesize nano-crystalline diamond films such as: Hot filament CVD, Microwave plasma CVD, Radio-frequency Plasma CVD and DC arc plasma.

2.4.1 Hot-filament CVD

Masumoto et al. [Masumoto 1982] gave the first description of a process using hotfilament CVD (Figure 2.5). The hot-filament assisted process operates at lower gas activation temperatures and low pressure (1-80 Torr). The substrate is between 5 and 20 to grow diamond has some advantages when compare with others like simplicity (Figure 2.5), low cost, scaleable and can be used to coat complex shapes and internal surfaces. Two major drawbacks of hot- filament CVD are: (1) material from the filament can contaminate deposited films and (2) the range of gases available for use in HFCVD is limited by the sensitivity of the filament to oxidising or corrosive species.



Figure 2.5: Hot-filament system diagram

The filaments (tungsten, tatalum, rhenium materials), evaporates to a small extent and contaminates the growing diamond film. This metallic contamination is not too much of a constraint for coatings used in mechanical applications such as tools or general wear parts; however, it is a nuisance when envisaging electronic applications such as active components, as well as optical or sensor devices.

Wang et al. [Wang 2004], have grown UNCD on 2" Si (100) wafers by decreasing the deposition pressure and increasing acetone in gas mixture with a hot filament technique. Average grain sizes of approximately 4-8 nm were achieved.

2.4.2 Microwave Plasma CVD

Microwave plasma assisted chemical vapor deposition (MPCVD) systems have more advantage than other chemical vapor deposition (CVD) systems like hot filament CVD, direct current CVD arts or combustion flame in terms of have a wide operating pressure regime and high growth rate [Grotjohn 2001]. The range of pressure operated in MPCVD systems range from 10 mTorr to over 240 Torr. MPCVD is one of the most popular techniques used to grow nanocrystalline diamond films in the laboratory.

The plasma is generated in a reactive gas mixture by a high-frequency electric field, such as microwaves (Figure 2.6), or by electron cyclotron resonance (ECR), i.e. a combination of electric and magnetic fields. By using these methods, the coatings are very uniform (± 10 % of average thickness), over large area (200 mm and more), smooth, and of high purity. By this process, the large areas of uniform, homogeneous, polycrystalline thin diamond films were obtained.



Figure 2.6: Microwave plasma CVD diagram

Gruen at al. [Gruen 1999] grew nano-crystalline and ultra-nanocrystalline diamond films with a argon-carbon (C_{60} in argon) microwave plasma and controlled the diamond crystal microstructure by argon additions to methane-hydrogen microwave plasma discharges in a microwave plasma CVD reactor (ASTeX PDS-17). It was found that nanometer sized diamond could be synthesized with either C_{60} or CH₄ carbon precursor. Cross-section and plane view SEM images show that the morphology, grain size, and growth mechanism are affected by the ratio of argon to hydrogen in the gas mixture. The transition from microcrystalline to nanocrystalline which depends on ratio of argon to hydrogen was confirmed by X-ray diffraction and Raman spectroscopy. The nano-crystalline diamond was synthesized at an Ar/H₂ volume ratio of 99% and CH₄ volume percentage of 1%. The nanocrystalline diamond was synthesized at 0-2% of H₂ and 1% of CH₄ (vol%). The C₂ dimer concentration is promoted significantly by increasing the argon concentration [Gruen 1999]. A critical process in this deposition is believed to be the continuous renucleation by the C₂ dimer.

Nanocrystalline diamond films were also synthesized on a 4" Si (100) wafer with a hydrogen flow rate of 100 sccm and a methane flow rate of 10 sccm using a microwave plasma CVD system. The basis of the nanocrytalline diamond deposition in this process was a very high nucleation density. The silicon substrate was scratched twice by dry diamond powders with the sizes of 250 nm and 5 nm respectively [Yoshi 2001]. The high nucleation density, approximately 1×10^{11} cm⁻², led to a smooth (RMS=8.4 nm by atomic force microscopy) and fine-grain (about 10 nm observed by field emission scanning electron microscopy) diamond film with 3.5 µm in thickness. The FTIR (fourier transform infrared spectrometer), spectra showed C-H bands: sp³ - CH₂ symmetric stretch at 2850 cm⁻¹ and sp³ -CH₂ asymmetric stretch at 2925 cm⁻¹, in the film.

Hong et al. [Hong 2002] used the same technique and similar conditions to deposit nanocrystalline diamond films on a 4" Si(100) wafer but modified the two-step scratch seeding procedure with dry diamond powders of the sizes of 1 μ m and 5 nm for tribological characteristics study. A slightly thinner film (2.2 μ m thick) with approximately the same size crystals (10-15 nm) showed a very low surface roughness value (10 nm).

Bhusari et al. [Bhusari 1998] deposited diamond films with grain sizes ranging from 4 nm to a few hundreds of nanometers in methane, hydrogen, and oxygen gas mixture by an AsTex 5 kW microwave reactor. The growth results of the quartz substrates pretreated with two different diamond-powder sizes, 4 nm and 0.1 μ m, were compared. The ultra-smooth and highly transparent nano-crystalline diamond films were coated on the quartz substrates (1) using 4 nm powder pretreatment and low (<20%) methane concentration, and (2) using 0.1 μ m powder pretreatment and high (>20%) methane concentration. According to the in situ OES (optical emission spectroscopy) study, the C₂ dimer continued to increase as methane concentration increased, while other hydrocarbon species that decreased significantly as methane concentration increased. Thus, it was speculated that C₂ may be the predominant growth species at higher methane fractions.

Sharda et al. [Sharda 2003] compared the optical properties of microcrystalline and nanocrystalline diamond films fabricated on silicon substrates by microwave plasma chemical vapor deposition with a mixture of 5% methane in hydrogen. The substrate was pretreated with bias enhanced nucleation. The nanocrystalline diamond film grown at 700 $^{\circ}$ C had a very

high optical absorption coefficient, i.e. $>10^4$ cm⁻¹ (higher than that of the microcrystalline diamond film) even though it was smoother than microcrystalline diamond film. Nevertheless, the nano-crystalline diamond film grown at 600 °C, was smoother, had 78 % transmittance in the infrared region, and thus had demonstrated a potential for application as optical windows.

Ulcznski [Ulczn 1998] reported to grow diamond on borosilicate glass substrates for protective coatings purpose. The glass substrates were Corning code 7059 and Corning code 7050. The films are grown by low-temperature microwave plasma-assisted chemical vapor deposition on seeded glass substrates. A smooth diamond films (the thickness less than 2 μ m), both patterned and unpatterned, achieved with near ideal transmission throughout the visible

2.4.3 Radio-Frequency Plasma CVD (RFPCVD)

The power source of radio-frequency plasma CVD uses with frequencies ranging from hundreds of kHz to tens of MHz. A schematic drawing of a Radio-Frequency Thermal Plasma CVD (RFPCVD) reactor is shown in Figure 2.7. Several types of RFPCVD systems have been used to deposit diamond such as RF thermal plasma and RF glow discharge plasma systems. The first reported growth of diamond using RF thermal plasma was in 1987 by Matsumoto [Matsumoto 1987]. High growth rates diamond deposition (in the tens of μ m/h) over substrates as large as 10 cm in diameter using RF thermal plasmas were achieved by a Toyota group [Kohza 1993]. Similar to DC thermal plasmas, RF thermal plasmas exposes the substrates to a high heat load, and the substrate temperature needs to cool down enough for diamond growth. So the challenge of this method is to control substrate temperature and boundary layer thickness.



Torch Head

Figure 2.7: Radio-Frequency Plasma CVD diagram

Using a radio frequency plasma assisted CVD (RFPACVD) method, an appropriate thickness of a nanocrystalline diamond layer was deposited as an anti-abrasive coating on cemented carbide substrates. The nanocrystalline coating reduced the friction coefficient in sliding against wood [Niedzi 2001]. The results of this study are helpful in the selection of the optimum thickness of the nano-crystalline diamond films to be coated on the cemented carbide tools to improve cutting of the mills used in the wood industry.

Erz et al. [Erz 1993] fabricated nano-crystalline diamond, optical transparent films on silicon and quartz substrates using methane-oxygen-hydrogen mixture by a remote tubular microwave CVD. In

this investigation, they used different diamond powder with grain sizes ranging from 0.01-3 μ m to enhance diamond nucleation on the substrates. The results showed that a nucleation density up to 3 x 10^{10} cm⁻² was achieved by scratching the substrates with 10 nm diamond powder. The high nucleation density led to a flat diamond film with a smooth surface. However, by increasing the film thickness from 1 μ m to 10 μ m, the surface roughness increases more than 6 times (30 ± 10 nm to 200 nm).

2.4.4 D.C Arc Jet Plasma CVD

A typical d.c arc jet plasma CVD reactor describes in figure 2.8. The gas mixture Ar/H_2 is incorporated into a primary Ar plasma flow in the twin torch assembly. These gas flow s are mixed and expansion into the main reaction chamber. Methane is introduced into the Ar/H_2 plasma through an annular injection ring positioned 10 cm downstream from the output nozzle.



Figure 2.8: D.C arc plasma CVD reactor [Mankel 2003]

Nistor et al. [Nistor 1997] grew fine-grain diamond films on silicon substrates in methanehydrogen-argon gas mixture with fixed argon flow (50 sccm) and varied methane flow from 5-50 sccm, and hydrogen flow at 45 sccm by a D.C. arc discharge plasma. After the ultrasonic seeding process (ultrasonic seeding with 5 nm diamond powder suspension in ethanol), a pulsed excimer laser irradiation generated by an excimer KrF laser (pulse duration 15 nanosecond) was used to remove the undesirable non-uniformities in the surface distribution of the seeded crystals, while leaving the uncoalesced particles for subsequent growth undisturbed. The two-step seeding procedure led to highly smooth films owing to the irradiation of pretreated substrates by laser assisted disintegration of the coalesced seeds and removal of too large residue diamond particles. The improvement of the growth of nano-crystalline diamond films was obtained by the combination of the uniformly seeded substrates and a high methane concentration (50% of argon-methane-hydrogen mixture).

2.5 Pre-nucleation Techniques

This section describes the pre-nucleation techniques used to prepare the substrate before growing nanocrystalline diamond films. The process plays an important role in enhancing the initial nucleation density.

Growth of diamond begins when individual carbon atoms nucleate onto the surface in such a way as to initiate the beginnings of a sp^3 tetrahedral lattice. When using natural diamond substrates (a process called "homoepitaxial" growth), the template for the

required tetrahedral structure is already present, and the diamond lattice is just extended atom-by-atom as deposition proceeds. But for non-diamond substrates ("heteroepitaxial" growth), there is no such template for the C atoms to follow, and those C atoms that deposit in non-diamond forms are immediately etched back into the gas phase by reaction with atomic H. So pre-treatment of the substrate is necessary in order to obtain a nucleation density sufficient to allow the growth of a continuous diamond film on nondiamond substrates [Liu 1995].

Once nucleation of carbon has occurred, the homoepitaxial diamond growth can proceeded. The individual crystals become progressively larger and eventually grow into each other, leading to characteristic columnar growth of polycrystalline diamond films. A continuous film is formed at this point. In UNCD diamond growth, pre-nucleation is also necessary as the first step get the smooth of UNCD films.

There are five techniques used for pre-nucleation on the substrate surface. The simplest and most commonly pre-nucleation technique to seed the substrate surface is using mechanical polishing with micro or nano-diamond powder. The second technique is pretreatment using the Rotter method [Rotter 1999] and then ultrasonic scratching with nano-powder liquid. The third technique is using a spin coating slurry containing nanodiamond powder. The fourth technique is using bias enhanced nucleation (BEN) method. And the last technique is using tungsten (W) films. Piazza [Piazza 2005] reported research of seeding on substrate surfaces by the scratching method for UNCD growth. The study focused on the effect of diamond powder crystal sizes for seeding on the substrate surface. The results show that the nucleation increases as the seed particle size decreases (Figure 2.9)



(a) (b) (c)

Figure 2.9: SEM pictures of film deposited after 01 hours using different powder

(a) using micro powder; (b) using nano power; (c) using ultra-nano powder

The results also show that the diamond powder size using for seeding effected the surface morphology of the diamond films (Figure 2.10)



Figure 2.10: SEM pictures of film deposited after 10 hours using different powder as seeds. (a) using micro powder; (b) using nano powder

Lee reported growing UNCD films using the BEN pre-treatment method [Lee-Y 2005]. The nucleation process was carried out with a CH_4/H_2 plasma and a negative DC bias voltage system. By using BEN method, the nucleation site density is greater than 10^{11} sites/cm² and growth rate is up to 1 µm/hr (Figure 2.11).





For comparison reason, various pre-treatment methods to enhance the surface nucleation density were studied by Chen et.al [Chen 2005]. UNCD films were grown by MPACVD system under the same conditions (Ar:CH₄% = 99:1%, 150 Torr) after pre-treated with four different methods: scratching, spin coating, ultrasonic, and bias DC. The results are show in Figure 2.12.



Figure 2.12: SEM morphology of UNCD films using different seeding methods (03 hrs)(a) scratching (using 0.1 μm powder); (b) spin coating (using 3 nm powder);

(c) ultrasonic (using 3 nm powder); (d) bias DC (-100V).

Other research about enhance nucleation of UNCD used tungsten (W) films. Naguib [Naguib 2005] studied the pretreated method using a thin tungsten film applied onto a silicon surface prior to ultrasonic seeding. The thickness of the tungsten layer varied from 36 to 100 angstroms. The results for nucleation density are from 10^{11} to > 10^{12} sites/cm². Figure 2.13 (a), (b) show the results of SEM images for two UNCD films grown at the same condition and for the same time, using two pretreated methods: a) without tungsten film added, (b) with tungsten film added. The nucleation density has been increased by using the tungsten film.



Figure 2.13: SEM morphology of UNCD films using tungsten seeding methods (a) without tungsten added; (b) with tungsten film added (100 angstroms thickness)

Table 2.3 summaries the results of nucleation density from difference pretreatment methods.

Pretreatment methods	Nucleation density (cm^2)	Substrate	References
No pretreatment	10 ³ -10 ⁵	Silicon	[Bauer 1993]
Scratching	$10^6 - 10^{10}$	Silicon	[Ascarelli 1993]
Ultrasonic scratching	$10^7 - 10^{11}$	Silicon	[Popovici 1992]
Spin Coating	$10^6 - 10^{10}$	Silicon	[Smolin 1993]
Biasing	$10^8 - 10^{11}$	Silicon	[Stoner 1992]
Tungsten film	$10^{11} - > 10^{12}$	Silicon	[Naguib 2005]

Table 2.3: Nucleation densities of diamond after various pre-treatment

2.6 UNCD at low temperature growth

In UNCD growth by a MPACVD system, the substrate temperature is typically around $700 \, {}^{0}$ C to obtain high quality diamond film at a good growth rate. For most microelectronic device applications, depended on materials, the substrate temperature needs to keep at 500 0 C or lower. So growth of UNCD at low temperature while maintaining good film quality (with reasonable growth rates) is a new challenge for UNCD researchers.

Xiao reported the growth of UNCD diamond at low temperature (i.e. substrate temperature range from 400 -800 ⁰C) [Xiao 2004]. The initial enhanced nucleation method plays a very important role for growth of UNCD at low temperature. Ultrasonic seeding with nano-diamond powder was utilized. The UNCD films growth was

performed using a Cyrannus Iplas MPECVD system. Since the thermal conductivity of argon is much lower than hydrogen, and the power levels are also lower for plasma formation, the gas mixtures Ar-CH₄ = 99:1% is used to reduce the substrate temperature. The results for growing UNCD diamond at 400 $^{\circ}$ C was a growth rate of 0.2 µm/h as compare with 0.25 µm/h at 800 $^{\circ}$ C.





(b)

Figure 2.14: SEM morphology of UNCD films

(a) UNCD film deposited at 800 0 C; (b) UNCD film deposited at 400 0 C Figure 2.14 shows the surface morphology of diamond films growth at 800 0 C (a), and 400 0 C (b). The surface morphology of UNCD at 400 0 C is similar with UNCD at 800 0 C.



Figure 2.15: Low temperature UNCD coating for bio-MEMS application.

Figure 2.15 shows the applications of low temperature UNCD. The low temperature UNCD film is used to fabricate hermetic protective coating for bio- MEMS devices (because the melting point of aluminum is very low).

2.7 Conducting UNCD films

The possibility of doping diamond and changing it from an electrical insulator to a semiconductor opens up a wide range of potential electronic applications.

Researchers at Argonne National Laboratory (ANL) reported growing conductivity diamond by adding nitrogen gas to Ar-CH₄ gas mixtures [Bhatta 2001]. The conductivity at room temperature increases dramatically with nitrogen concentration, from 0.016 (1% N_2) to 143 (o.cm)⁻¹ (20% N_2).



Figure 2.16: Surface morphology of conducting diamond film 1% and 20% N2.

Figure 2.16 shows the surface morphology of conducting diamond film with 1% and 20% nitrogen in Ar-CH₄-N₂ gas mixtures.

The diamond films changed from insulating to conducting because nitrogen atoms are incorporated into the narrow boundaries between the grains (Figure 2.17) leading to enhanced electron transport [Bhatta 2001].



Figure 2.17: Surface morphology of conducting diamond film

Chapter 03: System Operation/Experimental Method

3.1 Introduction

This chapter describes the experimental system used for this thesis research including the microwave plasma assisted chemical vapor deposition (MPACVD) reactor, microwave power supply, wave guide system, gas flow control system and computer control system. This chapter also describes procedures to set up the experiment and system operation.

3.2 Experimental Systems

The system as show in (Figure 3.1) is used in this thesis. It consists of (1) Microwave power supply, (2) Directional power coupler, (3) Flexible waveguide, (4) Transition unit, (5) Cavity side wall, (6) Base plate, (7) Water cooling pipes, (8) Quartz dome, (9) Excitation probe, (10) Air cooling entrance, (11) Sliding short, (12) Variable input gases, (13) Gas inlet valve, (14) MKS Mass flow controller, (15) Pressure controller, (16) Pressure read out, (17) Pressure gauge, (18) Monitoring computer, (19) Throttle valve, (20) Nitrogen purge system, (21) Roughing pump, (22) Exhaust gas, (23) Holder base plate, (24) Process chamber, (25) Chiller, and (26) Substrate holder.



Figure 3.1: MSU-Microwave Plasma Assisted CVD System

3.2.1 Microwave Power and Wave Guide System

The microwave power source used in this thesis experiment is a **Cober** model **S6F** 2.45-GHz, 6 kW supply (Figure 3.2). The Cober-SF6 supplies microwave energy into the cavity through a rectangular and coaxial waveguide (Figure 3.3).



Figure 3.2: Control Board of Microwave Generator model S6F

Coaxial Waveguide

Rectangular Waveguide



Cober Power Supply

Figure 3.3: Microwave Plasma Assisted CVD System.



Figure 3.4: Microwave power and Wave Guide System

The microwave power and wave guide system (Figure 3.4) consists of:

- (1) Magnetron
- (2) Circulator
- (3) Dummy load.
- (4) Directional power coupler
- (5) Rectangular Waveguide

The microwave generator Cober model S6F is a complete self-contained power source with 6 kW continuous power output and operates at 2.45 GHz frequency. The air cooling is mounted on top of the cabinet. A portion of the air is exhausted through the waveguide to the applicator. Two of the major components, the magnetron tube (1) and the circulator (2), are directly water cooled. All indicators and operating controls are mounted on the door for easy monitor (Figure 3.3). The power input is approximately 12 kVA. The microwave power Cober S6F is equipped with a waveguide arc detector. When an arc occurs, the control circuit is immediately disabled and the amber "arc" light comes on.

The microwave power supplied by the magnetron (1) is propagated into the cavity applicator through rectangular waveguides (5). The reflected power, which is reflected back from the cavity applicator, passes through the dual-directional coupler (4) and is directed by the circulator (2) into a matched dummy load (3), where it is absorbed and dissipated as thermal energy. The circulator and the matched dummy load protect the power source from being damaged by preventing the propagation of the reflected power back into the power supply. The dual-directional power coupler attenuation factors for incident and reflected power is 60 dB. The incident power P_{in} and reflected power P_{ref} are measured by incident and reflected power meter.

3.2.2 Transmission System

The transmission system guides the microwave energy into the cavity applicator (Figure 3.5).

The microwave energy from the generator is propagated through a rectangular waveguide (1), a flexible waveguide (2) and a transition unit (3). Microwave energy is then coupled into the cavity applicator (6) by the excitation probe (4) and coaxial waveguide (5). The excitation probe is located at the center of the sliding short (7). The excitation probe can move up and down along the reactor axis by manual adjustment in order to get the best position for incident power matching.



Figure 3.5: Transmission System

(1) Rectangular Waveguide	(2) Flexible Waveguide		
(3) Transition Unit	(4) Excitation Probe		
(5) Coaxial Waveguide	(6) Cavity Applicator		
(7) Sliding Short			

3.2.3 Vacuum pump and gas flow control System

3.2.3.1 Vacuum pump and nitrogen purge system

The vacuum pump system is very important in CVD diamond system. Through the control system, it will keep the pressure at the desirable constant pressure.



Figure 3.6: The Vacuum and Nitrogen purge System

(1) The process chamber	(2) Glass window		
(3) Throttle valve	(4) Nitrogen purge		
(5) Roughing pump	(6) Exhaust gas		

Figure 3.6 shows the vacuum and nitrogen purge system. The vacuum pump (5), used for this system, is two stage rotary vane vacuum pump (Alcatel 2063 CP).

The throttle valve (3) used in this system is a MKS 653 A. The nitrogen purge (4) is used to bring the pressure up to atmosphere pressure when the experiment is done.

3.2.3.2 The Gas Flow Controller System

Figure 3.7 shows the gas flow controller system used in the MPACVD system. The gases, used for nano-crystalline diamond film deposition experiments are H_2 or N_2 , Ar or He and CH₄. The gases from gas tanks (4) flow into the chamber through four MKS mass flow controllers (5) (range from 10 to 1000 sccm). The gas flow is automatically controlled by Lab-view software on computer (6) and gas flow controller (7).

The gas flow control is monitored by a 4-channel MKS type 247 C flow controller (7). The impurity of source gases used for PACVD system are: Hydrogen (99.999%), Methane (99.999%), Nitrogen (99.995%), Argon (99.999%) and Helium (99.995%). The source gases have high purity to minimize the introduction of impurities into the process chamber during film deposition.

Two baratron capacitance manometers MKS type 627B are used for monitoring the pressure inside the chamber. The Baratron capacitance manometer MKS type 627 B determines the pressure in the process chamber by measuring the change in capacitance between the diaphragms and an adjacent dual electrode. The differential capacitance

signal is converted into a useable output by signal conditioning circuitry and directly transferred to the MKS pressure controller (8).



Figure 3.7: The Gas Flow Control System

- (1) Cavity
- (3) Gas inlet valve
- (5) Mass flow controller
- (7) 4-channel read out
- (9) Baratron
- (11) Pressure read out

- (2) Process chamber
- (4) Gas Tanks
- (6) Monitoring Computer
- (8) Pressure Controller
- (10) Transducer
- (12) Throttle Valve

The MKS pressure controller MKS model 651 instrument used in this system is a selftuning pressure controller for throttle valves. It provides a read-out for an attached capacitance manometer.

The 4-channel readout MKS model 247C is used to control and display from the mass flow controllers (5). The flow rate set point can be adjusted either through front panel controls or remotely through the rear panel analog interface.

The mass flow controller MKS model 1159B (figure 12) is used to measure and control the flow of gases from gas tanks (4). It can also be used as a pressure controller when connected to a suitable pressure transducer. The gas flow range channel is shown in Table 3.1.

	Channel 1	Channel 2	Channel 3	Channel 4
Gas	H ₂	H ₂	Ar	CH4
Range (sccm)	10	1000	500	10

Table 3.1: The gas flow range

3.2.4 Computer control system

The computer is used to control and automatically monitor the experiment procedure in the MPACVD system from start to shut down. The program software used for control is Lab-View.



Figure 3.8: Computer Control System Diagram

Figure 3.8 shows the monitoring computer control flow chart used for the MPACVD system. The operating pressure and the run time are first set in the CVD program. The experiment system is then set up and the feed gas flow to the process chamber is established. After the CVD system is working with the Lab-View control program, the throttle valve operates in a remote mode to adjust the pressure in the chamber.

During the experiment, the pressure and running time are monitored and controlled as preset values. If for some reason, the reflected power is more than 25% of incident power value or operating pressure exceeds preset value, the microwave power will be shut down by computer. In that case, the throttle valve still maintains the pressure at the preset value. Under normal operation, the CVD program control directs the system into a normal shut down sequence at the end of the last state (when the running time is expires).

3.2.5 Microwave Plasma Cavity Reactor

Figure 3.9 shows the microwave plasma cavity reactor used for the PACVD system. The cavity is made of brass. The inside diameter of the cavity is 7 inches. The thickness of the cavity wall is 0.125 inches. The cavity, which forms the conducting shell, is electrically shorted to a water-cooled base plate and a water cooled sliding short via finger stock. The sliding short controls the applicator height L_s and the excitation probe extends below the sliding short a distance L_p . Both L_s and L_p can move up and down along the longitudinal axis of the applicator cavity wall. The applicator height L_s is adjusted to approximately 21.5 cm and the probe depth L_p is about 3.2 cm [Zhang 1993]. The cavity length is set to

get the TM_{013} mode. This mode reduces the near field effect caused by the coaxial excitation probe (Figure 3.9).

The microwave power is propagate into the cavity applicator through a mechanically tunable coaxial excitation probe which is inside a coaxial waveguide and is located in the center of the sliding short. The cavity, with volume bounded by the sliding short, side wall and base plate forms the cylindrical electromagnetic excitation region (Figure 3.10).

The base plate is internally water cooled and also air cooled from out side. It also included the input gas feed plate and gas distribution plate. A quartz dome (five inches inside diameter) is sealed by Buna-N O-ring (Copolymer of butadiene and acrylonitrile) in contact with base plate assembly.

The thermally floating substrate holder setup assembly (Figure 3.9 and 3.11) includes a flow pattern regulator, a metal tube (stainless steel, O.D = 64 mm, I.D = 57 mm and h = 47mm), a quartz tube with I.D = 95 mm, O.D = 100 mm, and height=50 mm, and a holder-base plate. The flow pattern regulator (made by molybdenum, I.D = 3.016" and O.D = 4.038") is a plate with a series of holes arranged in a circle right inside the big circumference.



Figure 3.9: Microwave Cavity Plasma Reactor



Figure 3.10: Cavity Applicator

There are five holes (D = 6 mm), one in the center and four holes symmetric and off the center by 28 mm, used to measured the temperature from the back side. The gas flow coming out the gas inlet, into the quartz dome, flows through the plasma. The configuration is designed to increase the uniformity of the film deposition by changing the flow pattern in the plasma discharge and influencing the shape of the plasma discharge [Zhang 1993].

The premixed input gases are fed into the gas inlet of the base plate assembly. The substrate is placed on top of the flow pattern regulator, which is supported by a quartz tube. Quartz tubes of different heights may be used to change the position of the substrate with respect to the plasma to optimize the film deposition (from 47 mm to 50 mm). A stainless steel tube which serves as an electromagnetic field resonance breaker is placed inside the quartz tube. The tube prevents the plasma discharge from forming underneath the substrate.



Figure 3.11: Substrate holder assembly (Top view)

The stainless steel tube and quartz tube are placed on a substrate holder base plate which has 30 mm diameter hole at its center to pass the hot gases from within the quartz dome to the exhaust roughing pump. The base plate, the annular input gas feed plate, and the gas distribution plate introduces a uniform ring of input gases into the quartz dome where the electromagnetic fields produce a microwave discharge. A screened view window (Figure 3.12 a) is cut into the cavity wall for viewing the discharge. During an experiment, the viewing window is used to observe the plasma size inside the quartz dome. The plasma size needs to be large enough to cover the substrate but small enough so *it* does not touch the dome. Figure 3.12 (b), (c) and (d) show the plasma with different gas mixtures as viewed through window.






Figure 3.12 b: Ar-H2-CH4 gas mixture plasma



Figure 3.12 c: He-H2-CH4 gas mixture plasma



Figure 3.12 d: Ar-N2-CH4 gas mixture plasma

An air blower (Dayton model 4C443A) with 100 CFM (cubic foot per minute) flow rate blows a cooling air stream into the air cooling inlet to cool the quartz dome and cavity side wall. The air exits the cavity through the air blower outlet and through four holes (optical access port) in the base plate. The air blower existing inside the Cober model S6F microwave power supply adds another air cooling stream into the microwave cavity plasma reactor. Three Teflon pieces in the coaxial waveguide were drilled with four of 1/8" diameter through holes. This allows the cooling air from the air blower in the microwave power supply to flow through the coaxial waveguide, onto quartz dome and cavity side walls. This air flow, then exit out of the air blower outlet and the optical access ports.

A re-circulating chiller (Nestlab model CFT 300), which controls the temperature of the input coolant liquid, is used for the cooling system (Figure 3.13). The cooling water flow is 3 gpm at 60 psi. The coolant temperature is range from 5 $^{\circ}$ C to 35 $^{\circ}$ C.



Figure 3.13 The chiller Neslab model CFT 300

A water flow indicator is used to monitor water cooling operation (Figure 3.14). During the experiment, when the cooling water flow is too slow or off for some reason, the operator can emergency shut down (manually) the system to avoid overheating.



Figure 3.14: The water flow indicator

In the future, the cooling water flow needs to be improved such that monitoring is done by the computer so that the system automatically shuts down when cooling flow is low.

3.2.6 Operating Field Map

This section describes the general operating field map for the determination of substrate temperature. Measurements were carried out with the microwave plasma reactor under thermally floating substrate holder set up and different gas mixtures (Figure 3.15, 3.16, 3.17). Each plot shows the substrate temperature measured as a function of pressure and absorbed microwave power for a set gas flow mixture.





 $Ar-H_2-CH_4 = 100-4-1$ (sccm)



Figure 3.16: The MPACVD operating field map system

 $He-H_2-CH_4 = 100-4-1$ (sccm)



Figure 3.17: The MPACVD operating field map system

 $Ar-N_2-CH_4 = 100-4-1$ (sccm)



Figure 3.18: Substrate temperature is measured from the back side

The deposition pressure, the microwave power P_{abs} and the substrate temperature T_s are interrelated and interdependent. Figure 3.15, 3.16 and 3.17 show the dependence of substrate temperature on the deposition pressure, input gas mixture and microwave power P_{abs} . The substrate temperature T_s increases with either increase in the pressure, and/or the microwave power P_{abs} . For a fixed pressure, the plasma discharge volume V increases with increases in the microwave power P_{abs} . The substrate temperature is measured from backside as shown in figure 3.18.

For a fixed microwave power P_{ates} the plasma discharge volume V decreases with increasing pressure. By the observation through the viewing window in the cavity wall, the lower absorbed microwave power limit is determined by the minimum power required to maintain a discharge volume that covers a 3" diameter substrate. The upper limit of the microwave power is determined by the maximum power that can be used to generate a discharge volume which is just big enough to fill the quartz dome without touching the quartz dome walls. The upper limit of the microwave power is used to operate the MPACVD system without over heating the quartz dome.

3.3 Experimental Procedures

3.3.1 Prepared sample

The seeding or pre-treatment method is the first step to prepare the sample before running experiments. In the nanocrystalline diamond growth process, seeding enhances the initial nucleation diamond density on the substrate surface which is critical in determining the quality and uniformity of the film after growth. Nucleation enhancement on the substrate surface is especially important to grow nanocrystalline diamond at low substrate temperatures.

Mechanical scratching using micron diamond powder (0.25 µm crystal size) and pretreatment by Rotter method [Rotter 1999] combined with ultrasonic nanopowder 3-5 nm crystal size procedures are introduced in this section.

3.3.1.1 Scratch seeding procedure

The procedure for mechanical scratch seeding (Figure 3.19) is as followed:

1. Place the substrate on the seeding stage.

 Connect the seeding stage to a pump and turn on the power. The vacuum sucks the substrate and keeps the substrate from moving.

3. Quickly clean the surface with acetone and methanol by Kim WipeTM.

4. Put some Amplex (0.25 µm crystal sized) micron diamond powder onto the substrate surface.

If the humidity in the room is high, bake the diamond powder at 150°C for 2 hours before usage.



Figure 3.19: Prepare for scratching method

5. Use a wrapped in Kim Wipe[™] finger to polish the substrate with the combination of several different angles of straight line motion and several different diameters of circular motion in 10 minutes. Make sure the substrate surface is scratched everywhere with a median force.

6. Pick up the substrate from the seeding stage and put it in the container, with the scratched surface facing down.

7. Fill the container with acetone (enough to cover above the substrate).

- 8. Put the container in an ultrasonic bath for 30 minutes for cleaning and agitation purpose.
- 9. Take the substrate out and put it in another container with the scratched surface facing up.

Fill the container with enough methanols to cover the substrate (5 minutes).

- 10. Use Q-tip to gently wipe the substrate surface to remove any dirt or diamond powder.
- 11. Put the substrate into an open container.
- 12. Rinse the substrate with acetone and methanol for 2 minutes each step.
- 13. Rinse the substrate with de-ionized water for 10 minutes.
- 14. Blow dry with a nitrogen gun (in clean room).
- 15. Check the substrate surface cleanness under optical microscopy. If there is dirt or diamond powder left on the substrate surface, repeat step 6 through step 15.

Figure 3.20 shows the result of a mechanical scratch seeding method (under optical microscope).



Figure 3.20: Silicon wafer substrate surface after using scratch seeding method.

(Optical microscopes 50X)

3.3.1.2 Ultrasonic seeding procedure

The procedure of this method is as follows:

- 1. Clean the substrate surface by acetone and methanol.
- Put the substrate onto the substrate holder, then pre-treatment the surface by Rotter method: in the MPACVD system use diamond growth depositions condition for 30 minutes with gas mixtures Ar-H₂-CH₄ = 100:4:1 and 120 Torr pressure.
- After pre-treatment, take the substrate out of the chamber and put it into an ultrasonic bath with ultranano diamond powder liquid (30 minutes).
- 4. Rinse the substrate with de-ionized water for 10 minutes.
- 5. Blow driy with a nitrogen gun (in clean room).

Figure 3.21 shows the result of a Ruttler and Ultrasonic seeding method



Figure 3.21: Substrate surface after using Ruttler and Ultrasonic method.

(Optical microscopes 50X).

3.3.2. Experimental Set-up

- 1. Clean the inside the quartz dome and process chamber using acetone.
- 2. Load the substrate sample (with seeding) into the process chamber.
- 3. Set up the mirror or thermocouple below the substrate (in the center).
- 4. Close the chamber window.
- 5. Pump down the pressure in the process chamber (usually for 3 or more hours)

3.3.3 Start up and shut down procedure

a. Start up procedure:

After the system is pumped down as low in pressure as possible then start to run experiment as follow:

- Turn on the water to microwave power supply.
- Turn on the microwave power supply. The power level control knob should be zero.
- Turn on the Neslab chiller and set the temperature at 18°C.
- Turn on the gas tank valves.
- Turn on the gas inlet valve.
- Set the gas flow for each channel of the 4-channel read out MKS 247C. Switch to automatic mode.
- Set the experimental running time, pressure, and gas flows for each channel in each run state of the CVD control software.
- Adjust the cavity length to 21.5 cm by moving the sliding short position.
- Open the roughing valve. Now the chamber pressure is controlled by the automatic throttle valve.
- Enable the microwave power supply when the system pressure reaches 5 Torr.
- Turn on the cooling fan.
- Slowly increase the input microwave power as pressure increases such that the plasma discharge covers the entire substrate surface (Look through the viewing window with safety glass).
- Fine tune the cavity length, L_s, to obtain the minimum reflected power.

• The experiment starts to run by itself as control by computer.

b. Shut down procedure:

When the experiment is completed, the system will perform the shut down procedure as follows.

- Turn off the microwave power
- Turn off the gas flow channel (set the key back to manual mode)
- Turn off the computer program
- Turn of the gas inlet valve
- Turn off the gas tank valves
- Turn off the chiller
- Turn off the air blower motor
- Open the knob of chamber window before using nitrogen to bring the chamber pressure up to atmosphere.
- Open the chamber window and unload the sample.

Chapter 4: Experimental Results

4.1 Introduction

This chapter describes the experimental results for nanocrystalline diamond synthesis from a microwave plasma assisted CVD system. The substrate material used for each experiment was Silicon 3" wafers (100) Boron doped (P Type); the wafer thickness was from 331 to 431 μ m. The gas inputs were H₂, N₂, Ar, He and CH₄. The cooling temperature of Chiller was usually control at 18 ^oC. The applicator height is L_s = 21.5cm.

4.2 Nano-crystalline diamond films growth by H₂/Ar/CH₄ gas mixtures

This section presents the results of MPACVD diamond growth experiments using $H_2/Ar/CH_4$ gas mixtures.

4.2.1 Film Morphology

Figure 4.1 (a), (b), and (c) displays the surface morphology of diamond films with hydrogen varied from 1 to 4 sccm (AFM microscope). Figure 4.1 (d), (e) and (f) shows the surface roughness increases with hydrogen flow rate. From Figure 4.1 (d), the average surface roughness (RMS) is 12.4 nm for a hydrogen flow rate of 1 sccm. When the hydrogen flow rate is increased to 4 sccm, the surface becomes roughly with an RMS of 19.6 nm (Figure 4.1 f). Figure 4.1 (g) shows the relation between surface roughness

and hydrogen flow rate. The surface roughness also increased with hydrogen flow rate at a higher pressure of 160 Torr as shown in Figure 4.1 (g).



Figure 4.1 a: Film Morphology (AFM)

Pressure =120 Torr, gas mixtures Ar:CH4:H2 =100:1:1sccm , deposition time = 8 hrs



diamondcoating_4_12_2004.000



Pressure =120 Torr, gas mixtures Ar:CH4:H2 = 100:1:2sccm, deposition time = 8 hrs



coating_03_08_2004.022



Pressure =120 Torr, gas mixtures Ar:CH4:H2 = 100:1:4sccm, deposition time = 8 hrs



Figure 4.1 d: Surface Roughness (AFM)

Pressure =120 Torr, gas mixtures Ar:CH4:H2 = 100:1:1sccm, deposition time = 8 hrs



Figure 4.1 e: Surface Roughness (AFM)

Pressure =120 Torr, gas mixtures Ar:CH4:H2 = 100:1:2sccm, deposition time = 8 hrs



Figure 4.1 f: Surface Roughness (AFM)

Pressure =120 Torr, gas mixtures Ar:CH4:H2 = 100:1:4sccm, deposition time = 8 hrs

Surface Roughness vs Hydrogen



Figure 4.1 g: Surface Roughness vs Hydrogen Flow Rate

Ar:H₂: CH₄ = 100:1-4:1 sccm

Figure 4.1 (h) shows the surface roughness versus thickness of UNCD film. The surface roughness is rougher as UNCD film get thicker.



Surface Roughness vs Thickness

Figure 4.1 h: Surface Roughness vs Film Thickness

 $Ar:H_2:CH_4 = 100:4:1-2$ sccm

4.2.2 Film Growth Rates

The growth rate varies depending on input factors like pressure, gas mixture and temperature. Figure 4.2 (a) shows the growth rate versus pressure. The growth rate increases with pressure and hydrogen flow rate. Figure 4.2 (b) shows the growth rate versus methane flow rate. The growth rate increases up to 1.06 μ m/h at a methane flow rate of 2 sccm. In the case of substrate temperature, there are also correlations with growth rate. Figure 4.2 (c) shows the growth rate increase with substrate temperature.



Growth Rate vs. Pressure

Figure 4.2 a: Growth Rate vs Pressure

 $Ar:CH_4:H_2 = 100:1:1-4$ sccm



Growth Rate vs Methane

Figure 4.2 b: Growth Rate vs Methane Flow Rate

 $Ar:CH_4:H_2 = 100: 1-2: 4 \text{ sccm}, 160 \text{ Torr}$



Growth Rate vs Substrate Temperature

Figure 4.2 c: Growth Rate vs Substrate Temperature

 $Ar:CH_4:H_2 = 100:1-2:1-4$ sccm

4.2.3 Thin and Thick UNCD film

This section describes the results of thin and thick diamond films. Diamond films of various thicknesses from 58 nm to 72.3 μ m were deposited. When the diamond films are less than 50 nm thick, the film surface is discontinuous (figure 4.3 a). Figure 4.3 (b) and (c) show two thin diamond films, with thickness 58 and 61.2 nm respectively. In figure

4.3 (d) and (e) the two thick diamond films with thicknesses 56 and 72.3 μ m are displayed. These two thick films retain small grain sizes on the surface. The surface roughness (RMS) is 50.46 and 60.88 nm respectively.



Figure 4.3 a: Thin Film Morphology (less than 50 nm)

Ar:CH₄:H₂ = 100:1:1 sccm , deposition time: 75 minute.



Figure 4.3 b: Thin Film Morphology (58 nm)

 $Ar:CH_4:H_2 = 100:1:1$ sccm, deposition time: 1 hour.



Figure 4.3 c: Thin Film Morphology (61.2 nm)

 $Ar:CH_4:H_2 = 100:1:1$ sccm , deposition time: 1.25 hours.



Figure 4.3 d: Thick Film Morphology (56 μ m)

 $Ar:CH_4:H_2 = 100:1.5:4$ sccm , deposition time: 52 hours.



Figure 4.3 e: Thick Film Morphology (72.3 μ m) Ar:CH₄:H₂ = 100:2:4 sccm , deposition time: 65 hours

Figure 4.3 (f) and 4.3 (g) show the surface thin and thick films measured with an AFM microscope. The roughness of the surface for the thin film is RMS = 12.12 nm and thick film is RMS = 60.88 nm. In the case of the thick diamond film, the surface roughness on the back side (after silicon substrate is removed) is a very smooth RMS = 11.8 nm as compared with front side is RMS = 50.46 nm for the film thickness 56 μ m (as show in figure 4.3 (h) and 4.3 (k)).



Figure 4.3 f: Thin Film Morphology AFM (58 nm)

Ar:CH₄:H₂ = 100:1:1 sccm , **RMS = 12.12 nm.**



Figure 4.3 g: Thick Film Morphology AFM (72.3 μ m) Ar:CH₄:H₂ = 100:2:4 sccm , **RMS = 60.88 nm.**



Figure 4.3 h: Thick Film Morphology in the back side AFM (56 µm)

Ar:CH₄:H₂ = 100:1.5:4 sccm , RMS = 11.8 nm.



Figure 4.3 k: Thick Film Morphology AFM (56 µm)

Ar:CH₄:H₂ = 100:1.5:4 sccm , RMS = 50.46 nm.



Figure 4.3 m: The UNCD thick film 72.3 µm (SEM image)

Figure 4.3 m shows the thick UNCD film (SEM image). The method to measure the thickness of this UNCD film based on weight gain with density of 3.51 g/cm³ gave an average thickness of the film as 72.3 µm. In the Figure 4.3 m, the thickness is 88 µm.

4.2.4 Young's Modulus of UNCD Films

Young's modulus is the stress of a material divided by its strain. It is a measure of material's strength. The Young's modulus of nanocrystalline diamond film is measured by LAwave instrument (Figure 4.4). The LAwave instrument introduces a sound wave into the sample's surface to measure the materials phase velocity dispersion curve. The built-in matching algorithm determines Young's Modulus of the film.

LAwave device includes a nitrogen-pulse laser, a digital oscilloscope, an micrometer translation stage, an ultrasonic signal transducer and computer. The system directs a laser beam onto a component for half a billionth of a second, causing the surface to vibrate. The form and duration of the wave pattern from the vibration is recorded and evaluated within seconds by an algorithm. The laser acoustic signals can be received at varying distances between the detector and source.



Figure 4.4: Fraunhofer's LAwave Instrument

Table 4.1 shows the Young's modulus of nanocystalline diamond films measured by LAwave device.
Substrate (Si wafer)				Film (diamond)			
C11	C12	C44	D (g/cm3)	Y. (GPa)	Poisson's	D (g/cm3)	h (um)
177.9	63.5	79.6	2.33	617.013	0.09	3.218	2.97
177.8	63.5	79.6	2.33	617.677	0.09	3.219	2.97
178.4	63.5	79.6	2.33	602.234	0.09	3.191	2.97
177.81	63.5	79.6	2.33	611.519	0.09	3.202	2.97
176.65	63.5	79.6	2.33	647.897	0.09	3.267	2.97
180.9	63.5	79.6	2.33	576.177	0.09	3.17	2.97
179.6	63.5	79.6	2.33	588.699	0.09	3.184	2.97
178.4				608.745		3.207	
156.3	63.5	79.6	2.33	864.349	0.09	3.52	1.05
156.5	63.5	79.6	2.33	861.879	0.09	3.52	1.05
156.8	63.5	79.6	2.33	868.748	0.09	3.52	1.05
156.5				864.992		3.52	
169.4	63.5	79.6	2.33	692.084	0.09	3.458	1.42
169.0	63.5	79.6	2.33	708.238	0.09	3.496	1.42
167.9	63.5	79.6	2.33	717.84	0.09	3.486	1.42
167.5	63.5	79.6	2.33	723.853	0.09	3.491	1.42
168.5				710.503		3.48275	

Table 4.1: Young's modulus results of UNCD film

The Young's modulus of UNCD growth with $Ar:CH_4:H_2$ measured range from 608 GPa to 864 GPa.

4.3 Nano-crystalline diamond film deposition from H₂/He/CH₄ gas mixtures

This section describes the results of nano-crystalline diamond film growth by MPACVD system using $H_2/He/CH_4$ gas mixtures. The resulting films were characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

4.3.1 Film Morphology

Figures 4.5 (a), (b) and (c) display the film surface morphology for different hydrogen flow rate, with the helium flow fixed at 100 sccm, methane flow fixed at 1 sccm and pressure at 120 Torr. The grain boundaries of crystal diamond become larger on the surface when the hydrogen percent in the mixture increases. This makes the surface rougher as the grain size becomes larger.



200 nm



Pressure =120 Torr, gas mixtures He:CH4:H2 = 100:1:1 sccm, deposition time = 8 hrs



200 nm



Pressure =120 Torr, gas mixtures He:CH4:H2 % = 100:1:2%, deposition time = 8 hrs

As see in figure 4.5 (a), (b) and c, films grown with helium replacing argon are consistent with the grain size expected for nano-crystalline diamond (less than 50 nm).



200 nm



Pressure =120 Torr, gas mixtures He:CH4:H2 sccm = 100:1:4%, deposition time = 8 hrs

Figures 4.5 (d), (e) and (f) show the surface morphology of diamond films measured using an AFM microscope. Figure 4.3.1 d displays the surface morphology of the diamond film when the hydrogen flow rate is 1 sccm. Figure 4.5 (e) and 4.5 (f) show the surface morphology of diamond films with 2 sccm and 4 sccm respectively.



d1amond_08_26_05.006

Figure 4.5 d: Surface Morphology (AFM Image)

Pressure =120 Torr, gas mixtures He:CH₄:H₂ % = 100:1:1%



diamond_08_26_05.007

Figure 4.5 e: Surface Morphology (AFM Image)

Pressure =120 Torr, gas mixtures He:CH₄:H₂ % = 100:1:2%



diamond_08_26_05.005

Figure 4.5 f: Surface morphology (AFM Image) Pressure =120 Torr, gas mixtures He:CH4:H2 % = 100:1:4%

Figures 4.6 (a), (b) and (c) show the surface roughness versus hydrogen flow rate with helium 100 sccm, methane 1 sccm and pressure 120 Torr. In figure 4.6 (a), the RMS surface roughness is 10.5 nm (1% hydrogen flow rate). The film is very smooth. When the hydrogen flow rate increases to 2%, the RMS surface roughness is 19.8 nm in figure 4.6 (b). The RMS surface roughness increases very fast to 49.8 nm with 4% hydrogen in figure 4.6 (c).



4.6 a: Film Surface Roughness (AFM image)



Pressure =120 Torr, gas mixtures He:CH4:H2 = 100:1:1 sccm



Pressure =120 Torr, gas mixtures He:CH4:H2 = 100:1:2 sccm



Figure 4.6 c: Film Surface Roughness vs % Hydrogen (AFM Image)

Pressure =120 Torr, gas mixtures He:CH4:H2 % = 100:1:4%

Figure 4.6 (d) shows the surface roughness versus hydrogen flow rate in case of He:CH₄:H₂ gas mixtures. When the hydrogen flow rate is increased, the surface roughness increases.

Surface roughness vs Hydrogen



Figure 4.6 d: Film Surface Roughness vs Hydrogen Flow Rate

Pressure =120 Torr, gas mixtures He:CH₄:H₂ = 100:1:1-4 sccm, deposition time = 8 hrs

4.3.2 Film Growth Rates

This section presents the relationship between growth rate and various input variables including hydrogen flow rate, temperature and pressure. Figure 4.7 (a) displays the growth rate versus hydrogen flow rate. The growth rate increases when the hydrogen flow rate is increased (The results are comparable with those of Ar-CH₄-H₂ gas mixtures). Figure 4.7 (b) shows the relation between growth rates versus temperature. Figure 4.7 (c) shows the growth rate versus pressure.

Growth Rate vs Hydrogen



Figure 4.7 a: Film Growth Rate vs Hydrogen

Pressure =120 Torr, gas mixtures He:CH₄:H₂ = 100:1:1-4 sccm

Growth Rate vs Temperature



Figure 4.7 b: Film Growth Rate vs Temperature

He:CH₄:H₂ = 50:3:50 sccm



Figure 4.7 c: Film Growth Rate vs Pressure

He:CH₄:H₂ = 50:3:50 sccm

The Young's modulus of UNCD growth with He: CH_4 : H_2 measured in the range from 636 GPa to 850 GPa.

4.4 Nano-crystalline diamond film deposition from N₂/Ar/CH₄ gas mixtures

This section describes the results of growing nanocrystalline conducting diamond films using nitrogen in the gas mixture. The substrate temperature ranges from 400 0 C to 635 0 C for these experiments.

4.4.1 Film morphology

Figure 4.8 a, displays the surface morphology for a conducting diamond film with a nitrogen flow rate of 1 sccm. Figures 4.8 (b) and (c) display the surface morphology for conducting films with nitrogen flow rates of 2 sccm and 10 sccm.



200 nm



Pressure = 100 Torr, gas mixtures Ar:CH₄:N₂ = 100:1:1 sccm



200 nm



Pressure = 100 Torr, gas mixtures Ar:CH₄:N₂ = 100:1:2 sccm



200 nm



Pressure = 100 Torr, gas mixtures Ar:CH₄:N₂ = 100:1:10 sccm

The surface roughness of conducting diamond films versus nitrogen flow rate was investigated. Figures 4.9 (a), (b), (c) and (d) show the surface roughness of conducting diamond films grown with nitrogen flow rates of 1, 2, 10 and 20 sccm. With 1 sccm nitrogen flow rate, the surface is very smooth (RMS = 12.6 nm). The surface roughness is seen to increase with nitrogen flow rate. When the nitrogen flow rate is 20 sccm, the surface roughness is 88 nm.



diamond_08_26_05.002



Pressure =100 Torr, gas mixtures Ar:CH₄:N₂ = 100:1:1 sccm, RMS = 12.65 nm



diamond_08_26_05.003

Figure 4.9 b: Film Surface Roughness (AFM Image)

Pressure =100 Torr, gas mixtures Ar:CH₄:N₂ = 100:1:2 sccm, RMS = 17 nm



tran_08_11_05.003



Pressure =100 Torr, gas mixtures Ar:CH₄:N₂ = 100:1:10 sccm, RMS = 37.35 nm



tran_08_11_05.000



Pressure =100 Torr, gas mixtures Ar:CH₄:N₂ = 100:1:20 sccm , RMS = 88 nm

Figure 4.9 (e) displays the surface roughness versus nitrogen flow rate. With more nitrogen flow rate in the gas mixtures, the surface roughness increases as seen in the diagram below.



Surface Roughness vs Nitrogen

Figure 4.9 e: Surface Roughness vs Nitrogen Flow Rate

Pressure 100 Torr, Ar:CH₄:N₂ = 100:1:1-20 sccm

4.4.2 Film Growth Rate

This section describes the growth rate versus nitrogen flow rate. The growth rate increases when nitrogen flow rate is higher (Figure 4.10).





Figure 4.10: Film Growth Rate vs Nitrogen Flow Rate

 $Ar:CH_4:N_2 = 100:1:1-20$ sccm

4.4.3 Film Conductivity

The electrical conductivity of diamond film is investigated in this section. The conductivity of nanocrystalline diamond films were measured by four point probes device. Figure 4.11 show the schematic of four point probe device. The resistivity (ρ) of the films determined by formula:

$$\rho = k (V/I) t$$

t: Thickness of the films

V: Voltage (V)

I: Current (A)

k: Constant (depend on the shape of the films)



Figure 4.11: Schematic of four point probe

Figure 4.12 shows the conductivity versus nitrogen flow rate. The conducting of the diamond films increase as the nitrogen flow rate input increased.





Figure 4.12: Conductivity vs Nitrogen Flow Rate Pressure 100 Torr, Ar:CH₄:N₂ = 100:1:1-20 sccm

Figure 4.13 shows the substrate temperature versus nitrogen flow rate. When increasing the nitrogen flow rate, the substrate temperature is increased.

Substrate temperature vs Nitrogen flow



Figure 4.13: Substrate temperature vs Nitrogen Flow Rate

Pressure 100 Torr, Ar:CH₄:N₂ = 100:1:1-20 sccm

The Young Modulus of conducting diamond film is varies from 545 GPa to 891 GPa.

Chapter 5: UNCD Film Applications

5.1 Introduction

This chapter describes the applications of nano-crystalline diamond films. Nanocrystalline diamond captures many of the best properties of natural diamond in thin film form. It is currently being evaluated for a wide variety of applications based on its super properties. Some of the applications of nano-crystalline diamond film include a hard coating material, a material/substrate for micromechanical systems, a surface acoustic wave (SAW) device substrate [Bi 2002], a robust conducting coating for electrochemical electrodes, and a freestanding film for vacuum windows or ion beam stripping foils (Figure 5.1).



Figure 5.1: UNCD freestanding film (Photograph provided by Dr. Reinhard)

Diamond can be doped from an insulator to a semiconductor, giving it the potential to be used in many electronic devices such as piezoelectric effect devices, radiation detectors, field effect transistors, field emission displays, and UV photo-detectors. Defects and surface roughness issues still need to be addressed before diamond electronic devices can be widely used. The surface acoustic wave (SAW) device is one type of electronic device which can use impure, thin UNCD diamond, known as the SAW filter.

The field emission display device is based on the electron emission properties of polycrystalline diamond. It consumes very low power levels, and employs the idea of using UNCD film as an electron emitter in flat-panel displays.

Generally, nano-crystalline diamond, with a smooth surface, is a suitable material for many applications. In this chapter, three applications of nano-crystalline diamond are briefly explored: (1) Surface acoustic wave (SAW) device based on UNCD, (2) Ultra high frequency micromechanical resonators and (3) UNCD coatings for atomic force microscope tips.

5.2 UNCD surface acoustic wave (SAW) devices

Surface acoustic wave (SAW) devices are critical components of many modern digital microwave and optical telecommunications systems. These devices perform complex signal processing functions through electro acoustic interactions in materials. Use of these devices reduces part counts in cellular telephones and other complex

communications systems, making these systems increasingly portable, powerful, and affordable.

Nano-crystalline diamond films are a good candidate in SAW applications because SAW devices require a smooth surface. Smooth surfaces reduce the propagation loss and ensure the correct generation and propagation of the surface acoustic wave. With micro crystalline diamond films, polishing to achieve a smooth diamond surface is very difficult, especially in large wafers. Therefore, nano-crystalline is a favored material for the SAW device application.

SAW devices, used in satellite communication or optical communication, require a high frequency filter (greater than 2.5 GHz) [Nakahata 1992]. As digital communications move to higher frequencies for more bandwidth, conventional SAW devices require more difficult and expensive lithography. Due to the smaller feature size required, diamond has the highest known speed of sound and other unique desirable acoustic properties, SAW devices, built on CVD diamond, provide operation at extremely high frequencies using existing low-cost lithography. Since diamond is not a piezoelectric material, diamond SAW filter requires a multilayer structure. Diamond must be incorporated with other piezoelectric materials like ZnO. Table 5.1 gives the comparison between a diamond SAW filter and other materials. Research on diamond SAW devices, carried out by Nakahata, is concluded that when diamond was combined with a piezoelectric thin film, the SAW velocities elevated to as high as 12000 m/sec [Nakahata 1995].

Material	Sound velocity	Frequency (GHz)	Feature size for
	(m/s)		2.5 GHz filter (µm)
LiNb O ₂	3500	0.9	0.35
Quartz	3200	0.8	0.32
ZnO/Sapphire	5500	1.4	0.55
ZnO/Diamond	10000	2.5	1.0

Table 5.1: Characteristics of SAW filter comparisons (Fujimori 1998)

SAW devices are most typically implemented on piezoelectric substrates (quartz, lithium niobate) on which thin metal film inter-digitated transducers (IDT) are fabricated using photolithography. With a surface wave velocity 1×10^4 m s⁻¹, diamond allows SAW device operation near 2.5 GHz (Bi 2002). Figure 5.2 shows the structure of a SAW device.



Figure 5.2: Structure of a surface acoustic wave (SAW) device (Bi 2002)

For application such as SAW device processes to grow thick nanocrystalline diamond film with thickness up to 56 μ m and surface smoothness of 50 nm were achieved in this investigation as described earlier in section 4.2.3.

5.3 Ultra high frequency micro-electro-mechanical (UHF-MEMS) resonators

Micro-Electro-Mechanical Systems (MEMS) are the integration of mechanical elements, sensors, actuators, and electronics on a common silicon substrate through micro-fabrication technology. While the electronics are fabricated using integrated circuit (IC) process sequences (e.g., CMOS, Bipolar, or BICMOS processes), the micromechanical components are fabricated using compatible "micro-machining" processes that selectively etch away parts of the silicon wafer or add new structural layers to form the mechanical and electromechanical devices.

MEMS promises to revolutionize many product categories by bringing together microelectronics with micro-machining technology, making possible the realization of complete systems-on-a-chip. MEMSis an enabling technology that allows the development of smart products. By augmenting of the computational ability of microelectronics with the perception and control capabilities of micro-sensors and microactuators, an expansion of the space of possible designs and applications occurs.

UNCD film is the most desirable material for many MEMS applications. The ultra high frequency mechanical (UHF MEMS) resonator device is one of them. The resonance

frequency is generally proportional to acoustic velocity, which is proportional to the square root of Young's modulus to density ratio. UNCD film provides the largest boost towards even higher resonance frequencies.



Figure 5.3: Structure of ultra high frequency MEMS device [Wang 2002].

Figure 5.3 shows the structure of an ultra high frequency MEMS device [Wang 2002]. A nano-crystalline diamond micro-mechanical disk resonator with a material-mismatched stem has been demonstrated at a record frequency of 1.51 GHz with an impressive Q of 11,555 (in resonant systems, Q is a measure of the ratio of the energy stored in it to the energy lost during one cycle of operation). This is more than 7X higher than demonstrated in a previous 1.14-GHz poly-silicon disk resonator. The nanocrystalline diamond films achieved a frequency-Q product of 1.74×10^{13} that exceeds the 1×10^{13} of some of the best quartz crystals. In addition, a 1.27-GHz version with a Q exceeding 12,000 exhibits a measured motional resistance of only 100 k Ω with a dc-bias voltage of 20V, which is more than 34X lower than measured on a pure poly-silicon counterpart at

1.14 GHz. At 498 MHz, Q is up to 55,300 in vacuum and 35,550 in air have been demonstrated, both of which set frequency-Q product records at 2.75×10^{13} (vacuum) and 1.77×10^{13} (air) [Wang 2002].

The objective of this project was to grow conducting UNCD at low temperature with a useful deposition rate of greater than 0.25 μ m/hr and with a high Young's modulus. Conducting UNCD films were deposited at a substrate temperature 635 ⁰C that yielded a Young's modulus of 891 GPa. The conductivity of film was 2 (Ω .cm)⁻¹ and the growth rate was 0.4 μ m/hr.

After more than six months of research, these results for the growth nanocrystalline conducting diamond film generally meet the UHF MEMS requirements.

5.4 UNCD Tips coated

Atomic force microscopy (AFM) is a method of measuring surface topography on a scale from angstroms to 100 microns. This technique involves imaging a sample using a probe, or tip, with a radius of about 20 nm. The tip is held a several nanometers above the surface using a feedback mechanism (Figure 5.4) that measures surface-tip interactions on the scale of nano-newtons.

Variations in tip height are recorded while the tip is scanned repeatedly across the sample, producing a topographic image of the surface. In its repulsive "contact" mode, the instrument lightly touches a tip at the end of a leaf spring or "cantilever" to the

sample (Figure 5.5). As a raster-scan drags the tip (Figure 5.6) over the sample, a detection apparatus measures the vertical deflection of the cantilever, which indicates the local sample height. Thus, in contact mode the AFM measures hard-sphere repulsion forces between the tip and sample.



Figure 5.4: Atomic force microscope (Baselt 1993)



Figure 5.5: AFM cantilever is touching on the sample (Baselt 1993)



Figure 5.6: The silicon AFM Tip (Baselt 1993)

In combination with tip-sample interaction effects, the sharpness at the end of the tips generally limits the resolution of AFM. The development of sharper and harder tips is currently a major concern. UNCD film with small grain sizes (nano-scale), high hardness and smooth surfaces is an ideal material for AFM tips. The UNCD-coated tips are expected to improve the accuracy of AFM-image results as well as to preserve the spatial resolution expected from the tips remaining sharp. The diamond coating tip also is used as a tool for fabrication. It can cut metal tracers to modify the circuit in an IC chip or form gaps for further fabrication. Since the silicon tip is not hard enough, they are worn out quickly when used for cutting.

Figure 5.7 and 5.8 show a silicon AFM tip coated by UNCD film in this project. The original silicon tip was seeded by dipping the tip into a nanopowder liquid (crystal size 3-5 nm). Then the seeded silicon tip is coated with UNCD thin film for 60 to 75 minutes. The conditions to grow a UNCD thin film on AFM tip are: a gas mixture of Ar-H₂-CH₄ =100:1:1, a pressure of 120 Torr and a 2 kW microwave power.



Figure 5.7: The AFM Tips coated UNCD (SEM image)



Figure 5.8: The silicon AFM Tip coated UNCD (SEM image)

Chapter 6: Conclusions

6.1 Introduction

UNCD thin films have a great potential for many application. The techniques to grow ultra nano-crystalline diamond (UNCD) film were reported in recent years. Huang [Huang 2004] reported on the growth of ultra-nano crystalline diamond using microwave plasma assisted chemical vapor deposition system with an Ar/H₂/CH₄ gas mixture. Huang explored a large experimental parameter spaces for the synthesis of smooth ultra-nano crystalline diamond films. However, in order to utilize previous developed techniques and to explore new process techniques to grow the ultra-nano crystalline diamond film for specific applications with varied thicknesses of film, more research needed to be done.

After two years, the objectives of this thesis which were to develop the process technologies and methodologies to grow a wide range of thicknesses and conductivities of ultra-nano crystalline diamond films have been achieved. Three gas mixtures including $Ar/H_2/CH_4$, $He/H_2/CH_4$ and $Ar/N_2/CH_4$ were investigated to grow UNCD films. Thickness studies of ultra-nano crystalline films were carried out with demonstrated thicknesses from 58 nm to 72 µm. Uniform, low-stress, UNCD films were deposited over a wide pressure range (60-180 Torr) and temperature range (400-850 C). Film surface roughnesses as low as 12 nm (AFM microscope) was obtained. The highest growth rate of 1.12 µm/h was achieved at 180 Torr, $H_2/Ar/CH_4 = 4/100/2$ sccm and 3 kilowatt

power. The routine and repeatable synthesis of smooth and uniform ultra-nano crystalline diamond films have been demonstrated for applications.

6.2 Summary

6.2.1 UNCD films growth by Ar-CH₄-H₂ gas mixtures

This section summarizes the results of nano-crystalline diamond films growth with Ar-CH₄-H₂ gas mixtures.

6.2.1.1 Effect of variable inputs:

a) Hydrogen flow rate

When hydrogen flow rates is increased from 1 to 4 sccm:

- The surface roughness increased 1.5 times (120 Torr) and 2.15 times (160 Torr)
- The growth rate increased 2.11 times (120 Torr) and 2.17 times (160 Torr)
- The substrate temperatures increased from 580 °C to 625 °C (120Torr) and from 543 °C to 660 °C (160 Torr).

b) Pressure

When the pressure is increased from 60 Torr to 180 Torr:

• The growth rate increased 13.33 times (Ar-CH₄-H₂ =100-1-4 sccm) and 17.5 times (Ar-CH₄-H₂ =100-1-2 sccm)
- The substrate temperature increased from 430 $^{\circ}$ C to 600 $^{\circ}$ C (Ar-CH₄-H₂ =100-1-1 sccm) and 470 $^{\circ}$ C to 700 $^{\circ}$ C (Ar-CH₄-H₂ =100-1-4 sccm)
- Surface roughness increased 6 times (Ar-CH₄-H₂ =100-1-4 sccm)

6.2.1.2 Results of thin and thick film

Continuous UNCD films were successfully grown with thicknesses ranging from 58 nm to 72 μ m.

- The thinnest continuous film with a thickness of 58 nm was achieved using a deposition pressure of 120 Torr, a gas mixture of Ar-CH₄-H₂ =100-1-1 sccm, an incident power of 1.5 kW, and a deposition time of 1 hr.
- The thickest film with a thickness of 72.3 μm was achieved using a deposition pressure of 180 Torr, a gas mixtures of Ar-CH₄-H₂ =100-2-4 sccm, an incident power of 2.2 kW, and a deposition time of 65 hrs.

The Young's modulus of ultra-nano crystalline diamond, with $Ar-CH_4-H_2$ gas mixtures, ranged from 608 to 864 GPa.

6.2.2 UNCD film growth by He-CH₄-H₂ gas mixtures

Helium is an inert gas and it was used to replace argon for UNCD deposition. This section summarizes the results of nano-crystalline diamond films growth with He-CH₄-H₂ gas mixtures.

6.2.2.1 Effect of variable inputs:

a) Hydrogen flow rate

When the hydrogen flow rates increased from 1 to 4 sccm:

- The surface roughness increased 4.7 times (120 Torr)
- The growth rate increased 2.3 times (120 Torr)
 - b) Pressure

When the pressure increased from 60 Torr to 120 Torr:

- The growth rate increased 36 times (He-CH₄-H₂ = 30-3-30 sccm)
- The substrate temperature increased from 430 °C to 800 °C (Ar-CH₄-H₂ =30-3-30 sccm)

The Young's modulus of ultra-nano crystalline diamond grown with He-CH₄-H₂ gas mixtures range from 771 to 850 GPa.

6.2.3 UNCD film growth by Ar-CH₄-N₂ gas mixtures

This section summarizes the results of nano-crystalline conducting diamond films growth with Ar-CH₄-N₂ gas mixtures.

6.2.3.1 Effect of variable inputs:

a) Nitrogen flow rate

When nitrogen flow rate is increased from 1 to 20 sccm (100 Torr):

- The growth rate increased 2.29 times
- The conductivity increased 35.5 times
- The substrate temperature increased from 450 °C to 650 °C
 - b) Pressure

When the pressure increased from 60 Torr to 120 Torr:

- The growth rate increased 2.8 times (Ar-CH₄-N₂ =100-1-1 sccm)
- The substrate temperature increased from 450 °C to 600 °C (Ar-CH₄-N₂ =100-1-4 sccm)

The Young's modulus for conducting UNCD film was measured to be 891GPa with the substrate deposition temperature at 635 ⁰C.

6.3 Discussion

This section gives some recommendations for future research. There still are some issues for growing UNCD using the MPACVD system that need to be investigated beyond this thesis such as:

(1) Growth Rate:

The maximum deposition rate achieved onto 3 inch silicon wafers was 1.12 μ m/h (180 Torr, Ar-CH₄-H₂ =100-2-4). With these results, the process costs are still too

high for some commercial applications of UNCD films using the Microwave Plasma Assisted CVD system. In the future, more research needs to be done to improve the growth rate of UNCD by modified the cavity, cooling system, substrate heater, and nucleation treatment method.

(2) <u>Thin film</u>:

The thinnest continuous UNCD film achieved in this research was 58 nm. More research needs to be invested for improve or enhance nucleation on the substrate surface to get even the thinner UNCD films.

(3) Growth diamond film at low temperature substrate conditions (below $400 \,^{\circ}C$):

Lower the substrate temperate decreases the growth rate for UNCD deposition. There are many applications for diamond coating where the substrate material must remain at or below 400 ⁰C. Improving the deposition rate at low substrate temperature is remaining an important direction for further investigation.

Appendix

Ar/H ₂ /CH ₄	Thickness	Time	Pressure	P _{abs}	Ts	Ls	RMS
(sccm)	(µm)	(hr)	(torr)	(watt)	(⁰ C)	(cm)	(nm)
100-1-1	0.058	0.75	120	1733	500	21.5	12.12
100-1-1	0.068	1.0	120	1793	506	21.5	
100-1-1	0.088	1.5	120	1899	515	21.5	
100-1-1	0.153	2	120	1701	510	21.5	
100-1-1	0.292	2.5	120	1760	520	21.5	12.36
100-1-1	0.153	16	60	1034	470	21.5	
100-2-1	0.178	3	120	1880	505	20.5	
100-1-1	0.181	4	160	1240	575	21.5	
100-4-1	0.215	8	120	1161	565	21.5	
100-4-1	0.275	8	120	1045	560	21.5	
100-1-1	0.318	4	160	1400	570	21.5	13.97
100-1-1	0.374	8	80	994	485	21.5	
100-2-1	0.418	4	120	1226	525	21.5	
100-2-1	0.470	4	120	1740	550	21	
100-4-1	0.524	4	120	1161	535	21.5	
100-2-1	0.563	4	120	1766	540	21	
100-2-1	0.849	8	120	1119	545	21.5	
100-2-1	0.854	8.	120	1326	560	21.5	12.90
100-1-1	0.912	8	160	1730	595	21.5	
100-2-1	0.943	8	160	1680	585	21.5	14.11
100-2-1	0.996	8	160	1941	613	21.5	15.08
100-1-1	1.068	8	120	1393	550	21.5	12.40
100-4-1	1.190	8	120	1361	555	21.5	19.60
100-2-1	1.212	8	120	1394	550	21.5	13.2

TABLE A.1: Experiment data for Ar/H₂/CH₄

100-2-1	1.237	8	160	1643	600	21.5	15.59
100-2-1	1.262	8	120	1295	550	21.5	13.7
100-2-1	1.284	8	160	1641	620	21.5	
100-2-1	1.425	16	100	1075	490	21.5	
100-2-1	1.768	8	160	1523	590	21.5	18.88
100-0-1	1.780	16	100	919	450	21	
100-4-1.6	2.580	24	160	1650	660	21.5	
100-2-1	2.855	8	160	1550	605	21.5	
100-2-1	2.950	8	160	1700	647	21.5	
100-4-1	2.980	8	160	1992	660	21	
100-2-1	3.042	8	160	1520	600	21.5	16.65
100-4-1	3.133	8	180	1987	705	21.5	
100-1-1	3.517	15	160	1560	580	21.5	
100-1-1	3.767	22	160	1760	623	21	
100-2-1	4.023	12	160	1550	572	21.5	
100-1-1	4.479	16	160	1700	585	21.5	· · · · · · · · · · · · · · · · · · ·
100-2-1	4.637	15	160	1800	615	21	
100-2-1	4.967	24	160	1740	620	21.5	
100-1-1.2	5.022	24	160	1650	610	21	
100-4-1	7.078	30	120	1556	560	21.5	33.5
100-1-1	7.550	22	160	1900	613	20.5	
100-2-1	7.600	20	160	1600	622	21	
100-4-1.4	8.962	12	160	2054	662	21.5	
100-2-1.4	9.200	24	160	1894	636	21.5	
100-4-1.4	10.70	12	160	1990	708	21	
100-4-1.4	16.8	24	160	1870	652	21.5	
100-2-1.5	17.08	30	140	2114	675	21	
100-4-1.5	17.57	25	160	2090	664	21.5	38.35
100-2-1	17.8	50	160	1835	626	20.5	
100-2-1	19.58	50	160	1990	624	20.5	

100-2-1.5	20.7	24	160	1820	685	21	
100-2-1	22.62	60	160	1854	623	20.5	
100-4-2	26.07	25	160	1970	690	20.5	44.52
100-4-2	26.47	25	160	2030	694	21.5	
100-4-1.4	33.70	48	160	1913	684	21	
100-4-1.5	45.10	48	160	1892	690	21	
100-4-1.4	50.46	65	160	1990	661	21.5	
100-4-1.4	50.87	55	160	1976	679	21.5	
100-4-1.5	56.0	52	160	2013	721	21	50.47
100-4-2	72.3	65	180	1979	740	21	60.88
100-4-2	77.74	70	180	1856	740	21	

 T_S : The temperature measured at center of substrate.

He/H ₂ /CH ₄ (sccm)	Thickness (µm)	Time (hr)	Pressure (torr)	P _{abs} (watt)	T _s (⁰ C)	L _s (cm)	RMS (nm)
100-1-1	0.050	1	120	1751	613	21.5	
100-1-1	0.058	3	120	1830	625	21.5	
100-1-1	0.146	2	120	1621	630	21	
30-30-2.25	0.148	3	30	1105	580	21.5	
100-1-1	0.290	4	120	2110	678	21.5	
30-30-2.25	0.397	3	40	1250	607	21.5	
30-30-2.25	0.484	6	30	1480	595	20.5	
30-30-2.25	0.564	65	10	825	430	21.5	
100-1-1	0.615	8	120	1717	630	21.5	10.57
100-2-1	0.837	8	120	1060	634	21.5	19.8
30-30-2.25	1.01	6	40	1350	641	20.5	
100-4-1	1.837	8	120	1940	685	20.5	49.8

TABLE A.2: Experiment data for He/H₂/CH₄

30-30-2.25	1.96	6	120	1180	800	21.5	
100-4-2	12.37	36	140	1777	850	21.5	
30-30-2.25	13.22	72	60	1540	705	20.5	

Ar/N ₂ /CH ₄	Thickness	Time	Pressure	P _{abs}	T _s	Ls	RMS
(sccm)	(μm)	(hr)	(torr)	(watt)	(⁰ C)	(cm)	(nm)
100-2-1	0.087	3	160	1880	645	21.5	
100-1-1	0.49	22	50	1113	400	21.5	
100-2-1	0.7	8	100	1070	465	21.5	17.0
100-1-1	0.8	22	60	1325	425	21.5	20.79
100-10-1	1.28	8	100	1698	640	21.5	37.35
100-1-1	1.58	12	100	1776	545	21.5	12.65
100-10-1.5	2.45	6	100	1435	635	21.5	13.49
100-5-1	2.49	20	100	1690	585	21.5	20.8
100-20-1	3.1	16	100	1430	630	21.5	88.0
100-2-1	3.49	84	60	970	413	21.5	
100-2-1.5	4.2	30	120	1650	560	21.5	

TABLE A.3: Experiment data for Ar/N₂/CH₄

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