Diamond Based-Materials: Synthesis, Characterization and Applications

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Diamond Based-Materials: Synthesis, Characterization and Applications

by

Qiang Hu

A dissertation submitted in partial fulfillment
of the requirements for the degree of
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DEDICATION

This dissertation is dedicated to those who keep on learning new knowledge, challenging and improving themselves in their lives.

Learning is like the sea without any horizon
ACKNOWLEDGMENTS

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ABSTRACT

The studies covered in this dissertation concentrate on the various forms of diamond films synthesized by chemical vapor deposition (CVD) method, including microwave CVD and hot filament CVD. According to crystallinity and grain size, a variety of diamond forms primarily including microcrystalline (most commonly referred to as polycrystalline) and nanocrystalline diamond films, diamond-like carbon (DLC) films were successfully synthesized. The as-grown diamond films were optimized by changing deposition pressure, volume of reactant gas hydrogen (H₂) and carrier gas argon (Ar) in order to get high-quality diamond films with a smooth surface, low roughness, preferred growth orientation and high sp³ bonding contents, etc. The characterization of diamond films was carried out by metrological and analytical techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM) and Raman spectroscopy. The results of characterization served as feedback to optimize experimental parameters, so as to improve the quality of diamond films. A good understanding of the diamond film properties such as mechanical, electrical, optical and biological properties, which are determined by the qualities of diamond films, is required for the selection of diamond films for different applications. The nanocrystalline diamond nanowires grown by a combination of vapor-liquid-solid (VLS) method and CVD method in two stages, and the graphene grown on silicon substrate with nickel catalytic thin film by single CVD method were also investigated in a touch-on level.
Microwave plasma enhanced chemical vapor deposition (MPECVD) polycrystalline diamond films were deposited with mixed gas CH₄ and H₂ at flow rate ratio 1:100 by changing the H₂ volume from 100sccm to 3000sccm. SEM micrographs revealed that the samples of 100sccm and 500sccm H₂ had agglomerates of a cauliflower-like surface, whereas samples with 1000sccm to 3000sccm H₂ had a faceted surface; the size of the faceted crystallites ranged from 200nm to 1500nm. Raman spectra indicated that the samples of 100sccm H₂ contain a certain amount of graphitic phase, whereas samples of more than 1000sccm H₂ had a concentration of crystalline diamond. The XRD patterns highly exhibited the crystallinity of deposited diamond with largely (111) and (220) plane; (220) plane accounted for three times more than (111) plane in the whole deposited surface.

MPECVD nanocrystalline diamond films displayed a nano peak at 1140cm⁻¹ in the Raman spectrum, and showed 100nm global particles on the surface in SEM images, presented (111) and (220) planes with a low ratio of 1:2 in the XRD pattern. Three-dimensional AFM images provided consistent grain size with that of the SEM images, and 94nm average roughness in the 10μm×10μm scan area.

Diamond-like carbon (DLC) did not exhibit any sharp peaks in the Raman spectrum, and only showed broad bumps in the position of D band and G band, illustrating that there was no crystalline structure formed on the surface. SEM disclosed a rough surface with scattered particles embedded in the tiny boundary-like ditches.

The morphologies of nanocrystalline diamond films changed from scattered global particles to texture with the Ar flow rate varying from 170sccm to 200sccm under 120HPa constant pressure. XRD pattern displayed similar height of (111) and (220)
plane. In another condition, keeping the Ar flow rate at 180 sccm constantly, a sample of 110HPa pressure presented a smoother surface, and the (111) plane was the primary structure of surface with the (220) plane dematerialized and a (311) plane generated.

Nitrogen-doped nanocrystalline diamond films, with 5%, 10%, 15% N₂ flow rate variation, were investigated, and it turned out with the increase of N₂, the nano peak in the Raman spectra dematerialized, the XRD pattern revealed that the (111) peak became the major component rather than the (220) peak; a sample of only 10% N₂ displayed texture structure.

15% N₂ doped nanocrystalline diamond films grown on SiO₂ demonstrated a smooth surface, high growth rate, and high (111) peak, indicating the SiO₂ layer changed the surface electron density and, therefore, changed the quality of the diamond film.

The surface residual stress evaluated by the Raman shift showed that HFCVD polycrystalline diamond film had tensile stress at the corner and compressive stress in the center, whereas MPECVD polycrystalline diamond film had compressive stress on the whole surface. The roughness of MPECVD was higher than that of HFCVD.

A capacitive micromachined ultrasonic transducer (CMUT) with a diamond membrane was successfully fabricated by overcoming the challenges such as diamond window etching, two-stage diamond depositing, and vacuumed cavity formation.
CHAPTER 1:
INTRODUCTION TO CVD DIAMOND

1.1 Overview of CVD Diamond

Electronic semiconductors are believed to have been experienced in three generations since the 20th century. Silicon is considered the first-generation semiconductor, which changes the world by the role it plays in modern life such as computer chips, data storage hard drives, cell phones, music players, communication devices and so on. The second-generation semiconductors are believed to be gallium arsenide (GaAs) and indium phosphide (InP), which contribute to the revolution of wireless and information communication, and are especially important in military applications. The third-generation semiconductors such as silicon carbide (SiC) and gallium nitride (GaN) are characterized by wide-band-gap and are widely employed in electronic and optoelectronic industries. Blossomed three decades ago, diamond films were expected to be a future-generation semiconductor by its many superior properties, not only limited to electronic and electrical applications, but also noticeable in their mechanical, thermal, chemical, physical and optical properties, as well as a wide range of applications especially in high-temperature or harsh environments. Though several research works on diamond remain in the early laboratory stage, diamond has already attracted much attention from the electronic, mechanical engineering, chemical and biological engineering, health care and medical device industries [1].
Artificial bulk diamond first appeared in the 1950s and developed under high-pressure and high-temperature conditions (referred to as HTHP technique). It has been primarily used in cutting, grinding and polishing tools [2]. Since the early 1980s, the chemical vapor deposition method of growing diamond films from gas mixture has been subjected to intensive worldwide research. The difference between the CVD method and the HTHP technique is that the CVD method yields diamond films on the substrates of various materials rather than bulk diamond, and it does not require high pressure, thus the CVD process is simple, relaxed and can be easily carried out for laboratory research [3].

With various reactant gas recipes and ratios, different forms of carbon materials can be made using the CVD technique, such as diamond-like carbon (DLC), polycrystalline diamond, intrinsic nanocrystalline diamond and extrinsic nanocrystalline diamond including p-type or n-type diamond.

Diamond-like carbon is an amorphous carbon mixture of cubic lattice and hexagonal lattice without long-range crystalline order. The content of various nano scale structures can be obtained by the variation of the gas reactants (CH₄:Ar at the ratio of 5%:95% for the CVD method), from cubic dominated to hexagonal dominated, thus variable desired properties of hardness and tribology can be achieved. The primary desirable applications of DLC carbon are based upon the properties of hardness, wear resistance and slickness. There are two main factors that will determine the quality of the DLC films. One factor is the amount of cubic lattice content, which the valence carbon atoms hybridize sp³ bonding and form a four C-C covalent bond known as tetrahedral amorphous carbon. Another structure is graphite of sp² bonding, which valence electrons distribute in the normal state of the carbon atom. 100% sp³ indicates the hardest and
100% sp$^2$ indicates the slickest due to the fact that the length of the sp$^3$ bond is significantly less than the length of the sp$^2$ bond. Further details will be given in chapter 1.2.1. The second factor that affects the quality of DLC films is the fractional content of hydrogen atoms and carbon hydrogen bondings (C-H) that result from the carbon source gas, methane (CH$_4$). The large amount of concentration of hydrogen atoms and C-H bondings in DLC will degrade the quality almost as much as the residual sp$^2$ bonded graphitic carbon does [4].

Since sp$^3$ diamond is the hardest known material in the world, it is used to make stylus for hardness measurement equipment such as a nanoindentation tester, or the stylus of a profilometer for the measurement of thin film thickness. DLC coatings are also applied to the edge of the cutting tools, the bits of the mining drills, etc. The superior anti-wear property of sp$^2$ graphite is utilized to make pencils, solid lubricants and so on.

DLC films of sp$^3$ tetrahedral diamond serve as a good insulator in electrical and electronic applications. On the contrary, sp$^2$ graphite is a good conductor by a special mechanism of hopping conductivity that electrons move in quantum mechanical tunneling between pockets of conductive material isolated in an insulator. Such a process characterizes graphite as a semiconductor; the electron emissions under high voltage and vacuum conditions make diamond electrodes a field emission device [4].

Polycrystalline diamond (PCD) consists of grain sizes from several hundred nanometers to several micrometers according to the gas recipe CH$_4$/H$_2$ at a ratio from 1/100 to 5/100 with different growth rate and sp bonding composition. One of the remarkable features of polycrystalline diamond is its high growth rate (1-3μm/hr), and a freestanding polycrystalline diamond plate of 300μm thick serving as output windows for
high-power microwave and laser radiation sources was reported [5]. A maximum 350μm thick polydiamond was reported as having identical optical emission properties to that of ideal single crystalline diamond [6]. The rough surface of the PCD films has grain sizes at the order of micron; this is the main limiting factor of diamond films in most electronic, optical, biomedical and tribological applications [7-9]. Nanocrystalline diamond (NCD) films, which possess smooth surface and high sp³ content, have therefore been recognized as the promising candidates for such applications [10].

As evident from its name, nanocrystalline diamond film consists of diamond grains in a range of size from several nanometers to several tens of nanometers. There is no strictly defined grain size between polycrystalline and nanocrystalline diamond. Due to the extremely high density of nano grain size, nanocrystalline diamond has superior outstanding properties compared with polycrystalline diamond, including its extreme hardness, low friction coefficient, chemical inertness and high thermal conductivity [11, 12]. The protocol of nanocrystalline diamond film synthesis by plasma enhanced chemical vapor deposition is as follows: the reactant gas chemistry recipe in flow rate is Ar/CH₄/H₂ at a ratio of 98/1/1; the deposition temperature is above 700°C; the pressure is in the range of 90HPa to 140HPa.

Intrinsic nanocrystalline diamond has a high concentration of sp³ bonding, thus high resistivity. In order to accomplish high conductivity of extrinsic diamond films for electronic applications, there are two types of doped diamond films that are fabricated, i.e., p-type and n-type diamond films. P-type diamond films are usually made in a hot filament CVD system and the dopant element is mainly boron. Conventional boron sources commonly used are triethylborane [B(C₂H₅)₃] and diborane (B₂H₆) [13, 14]. In
the past decade, a new approach of boron supply for p-type diamond films was reported. Herein, the boron source was obtained by forcing an H₂ stream through a bubbler containing B₂O₃ dissolved in methanol (CH₃OH). The system controls boron concentration by using a flow controller for the gas inlet, and the H₂ and B₂O₃/CH₃OH/H₂ flows are controlled in order to achieve the desired B/C ratios [15]. N-type diamond films are generally made both in hot filament and microwave CVD systems, and dopant element sources are largely molecular nitrogen gas or phosphorus-contained gas such as phosphine (PH₃) [13,16,17].

1.2 Structures, Properties and Applications

1.2.1 Crystalline Structure of CVD Diamond

A well-known fact is that structure determines the properties of materials, including mechanical, electrical, physical and chemical properties, and eventually determines the engineering performances of materials. For instance, both diamond and graphite are composed of carbon, but differ in their structures by various bonding types and arrangements of the atoms. Diamond is sp³ bonding and has a face-centered cubic structure, whereas graphite is sp² bonding and has a hexagonal structure. As a result, diamond serves as an abrasive because of its great hardness, whereas graphite is used as a lubricant. Diamond is the high-pressure polymorph, and hence has a denser structure than graphite.

The crystalline structure of diamond can be briefly described as a specially arranged face centered cubic (FCC) structure. To better understand diamond structure and its origin, a basic structural unit, tetrahedral, has to be introduced. A tetrahedral structure
is represented by one atom covalent bonded with the other four atoms with 109.5° in
three-dimensional space (Fig.1-1).

If four atoms are added interior to the FCC unit cell at (1/2, 1/2, 1/2) positions, each of the extra atoms is tetrahedrally coordinated with the other four atoms in FCC unit, and zinc blende structure (also called sphalerite) is formed. Zinc blende structure is named after the exact mineralogical term for zinc sulfide (ZnS); the four extra added atoms represent zinc ions, and one cornered atom and three centered atoms in the FCC unit cell represent four sulfuric ions (Fig.1-1). Similar compounds of equivalent structures also include silicon carbide (SiC), gallium arsenide (GaAs) and zinc telluride (ZnTe).

![Tetrahedral structure, Zinc blende structure, diamond cubic crystal structure](image)

**Figure 1-1. Formation of diamond cubic crystal structure**

The different types of bonding found in diamond and graphite are ascribed to the various types of electron distribution around carbon. The atomic number of carbon is six (C⁶); it has six electrons outside its nucleus. These six electrons configure in shell-subshell designation. According to the Pauli Exclusion Principle, each subshell can hold no more than two electrons, which must have opposite spins. Therefore, s, p,d and f
subshell may each accommodate, respectively, a maximum of 2, 6, 10 and 14 electrons. In most cases, the electrons preferentially fill up the lowest energy state (referred to as ground state) in the shell and subshell, two electrons having opposite spins per state. The normal electron configuration of the carbon atom is \(1s^22s^22p^2\) with four valence electrons (the number of electrons that occupy the outermost shell). It should be noted that p subshell has three electron states; only two of them are half occupied, thus it has one unfilled 2p electron state, which implies an unstable electron configuration. However, under special circumstances, electron transitions to higher energy states are possible to form a stable bonding structure. For instance, the s and p orbitals combine to form hybrid \(sp^n\) orbitals, where \(n\) indicates the number of electrons contained in p orbital, which may have a value of 1, 2, or 3. The driving force for the formation of hybrid orbital is a lower energy state for the valence electron bonding [18, 19]. In diamond, the \(sp^3\) hybrid bonding has an electron configuration of \(1s^22s^12p^3\). In the current research, graphite and diamond are mostly concerned and the corresponding \(sp^2\) and \(sp^3\) bonding can be described in terms of electron occupation in orbital.

<table>
<thead>
<tr>
<th>Carbon (sp^2) bonding (graphite): (1s^22s^22p^2)</th>
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<th>Carbon (sp^3) bonding (diamond): (1s^22s^12p^3)</th>
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Figure 1-1a. The electron distribution in \(sp^2\) and \(sp^3\) bonds of carbon atom
Further explanation of orbital hybridization in perspective of chemistry, especially for paraffin compound family ($C_nH_{2n+2}$), can be found a little different from this due to the C-C bonding, C=C ($\pi$ bond), and C-H ($\sigma$ bond) bondings involved [20].

1.2.2 Properties and Applications

Diamond is well known as the hardest material in the world. In addition to that, diamond has numerous outstanding properties such as mechanical, thermal, optical, electronic, electrochemical and biocompatible properties presented by high Young’s modulus, low coefficient of friction, anti-wearing, high thermal conductivity, high refractive index, high dielectric constant, chemical inertness and biological compatibility that make it a promising material in many applications of industries. Each aspect of diamond properties corresponds to a certain series of applications that can be applied to industry, medical health, civil life, etc.

Remarkable mechanical properties are characteristic of diamond as a conventional material including specific values of the hardest hardness (10,000 kg/mm$^2$), high tensile strength (1.2GPa), compressive strength (110GPa), Young’s modulus (1200GPa) and a low coefficient of friction (0.05 dry)[21]. Diamond is extremely hard, so it is an ideal material used for cutting tools such as scalpels, knives and tips of mineral drills. On the other hand, the thermal conductivity of diamond is about 20W/cm-K at room temperature; this value is believed to be the highest in any known materials, and is significant to heating dissipation in cutting tool applications [21, 22]. Conventional cutting tool materials are high-speed steel and tungsten carbide (WC), which are not suitable for new materials such as Al-Si alloys, metal matrix composites and fibre-
reinforced plastics [23]. During the high-speed cutting process, the friction between the cutting edge and workpiece generates a large amount of heat; the high temperature that results from this friction softens the workpiece material that will influence the precision of the parts, and forms a strong adhesion to the surface of the cutting edge. Diamond is expected to alleviate this problem, increasing productivity and improving the quality of the machined surface due to its extraordinary mechanical properties and high thermal conductivity as mentioned above [24]. Diamond, with its special tetrahedral crystal structure, is not readily coated on classical substrate materials. The most favored material for diamond coating is Co-cemented tungsten carbide (WC-Co), which can form strong adhesive bonding with diamond. The element Co has a catalytic effect that induces carbon diffusion into substrate and forms a graphite layer that weakens the diamond coating. Chemical solutions can be applied to reduce the Co effect [24]. Alternative solutions also include the insertion of interlayer materials such as amorphous carbon, metallic materials and ceramics [26].

The tribological property of low friction coefficient (0.12-0.2) of diamond makes it a good choice of solid lubricant in-between surfaces. These films could find applications as ultrathin anti-friction and anti-wear protective coatings, hydrophobic coatings, gas diffusion barriers and dielectric layers in electronic devices [27].

The thermal conductivity of diamond is ranged from 10-20 W/cm-K, depending on the impurity content and crystalline defects on the surface. Copper, the most commonly used metal for heat dissipation, has a conductivity of 4 W/cm-K. By comparison, diamond is believed to be the highest thermal conducting material in the industry. This characteristic finds its application in semiconductor devices and circuits as
a heat sink to avoid the efficiency loss of devices due to heat generation. Heat is believed to be transferred in solid by charge particles, electrons, and vibration of phonon. For diamond, the decrease of impurities increases the thermal conductivity and causes less grain boundary and thicker film, resulting in higher thermal conductivity [21, 22, 28]. Other applications of diamond utilizing its excellent thermal properties include heat exchanger, heat spreader, even in a dosimetric medical device that counts the number of the released photons on the sample during the heat delivering process [29].

Each material has its own characteristic wavelength that determines its optical property. For instance, people standing under sunlight can see their shadows, indicating that sunlight cannot transmit through the human body. But when people get a physical check in the hospital, an X-ray can easily go through a person’s body. Diamonds, with different structures and grain sizes (nanocrystalline, polycrystalline and amorphous), have their own characteristic wavelength. Nanocrystalline has a wavelength of 546nm, polycrystalline 552nm and amorphous diamond 557nm according to the Raman shift calculation using the equation,

\[
D \text{ (cm}^{-1} \text{)} = (1/l_o - 1/l_R), \quad \text{Eq. 1}
\]

where D is the Raman Shift in units of wavenumber (cm\(^{-1}\)), \(l_o\) is the laser wavelength which is 514nm in the Renishaw Raman Spectrophotometer, and \(l_R\) is the Raman radiation wavelength.

DLC films are typically transparent in the infrared region (wavelength 700nm ~ 106nm), weakly absorbed in the visible spectrum (wavelength 380nm ~ 750nm), and increasingly absorbed with decreasing wavelength in the UV (wavelength range 10nm ~ 400nm). Wavelength spectra are not exactly defined, so an overlap can be seen in
different sections. The refractive index of diamond is 2.4, which has been found to be
dependent on the preparation, hydrogen content and CH bonding of the films, and can be
adjusted from 1.7 to 2.4 due to growth conditions. A higher index of refraction usually
indicates DLC with stronger crosslinking, greater hardness, and better wear resistance
[30-32].

Due to its IR transparency, DLC can be used for optical applications, such as antireflective and scratch-resistant wear protective coatings for IR optics. Besides their application as protective optical coatings, diamond-like carbon films can be used for the fabrication of optical components. Using anisotropic O$_2$ RIE etching in combination with hard masks such as SiO$_2$ or Al, patterns with well-defined rectangular profiles can be obtained. In combination with the IR transparency of the films, this enables the recording of IR diffractive optical components with good control of surface and pattern quality [30, 33]. Based on a similar principle, other optical applications of diamond include infrared windows, lenses, ATR units, X-ray windows, etc.

CVD diamond films, particularly heavily boron-doped diamond films, are being used increasingly in electrochemical research because of the excellent electrochemical properties exhibited such as high conductivity, sensitivity and reproducibility, low background currents, chemical inertness and biocompatibility when immobilized and functionalized with biological substances. Applications utilizing electrochemical properties of diamond include electrodes, electro-chemical detectors, bio-chemical sensors, and waste water treatments. Diamond electrodes have an advantage over the conventional electrode materials that are easily poisoned or corroded, and in addition, the
wide range of operating potentials increase the versatility of application, especially in harsh environments.

One challenge in diamond biosensor application (electroanalysis) is its selectivity toward the target analyte. A general approach to solving this problem is to chemically functionalize the electrode surface in order to incorporate a selective chemical that responds to the analyte concerned. The strategies can be divided into the physical adsorption of the electrode modifier onto the carbon surface, or the covalent binding of the species concerned [34].

A diamond group in Argonne National Lab claimed that a new innovative method has been developed to construct hybrid organic-inorganic interfaces on conducting diamond thin films. The UNCD films are immersed into a special chemical solution and voltages are applied, then radicals of the solution react with the diamond surface to form strong carbon-carbon bonds. These C-C bonds attract biomolecules such as proteins that are covalently bound in a process called functionalization [35].

Small biological molecules such as amino acids, DNA, are considered building blocks of molecular engineering on surfaces due to their inherent nature for molecular recognition and self-assembly. The interaction between molecules and solid surfaces is significant to understand the protein surface bonding and the development of bioanalytical devices as well as biocompatible materials. Figure 1-2 is an example of a diamond cantilever biosensor that measures the frequency response.
Figure 1-2. Prototype biosensor of diamond cantilever functionalized with crosslinker to detect target analytes

Receptor biomolecules, such as antibodies, are attached to a micro-cantilever made of ultrananocrystalline diamond thin-film (UNCD). The cantilever is vibrated by an electrical field. When the sensor is exposed to a gas or liquid containing biological toxins (targeted analytes), the toxins are selectively captured by the receptor biomolecules, which makes the cantilever heavier and changes its vibration frequency. Different biological toxins and other biomolecules can be detected by attaching different receptor molecules to the cantilever.

CVD diamond film is expected to be an ideal material for radiation detectors or dosimeters, because of its excellent features such as high radiation resistance, low leakage current, high operating temperature, and high radiation stability. The high resistivity and high band gap of diamond allows for a simple structure and extremely low
number of free carriers that will result in very low noise and power dissipation. Different thickness of intrinsic diamond or extrinsic diamond with various degree of doping can be utilized to investigate for ionizing α, β, γ and X-ray and non-ionizing UV radiation. The thickness of polycrystalline diamond free standing window can be as much as several hundred micrometers [36, 37].

Among all materials, diamond possesses the highest surface acoustic wave (SAW) velocity, which is about 18,000 meters/second in longitudinal elastic wave [38]. Longitudinal wave is an elastic wave such that the direction of displacement at each point is normal to the direction of wave propagation. This feature can be utilized to fabricate surface acoustic wave (SAW) devices such as GHz-band signal filters, optical and telecommunications, even biosensors.

The brief principle of the SAW filter is to convert an input electric radio frequency (RF) signal to a SAW at the input interdigital transducer (IDT), which propagates along the surface to the output IDT and then reconverts it to an output electric RF signal there. In this process, the signal frequency that can be effectively converted from the input RF signal to the SAW and effectively reconverted from the SAW to the output RF signal is determined by $f = \frac{v}{r}$ (where $v$ is the phase velocity of the SAW and $r$ is the wavelength: wavelength = electrode width × 4), so that only this frequency signal can pass through this device. The function flow chart is as follows:

```
Input RF signal  IDT  SAW  IDT  output RF signal
```

Because the frequency is determined by the velocity of SAW and the wavelength that can be obtained by adjusting the electrode width, in order to get the expected high frequency, to find the high-velocity material such as diamond film for the SAW substrate
can offer the best solution for this approach. Figure 1-3 shows the schematic diagram of diamond films integrated SAW frequency filter.

![Diagram of diamond films integrated SAW frequency filter](Image)

Figure 1-3. The schematic diagram of diamond films integrated SAW frequency filter

As evident in figure 1-3, a typical layer structure of commercial product of a diamond SAW device is the IDT/ZnO/diamond/Si structure. IDTs can be aluminum, gold, silver, titanium, copper, etc. The commonly used materials for piezoelectric layers can be zinc oxide (ZnO), silicon dioxide (SiO₂), aluminum nitride (AlN) or gallium nitride (GaN), and lithium niobate (LiNbO₃) as well as lithium tantalate (LiTaO₃) for surface acoustic wave. A typical high-temperature piezoelectric material is langasite (lanthanum gallium silicate, also referred to as LGS in literatures), which can work at 1400°C and match the excellent high-temperature performance of diamond [39-41].

Some other novel properties of diamond that have been reported in prestigious academic journals such as Science or Nature, but have not been fully investigated, are superconductivity at low temperature and light emitting diode (LED) of diamond.
Diamond is well known as an insulator. Boron has one less electron and a smaller atomic radius than carbon, and is easily incorporated into diamond. As boron acts as a charge acceptor, boron-doped diamond presents a p-type semiconductor, i.e., it is featured by hole carriers. When boron-doped diamond was synthesized at high pressure (nearly 100,000 atmospheres) and temperature (2,500–2,800 K), superconductivity was discovered below the transition temperature at 4k. The discovery of superconductivity in diamond-structured carbon suggests that Si and Ge, which are located in the same group in the periodic table and have a similar diamond structure, may similarly exhibit superconductivity under the appropriate conditions [42].

LED is an acronym for light-emitting diode. When a semiconductor diode, which is a p-n junction in physical nature, is forward biased (switched on), a current is generated when electrons recombine with holes. In the meantime, energy releases in terms of photons, and light with different color (wavelength) is emitted. This effect is called electroluminescence, and the color of light (commercially red, green and blue) is determined by the energy gap of the semiconductor. In a diode, the current flows easily from the p-side to the n-side, but not in the reverse direction. LEDs present many advantages over incandescent light sources including lower energy consumption, longer lifetime, improved robustness, smaller size, faster switching, and greater durability and reliability [43]. Figure 1-4 shows the structure of the p-n junction and the working principle of LED.
Most light-emitting elements are located in the main groups II to V in the Periodic Table. The larger the band gaps of these insulating materials, the shorter the wavelength of the emitted light is. Shorter wavelengths are desirable because they potentially allow greater data storage, but suitable materials at these wavelengths are harder to find. Blue lasers are thus a much greater challenge than red or green ones. GaN can emit blue lasers at wavelengths below 450 nm at room temperature [44].

For light emission at even shorter wavelengths, diamond is a potentially promising material because of its large band gap (about 5.47 eV). Koizumi et al. report a diamond-on-diamond (homoepitaxial) pn junction made by CVD that emits at 235 nm, which is located in the ultra-violet spectrum. The pn junction was formed from a boron-doped p-type diamond layer and phosphorus-doped n-type diamond layer grown epitaxially on the (111) surface of a single crystalline diamond. The pn junction exhibited good diode characteristics, and at a forward bias of about 20 volts, strong ultraviolet light
emission at 235 nanometers was observed and was attributed to free exciton recombination [45].

There are two types of band gap in semiconductor materials: direct band gap and indirect band gap. If the minimal energy state of conduction band has the same value of $k$-vector as the maximal energy state of covalence band, this band gap is defined as direct band gap. $K$-vector is crystal momentum that describes the electrons (waves) in crystal lattice. Theoretically, only semiconductors having direct band gap can be made to emit light. Diamond is not direct band material. The ultraviolet light emission of a diamond pn junction was ascribed to the recombination of free exciton [45], which is an electrically neutral electron-hole pair that exists in semiconductors, insulators or liquids. Exciton can transport energy without transporting net electric charge [46].

As stated above, structure determines properties, and properties determine applications; diamond film by chemical vapor deposition method is an amazing material that has many excellent properties that cause it to have a few potential, novel applications in almost all walks of life. Of course, there are still several challenges that need to be overcome before diamond films achieve their market value. Further research should be conducted in order to make practical application of diamond films to better serve the lives of human beings.

1.2.3 Research Objectives

A good understanding of the diamond film properties such as mechanical, electrical, optical and biological properties, which are determined by the qualities of diamond films, is significant to the choice of diamond films for different applications.
One of the most important approaches to growing diamond films is microwave plasma enhanced chemical vapor deposition method (MPECVD). In the current dissertation, using MPECVD method, diamond films with different crystallite sizes and structures such as amorphous diamond, polycrystalline diamond and nanocrystalline diamond were synthesized in order to get different properties for various purposes of application. Intrinsic diamond is a good insulated material, by adding the dopant elements, typically boron and nitrogen or phosphorus, p-type and n-type semiconductor diamond films with certain conductivities can be fabricated for electronic devices. The characterization of as-grown diamond films have been carried out by Raman spectroscopy, scanning electron spectroscopy (SEM), X-ray diffraction (XRD) and atomic force microscopy (AFM). The optimized parameters have been obtained to grow the expected high-quality films according to the results of characterization techniques. For nitrogen-doped diamond films, the electrical properties, ohmic contact and surface features on SiO₂ layer were investigated. Residual stress analyses of polycrystalline diamond films by HFCVD and MPECVD were evaluated by Raman spectra. The application part is mainly about the design and fabrication of capacitive micromachined ultrasonic transducer with integrated diamond membrane.

1.3 Growth of Diamond - Chemical Vapor Deposition Method

Chemical Vapor Deposition (CVD) is a method of growing semiconductor thin films, such as silicon carbide (SiC), silicon dioxide (SiO₂), silicon nitride (Si₃N₄), gallium nitride (GaN), and diamond (C), etc., on a substrate by the reaction of vapor phase chemicals that contain the required constituents. The structural forms of the films
deposited by the CVD method can be amorphous, polycrystalline and monocrystalline. The reactant gases are activated by various energy forms such as thermal, plasma and reacted on and/or above the temperature-controlled surface to form the thin film. The reactive gas species of intrinsic diamond film include methane (CH₄, which is a carbon source), hydrogen (H₂) and argon (Ar); sometimes, donor gas such as nitrogen (N₂) or phosphine (PH₃) is introduced for n-type diamond films, whereas diborane (B₂H₆) or boron trioxide (B₂O₃ powder, mixed with methanol or acetone to be volatile) is introduced for p-type diamond films. Changing the gas recipe results in different forms of diamond films such as amorphous diamond (CH₄:Ar at 5%:95%), polycrystalline diamond (CH₄:H₂ at 10%:100%) and nanocrystalline diamond films (CH₄:H₂:Ar at 1%:1%:98%). By regulating the process conditions, such as the gas recipe introduced, pressure of the reaction chamber, temperature of the substrate and the way the plasma generated, different qualities and forms of diamond films can be grown on the silicon substrate.

A typical chemical vapor deposition system mainly includes four sections: reactor gas supply, power energy supply (microwave plasma or thermal hot filament), vacuum and exhaustion, and heating and cooling parts. Figure 1-5 illustrates the major components of a typical CVD system.

The gas supply section is composed of cylinders of various reactant gases (such as argon, hydrogen, methane and nitrogen), stainless pipelines, mass flow controllers and several valves. Its function is to offer gases required for chemical reaction at a certain flow rate in order to achieve high-quality diamond film formation. Among them, methane is the carbon source gas. Hydrogen is the plasma precursor and argon can adjust the
pressure in the chamber. The stainless steel chamber is the place where deposition happens. Concerned with the chemical reaction process, the chamber is also referred to as the reactor.

![Diagram of a plasma-enhanced CVD system]

Figure 1-5. Component-construction of a typical plasma-enhanced CVD system

The mass flow controller (MFC) can offer a desired gas flow rate in a unit of sccm, which means standard cubic centimeters per minute. Sometimes a unit of slpm is also used, which means standard liters per minute; one slpm equals to 1000 sccm. Gas and liquid can be measured in volumetric or mass flow rates such as liters per second or kilograms per second. Two measurements can be converted by the density of material. There are two types of mass flow controllers: digital and analog; the digital mass flow controller is able to measure more than one type of gases without calibration, whereas the analog mass flow controller can only be valid for one specific gas. The mass flow controllers in our lab are analog, so they are for specific gases. Each mass flow controller
has its maximum value (for instance 100 sccm) and its percentage scale range from 0 to 100%. The real flow rate is calculated by the readout value (percentage value) times the maximum value. For example, when the readout value is 50 (50%), and the maximum value of this mass flow controller is 30 sccm, the real mass flow rate is 30 sccm times 50%, i.e., 15 sccm. The flow rate of the analog mass flow controller is specified as a percentage of its calibrated full-scale flow rate. The mass flow controller is calibrated with nitrogen N₂ gas, because the k-factor of other gases is nearly linear to N₂. In order to use the specific mass flow controller for another gas, a calculation has to be made according to the k-factor charter in the manual of the mass flow controller.

The second part of the CVD system is the energy supply that is mainly an RF generator to produce plasma. Plasma is highly ionized gas (or a mixture of several gases) composed of ions, electrons and neutral particles, that is generated by microwave radiation from normal gas; it is believed to be the fourth state of matter, in sequence of solid, liquid and gas. The maximum power of the Astex CVD system is 1.5 kilowatts with a frequency of 2.45 GHz. Microwave radiations from the RF generator go through a waveguide, which is normally a rectangular pipe made of metals or dielectric materials and functions as a transportation tunnel of radiation, runs into reactant gas mixture in the CVD chamber, and finally yields the plasma. Carbon ions bombard onto the surface of the substrate and experience complex chemical reactions, such as surface reactions, nucleations, diffusions, step growth, and eventually form the diamond films. The unreacted particles are pumped out of the chamber by vacuum system.

Each CVD reactor needs a mechanical pump to get a desired vacuum level. Astex CVD diamond deposition requires 1 mTorr of pressure before inputting the reactant gas.
The pressure is measured by a mechanical pressure gauge that is connected to the chamber. The pressure can also be minorly adjusted by a needle valve in order to get an expected pressure during the deposition process. The unreacted particles, impurities, and some other by-products of plasma reactions are exhausted by a mechanical pump through the pipelines.

Microwave plasma-enhanced CVD diamond deposition requires a high temperature, approximately above 700°C. When the power of the RF generator and the frequency of microwave radiation are not powerful enough (for instance, Astex CVD has only 1.5kw and 2.45GHz), a heater is needed to increase the temperature of the sample in order to meet the temperature requirement of diamond deposition. The heating section is made of DC bias power convert, sample stage, conduction metal wires sheathed by ceramic beads that hook up the converter and sample stage. The sample stage is made of graphite, which is a material of high electrical resistance, so as to absorb energy from the converter and release the heat to the sample. A chromium-alumina thermal couple is fixed on the bottom of the stage and the sensible tip of the thermal couple stands up above the surface of the stage to monitor a real-time temperature inside the chamber. Tap water or chilly water is supplied to run through pipelines wound inside the stainless steel wall of the CVD chamber to cool down the system. The Astex CVD system utilizes tap water because of the low power of the RF generator and relatively low working temperature of the system.
Characterization Techniques

After diamond films were deposited on the silicon substrates, characterization techniques have to be carried out to prove that what were deposited by chemical vapor deposition system under certain conditions were in fact diamond, rather than some other material. Characterization techniques for diamond films include Raman spectroscopy, atomic force microscopy (AF), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Raman spectroscopy can offer information on the bond type of the film; sp$^3$ represents diamond, whereas sp$^2$ indicates graphite. Atomic force microscopy can tell the topography of the deposited films such as roughness, grain size, etc. X-ray diffraction provides the crystalline structure of the thin films, which determines what material it is. Scanning electron microscopy tells the morphology of the film surface. Each technique has its own special features and advantages based on totally different principles. A combined implementation of all these techniques will provide a comprehensive description, determination and understanding of observed material.
1.4.1 Raman Spectroscopy

When a light with a certain wavelength or frequency, whether it is visible light or X-ray or electron beam, hits on the atoms, the elastic or inelastic scattering of radiation occurs. Elastic scattering that has no energy loss leads to the application of optical image, X-ray diffraction and transmission electron microscopy. Inelastic scattering that loses part of the incident beam energy is utilized to characterize the electron level energy change and leads to the techniques of scanning electron microscopy and Raman spectroscopy.

Raman scattering phenomenon was found in 1928 by Indian physicist and Nobel laureate C.V. Raman. When a monochromatic (single wavelength) laser hits on an electron, a photon is excited and the electron energy state jumps from ground state to a new state. The energy difference between the two states causes a wavelength shift in the emitted photon from the excitation wavelength. If the final state is in a higher energy status than the original state, which means absorption of energy, the excited photon will shift to a lower frequency in order to maintain an energy balance. Because of the energy change, it is believed to be an inelastic scattering. This phenomenon offers information about the internal microstructure of the crystals, molecules such as chemical bonding types, vibrational or rotational modes. Inelastic Raman scattering is very weak compared with elastic Rayleigh scattering—about 1 inelastic photon found in 10 million elastic photons. The most common light source in Raman spectroscopy is an Ar-ion laser. Raman analysis is an ideal analytical technique because it is non-contact and non-destructive, requires a small sample area, and provides quick outcome. Figure 1-7 illustrates the working mechanism of Raman scattering phenomenon.
Figure 1-7. Working mechanism of Raman scattering

Figure 1-8 shows the orbital jump of electrons in terms of energy change during the process of photon emission. Raman scattering can be classified as Stokes Raman scattering for energy-loss photon emission, and Anti-Stokes scattering for energy-gain emission. Elastic Rayleigh scattering has no energy change with electron transportation.

Figure 1-8. The orbital jump of electrons with respect to energy change
The commonly used wavelengths of lasers that excite the Raman scattering can be 514nm, 633nm, 780nm. The shorter the wavelength, the more powerful energy the laser has; thus, laser with shorter wavelengths can excite more efficient Raman scattering. The intensity of the Raman peak reflects the number of photons generated. The characteristic Raman frequency can tell the composition of material. Frequency changes in Raman peaks can be utilized to calculate the stress/strain status of films; for instance, a 10cm\(^{-1}\) peak shift for silicon represents 1\% strain [47]. Polarization of Raman peaks indicates the symmetry and orientation of the crystal lattice. The width of Raman peaks provide information about the quality and crystal degree of films [48-50]. Raman analysis for CVD diamond films will ascertain the type of C-C bonding (either sp\(^3\) or sp\(^2\)). Figure 1-9 is a typical Raman spectrum for polycrystalline diamond film.

![Raman spectrum](image-url)

**Figure 1-9.** A typical Raman spectrum for polycrystalline diamond film
As evident in figure 1-9, the Raman spectrum is expressed in wavenumbers, which can be explained as the number of wavelengths per unit distance and which have units of inverse centimeters (cm\(^{-1}\)). In order to convert between spectral wavelength and wavenumbers of shift in the Raman spectrum, the following formula can be used:

\[
\Delta w = \left( \frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right),
\]

where \(\Delta w\) is the Raman shift expressed in wavenumber, \(\lambda_0\) is the excitation wavelength, and \(\lambda_1\) is the Raman spectrum wavelength [48]. An example calculation is given to diamond film by the Renishaw Raman spectroscopy, which has an incident laser with a wavelength of 514nm. If the Raman shift (wavenumber) of nanocrystalline diamond is 1140cm\(^{-1}\), then the wavelength of the excited photon is 546nm; if the Raman shift of polycrystalline diamond is 1350cm\(^{-1}\), then the wavelength of the excited photon is 552nm; if the wavenumber of graphite is 1500cm\(^{-1}\), then the wavelength of the excited photon is 557nm. A simple conclusion can be made from above calculation that nanocrystalline diamond has more solid structure, and releases more energy to break it up.

1.4.2 Atomic Force Microscopy (AFM)

Atomic Force Microscopy, abbreviated as AFM, was invented in 1986 by G. Binnig and H. Rohrer at IBM. It was one of the most important tools for imaging and measuring the surface of material on the order of nanoscale. The theory and operation of an AFM are similar to those of a stylus profilometer. An AFM generates a very small electrostatic force (nano Newton) between the probe tip and the scanned surface, hence a much higher resolution can be achieved. The most important component of AFM is a
cantilever with a sharp tip (probe) at its end. Generally the cantilever is made of silicon or silicon nitride (Si$_3$N$_4$) with a tip 1-10 nm in diameter, which is used to scan on the surface of a specimen. When the tip approaches a sample surface, there exists a force between the tip and the sample; this force leads to a deflection of the cantilever. A smart laser beam deflection system is introduced to measure the deflection of the cantilever. An incident laser hits on the polished back (like a mirror) of cantilever, and then is reflected to a position detector. The position detector reads out the deflection and calculates the force according to Hook’s law $F = -kz$, where $F$ is the force, $k$ is the stiffness of the lever, and $z$ is the distance the lever is bent. The calculated forces are mapped to form the topography of the surface.

The operation mode of cantilever can be classified into contact mode and non-contact mode. Contact mode is for hard materials, and non-contact mode is generally for moist surfaces. Diamond film, due to its extreme hard property, is recommended to use in non-contact mode in order to reduce the wear-out of the tip. In contact mode, the force between the tip and the surface is kept constant by maintaining a constant deflection, and therefore constant height above the surface. The topography is mapped by measuring direct deflection of the cantilever. In non-contact mode, the cantilever oscillates at a frequency slightly above its resonance frequency with an amplitude of a few nanometers ($<$10 nm). When the cantilever comes close to the sample surface, the amplitude and phase of the vibrating cantilever change; this change is related to the force on the surface and can be easily measured to construct a topographic image of the sample surface. Due to the principle of scanning, images of non-contact mode are referred to as phase image,
amplitude image and frequency image [51, 52]. One of the advantages of AFM is the formation of three-dimensional images on material surfaces.

1.4.3 X-Ray Diffractions (XRD)

X-rays are electromagnetic radiation with wavelengths in the range of 0.1 angstrom to a few angstroms, which are comparable to the size of atoms and are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the crystallographic structure, crystallite size (grain size) and preferred orientation of film or bulk materials.

X-rays are produced generally by X-ray tube where electrons from heated cathode filaments are focused and accelerated through a high-voltage potential of tens to hundreds of kilovolts. When incident electrons beam strikes on a stationary or rotating solid target (usually powdered Cu and Mo [molybdenum] with corresponding wavelengths of 1.54 Å
and 0.8 Å and served as anode), the incident electrons can eject electrons from the inner shell of the target atoms; then electrons from the high-energy level of target atoms fill the vacancies left by incident electron beams, and in the meantime, X-ray photons with the same wavelength of target atoms are emitted in all directions and go through a small, round window where X-rays exit. Since powders contain large amounts of fine and randomly oriented particles and each particle can be seen as a crystal, it ensures some particles are properly oriented such that a possible set of crystallographic planes will be available for diffraction. Diffraction conditions of X-rays for a periodic arrangement of atoms are based on the famous Bragg’s Law:

\[ n\lambda = 2d \sin \theta, \]

where \( n \) is an integer, \( \lambda \) is the wavelength, \( d \) is the interplanar spacing and \( \theta \) is the diffraction angle. It shows that diffraction occurs only when traveled distances of rays reflected from successive planes are integer number \( n \) of wavelength \( \lambda \).

XRD pattern is a plot of scattering intensity versus the scattering angle \( 2\theta \). By varying the incident X-ray angle \( \theta \), planes with different d-spacing in polycrystalline material can be identified. Identification of materials is achieved by comparing X-ray diffraction pattern with an internationally recognized database containing reference patterns for more than 70,000 phases. The widths of peaks in particular phase patterns provide the crystallite sizes. Large crystallites give rise to sharp peaks, whereas wider peaks correspond to reduced grain sizes. Peak broadening also occurs as a result of variations in d-spacing caused by micro-strain. In general, the XRD pattern indicates phase presence by the position \( 2\theta \), phase concentrations by peak heights, amorphous content by background hump, and crystallite size/strain by peak widths [51-55].
Figure 1-11. XRD pattern of intrinsic nanocrystalline diamond synthesized at 110Torr

1.4.4 *Scanning Electron Microscopy (SEM)*

The scanning electron microscope (SEM) is a technique to get images of a sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. An electron beam in a typical SEM is thermionically emitted from an electron gun made of a tungsten filament cathode. Thermionic emission is the heat-induced flow of charge carriers such as electrons and ions, from a hot metal cathode under vacuum. Tungsten is normally selected in thermionic electron guns because of its high melting point and low vapour pressure of all metals, thereby allowing it to be heated for electron emission. Other materials for electron emitters such as cathodes include lanthanum hexaboride (LaB$_6$) and Zirconium dioxide (ZrO$_2$). Figure 1-12 displays different penetration depths of various particles.
When a focused electron probe with a condensed diameter of about 0.4nm to 5nm is incident on the surface of a specimen, various signals such as Auger electrons, secondary electrons, backscattered electrons and X-rays are generated. The depths of the signals depend on the acceleration voltage or energy, which usually ranges from 0.5keV to 40keV. When a primary beam electron collides inelastically, the energy imparted to the specimen atom will cause it to emit electrons that are referred to as “secondary electrons.” They are generally characterized by possessing energies of less than 50 eV. Since secondary electrons do not diffuse deep inside the specimen, they are most suitable for observing the fine structure of the specimen surface. The generation of secondary electrons increases with a higher specimen atomic number. The secondary electron reaction can produce secondary electrons, X-rays, Cathodoelectroluminescense and Auger electrons.

Figure 1-12. Penetration depths of various signals beneath the surface
Auger electrons from top shallow layer of the surface provide compositional information; backscattered electrons give atomic numbers and topographical information of materials, Cathodeelectroluminescence offers electrical information, X-rays from the thickest place under the surface tell elemental composition of materials, which refer to an important analysis function as Energy Dispersive X-ray Spectroscopy (EDS or EDX) [56-60]. Figure 1-13 is the SEM micrograph of intrinsic nanocrystalline diamond synthesized at 100Torr.

![SEM image of intrinsic nanocrystalline diamond synthesized at 100Torr](image)

Figure 1-13. SEM image of intrinsic nanocrystalline diamond synthesized at 100Torr

SEM provides structural analysis of CVD diamond films such as surface morphology, grain shape, boundaries, crystallite sizes and features, and a high-magnification image can even display fine crystalline defect features, the preferred growth orientation or texture structures; EDS (energy dispersive spectroscopy) analysis is able to determine the elemental and compositional information of the diamond surface.
1.5 List of References


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CHAPTER 2:
VARIOUS FORMS OF CARBON

2.1 Polycrystalline Diamond Film

2.1.1 Introduction to Polycrystalline Diamond Film

The polycrystalline diamond was the first one to be studied in all forms of diamond materials. Polycrystalline diamond films deposited by the plasma-enhanced microwave chemical vapor deposition (PEMCVD) method have characteristics such as a rough surface, large and coarse grain size. The polycrystalline material differs from single-crystal material in that it is polycrystalline in nature with many grain boundaries and defects. These properties determine that polycrystalline diamond films must be smooth-treated before applications in electrical micro devices. Most of the applications of polycrystalline diamond films reported in literatures concentrated on the cutting tools. The main challenge to diamond-coated cutting tools is the adhesion of diamond films onto the metal substrates because of the great difference in thermal coefficient of diamond and substrate materials (particularly metallic substrate); another reason is the high deposition temperature of diamond (above 750°C), causing thermal residual stress during the cooling process that leads to the delamination of diamond films from the substrates [1-4].
2.1.2 Growth Conditions of Polycrystalline Diamond Film

A characteristic of the polycrystalline diamond film growth is that its chemistry gases only contain methane (CH\textsubscript{4}) and hydrogen, without any addition of argon. The ratio of CH\textsubscript{4} to H\textsubscript{2} is approximately 1\%CH\textsubscript{4} to 99\%H\textsubscript{2}, not exactly, so sometimes a CH\textsubscript{4}:H\textsubscript{2} recipe at 1sccm:100sccm or 2sccm:100sccm can be found in literatures. Since the low volume of reactant gases and both of these two gases join the chemical reaction, the pressure during deposition is very low, in the range of 30Torr to 50Torr. The deposition temperature is above 730°C up to 800°C.

Polycrystalline diamond films can be successfully grown by Astex CVD system using various chemistry gases according to the protocol stated above. Table 1 lists the gas recipe and deposition conditions.

<table>
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<tr>
<th>H\textsubscript{2} (sccm)</th>
<th>CH\textsubscript{4} (sccm)</th>
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<th>Temperature (°C)</th>
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An ultrasonic slurry seeding method for diamond nucleation on Si substrate was carried out to prepare the sample. Commercial available (Sigma Aldrich) nano-diamond powder (5 nm) was mixed in methanol to make the slurry. The Si wafer was cut into 2cm×2cm square pieces to serve as samples. A beaker with Si pieces submerged in methanol diamond slurry was put in Bransonic 1510, a tabletop ultrasonic cleaner. The Si
samples were ultrasonic agitated for 15 minutes in order to get uniformed seeding. After oscillation seeding, the samples were rinse-cleaned by methanol to remove the residues such as contaminants or impurities on the surface, and then they were dried by compressed nitrogen just before setting into the CVD chamber. The CVD process was carried out under the pressure of 50 Torr at 650 °C for one hour. Torr and Pascal are different units for measuring the pressure. In engineering, one Torr is considered equal to one HPa; in the present dissertation, Torr and HPa are used as equivalent units unless special notification.

2.1.3 Characterizations of Polycrystalline Diamond Film

Characterization of polycrystalline diamond films by Raman spectroscopy, AFM, XRD and SEM indicated that the chemical combination of H₂ (3000 sccm) and CH₄ (30 sccm) produced the best quality films. The high Raman peak indicates that more sp³ bonding existed in the film, which means there is more diamond structure presented. Compared with the H₂ flow rate recipe, the background hump of 100 sccm and 500 sccm H₂ indicates a certain amount of amorphous carbon existed in the film. Wavenumber is the reciprocal of wavelength, which is proportional to the frequency. The interaction between laser and atoms produces photons; if the emitted photons contain higher energy, it means they are hard to be generated; if the released photons have less energy, it means they are readily to be activated. So the right shift of Raman peak indicates that it releases less energy to activate the Raman scattering, and the bonding between atoms is at a higher energy level. The peak corresponding to the 3000 sccm located at the left-most side
of the figure indicates that it has the most solid and stable structure. Figure 2-1 is a Raman spectroscopy for polycrystalline diamond film.

![Raman spectroscopy for polycrystalline diamond film](image)

Figure 2-1. Raman spectra for polycrystalline diamond with various H₂ flow rate

An SEM image of polycrystalline diamond film reveals the morphology of the surface as well as the shape and size of crystallites. As evident from SEM images, polycrystalline diamond has faceted crystallites. Figure 2-2 is an SEM image of polycrystalline diamond.
a. 1000sccm H₂ with 30k magnification   b. 2000sccm H₂ with 30k magnification

c. 3000sccm H₂ with 30k magnification   d. 3000sccm H₂ with 50k magnification

Figure 2-2. Morphological images of polycrystalline diamond by SEM

Polycrystalline diamond crystallites with 1000sccm H₂ shown in figure 2-2a are multiple faceted with diameters more than 0.5µm; the crevice can be clearly seen and the surface is rather rough. Crystallites displayed in figure 2-2b with 2000sccm H₂ are a mixture of middle-size (about 0.2 µm diameter) and small-size grains—each of them accounts for approximately half of the surface. The polycrystalline diamond with 3000sccm H₂ in figure 2-2c has a similar grain size to that in figure 2-2b, but it is more closely packed than that of figure 2-2b. It is also apparently observed in figure 2-2c that
many dimples and rectangular flats exist on top of the crystallites. The dimples might result from H₂ etching effects during deposition. It can be concluded that CVD is a self-conflicted process; during this process, plasma etching and chemical deposition occur simultaneously; diamond formation is an outcome of a dynamic balance of etching and deposition. With reference to the Raman spectra in figure 2-1, it is conclusive that the polycrystalline diamond with 3000sccm H₂ obtains the best quality of films.

The chemical deposition of CH₄/H₂ at 1/100sccm and 5/500sccm at low pressure and low H₂ volume in the reactor during the deposition process yielded a polycrystalline diamond whose surface topography is absolutely different from that of the faceted morphology. Particularly for the sample of CH₄/H₂ with 1/100sccm, the diamond peak in Raman spectra (figure 2-1) was almost inhibited by the broad G band. Figure 2-3 illustrates the surface view of these two samples that were subjected to 100sccm and 500sccm H₂ flow rates.

![SEM morphology of polycrystalline diamond synthesized with low H₂ flow rate.](image)

Figure 2-3. SEM morphology of polycrystalline diamond synthesized with low H₂ flow rate.
The temperature and pressure of CVD-grown diamond located in the zone in the carbon phase diagram that is good for growth of stable graphite, however, is metastable for diamond. The atomic hydrogen functions as the graphite-etching phase and forms the diamond structure in the CVD process. Because of the low flow rate (in fact low volume) of H₂, the graphite-etching action does not proceed thoroughly, leaving most parts of the surface in graphitic form and amorphous carbon. For the same reason, the sample of 500sccm H₂ yields identical surface morphology to that of the 100sccm sample, but produces more diamond phase as illustrated in the Raman spectra in figure 2-1.

XRD shows the crystalline structure of the CVD polycrystalline diamond film. Figure 2-3 is the XRD pattern of polycrystalline diamond film.

![XRD pattern of polycrystalline diamond film](image)

Figure 2-4. XRD pattern of polycrystalline diamond film

The sample was prepared by ultrasonic slurry seeding for 10 minutes. The reactant gas chemistry is CH₄/H₂ with 15sccm/1500sccm ratio of flow rate. The deposition was carried out at 650°C temperature and 50torr operating pressure for 10
hours. As can be observed, the polycrystalline diamond film primarily consisted of (111) and (220) oriented plane, and (220) plane accounted for almost three times more than (111) plane. Both peaks were rather sharp indicated that perfect symmetric crystalline were being formed, therefore the as-deposited polycrystalline diamond film has a high quality.

2.2 Nanocrystalline Diamond Film

2.2.1 Introduction to Nanocrystalline Diamond Film

Polycrystalline diamond has a coarse grain size and it is difficult to avoid the cavities in the as-deposited diamond layer during the growth process. The introduction of Ar into the gas chemistry recipe of polycrystalline diamond results in the formation of ultra fine nanocrystalline diamond. Compared with the micro-scale grain size (>1μm) and rough surface(0.5-1μm) of polycrystalline diamond films, nanocrystalline diamond films have a much smaller grain size, which can be less than 5nm in diameter and smooth surface (15-30nm). Since nanocrystalline diamond films are expected to exhibit superior performance in physical, chemical, electrical and mechanical properties than polycrystalline diamond films do, nanocrystalline diamond films have been most extensively studied and employed in almost all industries [5-8].

2.2.2 Growth Conditions of Nanocrystalline Diamond Film

Intrinsic nanocrystalline diamond films are grown by a chemistry gas mixture of CH₄, H₂ and Ar. Among them, CH₄ always accounts for 1% in flow rate (sccm), H₂ can take 1% up to 5%, and the remaining part is Ar. In the current experiment,
nanocrystalline diamond film was prepared by CH$_4$/H$_2$/Ar at 2sccm/2sccm/200sccm for 3 hours. The deposition pressure was 120HPa and the temperature was 750°C. The pressure of nanocrystalline diamond deposition is much higher than polycrystalline diamond, because of the introduction of argon, which has big molecules and accounts for 98% of the total gas chemistry. Many researchers concluded that hydrogen plays an important role in decreasing diamond grain size to the nano scale. The seeding and cleaning procedure of nanocrystalline diamond deposition is the same as the polycrystalline process described before.

2.2.3 Characterizations of Nanocrystalline Diamond Film

Unlike the Raman spectroscopy of polycrystalline diamond film that only displays one peak at 1330cm$^{-1}$ presenting polycrystalline diamond, the nanocrystalline diamond Raman spectroscopy has four peaks that indicate nanocrystalline diamond, polycrystalline diamond, G band (graphite) and D band (diamond structure) respectively. In the crystalline solids, the Raman bands are relatively sharp; the widths broaden with the increasing temperature and decreasing grain size. However, the presence of impurities, vacancies or some other imperfections in the crystal lattice results in additional broadening of the Raman bands. In particular, amorphous materials are characterized by very broad features that are difficult to give a quantitative interpretation [9]. The laser wavelength of Raman is 514nm, which is located in the range of visible electromagnet spectrum from 380nm to 740nm. This wavelength is believed to readily present graphitic phase rather than diamond structure, especially the nanocrystalline
diamond bond, which is shorter and stronger than that of the polycrystalline diamond bond.

![Raman spectrum for nanocrystalline diamond](image)

**Figure 2-5.** Raman spectrum for nanocrystalline diamond

The morphology of nanocrystalline diamond observed using SEM is absolutely different from that of polycrystalline diamond. Figure 2-6 is a sample synthesized by CH$_4$/H$_2$/Ar at 2sccm/2sccm/180sccm under 110HPa. The surface displays uniform distribution of cauliflower-like diamond crystallites with 100nm to 200nm diameter of cluster, which are composed of hundreds of grains. The grain boundaries can be observed in dark color with about 0.5nm wide, which is rich in sp$^2$ bondings.
Figure 2-6. Morphology of nanocrystalline diamond by SEM

Figure 2-7 is the AFM images of nanocrystalline diamond film measured by non-contact mode, which can precisely record the tip-sample distance by controlling atomic forces between the cantilever tip and sample surfaces. Figure 2-7a is a two-dimensional AFM image with 10µm×10µm scanning area displaying a cauliflower-like surface morphology of nanocrystalline diamond films; figure 2-7b is a three-dimensional image showing the maximum height of 893.81nm in the scanned area; the height gradient can also be observed on the surface. The average roughness of this specimen is about 94nm, and the surface is covered by mixed different sizes of diamond grains.
a. Two-dimensional AFM image 

b. Three-dimensional AFM image

Figure 2-7. AFM images of nanocrystalline diamond film measured by non-contact mode

Figure 2-8 represents the XRD pattern of nanocrystalline diamond film synthesized by feeding a gaseous mixture of CH₄/H₂/Ar with a 2sccm/2sccm/200sccm flow rate ratio. The deposition was carried out at 700°C temperature and 130torr operating pressure for 26 hours. As can be observed, identical to the XRD pattern of polycrystalline diamond film in figure 2-4, nanocrystalline diamond film primarily consisted of (111) and (220) oriented plane, and (220) plane accounted for almost three times more than (111) plane. Both peaks displayed broad width, rather than sharp peaks illustrated by polycrystalline diamond film, indicating much smaller diamond crystallites were being formed; therefore the as-deposited nanocrystalline diamond film has a higher surface density and quality.
2.3 Diamond-Like Carbon (DLC)

2.3.1 Introduction to DLC

Amorphous carbon film is also referred as diamond-like carbon (DLC) film, which is a metastable form of amorphous carbon with a significant fraction of sp\(^3\) bonding. Crystalline materials have atoms with long-range order in a repeated or periodic way over long atomic distances. In amorphous materials there is no long-range atomic order. These materials are characterized by lack of a systematic and regular arrangement of atoms over long atomic distances. Amorphous carbon film can be seen as short-range ordered diamond film, because it has sp\(^3\) bonding as well as similar properties of diamond such as a high mechanical hardness, elastic modulus, chemical inertness, and optical transparency, etc., even though properties of amorphous carbon film are not as good as those of nanocrystalline diamond film or polycrystalline diamond film. Bondings in amorphous carbon consist of a fraction of sp\(^3\) bonded carbon sites and the hydrogen
content, C-H bond; sp² sites are a third significant factor in amorphous carbon, particularly for the electronic properties [10-12].

2.3.2 Growth Conditions of DLC

The deposition of amorphous carbon film can be achieved by a CVD technique by feeding a mixture of methane (CH₄) and argon (Ar) with a typical flow rate of 5% to 95% respectively. For example, the following characterized amorphous carbon film was synthesized by CH₄/Ar at 10sccm/190sccm for 2 hours. The deposition pressure was 120HPa and the temperature was 900°C. Even though amorphous carbon film deposition is similar to that of polycrystalline diamond film, both have two reactant gases: amorphous diamond has argon and methane; whereas polycrystalline diamond has hydrogen and methane, but the pressure difference is very high (polycrystalline 50HPa, amorphous carbon 120HPa) due to a great atom size difference between argon and hydrogen.

The Astex CVD system is equipped with a 1KW, 2.45GHz microwave generator. Usually the H₂ plasma is ignited at 400 watts for diamond growth. However, the output energy at this level is not powerful enough to generate argon plasma, because argon is a kind of noble gas that is chemically inert and difficult to be ionized by low power and low frequency microwave. In order to successfully deposit amorphous diamond with stable plasma of mixed chemistry consisting only of Ar and CH₄, an alternative approach of H₂ plasma ignition has to be adopted. Similar to the H₂ plasma generation as that of polycrystalline diamond and nanocrystalline diamond described above, once H₂ plasma is ignited, the Ar and CH₄ is fed into the CVD reactor subsequently according to the flow
rate of the recipe; then the H\textsubscript{2} molecular supply is reduced to a zero flow rate, leaving behind CH\textsubscript{4} and Ar in the chamber. Making a sensitive balance of pressure, gas flow rates, power supply and depositing temperature so that the value of reflected watts on microwave generator panel is not over 3 (indicating a stable plasma); the amorphous diamond film is finally being grown by Astex system.

2.3.3 Characterizations of DLC

Figure 2-9 is the Raman spectrum of diamond-like carbon grown by 10sccm CH\textsubscript{4} and 190sccm Ar under 120HPa at 900°C. From the figure, it is evident that there are no apparent sharp peaks. Three broad bumps corresponding to nano-diamond, polydiamond and graphite can be observed, illustrating that the Raman spectrum analysis is good at revealing the bonding types of materials such as sp\textsuperscript{3} or sp\textsuperscript{2} bonds, rather than crystallinity of material. From the obvious height and width difference of the peaks, Raman spectra can still provide information about long-range ordered atom arrangement (crystalline with sharp and high peak) and short-range disordered atom arrangement (amorphous phase with broad bump), even though both carbon phase forms are sp\textsuperscript{3} and sp\textsuperscript{2} bondings.
Figure 2-10 illustrates the SEM image of DLC. The top view of DLC demonstrates neither faceted particles like polycrystalline diamond, nor regularity crystallites like nanocrystalline diamond. The surface of DLC displays coarse and irregular clusters. Big island-like agglomerates are the main feature of the surface separated by boundary-like ditches that consist of tiny particles randomly oriented. The dark groves predominantly consist of sp² bondings (graphitic phase), whereas the tiny particle is rich in sp³ bondings (diamond phase). The entire surface exhibits a rough and homogeneous distribution of small particles.
Figure 2-11 reveals two-dimensional (figure 2-11a) and three-dimensional (figure 2-11b) images of DLC by AFM technique respectively. Figure 2-11a shows large agglomerates embedded in the background of uniform small particles; figure 2-11b demonstrates the roughness of surface and particle sizes of DLC film, but the big island is not accurately reflected because it is out of the measurement range, leaving an artifact in corresponding position. The total scanning area is 3µm×3µm with an average roughness of about 217nm.
2.4 Diamond Nanowires

2.4.1 Introduction to VLS and Nanowires

The growth of diamond wires can be divided into two stages: first, the growth of Si nanowires by the vapor-liquid-solid (VLS) method in a thermal furnace; second, the coating of nanocrystalline diamond on the shell of Si nanowires by the CVD method, which has exactly the same gas recipe as the deposition of diamond. The vapor-liquid-solid method (VLS) is a description of a mechanism for the growth of one-dimensional nanowires such as Si nanowires or ZnO nanowires, so called because it involves a vapor phase precursor, a liquid catalytic metal droplet and a solid one-dimensional nanowire. VLS can occur in a thermal furnace or a CVD chamber, but both of them follow the same growth process in terms of variation of material forms, vapor-liquid-solid. The VLS growth process of Si nanowires can be briefly described as follows: first is the preparation of the thin metallic catalyst thin film (for instance Au) on the Si substrate
surface. When the sample is annealed at a temperature above the eutectic point, a liquid Au-Si droplet of nano-size is formed functioning to lower activation energy for growth of nanowires. After the Si contained material such as SiO powder is heated and evaporated into gas phase, with the help of carrier gas Ar, Si atoms are adsorbed at the liquid-alloy/solid-Si interface, and the droplet rises from the surface to grow up as Au tipped Si nanowires [13].

Si nanowires have been expected for many applications, but the original function was to serve as interconnectors between nanoscale components. In addition, the high surface-to-volume ratio of nanowire makes it an interesting nanostructure for solid surface reaction and sensing. Up to now, even though production-scale nanowire applications with market value have not achieved, but many simple device structures have been demonstrated, illustrating the possibilities might be available in the near future [14].

Electronic applications of Si nanowires have been reported to make p–n junctions within single wires [15-17] and between wires [18] field-effect transistors (FETs) [15, 19-21]. Si nanowires can also be applied in the development of optical and optoelectronic devices such as light-emitting diodes (LEDs) [18, 22-24], heterostructure nanowire-based solar cells [25, 26]. The mechanical properties of nanowires have also been employed to demonstrate device concepts such as mass sensors for particles of very small mass [27], nanowire power generators [28]. Finally, the electrochemical applications of nanowires have been investigated. Law et al. demonstrated molecular sensors based on nanowires [29]. As well, pH sensors based on Si nanowires have been fabricated [31]. In addition to the above-mentioned applications, diamond nanowires compared with Si nanowires are
also an ideal material for chemical/bio-chemical, biomedical applications due to its special chemical inertness/stability, bio-compatible and strong bonding ability to DNA properties [31].

2.4.2 Growth Conditions of Diamond Nanowires

In the present study, Si nanowires were grown by the VLS method in a Lindburg thermal furnace. The VLS growth of Si nanowires in the thermal furnace can be described briefly as follows. First of all, a catalytic metal thin layer around 1-10 nanometers thick on the Si substrate was prepared by an electron beam evaporation method (E-beam evaporator). The generally used catalytic metal can also be Au, Pd, Al, Ga, etc. A gold catalytic thin layer with 5nm thick on Si substrate was selected to serve as the sample. The Si nanowire growth process was carried out in a vacuumed horizontal tube furnace about $10^{-3}$ Torr by a mechanical pump. The source material was the high purity SiO powders (120mg), which was contained in an alumina boat (also called a combustion boat). The boat with SiO powders was inserted into the horizontal tube furnace and kept in the middle of the furnace in order to absorb the highest amount of energy. Another boat with the sample was set next to the first one downstream of the carrier gas so that Si atoms decomposed by heat could drop on the surface of the sample. Prior to heating, the reaction chamber was vacuumed, and then the carrier gas Ar was introduced through the tube at a flow rate of 170 sccm. The source material was rapidly heated to 1030 °C from room temperature within 2 hours and was kept at 1030 °C for 1 hour. finally, the furnace was cooled down to room temperature in 2 hours. The chamber pressure was kept at about 30 mTorr during the entire process.
Once the Si nanowires had been successfully grown, the sample with Si nanowires was immersed into the uniformed diamond slurry and was then dried at room temperature in a natural way to avoid nanowires broken by blowing compressive nitrogen. After the naturally dried Si nanowire sample was placed into the Astex CVD chamber, the procedure of intrinsic nanocrystalline diamond deposition was started with \( \text{H}_2 \) (2sccm)/\( \text{CH}_4 \) (2sccm)/\( \text{Ar} \) (180sccm) under the operating temperature 770°C and pressure 120HPa. The nanocrystalline diamond growth time lasted 15 minutes.

2.4.3 Characterization of Diamond Nanowires

Figure 2-12 is the SEM image of Si nanowires grown in the above-described conditions. The maximum diameter is 323nm and the minimum diameter is 158nm. It is difficult to measure the practical length of Si nanowires because most of them entangled with and overlapped each other, and it is also impossible to find the roots of nanowires; therefore, only the length of the section of nanowires on the surface could be measured. The maximum length observed in this image is about 4 \( \mu \)m, when actually the real length of Si nanowires can reach from several tens of micrometers to more than one hundred micrometers.
Figure 2-12. Image of Si nanowires by SEM

Figure 2-13 is SEM image of the diamond nanowires grown according to the above-mentioned conditions. Nano-sized diamond particles coated around the shell of Si nanowires in a uniform and continuous way because the diamond and Si have identical microcrystalline cubic structures, and because the growth conditions were optimized. If the microstructures of two elements are not matched, such as diamond coating on ZnO nanowires, which have a hexagonal crystalline structure, diamond will present scattered particles around the shell of the ZnO nanowires. The maximum length of diamond wire in this photo is 14µm; the maximum diameter of diamond knot is more than 2 µm.
2.5 Graphene

2.5.1 Introduction to Graphene

Graphene is believed to be a new form of carbon allotropy subsequent to graphite, diamond, carbon nanotubes and fullerenes. It is a freestanding single atomic carbon layer with a hexagonal structure, which can be visualized as an individual layer extracted from graphite. There are several ways to produce graphene, including mechanical exfoliation of graphene from graphite, high temperature (>1100°C) extraction from SiC, chemical vapor deposition on a metal surface such as nickel and copper. In the present research, graphene was grown on Si substrate with a nickel layer by the CVD method.

Graphene has been found to have prominent mechanical and electrical and optical properties, which make it a promising material for many applications such as biosensor, gas sensor, transistor, conducting electrode, capacitors, etc. [32, 33]. Due to the limitation of application facilities, the current study only focuses on the characterization of graphene, and thus is not concerned with the practical applications.
2.5.2 Growth Conditions of Graphene

First, the Si substrate with an Ni thin layer was heated in the Astex CVD chamber for 30 minutes in H₂ plasma of 200sccm. The pressure of the chamber was 40HPa. The temperature of the sample surface was 700 ºC measured by pyrometer. Immediately after the heating treatment, a CH₄ mix was introduced into the chamber with 22.2sccm. In the meantime, in order to keep a CH₄/H₂ ratio at 1/8 and a total flow rate of 200sccm (the sum of CH₄ and H₂), the H₂ was adjusted to 177.8sccm from the previous heating flow rate of 200sccm. This is the reactant chemistry gas recipe of graphene growth [34], and the growth time was 5 minutes. Finally, the CH₄ and H₂ supply, was shut off, then Ar was put in at 10,000sccm to cool down the temperature and purge the chamber and pipelines.

2.5.3 Characterization of Graphene

Graphene created by the CVD method can produce a flake with several layers, as can be observed in an optical image with 50 magnification in figure 2-14. Several factors influence the graphene synthesis greatly; for instance, the growth rate and adhesion of graphene depend on the different catalytic metals. Temperature and carbon atom nucleation also play an important role in the growth process. Different orientations of graphene exhibit various growth rates; this point is similar to the growth of CVD diamond films and can be clearly viewed in figure 2-15 by the wave-like surface [35, 36].
Raman spectroscopy is a powerful tool for characterizing graphene and helping to understand the behavior of electrons and phonons. Because graphene fabricated by the CVD method usually contains multiple layers, it is important to clarify the number of layers and the features of different orders of layer when analyzing the graphene.

As evident in figure 2-15, there are three peaks positioned at 1351, 1571, and 2417 cm$^{-1}$, which are defined as D, G and 2D (two-dimensional) correspondingly. The remarkable sharp and symmetric 2D peak indicates the presence of single crystal graphene, which might be multiple layers. D peak is attributed to the defects and structural disorders in graphene. The intensity ratio of D-to-G peak increases with the rise of disorder degree in graphene, which may include distortions, corrugations (puckers) and non-uniformity developed during the growth process [37-39]. The G and 2D Raman peaks change in shape, position and relative intensity with the number of graphene layers. This reflects the electronic structure and electron–phonon interactions. Disorder can be monitored via the D peak [40].

Figure 2-14. Optical image of graphene flake made by CVD
The SEM image in figure 2-16 reveals the fact that the highly crystalline graphene accounts for most of the sample, and the corrupted region that is proportional to the intensity ratio of D-to-G peak in the Raman spectrum only takes up a small portion in the sample. The SEM image also reveals the multiple layer structure of graphene made by the CVD method.
2.6 Summary

Polycrystalline diamond films produced by the MPECVD method utilizing gas chemistry CH$_4$/H$_2$ at a ratio of 1/100 were deposited by changing the H$_2$ volume from 100sccm to 3000sccm. It turned out that the sample of 100sccm H$_2$ was composed of a large amount of graphitic phase and the surface presented cauliflower-like morphology. The samples fabricated by a more than 1000sccm H$_2$ flow rate showed classic faceted surfaces with the size of diamond crystallites ranging from 200nm to 1500nm. The XRD patterns exhibited high crystallinity of deposited diamond with mostly (111) and (220) plane, and the (220) plane accounted for three times more than (111) plane in the whole deposited surface.

Nanocrystalline diamond film produced by the MPECVD method using gas chemistry CH$_4$/H$_2$/Ar at 2sccm/2sccm/180sccm was deposited under 110HPa pressure. The Raman spectrum revealed a nano diamond peak at the position of 1140cm$^{-1}$. The SEM displayed cauliflower-like surface morphology with 100nm to 200nm diamond crystallites. Two- and three-dimensional AFM images showed that the average roughness was 94nm with a 10μm×10μm scan area. Identical to the XRD pattern of polycrystalline diamond film, nanocrystalline diamond film also primarily consisted of (111) and (220) oriented planes, and (220) planes accounted for almost three times more than (111) plane. Different from polycrystalline diamond film, both peaks displayed broadened width, indicating that much smaller diamond crystallites were being formed; therefore, the as-deposited nanocrystalline diamond film has a higher surface density and quality than that of polycrystalline diamond films.
Diamond-like carbon (DLC) exhibited in the Raman spectrum only broad bumps in the position of D band and G band, illustrating that no crystalline structures were formed on the surface. The SEM disclosed a rough surface with scattered particles embedded in the tiny boundary-like ditches. AFM demonstrated an average roughness of about 217nm in a 3µm×3µm scanning area, which was rather high compared with nanocrystalline diamond film.

Nanocrystalline diamond nanowires were successfully coated in a MPECVD reactor around the shell of Si nanowires produced by the VLS method in the thermal furnace. The maximum length of diamond wire that we have visualized in SEM was 14µm; the maximum diameter of diamond knot was more than 2µm. The uniformity of diamond coating on the shell of the Si nanowires was ascribed to the structure match between diamond and Si.

2.7 List of References


CHAPTER 3:
THE ROLE OF ARGON IN THE GROWTH OF NANOCRYSTALLINE DIAMOND FILMS

3.1 The Role of Ar in Nanocrystalline Diamond Film

Argon is a noble gas with atomic number 18, and it plays an important role in the chemical vapor deposition process of ultra fine nanocrystalline diamond films. Unlike hydrogen and methane, which are active species in the formation of the diamond film, argon does not directly participate the chemical reaction in the reactor; it is a medium to contain energy so that the chemical reaction can occur at a desired temperature. Argon is also used to strike the initial plasma and purge the system after the deposition. Plasma may be ignited by argon at 100-200 watts with a flow rate in the range of 1500-2500sccm. Another important role argon plays in the chemical vapor deposition process is that, by changing the volume of argon, the pressure in the reactor can be adjusted to an expected value. Temperature and pressure are two critical physical parameters to determine the quality of diamond films during the chemical vapor deposition process. The size of plasma can be tuned by the pressure; higher pressure results in smaller plasma, which has higher density, yields higher growth rate and a smaller deposition area. In the present section, the influences of argon on the intrinsic nanocrystalline diamond films are studied with variation of temperature and pressure.
3.2 Experimental Descriptions

A series of experiments with various volumes of argon were carried out in the Astex chemical vapor deposition system; the Astex CVD system is ideal for small size samples and exploring the properties of diamond films. All samples follow the same preparation procedure as stated in section 2.1.2. Each sample was cut into 2cm×2cm square pieces and was put into slurry made up with the mixing of methanol and diamond powder (5nm) to ultrasonic agitation for 15 minutes in order to get uniformed seeding on the surface of substrate. After oscillation seeding in an ultrasonicator, the samples were rinse-cleaned by methanol to remove the residues such as contaminants or impurities on the surface, and then they were dried by compressed nitrogen just before being placed into the CVD chamber. The above description of sample preparation can be seen as standard protocol of pretreatment before loading samples into the CVD chamber. Table 2 illustrates the gas chemistry, pressure and temperature of the deposition process. The deposition time for each sample was three hours.

Table 2. The depositing conditions of pressure, temperature and Ar variations

<table>
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<tr>
<th>Ar</th>
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<th>H\textsubscript{2}</th>
<th>Temperature</th>
<th>Pressure</th>
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<td>2sccm</td>
<td>750°C</td>
<td>120HPa</td>
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<td>767°C</td>
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<td>2sccm</td>
<td>770°C</td>
<td>120HPa</td>
</tr>
<tr>
<td>170sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>766°C</td>
<td>120HPa</td>
</tr>
</tbody>
</table>
3.3 Raman Analyses of Nano-Diamond Films on Ar Variation

There are two important peaks named D band and G band in the Raman spectra of nanocrystalline diamond, in which G band is not presented in the Raman spectrum of polycrystalline diamond films, corresponding to a Raman shift of 1350 cm\(^{-1}\) and 1500 cm\(^{-1}\) respectively. D and G band were first reported by F. Tuinstra and J. L. Koenig in 1970 on a paper of graphite study by the Raman spectrum [1]. When the CVD diamond study became prosperous, especially nanocrystalline diamond films, D band and G band have garnered greater interest. According to Tuinstra and Koenig [1], D band at around 1350 cm\(^{-1}\) is attributed to a particle size effect; the intensity of D band is inversely proportional to the crystallite size in the direction of the graphite plane. In the Nano-Diamond films, D band in the range of 1200-1400 cm\(^{-1}\) is believed to be induced by disorder such as nano-size crystallites, impurities, imperfections, edges, and related to the laser excitation energy; the intensity ratio \(I_D/I_G\) is proportional to the graphitic in-plane crystallite size [2]. In carbon allotropes, 0D defines fullerenes, 1D indicates nanotubes, 2D represents two-dimensional graphene, and 3D is stacked graphene into 3D graphite. G band is considered 2D graphite of first order Raman peak, which means one phonon is involved in the Raman scattering [3]. The full width at the half maximum (FWHM) intensity of the G band is also dependent on excitation wavelength [4].

In Raman spectra of intrinsic nanocrystalline diamond as demonstrated in figure 3-1, diamond has a characteristic emission at 1140 and 1332 cm\(^{-1}\); graphite has a characteristic emission at about 1580 cm\(^{-1}\). By comparing the height and sharpness of diamond peaks at 1140 cm\(^{-1}\), the samples with 170 sccm and 180 sccm Ar flow rate produced the best quality of diamond film and contained the lowest percentage of
graphite. The Raman lasers with 514nm and 488nm wavelength are only sensitive to sp² bonding because the cross-sectional area of sp² is much bigger than sp³ [5]. The Raman laser of 244nm wavelength (sometimes called UV Raman) provides higher energy and thus allows sp³ bonding to be effectively observed [6-7].

![Graph showing Raman spectra](image)

**Figure 3-1.** Raman spectra of nano-diamond grown at same pressure

### 3.4 SEM Morphologies of Nano-Diamond Films on Ar Variation

Magnification with an SEM of about 500 times is good enough to observe whether the coating is continuous or not. SEM magnification of about 1,000 times or more is sufficient to determine the crystal type. In order to compare the grain shapes, sizes and boundaries, images at 50k magnification were selected to make a thorough comparison.

In figure 3-2, SEM images of 170sccm and 180sccm Ar did not show much difference on morphology due to the variation in Ar flow rate. Both of them have a
cauliflower-like surface with round or global grains, and the surfaces are rather rough—
grain boundaries can be clearly observed. The image of 190sccm Ar is flatter than those 
of 170 and 180sccm. The grain shape is similar to 170 and 180 sccm, but the sizes are 
much smaller, and therefore grain boundaries are difficult to observe. It also showed that 
many long grains exist and mix with round grains. The image of 200sccm Ar has a totally 
different morphology from all of the above specimen. It has a surface like the ear-of-
wheat, which some literatures also prefer to call feather-like topography. Grain 
boundaries are rather short and smaller than those of cauliflower-like grains. From the 
perspective of a smooth surface, 190sccm Ar provides the best quality of Nano-Diamond 
films.

However, like the composition of surfaces such as different sp bondings or 
graphite, or DLC, generally the presence of amorphous carbon or graphite can be visually 
observed since it blackens the surface of the film. Diamond with significant indication of 
multiple bonds with sp and sp\(^2\) configuration forms a spherulitic or amorphous crystal 
structure considered as a defects-matrix in which sp\(^3\) diamond crystallites are embedded 
\[8, 9\]. On the other hand, diamond film with a low sp\(^2\) (graphitic) signal by Raman 
exhibits a faceted crystal structure like the polycrystalline diamond in chapter two.
a. SEM image with 170sccm Ar  

b. SEM image with 180sccm Ar  

c. SEM image with 190sccm Ar  

d. SEM image with 200sccm Ar  

Figure 3-2. SEM images of nano-diamond grown with various argon

3.5 XRD Comparison of Nano-Diamond Films on Ar Variation

A measurement of the diffraction pattern of X-rays exposed to the diamond film can be used to determine the components of diamond films. Diamond diffracts X-rays at approximately 44°, 75° (and 92°) two-theta when irradiated by copper radiation. The presence of graphite is indicated by a peak at approximately 27°. The presence of amorphous carbon is difficult to determine by X-ray.

Comparison of XRD patterns on the height of diamond (111) peaks in figure 3-3, illustrate that a 190sccm argon flow rate created the best quality of diamond. However, it
also contains a certain amount of diamond (311) peak. Considering the single orientation diamond crystal, 180sccm and 200sccm recipes exhibit better performance than other recipes. The peaks of 170sccm also display that a tiny amount of (311) orientated diamond existed. Because diamond can be seen as an FCC structure, taking into account planar density of (111) and (220) in FCC, (111) equals to 0.29/ (R^2), and (220) is 0.177/ (R^2), so (111) is supposed to grow much slower than (220). With the increase of growth time, (220) will become a major component of nanocrystalline diamond film. In the current case, for three hours deposition time, both planes were in same level of occupation.

![XRD pattern of nano-diamond grown at 120HPa](image)

**Angles (2θ)**

Figure 3-3. XRD patterns of nano-diamond grown at 120HPa

**3.6 Pressure Influences on Nano-Diamond Films**

Pressure is a most important factor in determining the formation of diamond films. Higher pressure causes the increase of the plasma density, which promotes the carbon dimers in the gas phase. Carbon dimers are believed to be the precursors for...
diamond growth and will increase the growth rate of diamond films [10-12]. The high gas pressures may cause an etching effect on the graphite susceptor by atomic hydrogen, which can be treated as an independent process parallel to diamond deposition [12]. Research also indicated that diamond crystallite size decreased with increasing pressure [13]. A pressure change from 5torr to 20torr also presented a texture orientation change from (111) to (100) for HFCVD polycrystalline diamond films [15]. More extensive studies on process parameters such as input power, substrate temperatures, gas pressures and gas flow rates can be referred to literatures [15-19]. In the current work, various pressure effects on nanocrystalline diamond films were examined while keeping the same Ar, CH₄ and H₂ flow rate.

<table>
<thead>
<tr>
<th>Ar</th>
<th>CH₄</th>
<th>H₂</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>180sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>770°C</td>
<td>120HPa</td>
</tr>
<tr>
<td>180sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>770°C</td>
<td>110HPa</td>
</tr>
<tr>
<td>180sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>700°C</td>
<td>100HPa</td>
</tr>
<tr>
<td>180sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>745°C</td>
<td>90HPa</td>
</tr>
</tbody>
</table>

3.6.1 Raman Analyses of Nano-Diamond Films on Pressure Variation

The comparison of Raman spectra under various pressures is presented in figure 3-4. The nanocrystalline peaks of 90HPa and 110HPa are almost overlapped, illustrating that the contents of nano-size diamond crystallites grown under these two pressures are almost the same amount. The peak of microcrystalline diamond of 90HPa is higher than that of 110HPa, indicating that microcrystalline diamond in 90HPa contains more than
that in 120HPa. The peak of G band in 90HPa is higher than that in 110HPa, meanwhile, the width of G peak in both pressures are almost the same, disclosing the fact that the graphite structure in 90HPa exists more than 110HPa. The as-grown diamond films under 100HPa and 120HPa own the highest nano-diamond peak in the Raman figure, but both the microcrystalline diamond peak and G peak of 120HPa are higher than those of 100HPa, revealing that the diamond films of 120HPa consist of crystalline structures more than that of 100HPa.

![Figure 3-4. The comparison of Raman spectra under various pressures](image)

**3.6.2 SEM Images of Nano-Diamond Films on Pressure Variation**

Figure 3-5 shows the micrographs of nanocrystalline diamond films grown with Ar 180sccm under 90HPa, with magnification of 10k, 20k, 30k and 50k respectively. In the image of 10k, the entire film consists of many big grains about 1µm to 2µm in diameter, and the grain boundaries can be clearly observed. The high magnification images show that the surfaces are full of ear-of-wheat-like diamond texture.
Ar 180sccm at 90hpa

Figure 3-5. Micrographs of nanocrystalline diamond films grown with 180sccm Ar at 90Hpa

Ar 180sccm at 100hpa

Figure 3-6. Micrographs of nano-diamond films grown with 180sccm Ar at 100Hpa
Figure 3-6 displays images of diamond at 100HPa, with magnification of 10k, 20k, 30k and 50k respectively. Compared with images of 90HPa, in the image of 10k, it contains much smaller grains with a maximum diameter of 1µm, and grain boundaries are not as clear as that of 90HPa. In the high-magnification images, surfaces also exhibit ear-of-wheat-like clusters, but many tiny round nano-sized round diamond crystallites can be observed in the image of 50k, which are not observed in the images of 90HPa. It should be noted that, in the image of 30k at the bottom of right corner, and also in the image of 50k at the bottom of left corner, the growth of extra large diamond grains was observed due to the increase of pressure, from 90HPa to 100HPa.

**Ar 180sccm at 110hpa**

Figure 3-7. Micrographs of nano-diamond films grown with 180sccm Ar at 110HPa

As can be observed, big differences of the surface appearance of nanocrystalline diamond films in figure 3-7 exist, compared with those in figure 3-5 and figure 3-6. In figure 3-7, the ear-of-wheat-like surface feature disappeared in place of a mixture of tiny-
sized (several tens of nanometers) and middle-sized (ranging from one to two hundred nanometers) diamond agglomerates uniformly distributed in a random orientation.

**Ar 180sccm at 120hpa**

**Figure 3-8. Micrographs of nano-diamond films grown with 180sccm Ar at 120HPa**

Figure 3-8 is the nano diamond morphology of 180sccm Ar at 120HPa. As a result of increased pressure to 120HPa, large diamond agglomerates can be obviously noticed and account for more than half a percent of the total area. On the other hand, the tiny-sized diamond particles decreased to 30% from almost 50% in the sample of 110HPa.

In conclusion, nanocrystalline diamond depositions with 180sccm Ar flow rate display various surface morphologies and structures under different pressures. At the low pressure of 90HPa and 100HPa, diamond films show an ear-of-wheat-like feature, indicating that nano diamond grew in a preferred orientation, and texture structures existed in the films. However, at the pressure of 110HPa and 120HPa, the ear-of-wheat-
like feature disappeared in place of a mixture of different-sized diamond agglomerates. With the increase of pressure, the evenly distributed surface became rough due to the growth of extra large sized diamond grains.

3.6.3 XRD Comparison of Nano-Diamond Films on Pressure Variation

XRD is an extensively utilized nondestructive technique that provides crystalline information such as phase presence, grain size, strain and preferential growth orientation in the research of CVD diamond films. Special attention should be paid to the fact that an X-ray can penetrate diamond more than 100µm in depth; the peaks of substrate sometimes exhibit stronger peaks than those of diamond [20]. For boron-doped microcrystalline diamond films, low gas pressure was proved to be advantageous to the growth of (220) plane [21]. For HFCVD microcrystalline diamond, the grain size and surface roughness decreased in accordance with the decrease of gas pressure, meanwhile enhancing the secondary nucleation rate [22]. Pressure influence on the growth rate presented discrepancy in the previous reports [23-27]; the reasons still remain inconclusive due to so many affected factors such as growth approaches, different gas reactants, various substrates, etc. It seems that the growth dependence on pressure is nonlinear; however, it has an optimized pressure value for specific conditions.

Figure 3-9 shows XRD patterns of nano-diamond grown with 180sccm Ar at various pressures. For samples of 90HPa and 120HPa, (311) plane was not presented; whereas, for samples of 100HPa and 110HPa, the (111) plane seemed the preferential growth orientation. In addition to the above-observed phenomena, the intensity ratios of the corresponding two diamond peaks, i.e., (111) and (220), for any samples are
proportional to each other, thereby confirming the fact that the variation of pressures will not affect the orientation of diamond growth and their concentrations. Judged from the full width at half maximum (FWHM) of diamond peaks in figure 3-9, the specimen of 110HPa demonstrated the smallest grain size and best crystallinity.

Figure 3-9. XRD patterns of nano-diamond grown at various pressures

3.7 Summary

Under constant depositing pressure of 120HPa, argon changed in the range of 170sccm to 200sccm with an increment of 10sccm for each sample. Raman spectra showed that samples of 170sccm and 180sccm Ar contained a low level of graphite and high volume of diamond. These two samples also displayed a cauliflower-like surface with round or global grains. The ample of 190sccm Ar presented a flattened surface in the SEM image, whereas the sample of 200sccm Ar displayed a texture structure of ear-of-wheat-like surface. XRD patterns illustrated that all samples consisted of mainly (111)
and (220) diamond planes; only sample of 190sccm Ar presented a high sharp (311) plane. As evident from the intensity and ratio of different peaks, the 190sccm sample is found to be the best quality. This conclusion was also consistent with the SEM image.

With a constant Ar flow rate of 180sccm, the depositing pressures varied from 90HPa to 120HPa with an increment of 10HPa for each sample. Raman spectra revealed that the sample of 120HPa produced the highest quality of nano scale diamond films. The SEM images of 90HPa and 100HPa samples exhibited texture structure, the 110HPa sample exhibited a flat cauliflower-like outlook and the 120HPa sample exhibited a rough cauliflower-like surface. XRD patterns disclosed that of the samples composed of (111) and (220) plane, the sample of 110HPa presented the highest peak intensity and unique (311) peak, whereas 90HPa showed the lowest peak intensity. The peak ratios between (111) and (220) for all samples were identical and thereby demonstrated that the change in pressure has no effect on the texture orientations.

3.8 List of References


CHAPTER 4:

NITROGEN-DOPED NANOCRYSTALLINE DIAMOND FILMS

4.1 Introduction to Nitrogen Doped Nano-Diamond Films

Theoretically intrinsic CVD diamond is an insulator, because of the introduction of graphitic phase in the deposition process, it exhibits very low conductivity; for example, an intrinsic CVD diamond sample can be observed directly by SEM without any special metallic coating treatment. Sometimes, the conductivity of diamond is desired for applications such as MEMS, biosensors, biochemical and electrochemical electrodes without spoiling the excellent properties of diamond. The addition of an impurity, called dopant, will dramatically increase the conductivity of pure semiconductor materials. Diamond, which is a specific cubic structure of carbon, is a kind of pure semiconductor. The doped diamond can be classified into two different types: the n-type and p-type. The typical dopant of p-type diamond is boron, which has been extensively studied and well-accepted with a high conductive property. Nitrogen and phosphorus are the widely preferred dopants. Until now, nitrogen-doped diamond has been left much to be desired to improve conductivity.

Nitrogen is an interesting element in the process of CVD diamond in two extreme aspects. First, it is hard to completely avoid, sometimes even the impurity of the ppm level in gas resource can result in 0.1% to 0.3% existence of nitrogen in diamond films. Nitrogen can also be seen ubiquitously in the natural diamond in the presence of a blue
color. Nitrogen is believed to modify the morphology and texture of polycrystalline (micro and nano size) diamond films, increase the growth rate and weaken the boundaries [1-7]. On the other hand, nitrogen sometimes is purposely added into the gas chemistry as a dopant to grow n-type extrinsic diamond films; during this process the content of nitrogen becomes saturated at 0.2% in diamond films when the nitrogen flow rate reaches no more than 20% in gas flow mixtures. Incorporation of nitrogen in nanocrystalline diamond films is inhomogeneous and rich in boundaries in the form of interstitial rather than substitutional distribution. The energy level of nitrogen is 1.57 eV below the minimum conduction band, making it virtually poor electrical conductivity of n-type semiconductor material [8-15].

The nitrogen-doped nanocrystalline diamond films were fabricated by the Astex CVD system. The nitrogen composition during the CVD process is conventionally defined in terms of gas flow rate with the unit of sccm, because it is technically difficult to quantify the content of nitrogen on the diamond surface. In the present study, the effects of various N₂ concentrations such as 5%, 10% and 15% on the quality of nanocrystalline diamond films were characterized by Raman spectroscopy, SEM, XRD as well as AFM techniques.

4.2 Experimental Descriptions

The preparation of specimen prior to being loaded inside the reactor can be referred to in the description in chapter 2.1. The reactant gases include H₂, CH₄, Ar and N₂ to ensure that the diamond grown consists of nanosized grains; the concentrations of N₂ that fed into the CVD chamber are at the 5%, 10% and 15% in sccm flow rate. The
details such as gas recipe flow rates, temperatures, pressures are listed in the following table 4. The deposition time for each of samples is three hours.

Table 4. Deposition parameters of nano-diamond films with various N\textsubscript{2} concentrations

<table>
<thead>
<tr>
<th>N\textsubscript{2}%</th>
<th>CH\textsubscript{4}</th>
<th>H\textsubscript{2}</th>
<th>N\textsubscript{2}</th>
<th>Ar</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% 2sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>0</td>
<td>180sccm</td>
<td>750°C</td>
<td>120HPa</td>
</tr>
<tr>
<td>5% 2sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>10sccm</td>
<td>186sccm</td>
<td>800°C</td>
<td>120HPa</td>
</tr>
<tr>
<td>10% 2sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>20sccm</td>
<td>176sccm</td>
<td>850°C</td>
<td>120HPa</td>
</tr>
<tr>
<td>15% 2sccm</td>
<td>2sccm</td>
<td>2sccm</td>
<td>30sccm</td>
<td>166sccm</td>
<td>885°C</td>
<td>120HPa</td>
</tr>
</tbody>
</table>

4.3 Raman Analyses on N\textsubscript{2} Variation

Figure 4-1 shows the Raman spectra for three different concentrations of N\textsubscript{2}. As can be observed, with the increase of N\textsubscript{2} concentration, nano-diamond peaks around 1140 cm\textsuperscript{-1} were strongly inhibited. The nano-peaks of the samples with 10% N\textsubscript{2} and 15% N\textsubscript{2} are hardly discernible. D band in 5% N\textsubscript{2} has a remarkable shift compared with 10% and 15%N\textsubscript{2}, indicating that higher surface compressive stress lowered due to nitrogen highly incorporated into the diamond films; additional nitrogen creates more boundaries and thus set up more space and this space relaxed the thermal stress between the diamond layer and Si substrate during the cooling process \cite{16}. G band in 5%N\textsubscript{2} is more highly oriented than those in the other two N\textsubscript{2} concentrations, illustrating that crystalline graphitic phase reducing with the increase of nitrogen concentration.
Figure 4-1. Raman spectra of nano-diamond for three different concentrations of N\textsubscript{2}.

Because the sample of 5\% N\textsubscript{2} has the highest nano-diamond peak in figure 4-1, a comparison is made in figure 4-2 between 5\% N\textsubscript{2} and intrinsic nano-diamond with 180sccm Ar so that the function of N\textsubscript{2} can be further clarified in the process of CVD.

It is obvious that the intrinsic diamond has an apparent nano-diamond peak whereas the nano-peak of extrinsic diamond is shown as severely prohibited; this might be caused by the large diamond grain grown due to atomic N. The sharpness of the peak can explain the crystallinity of crystal phase in the Raman spectrum. The heights of both D band and G band in intrinsic diamond are much higher than that of doped diamond, indicating that with the addition of nitrogen, the crystallinity of nano-diamond film becomes degraded. There still exists a microdiamond peak shift in D band; the same explanation in figure 4-1 can be applied to this figure.
Figure 4-2. Comparison of intrinsic and 5% nitrogen doped nano-diamond

4.4 SEM Morphologies on N₂ Variation

Figure 4-3 presents SEM images of various N₂ concentrations at the same pressure of 120HPa. The image of 5% N₂ has a relatively smooth surface and almost invisible boundaries, whereas the image of 10% N₂ has a rough surface and big grain size; with the N₂ concentration increasing to 15%, the image displays a cragged surface and darkened boundaries, which indicate sp² bondings. It can be concluded that the increased additions of N₂ result in a rough surface, big grain size and weak boundaries.
Figure 4-3. Micrographs of N-doped nano-diamond films grown at 120HPa

In order to further clarify the function of N₂ in CVD diamond deposition, nitrogen-doped diamond samples with various pressures are presented below. The gas recipe is the same as that listed in table 4 for each sample.

Figure 4-4 shows SEM images of the 5% N₂ incorporated sample with magnification of 20k and 50k respectively. As evident from the SEM images, the diamond grains are elongated compared with the image in figure 4-3 with the same N₂ concentration due to the increase of pressure. The preferentially diamond growth results in roughness of surface.
Figure 4-4. Micrographs of 5% N$_2$ doped nano-diamond films grown at 130HPa

Figure 4-5 reveals the surface feature of the 10% N$_2$ incorporated sample with magnification of 20k and 50k respectively. Compared with images of the same N$_2$ concentration in figure 4-3, the diamond grain shape and size are almost the same regardless of a 10HPa pressure difference between the two samples. Upon comparing the images of the sample without the N$_2$ addition (figure 3-7), we found that the grains are elongated in the case of the sample with the N$_2$ addition.

Figure 4-5. Micrographs of 10% N$_2$ doped nano-diamond films grown at 110HPa

Figure 4-6 displays the surface morphology of the 15% N$_2$ incorporated sample at 100HPa. As illustrated above, the increase of pressure will produce large diamond
agglomerates. In this case, the pressure is 20HPa less than the sample in figure 4-3, but it large diamond clusters and obvious boundaries can still be observed.

Briefly, SEM images indicated the role of N\textsubscript{2} during the deposition of diamond as follows: N\textsubscript{2} addition causes elongated diamond grains as a surface feature, produces a large cluster with increased boundaries; consequently, the roughness also seems to increase due to the rise of N\textsubscript{2} composition.

Figure 4-6. Micrographs of 15% N\textsubscript{2} doped nano-diamond films grown at 100HPa

Although there still remains controversies about morphological dependence on the N\textsubscript{2} concentrations, excluding the influence of surface contamination and oxidation, atomic nitrogen did change the surface feature by incorporating into boundaries, maybe sometimes, it is not apparent because of the low differences of gas composition pressures [17-23].

4.5 XRD Comparison on N\textsubscript{2} Variation

Figure 4-7 presents the XRD patterns of nano-diamond grown at 5%, 10%, and 15% N\textsubscript{2} concentration respectively. It can be observed that for the XRD pattern of 5% N\textsubscript{2}, (111) planes account for the films less than (311) planes, approximately half in half.
However, for samples of 10% and 15% N\textsubscript{2}, the (111) planes occupy the majority of the films, while the (311) planes only account for 1/3 of the total area.

Figure 4-7. XRD patterns of nano-diamond grown at various N\textsubscript{2} concentrations

4.6 I-V Characteristics and Ohmic Contact of NNCD Films

In CVD diamond, sp\textsuperscript{3} bondings are believed to be responsible for the mechanical properties, whereas sp\textsuperscript{2} bondings, which lie near the Fermi level, determine the optical and electronic properties of the films [24]. The addition of N\textsubscript{2} into intrinsic nanocrystalline diamond films is expected to incorporate atomic N in the boundary areas in the form of sp\textsuperscript{2} bonding, thus increasing the conductivity of nano-diamond films.

In order to make a satisfying integration of diamond into semiconductor devices, high-quality contacts are required. Most semiconductor materials are non-ohmic contact due to the complexes of carrier transportation mechanism. Ohmic contacts to p-type diamond have been achieved by using carbide-forming metals (such as Mo, Ta, Ti) in combination with annealing [25-27]. Ohmic contacts to n-type diamond are believed to
be much more difficult to realize due to the lower conductivity than that of p-type (boron doped) diamond. Nitrogen and phosphorus are the two most promising elements to be used as donors for n-type diamond in the Periodic Table. Titanium ohmic contacts to heavily phosphorus-doped diamond films have been reported as exhibiting low contact resistances [28, 29]. Silver (Ag), which is believed to not form carbide compounds, is an attractive metal to be employed for ohmic contact in the semiconductor industry. Ohmic contacts of Ag monolayer by RF sputtering to B ion implanted p-type diamond have been successfully fabricated [30, 31]. However, Ag thin layer by PLD (pulsed laser deposition) ohmic contact to nitrogen-doped n-type diamond films have not been reported. In the present study, ohmic contacts of Ag thin layer by PLD combined annealing to nitrogen-doped n-type diamond films are successfully achieved.

The advantage to using PLD to make a metallic contact is that the deposition takes place in a highly vacuumed environment (can reach $10^{-9}$ mbar by turbo-pump), thus is avoids any impurity and contamination. The high-quality contact thin film is prepared by ablation of the Ag target focused by pulsed laser beam in a controllable process of tuning the inert gas pressure and kinetic power of the laser. Table 5 is the silver contact deposition parameters by the PLD method.

The samples were grown using the gas mixture $\text{H}_2/\text{CH}_4/\text{Ar}/\text{N}_2$ with the flow rate ratio at 2.5sccm/2.5sccm/165sccm/30sccm, hence, it contained 15% $\text{N}_2$. After PLD deposition, the samples were annealed at temperatures of 100°C, 150°C, 250°C and 300°C in order to find the optimized temperature for silver deposition to obtain an ohmic behavior for Ag/ NCD interface, and 250°C was found the best temperature for ohmic contact.
### Table 5. Silver contact deposition parameters by PLD method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser energy (mJ)</td>
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</tr>
<tr>
<td>Deposition time (min)</td>
<td>10</td>
</tr>
<tr>
<td>Repetition rate (Hz)</td>
<td>10</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Target</td>
<td>Ag</td>
</tr>
<tr>
<td>Substrate</td>
<td>NNCD film/p-Si substrate</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>Distance from target to substrate (mm)</td>
<td>40</td>
</tr>
</tbody>
</table>

Current-voltage (I-V) characteristics were studied for the various interfaces as shown in figure 4-8. Figure 4-8a shows the Ohmic behavior of silver for the silicon substrate and figure 4-8b shows the I-V curve for the interface Ag/NNCD, which is also a straight line suggesting the Ohmic behavior for the junction. Since silver was annealed at 250°C as the optimized temperature to obtain ohmic contacts, the annealing effect of the high temperature functioned on the interface of Ag electrodes and NNCD film, which could possibly rule out the residual stress and microstructure imperfections. Here, it is worthwhile to mention that the electrical resistance on Ag contact reduced 10 times measured at a heated temperature of 250°C [32]. It can be seen from the observed I-V behavior that it is linear for both forward and reverse bias. This suggests that NNCD films are compatible to the Ag thin film contact, which has a high significance for the practical application of N-doped NCD film. It was observed that the current value for Ag/Si and Ag/NNCD presents a big difference as shown in figure 4-8a and b; the
Ag/NNCD film can have nearly 100 times less electrical conductivity than that of the Ag/Si substrate. This high resistivity feature of NNCD film combined with excellent thermo-mechanical property makes it a promising material for specialized dielectric applications [33]. Under the as-grown conditions, the room temperature resistivity of NNCD film was calculated as 17Ω·cm.

A Schottky type I-V curve shown in figure 4-8c was obtained for p-n heterojunction between the NNCD film and p-type Si substrate. The rectifying I-V curve induced by the heterojunction structure proves that the majority of carriers for the NNCD film are electrons. It presents a perfect rectifying property at the voltage range from -0.5 to 0 V and indicates that the NNCD film can be used as a potential rectifier. The turn-on forward voltage is about 0.2 V, which is close to the value of 0.3 V of turn-on voltage of Ge/SiC heterojunction diode in reference [34]. This result indicated that nitrogen-doped nanocrystalline diamond films might serve as an n-type semiconductor material.
(a) interface of Ag /p-Si  

(b) interface of Ag/NNCD  

(c) heterojunction of NNCD /p-Si

Figure 4-8. I-V characteristics for various interfaces

4.7 NNCD Films Grown on SiO₂ Layer

Interests in nanocrystalline diamond integrated MEMS devices have been increasing over the past decade due to the excellent properties of diamond, such as super hard, wide bandgap, high mechanical strength, high thermal conductivity, chemical stability and biocompatibility [1-4]. To fulfill the requirement of MEMS applications, one of the basic practical goals of nanocrystalline diamond film deposition (NCD) is to
obtain a large area of film with uniform thickness for diamond-based micro device. This goal has not been completely achieved partly due to the limitation of CVD technique itself like the size of plasma [5], mostly for the complexity of the growth mechanism of CVD deposition. Nanocrystalline diamond films grown by the microwave plasma enhanced chemical vapor deposition (MPECVD) technique have been extensively studied to understand the growth mechanism, surface characteristics, $sp^3/sp^2$ ratio, electrical properties, optical properties, and mechanical properties such as morphology, roughness, hardness, tribology [6-17]. Many researchers demonstrated that the growth morphology of NCD films have a strong dependence on the substrate temperature, reactant gas mixture, pressure and the hydrogen treatment [18-20]. Other investigations suggest that the diamond powder seed size and the seeding preparation method such as the mechanical seeding or the ultrasonic vibration seeding can have a great influence on the nucleation of diamond film [21, 22]. On the other hand, interests are focused on the surface charge carrier diffusions or hydrogenation treatments to explore the electrical properties of diamond films [23-28]. However, the distribution and concentration of electrons or ions on surface and their correlation with the morphology and structural feature of the diamond films have not been explored. In reality the chemical vapor deposition is not only a simple mechanical or chemical process, but it also involves a surface electric reaction that is critical for the growth process.

Since SiO$_2$ is the most commonly applied layer in MEMS, variations of diamond film on SiO$_2$ were significant to MEMS fabrication. In this section, nitrogen-doped nanocrystalline diamond films (NNCD) with interface structures like 1) NNCD/Si, 2) NNCD/SiO$_2$/Si, and 3) NNCD/NCD/Si were grown using the microwave plasma
enhanced chemical vapor deposition method. By particularly designing the diverse layer structures, the important role of electron diffusion during the CVD process of diamond films was investigated. The gas chemistry for NNCD was $\text{H}_2/\text{CH}_4/\text{Ar}/\text{N}_2$ with the flow rate ratio at 2.5sccm/2.5sccm/165sccm/30sccm, which contained 15% $\text{N}_2$; for NCD (intrinsic nanocrystalline diamond) film it was $\text{H}_2/\text{CH}_4/\text{Ar}$ at 180sccm/2sccm/2sccm ratio. The deposition temperature was in the range of 750°C~800°C, the pressure was around 110HPa, and the power supply was 800 W.

In contrast with the intrinsic nanocrystalline diamond films, the addition of $\text{N}_2$ is believed to increase the grain size of diamond [29-33]. Simulations of the kinetic Monte Carlo and molecular dynamics method under various loading conditions also proved that $\text{N}_2$ addition increased grain size and weakened the mechanical properties of nitrogen-doped diamond films [34]. In addition, many reports demonstrated that diffusion did happen during the CVD process on the subsurface of diamond films [23-26, 35, 36].

Figure 4-9a shows the SEM image of the NNCD/Si structure. Diamond agglomerates can be observed with a diameter of more than 1μm. Each grain might consist of several hundreds of crystallites. Crevice-like dark boundaries indicate that the compositions and structure in boundary are not similar to the surface of the film. Amorphous diamond boundaries that are rich in N atoms and sp$^2$ graphite bondings establish the conductive tunnel for charge carriers and electrons. Once diffusion occurs, charge carriers accumulate and cause diverse morphologies due to the existence of a blocked layer underneath nitrogen-doped diamond films such as intrinsic diamond or $\text{SiO}_2$ thin films. Figure 4-9b shows the surface morphology of the NNCD/NCD/Si structure. It can be seen that the diamond agglomerates are much smaller, and the width
of boundaries are narrow and not as clear as that of the NNCD/Si structure. The NNCD/NCD/Si structure was formed by first depositing intrinsic nanocrystalline diamond film for two hours according to the gas chemistry Ar/CH₄/H₂ at a ratio of 180sccm:2sccm:2sccm, then depositing nitrogen-doped nanocrystalline diamond film for another two hours in the gas chemistry of N₂/Ar/CH₄/H₂ at a flow rate of 30sccm:165sccm:2.5sccm:2.5sccm. Intrinsic diamond films by the CVD method consist of many sp² bondings, i.e., a graphite structure that is highly conductive. Similar to the case of NNCD films, there exist more sp² bondings of graphite than sp³ bondings of diamond in the boundary region of intrinsic nanocrystalline diamond films. The boundary region of intrinsic nanocrystalline diamond serves as a channel for the migration of charge carriers and electrons and thus reduces the density of charge carriers and electrons on the surface of diamond films. This causes the non-uniformity in density in various parts of the surface and results in different morphology and roughness of the diamond surface. Figure 4-9c shows the SEM image of the NNCD/SiO₂/Si layer structure. There is no crevice-like grain boundary observed and the roughness of the surface is smaller as compared to the previous two layer structures, i.e., NNCD/Si and NNCD/NCD/Si. In perspective of charge carrier diffusion, it is proposed that the 100nm thick SiO₂ layer has blocked the diffusion and formed a uniform density of charge carrier on the surface of the diamond film, thus resulting in a better quality of nanocrystalline diamond film.
Figure 4-9. SEM images of NNCD films for (a) NNCD/Si, (b) NNCD/NCD/Si, (c) NNCD/SiO$_2$/Si

Figure 4-10a shows the atomic force microscopy image of the NNCD/Si structure. The dark brown area corresponds to the boundary region in the SEM, which is rich with charge carriers. Figure 4-10b is the AFM image of the NNCD/NCD/Si structure, within the same scanning area of 10µm×10µm. The surface feature indicates that the partial diffusion appears at the interface layer of intrinsic nanocrystalline diamond films while the concentration of charge carriers was not observed to change as much as in the case of the NNCD/Si structure. In figure 4-10c for the NNCD/SiO$_2$/Si structure, the
nanocrystalline diamond displays identical grain size. The average roughness of ~ 29 nm is the smallest among these three layer structures. This suggests that the SiO$_2$ thin layer prohibited the charge carriers’ migration toward the p-type silicon substrate and formed an identical density on the surface.

Figure 4-10. AFM topographic images of NNCD films for (a) NNCD/Si, (b) NNCD/NCD/Si, (c) NNCD/SiO$_2$/Si
The XRD diffraction pattern (figure 4-11) reveals that the major phase in as-deposited films is diamond (111). The highest intensity peak occurs in the NNCD/SiO\(_2\) layer structure, indicating high phase concentration in this structure. X’Pert HighScore analytical software was employed to obtain the data such as intensity, space distance, half width at full maximum. Grain size can be calculated by the Scherrer formula

\[ t = \frac{0.9 \lambda}{B \cos(\theta)} \]

where \( t \) = the diameter of grain, \( \kappa \) = Scherrer constant, \( \lambda \) = the wavelength, which is 1.54 Å, and \( B \) = full width at half maximum (FWHM). Table 6 presents the calculated results of the grain size. As seen in table 6, NNCD/SiO\(_2\)/Si has the lowest roughness, smallest crystallite and highest growth rate.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Roughness</th>
<th>Crystallite</th>
<th>d-spacing(Å)</th>
<th>Growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NNCD/Si</td>
<td>76nm</td>
<td>2.079nm</td>
<td>2.04</td>
<td>0.33 μm/hr</td>
</tr>
<tr>
<td>NNCD/NCD/Si</td>
<td>46nm</td>
<td>1.038nm</td>
<td>2.06</td>
<td>0.32 μm/hr</td>
</tr>
<tr>
<td>NNCD/SiO(_2)/Si</td>
<td>29nm</td>
<td>0.3163nm</td>
<td>2.05</td>
<td>0.37μm/hr</td>
</tr>
</tbody>
</table>

From this, it can be concluded that the diffusion has a great influence on the growth of diamond films, and the SiO\(_2\) layer blocks the migration of charge carriers toward the p-type Si substrate. It should be pointed out that diamond at (111) plane appeared highest in the NNCD/SiO\(_2\)/Si structure and lowest in the NNCD/Si structure. It can be explained that the SiO\(_2\) layer successfully blocks hydrogen and electron diffusion toward the p-type silicon substrate, and causes high a concentration of hydrogen on the diamond film surface in the form of H\(^+\), H\(^-\), H\(^0\) as well as electrons, resulting in negative
affinity of substrate surface. This leads to the enhancement of nucleation and formation of sp³ bondings, and further develops into a higher concentration of diamond structure.

![XRD pattern of NNCD films for different layer structures](image)

Figure 4-11. XRD pattern of NNCD films for different layer structures

In a brief summary, diffusion of charge carriers during the CVD process has great influence on the topographic feature as well as crystallites of nanocrystalline diamond film. Three different layer structures, NNCD/Si, NNCD/NCD/Si and NNCD/SiO₂, were especially designed to study this phenomenon. Diffusion does not change the d-spacing of diamond but greatly affects the morphology, size of diamond crystallite, and the growth rate of diamond film. The SiO₂ layer underneath the diamond film prohibited the migration of charge carriers toward the silicon substrate. Understanding this phenomenon is significant in making higher quality nanocrystalline diamond films.

Figure 4-12 indicates the Raman spectra of three layer structures, NNCD/Si, NNCD/NCD/Si and NNCD/SiO₂. It is evident from figure 4-12 that the NNCD/Si has no
nanopeak, whereas, both NNCD/NCD/Si and NNCD/SiO₂/Si contains the nanopeak. This can be explained as the SiO₂ layer and NCD layer successfully prevented the electrons and negative atomic hydrogen from migrating downward to Si substrate, and consequently the higher density of negative charges on the surface enhanced the growth of nanosized diamond. The identical shape and feature of the Raman spectrum of the NNCD/NCD/Si and NNCD/SiO₂/Si structures indicated that the SiO₂ layer and NCD layer played a similar role in blocking electron diffusion in the CVD deposition process.

Figure 4-12. Raman spectra of three layer structures

Figure 4-13 is the Raman spectrum of nitrogen-doped nanocrystalline diamond film on quartz; quartz can be usually considered as SiO₂ bulk material. The gas chemistry is similar to the one described earlier, i.e., H₂/CH₄/Ar/N₂ with a 2.5sccm/2.5sccm/165sccm/30sccm flow rate ratio, which contains 15% N₂. As evident from the Raman spectra, the nanopeak was sharp and high and the HWFM was broadened, indicating that the concentration of nanosized diamond accounted for a large
percentage of film and the grain size was rather small. This figure furthered the conclusion that substrate with different materials can greatly alter the feature, quality and property of diamond film, and the reason for that might be the variation of density of charge particles such as electrons, atomic hydrogen caused by atomic diffusion toward the substrate.

![Raman spectrum of nanocrystalline diamond film on quartz](image)

**Figure 4-13.** Raman spectrum of nanocrystalline diamond film on quartz

### 4.8 Summary

Nitrogen-doped nanocrystalline diamond films with three different concentrations of 5% N₂, 10% N₂, and 15% N₂ were deposited at 120HPa. In the 10% N₂ and 15% N₂ samples there are no nano peaks due to the increase in diamond grains. The SEM images further proved the growth of diamond crystallites accompanying the increase of N₂ flow.
rate. The sample of 5% N\textsubscript{2} presented elongated grains due to 10HPa decrease of pressure, and similar symptoms were observed in the sample of 10% N\textsubscript{2} and 15% N\textsubscript{2} with the increase of 10HPa and 20HPa respectively. The XRD patterns showed that the major crystalline structures were (111) and (311) planes for all of the three N\textsubscript{2} concentrations. Each of (111) and (311) accounted for a half percent in the 5% N\textsubscript{2} sample; whereas in the 10% N\textsubScript{2} and 15% N\textsubScript{2} samples, the (111) planes occupied the majority of the films, and the (311) planes only accounted for 1/3 of the total area.

Ohmic contact of silver on nitrogen-doped nanocrystalline diamond films was successfully achieved using the PLD method, and I-V characteristics between diamond film and Si substrate were also obtained.

Nanocrystalline diamond films of 15% N\textsubscript{2} grown on different layer structures, NNCD/Si, NNCD/NCD/Si and NNCD/SiO\textsubscript{2}, were especially designed to study the surface change. It turned out that different structural substrates would greatly influence the surface morphology due to the charge atomic particle variation resulting from the diffusion. Characterization of SEM, AFM, Raman spectra and XRD illustrated that the SiO\textsubscript{2} layer would enhance the growth of nano scaled diamond crystallites, decrease the roughness and increase the growth rate.
4.9 List of References


CHAPTER 5: POLYCRYSTALLINE DIAMOND FILMS SYNTHESIZED BY MICROWAVE AND HOT FILAMENT CVD

5.1 Introduction to HFCVD Technique

Hot filament chemical vapor deposition (HFCVD) is another popular alternative method of diamond synthesis because of its low capital cost and simple operation. Similar to microwave chemical vapor deposition, it also consists of four major subsections: reactant gas supply, power energy supply, vacuum exhaustion system, and heating and cooling components. Power energy supply distinguishes these two systems by different energy sources to activate the gas chemistry. Microwave CVD utilizes microwave radiation generated by a magnetron to dissociate the reactant molecular gases, whereas HFCVD uses a tungsten (W) filament glowed by dc or ac current to about 2000-2300 °C to decompose carrier molecules into atomic ions [1]. It should be noted that the temperature of deposition on the substrate surface is between 700-1300°C, which is much lower than the temperature of filament and the gas activation temperature. By changing the length, shape and size of the tungsten filament, like a function of tuning, the deposited diamond in various areas with different qualities can be achieved. However, the glowed tungsten wire is readily being oxidized by oxygen and some other oxidant gases; a highly vacuumed ambient environment is necessary for the HFCVD process. In addition, the tungsten filament was discovered to react with methane and result in carburization of the
tungsten wire during deposition process; this phenomenon will absolutely induce contaminations on the deposited diamond surface [1-6].

A silicon wafer was cut into several pieces. The dimension of each piece will be kept at 2.5cm×2.5cm a piece and each piece will be treated according to the standard seeding process described in chapter 2.1.2. For HFCVD, the gas recipe is CH₄/H₂ at 5sccm/60scccm, the temperature is 730°C, and the pressure is 20HPa. The experiment was carried out by an HFCVD-008 system manufactured by Blue Wave Semiconductors Inc. Figure 5-1 is the outlook of the system.
For microwave CVD, the gas chemistry was CH\textsubscript{4}/H\textsubscript{2} at ratio of 10sccm/1000sccm as illustrated in table 1 of chapter 2.1.2. The deposition temperature was 650°C, and the pressure was 50HPa.

**5.2 Raman Spectra and Stress Evaluation of Polycrystalline Diamond Film**

Figure 5-2 displays the Raman peaks at four corners of the specimen. As can be observed, the upper-left and bottom-left corners have the same micro diamond peak at 1330.15 cm\textsuperscript{-1}. The upper-right and bottom-right corners have the same peak at 1331.69 cm\textsuperscript{-1}. The Raman shift is 1.54 cm\textsuperscript{-1}, indicating that a residual stress gradient exists on the diamond film surface because of the different thermal coefficient of diamond and Si substrate. Diamond film was grown at 730°C in this case, during cooling process, compressive thermal residual stress was yielded on the diamond surface, because diamond has higher thermal conductivity than that of Si substrate, thus diamond cooled faster than Si substrate. If the Raman peak shifts to a higher frequency, it indicates compressive stress; if the Raman peak shifts to a low-wave number, it represents tensile stress [7].
Figure 5-2. Raman peaks of HFCVD polycrystalline diamond at four corners of specimen

Figure 5-3 shows the Raman peak in the center of the specimen at 1333.23 cm\(^{-1}\). Compared with the peaks at the four corners, the center of the specimen had the compressive stress. In this case, the lowest stress is at the right side with 1331.69 cm\(^{-1}\); with respect to the point of center to the edge, the biggest difference of the Raman shift $\Delta \omega$ is 1.54 cm\(^{-1}\), toward a higher frequency, hence the residual stress at the center is supposed to be compressive.
Figure 5-3. Raman peaks of HFCVD polycrystalline diamond at center and corners of specimen

Figure 5-4 indicates the Raman peaks of polycrystalline diamond film by the MPECVD method. The peaks were measured at the four corners as well as the center of the sample. As can be observed, the corner peaks are positioned at 1337.85 cm\(^{-1}\); the center peak is located at 1333.23 cm\(^{-1}\). The Raman shift \(\Delta \omega\) between the corners and the center equals 4.62 cm\(^{-1}\). If the center peak is considered to be moving toward to the lower frequency, the surface stress in the center is supposed to be in a tensile status compared with those of the corners.
The residual stress of CVD diamond films can be categorized into two different parts; one is the thermal stress resulting from the different thermal expansion between diamond and substrate; another one is the intrinsic stress due to the growth process, for instance, grain protrusion. The stress reflected by the Raman shift is the resultant stress of thermal and intrinsic stress [7].

There are several different models to evaluate stress by the Raman peak shift, but the results of them contradict each other due to complexities such as local microstructure, crystalline orientation, film thickness and boundary conditions [8]. A reference to the Raman peak of stress-free diamond film is necessary to calculate the exact value of surface residual stress. In consideration of (111) planes in polycrystalline diamond films, according to model in [9-11], the stress-free Raman peak is defined at 1332 cm$^{-1}$($\omega_0$). The stress can be calculated by the equation,

$$\sigma = -0.567(\omega - \omega_0) \text{ GPa}$$  \hspace{1cm} \text{Eq. 3}
The constant is evaluated by biaxial stress of diamond films on Si substrate as a plate bending model [7, 11, 12]. Stress distribution can be calculated from the Raman peak in the following way: for HFCVD, the stresses at the corners are 1.049GPa (tensile) and 0.175GPa (tensile); the stress at center is -0.663GPa (compressive). For MPECVD, the stress at the corner is -3.316GPa (compressive); the stress at the center is -0.697GPa (compressive).

The stress deviation from its true value is attributed to the impact of several complicated factors. It is impossible to find a model that can exactly describe the CVD process and diamond film on Si substrate contraction during the cooling process. In this case, the constant for calculating surface residual stress was derived based on plate bending theory; actually, in the structure of thin diamond film adhering on the thick solid Si substrate, the Si foundation will not shrink or extend along with diamond thin film, the stress will mostly be relaxed and absorbed within the bulk of diamond material. As a result, the calculated stress distribution is nonlinear and does not completely obey a simple plate bending model. The reference peak at 1332cm\(^{-1}\) is also dependent on CVD growth techniques, conditions and texture orientation [13-17].

In addition, Raman spectra of MPECVD samples exhibited a smaller sp\(^2\) carbon peak than the HFCVD samples grown under analogous conditions. Upon comparison, it is evident that high quality of diamond is obtained by the MPECVD technique. The G bands in the HFCVD present sharp triangle peaks rather than broad band with a range of wavelength, illustrating the presence of graphitic crystalline rather than the scattered amorphous carbon phase of sp\(^2\) bonds.
5.3 SEM of Polycrystalline Diamond Film

SEM images of MPECVD polycrystalline diamond in figure 5-5 may be helpful in explaining residual stress distribution results by the peak shift of Raman spectra.

Figure 5-5. MPECVD polycrystalline diamond growth evolution

From the images, many facets with different orientations can be observed. The presence of crystal twin, tetrahedron and pentahedron (pyramid-like grain), which are formed by facets such as (111), (220), (311) and (001) planes are also visible in the SEM images. Since different orientations have different growth rates in the crystal growth, it is impossible to grow a flat surface without any post-deposition treatment. With the growth of diamond grains in the limited space, crystal planes with different orientations will meet
and merge into crystal twin, causing the intrinsic stress on the surface. The intrinsic stress is easily relaxed at the boundary rather than in the center of the sample due to the free space. On the other hand, because of the irregular shape and size of diamond crystallites, several cavities are formed inside of the diamond bulk, and these spaces are beneficial in relaxing the thermal stress when the cooling process happens; and grains at the boundary have less bondage than those in the center of specimen. This can partly explain why at the center point of the sample, residual stress is always compressive and is always higher than points at the boundary; stresses at boundaries sometimes present tensile behavior.

5.4 AFM of Polycrystalline Diamond Film

AFM provides information on the roughness of samples utilizing its unique technique of three-dimensional imaging. Figure 5-6 presents the profile of a three-dimensional image within a 3×3μm² scanning area of HFCVD polycrystalline diamond film. As evident from the two-dimensional image, many tiny particles, considered second nucleation, embed around the big diamond crystallites resulting in triangle peaks of G band in Raman spectra (figure 5-3). The average roughness is 35.5 nm in this image.
Figure 5-6. Two- and three-dimensional AFM images of HFCVD polycrystalline diamond film

<table>
<thead>
<tr>
<th></th>
<th>Whole Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Area St.</td>
<td>9.0420 µm²</td>
</tr>
<tr>
<td>Roughness Avg. Sq.</td>
<td>35.5328 nm</td>
</tr>
<tr>
<td>Root mean square Sq.</td>
<td>44.9126 nm</td>
</tr>
<tr>
<td>Ten Points Height Sq.</td>
<td>251.4446 nm</td>
</tr>
<tr>
<td>Range Sq.</td>
<td>253.6536 nm</td>
</tr>
</tbody>
</table>

Figure 5-7 displays two and three dimensional images of MPECVD polycrystalline diamond. As demonstrated in the two dimensional image, it presents fewer small graphitic particles among big diamond crystallites than that of HFCVD diamond (Fig. 5-6), resulting in the disappearance of G band in Raman spectra (Fig. 5-4). With the same scanning area, the average roughness in the MPECVD sample is 55.4nm, about 20nm higher than that of HFCVD sample.
Figure 5-7. Two- and three-dimensional AFM images of MPECVD polycrystalline diamond film

<table>
<thead>
<tr>
<th></th>
<th>Whole Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Area St.</td>
<td>9.0420 μm²</td>
</tr>
<tr>
<td>Roughness Avg. Sq.</td>
<td>55.4372 nm</td>
</tr>
<tr>
<td>Root mean square Sq.</td>
<td>70.5638 nm</td>
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<tr>
<td>Ten Points Height Sq.</td>
<td>420.7843 nm</td>
</tr>
<tr>
<td>Range Sq.</td>
<td>425.1042 nm</td>
</tr>
</tbody>
</table>

5.5 XRD of Polycrystalline Diamond Film

Figure 5-8 displays the XRD pattern of MPECVD diamond film grown with a mixture of CH₄/H₂ at a ratio of 10sccm/1000sccm under 650°C and 50HPa. The deposition time was 10 hours. As can be seen, the (220) peak was three times as high as that of (111) peak, indicating (220) texture was dominantly consisted of the diamond.
5.6 Summary

In conclusion, both polycrystalline diamond films by the HFCVD and MPECVD methods presented a faceted surface. Raman spectra indicated that the HFCVD polycrystalline diamond film contained a certain percentage of crystal graphite, whereas the MPECVD polycrystalline diamond did not have the same. The MPECVD polycrystalline diamond has bigger crystallites and a rougher surface than the HFCVD diamond. The MPECVD diamond also presents bigger compressive residual stress on the whole surface of the sample than that of the HFCVD diamond, the (220) plane accounts for mainly texture structure in the as deposited polycrystalline diamond film.
5.7 List of References


CHAPTER 6:
FABRICATION OF CMUTS

6.1 Introduction to CMUTs

“CMUTs” is the abbreviation for capacitive micromachined ultrasonic transducers, which is essentially a capacitor with one vibrating electrode serving as a membrane. Figure 6-1 is the basic schematic structure of CMUTs, which is primarily a cavity formed by a membrane and substrate serving as positive and negative electrodes. The working principle of CMUTs is that, when an alternating voltage is applied to both electrodes, the charges on the electrodes change, causing the variation of an attractive force between the two electrodes, and thus one flexible electrode will deflect and bend following the alternating voltage, therefore, the ultrasonic vibration is generated.

Figure 6-1. Schematic structure of a CMUT unit cell
As evident from figure 6-1, a CMUT unit cell, serving as an individual capacitor, consists of three main elements: the cavity, the membrane, and the electrode. Using a general integrated circuit (IC) fabrication process, a capacitor cell appears as a membrane with a metallic contact (top electrode) suspended above a heavily doped silicon substrate (bottom electrode). An insulating layer is necessary to prevent the two electrodes from an electrical short in case of contact, especially when the patterned bottom electrodes are made of metallic materials such as aluminum, chromium, and gold; whereas when heavily doped silicon substrate serves as the bottom electrode, the isolation layer is not required. CMUTs are constructed by organizing many units in a series or parallel way with different geometries and array of shapes as illustrated in figure 6-2.

Figure 6-2. A CMUT constructed by connecting units in series and parallel way

CMUTs cause extensive attention and interest as an alternative method to conventional piezoelectric transducers because they are small and cheap to produce in bulk quantities using photolithographic fabrication techniques with good quality and reproducibility. CMUTs have advantages over piezoelectric transducers such as high frequency ultrasonic, wide bandwidth, CMOS compatibility, a very high level of integration and batch fabrication (low cost). Ultrasonic vibration, similar to RF and surface acoustic wave (SAW) technology, can be utilized in almost all walks of life such as pressure sensor, fluid flow meter, non-destructive material diagnosis, distant
measurement, medical imaging, wireless communications, infrared cargo screening and airport security, etc. [1-7].

6.2 CVD Diamond Film Grown for CMUTs

Diamond film becomes the material of choice for the CMUTs design due to its extraordinary properties such as chemical inertness and acoustic wave transportation property. The chemical inertness makes diamond-membrane CMUTs perform properly in harsh environments. The acoustic wave transportation velocity in diamond can reach 17.5 km/s [8], which makes diamond-CMUTs generate higher frequency signals than other materials. CMUTs expect a membrane made of insulating materials, but CVD diamond films with diverse structural forms such as nanocrystalline, polycrystalline and diamond-like carbon (DLC) contain a different concentration of sp² bonds, which make diamond low conductive with different levels. It is necessary to deposit different forms of CVD diamond films to make the best quality for CMUTs application. Nanocrystalline, polycrystalline and DLC CVD diamond films were deposited with the following descriptions.

Nanocrystalline diamond film depositions were carried out by the Astex CVD system in gas chemistry CH₄/H₂/Ar at a flow rate ratio of 2sccm/2sccm/196sccm. The working pressure was 135 HPa and the deposition temperature was 720°C. Deposition time was one hour for each patterned wafer.

Polycrystalline diamond films were synthesized in the same Astex system with the gas chemistry CH₄/H₂ at a flow rate ration of 15sccm/1500sccm. The working
pressure was 40HPa and the deposition temperature was 600°C. Growth time was one hour for each patterned specimen with a growth rate 0.75μm/hr.

Table 7. Experimental conditions of diamond deposition for CMUTs

<table>
<thead>
<tr>
<th>Phases</th>
<th>CH₄</th>
<th>H₂</th>
<th>Ar</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-Dia</td>
<td>2sccm</td>
<td>2sccm</td>
<td>196sccm</td>
<td>720°C</td>
<td>135HPa</td>
</tr>
<tr>
<td>Ploy-Dia</td>
<td>15sccm</td>
<td>1500sccm</td>
<td>0</td>
<td>600°C</td>
<td>40HPa</td>
</tr>
</tbody>
</table>

6.3 Structure Design and Fabrication Process

L-Edit is the popular software used to design the masks and layout of micro devices that are fabricated by the IC process technique. It has a unique feature to provide a cross-sectional view of a designed multiple layer structure. All the figures of masks and structures of CMUTs used in the micro fabrication were drawn by the L-Edit software, excluding the schematic demonstrating figures presented in this chapter.

All the process steps, including spin-coating photoresist, mask alignment exposure, wet etching, plasma dry etching, electrode metallization, were carried out in the Nanotechnology Research and Education Center (NREC) in University of South Florida (USF), except the CVD diamond film depositing. Only nanocrystalline diamond form was selected as an example in the subsequent description.
6.3.1 First Mask and Unit Cell Pattern

First, SiO$_2$ sacrificial layers of 0.5μm and 1μm thickness were deposited on two inches of Si wafer respectively by a thermal oxidizing method. Second, the HMDS was deposited on the SiO$_2$ surface in order to increase the adhesion of the positive photoresist. After that, the positive photoresist, coatshipley 1813, was spin-coated on the SiO$_2$ layer with a thickness of 1.6μm by using a Laurell spinner. Both the HMDS and coatshipley 1813 followed the same procedure programmed on the Laurell spinner as follows: 10 seconds at 700rpm with an acceleration parameter of 4rpm/sec$^2$; 40 seconds at 3000rpm with an acceleration of 40rpm/sec$^2$; then 10 seconds at 700rpm with an acceleration of 4rpm/sec$^2$. The spinned photoresist wafer was then soft baked for one minute at 115°C, and then it was moved and settled on the stage of a Karl Suss mask aligner, exposed to ultraviolet rays under the first mask for 4 seconds at 25mv. The exposed photoresist was stripped away in MF-319 developer for 70 seconds. A rectangular pattern with four anchors was formed on the surface. Figure 6-3 illustrates the one unit cell of pattern by the first mask. Figure 6-4 is the real SiO$_2$ pattern with the removal of exposed photoresist. As evident in figure 6-4, the substrate was SiO$_2$, the pattern was the unexposed photoresist left on the SiO$_2$.

The subsequential process was to etch off the SiO$_2$ in the buffered oxide etchant (BOE), which was comprised of a standard mixture of hydrofluoric acid and water (HF:H$_2$O) at a ratio of 6:1 in volume. The SiO$_2$ etching rate is about 750Å/min; so for the sample of 1μm SiO$_2$ thickness, the approximate etching time was 13 minutes and 20 seconds. At last, the unexposed photoresist on the soft bake-hardened positive
coatshipley 1813 was washed away in acetone. Now the wafer was only left with the SiO$_2$ pattern on Si substrate, and ready to deposit diamond film.

Figure 6-3. One unit cell of SiO$_2$ pattern by first mask

Figure 6-4. First mask pattern after removal of exposed photoresist
6.3.2 Diamond Deposition and Second Mask for Opening Window

Nanocrystalline diamond film was deposited in the gas chemistry CH₄/H₂/Ar at a flow rate ratio of 2sccm/2sccm/196sccm for one hour to synthesize 0.3μm thick diamond film on the SiO₂ pattern. Similar to the descriptions in 6.3.1, the sample was again spin-coated with HMDS for adhesion and positive photoresist (coatshipley 1813), and after soft baked, then was exposed to UV under second mask for the opening window on the diamond film. After the removal of exposed photoresist in developer MF-319, the sample was ready to etch an opening on the diamond film. Figure 6-5 demonstrates the schematic diagram of the unit cell with an opening by second mask. Figure 6-6 illustrates the real unit cell after the removal of photoresist on the opening window. As evident in figure 6-6, the photoresist still remained on the membranes, whereas the anchor areas were SiO₂ with the removal of photoresist.

![Diagram](image.png)

Figure 6-5. Unit cell with an opening window by second mask
6.3.3 Diamond Etching and Membrane Release

Diamond etching to open a window for the SiO₂ sacrificial layer removal is the most challenge step in CMUTs fabrication process due to the extraordinary structural and compositional characteristics of CVD diamond. Because of chemical inertness of diamond, wet chemistry etching of diamond is not available. Plasma dry etching of diamond has been reported with a low etching rate due to the high strength of diamond. Several different techniques generally combined with biased-voltage substrate have been employed to diamond dry etching such as plasma assisted reactive ion etching (RIE), ECR (electron cyclotron resonance) plasma etching, Xe⁺ ion-beam etching (also referred as milling), inductively coupled plasma etching and microwave plasma enhanced CVD etching. These etchings usually activate O₂, H₂, Ar, F₄, CF₄, SF₆, NO₂, Cl₂ gases as plasma chemistry, either individually or in a mixture with different recipes and flow rate...
Diamond etching was carried out by a plasma dry etching method in NREC USF. The nanocrystalline diamond film was deposited one hour. Based on the gas recipe and previous experimental records, the film thickness was supposed to be 0.25μm~ 0.30μm, in which the section over SiO₂ is thicker than that of Si substrate in accordance with the results of chapter 4.7. The RIE etching was implemented only by O₂ at an 80sccm flow rate under 65mtorr for three five-minutes stop checking. Because of the low etching rate, the plasma etching chemistry gas was changed to a mixture of O₂ / CF₄ at 50sccm/1sccm under 50mtorr for two three-minutes. The diamond was completely etched away under the observation of a microscope. Figure 6-6 is the unit cell with released diamond membrane. The membrane was still covered by diamond film; the anchor was exposed by Si substrate. Some damaged defects caused by plasma etching can be observed on the diamond membrane. Using the argon–chlorine-based plasma will not damage the diamond surface and sub-surface regions can also avoid the formation of undesirable etch pits [18].
The sample was immersed into acetone to clean the residual photoresist remains on the membrane. Condensed buffered oxide etchant mixed by hydrofluoric acid and water with HF:H_2O at 10:1 in volume was employed to etch away SiO_2 to form the gap of membrane. Polycrystalline diamond film was then deposited with the gas chemistry CH_4/H_2 at a flow rate ratio of 10sccm/1000sccm. The reason for selecting polycrystalline diamond deposition to finally form the diamond membrane rather than nanocrystalline diamond is because the deposition pressure of polycrystalline diamond was 40HPa, whereas the pressure of nanocrystalline deposition was usually 100HPa. For safety consideration, to avoid the collapse of the diamond membrane during the second diamond deposition, polycrystalline diamond was deposited for one hour so that a 0.75 μm thick diamond layer was formed.
6.3.4 Electrode Metallization

The commonly used metals for CMUTs electrode metallization are aluminum, gold, silver, titanium and copper. Aluminum was selected and sputtered 200nm thick by thermal evaporator equipment in the thin film lab of NREC. To produce the metal electrode by the third mask, spin coating photoresist process was carried out again. Because this time positive photoresist coatshipley 1813 was coated on aluminum, the adhesion HMDS coating was skipped. The spinner program was also changed as follows: 10 seconds at 500rpm with an acceleration parameter of 6rpm/sec²; 40 seconds at 2500rpm with an acceleration of 30rpm/sec²; then 10 seconds at 500rpm with an acceleration of 6rpm/sec². The subsequent processes were the same as the descriptions in chapter 6.3.1. The aluminum etchant was lab-made with a mixture of H₃PO₄:HNO₃ at a proportion of 80%:20%, and the etching time was 20 minutes. Figure 6-7 displays the patterned aluminum electrode of the as-fabricated CMUTs. In figure 6-7a, the substrate was covered by aluminum; the metallic contact on the membrane was covered by photoresist. In figure 6-7b, the aluminum on substrate and photoresist on the membrane were all etched away, aluminum contact was formed on the membrane, and all of the unit cells were connected by an aluminum electrode.
a Aluminum and photoresist pattern  b. Final aluminum contact on unit cell

Figure 6-8. The patterned aluminum electrode

6.4 Summary

In summary, CVD diamond films were successfully integrated into CMUTs by the IC processing technique. The advantages of CVD diamond were considered in two aspects: first, CVD diamond was chemically inert, which allows diamond-CMUT to work under harsh environments; second, the acoustic wave transportation velocity was believed to be the highest (17.5km/s) in the current materials. This merit makes diamond-CMUT generate high-frequency output signals, which is significant for medical imaging applications. During the fabrication process, several technical challenges were overcome by many times of repeated experiments. For instance, the plasma etching of diamond opening; two times of deposition of diamond to seal the anchor and form the cavity, and, in the meantime, avoid membrane collapse under the CVD deposition pressure; photoresist spin coating on the aluminum emboss; aluminum electrode center positioned on the membrane. It proved that the two-step CVD diamond depositing solutions was simply designed and operational to form a cavity within the lower pressure ambient circumstances inside the CVD chamber. Various selections of diamond forms leave potential to improve the performance of diamond-membrane CMUTs.
6.5 List of References


CHAPTER 7:
CONCLUSIONS AND FUTURE WORKS

7.1 Conclusions

The quality of diamond films synthesized by the MPECVD and HFCVD methods are greatly affected by the experimental parameters such as the reactant gas H₂, carrier gas Ar, depositing pressure; they can also be characterized by Raman spectra to determine the electronic structure of surface in terms of sp² and sp³ bondings, by XRD patterns to investigate crystalline orientation, content and texture structure, by AFM to investigate average roughness and three-dimensional morphology, and by SEM to display the texture structure and grain size and boundaries. Micro structures determine the properties, and properties determine the applications. By utilizing characterization techniques, the deposited diamond films’ qualities were optimized to better serve specific applications.

In this dissertation, a systematic research on the influential factors such as H₂, Ar volume, and depositing pressure on the quality of diamond films were investigated by metrological and analytical techniques largely including SEM, AFM, XRD, Raman spectroscopy, etc. For polycrystalline diamond syntheses, H₂ volumes less than 500sccm generate a cauliflower-like surface; more than 1000sccm H₂ volumes yield a faceted surface; mainly crystal planes include (111) and (220), (220) planes occupy more than (111). For intrinsic nanocrystalline diamond film growth, the change of Ar volume will
vary the surface morphology such as cauliflower-like or ear-of-wheat-like texture structure; (111) and (220) planes exhibit the same amount of content in the nanocrystalline diamond films. Similar symptoms accompany the change of deposition pressure.

For nitrogen-doped nanocrystalline diamond films, the grains grow with the increase of N\textsubscript{2} volume, and the preferential growth plane is (111). 15% N\textsubscript{2} doped diamond films grown on different substrate structures present morphology, roughness and growth rate change due to atomic charge particle diffusion. MPECVD and HFCVD polycrystalline diamond display similar surface features, different roughness and residual stress.

CMUTs built up by a diamond membrane with 1μm gap distance was successfully fabricated utilizing IC processing techniques, and overcoming several technical challenges such as diamond window etching, two-stage diamond depositing, vacuumed cavity formation and alignment of electrode of metallization with the pattern. The outstanding properties of CVD diamond films are expected to enhance the potential developments and applications of micro devices in the semiconductor industry.

7.2 Future Works

The resultant surface residual stress of CVD diamond films derived from lattice mismatch and different thermal coefficients between diamond and substrate is a big challenge that prevents the practicable application of diamond films. Current evaluations of residual stress of diamond films are mostly calculated by XRD curvature measurement and Raman spectra peak shift. Due to the complexity of the CVD process and simplicity
of the simulation model, the calculated results are greatly deviated from the real situation. Further in-depth investigation is needed to develop a new method that can reach a consistent result for both XRD and Raman method and closely describe the real stress field of diamond surface.

Growing CVD diamond films on commonly applied MEMS layer such as SiO₂, Si₃N₄, polysilicon, metal and metal oxide will generate different surface structure features, which are significant to the fabrication and performance of micro devices. This surface change is most probably caused by the electrons, atomic H density on the surface and their correlations with atomic charge particles’ diffusion toward substrate. This phenomenon has not been given extensive attention and the knowledge about the functioning mechanism under it is even more lacking. It is necessary to make a systematic investigation on this phenomenon and clarify the principles in order to better serve the CVD diamond film applications.

Other interests also include metal particle modified extrinsic diamond electrode on the electrochemical applications, diamond film integrated micro device fabrications, simulations, measurements, and applications.
ABOUT THE AUTHOR

Qiang Hu majored in mechanical engineering in his bachelor degree and received an M.S. in solid mechanics from Northeastern University in 1998, China. He started research on fatigue and fracture, transformation behavior of TiNi shape memory alloys based on cyclic stress and strain in the Institute of Metal Research (China). He entered the Ph.D. program at the Department of Mechanical Engineering in the University of South Florida in fall 2006.

While in the Ph.D. program at the University of South Florida, Mr. Hu was very active in academic research; he published two papers as first author, and two papers as coauthor in peer-viewed prestigious journals, and also has several papers in review. He attended five national academic conferences with poster exhibitions. He was granted the Graduate Multidisciplinary Scholars (GMS) fellowship by the Graduate School of USF from the fall semester of 2007 to the summer semester of 2009 based on his outstanding academic performance.