Chapter 1

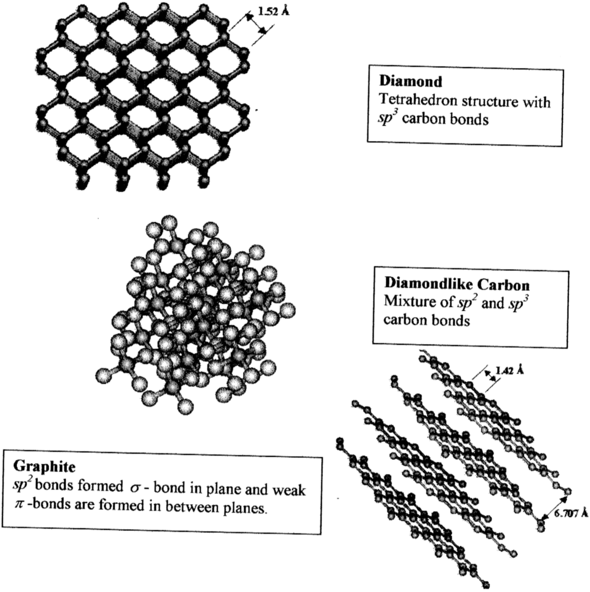
Introduction

1.1 Graphite, diamond and diamondlike carbon

The carbon atom has an electron configuration of $1s^2 2s^2 2p^2$, essentially a helium noble gas core with four outer electrons for bonding. These outer electronic orbits ($2s$ and $2p$) hybridize to various extents, allowing pure carbon to assume a number of crystalline and amorphous structures. The two most common crystalline forms of carbon are graphite and diamond. In graphite, each carbon atom has a sp^2 electronic configuration and forms strong covalent σ-bond with three other carbon atoms in plane. The remaining electrons, one for each carbon atom, form weaker π-bonds with each other above and below planes and are held together by Van der Waals forces. The properties of graphite are highly anisotropic due to the difference in chemical bonding within and between the carbon planes. For example, graphite has a high electrical conductivity parallel to these planes but not perpendicular to them. This is because the π-bonded electrons are delocalized and can move easily within the planes. Delocalized electrons also absorb electromagnetic radiation throughout the visible range causing graphite to appear black. Since the carbon planes are held together only by weak van der Waals forces, they can easily slip past one another; this makes graphite a soft material with lubricity [1].

In diamond, each carbon atom is sp^3 hybridized and forms strong σ-bonds to four other carbon atoms arranged in the form of tetrahedron. Consequently, a strong three-dimensional covalent network is produced. Since all four outer electrons of each carbon atom participated in covalent bonds, in its pure form carbon is an electrical insulator and is transparent throughout the visible and infrared spectrum, except for two-phonon absorption. The strong bonding, dense packing of atoms, and high cohesive energy, make diamond the hardest, stiffest, and least compressible material ever known and are responsible for its very low thermal expansion coefficient. The strong, short, stiff bonds also give rise to diamond's most important property for electronic packing applications, its extremely high thermal conductivity, which at room temperature is five times greater than pure copper [1].

The term Diamondlike carbon (DLC) embraces a class of material which range from one extreme, crystalline diamond to another extreme of amorphous carbon or graphite. Diamondlike carbon consists mainly of a mixture of "diamond" sp^3 and "graphite" sp^2 hybrid carbon atoms. The level of hardness of hard carbon films depends on the sp^3 concentration in the deposited film. As a result, they can be classified according to their hardness. Hard carbon films with a hardness of 1500-3000HV contain between 5 and 10% unhydrogenated sp^3 carbon. Hard carbon coatings with a hardness of 3000-5000 HV have a sp^3 / sp^2 ratio of about 15-20%. If the sp^3 concentration is close to 100%, then the hardness and elasticity of the DLC coating are very similar to diamond (8000-9000HV)[2].



Diamond
Tetrahedron structure with sp^3 carbon bonds

Diamondlike Carbon
Mixture of sp^2 and sp^3 carbon bonds

Graphite
sp^2 bonds formed σ - bond in plane and weak π -bonds are formed in between planes.

Figure 1.1: Model of the structure of diamond, diamondlike carbon and graphite

1.2 Plasma synthesis of diamond or diamondlike carbon films

1.2 Plasma synthesis of diamond or diamondlike carbon films

Diamond is the hardest known material and exhibits a unique combination of optical, physical and electronic properties. Therefore the synthesis of diamond films is arousing great interest because of their wide range of promising industrial applications owing to their high quality tribological characteristics and corrosion-protective layers.

Since the mid-1950's various methods of low pressure diamond synthesis have been studied at the Physical Chemistry Institute of the Academy of Sciences in Moscow. The major advancement achieved by the team working there was to prepare the basis for the methods now in use for low pressure diamond synthesis. In the 1960's, vapour transport reactions allowing discontinuous diamond growth on diamond substrates were known. In 1971, Deryagin, Spitzin, Fedosayev *et al.* demonstrated the possibility of continuously growing low-pressure diamond on diamond substrates, and in 1976, Deryagin, Spitzin and Bouilov *et al.* showed that diamond nucleation and growth is also possible on non-diamond substrates such as copper. After that, widespread attention was drawn to these possibilities when the information contained in the early work became known outside the U.S.S.R. Intensive research activities began in the early 1980's in Japan, Western Europe and more recently in the United States[3].

Three methods of syntheses of diamondlike carbon film have emerged. First to gain commercial importance was the high pressure / high temperature (HPHT) growth process. At atmospheric pressure, graphite is the thermodynamically stable form of pure carbon and diamond is metastable. High pressure, of the order of 10^4 atmospheres, is required to make diamond the stable form of carbon. To convert graphite to diamond at such a high pressure, high temperature is needed to overcome the activation energy barrier. High pressure and high temperature can be generated statically, with a heated hydraulic press, or dynamically, by propagating a shock wave in graphite material. In the static HPHT process, the solvent/ catalyst approach is used to lower the temperature and pressure from that required for direct conversion of graphite and diamond. In this technique, a metal such as nickel or iron is mixed with graphite before it is placed in the die cavity. The mixture forms a eutectic melt around 1300-1500°C and under the high pressure (30,000 – 40,000 atmospheres) diamond precipitates out. Dissolution into the molten metal reduces the activation energy barrier, which lowers the necessary processing temperatures and significantly improves the kinetics for conversion of graphite to diamond. Diamond produced by HPHT processes is primarily used for industrial cutting and grinding applications. It can also be used as substrate for electronic devices, but the crystal is expensive and is only a few square millimeters in size[1].

Syntheses based on physical vapour deposition of carbon species at low pressures can produce diamond thin films. These processes involve some form of ion bombardment to achieve conditions necessary for the formation of sp^3 bonded carbon. The films formed are typically amorphous networks with variable ratio of sp^2 and sp^3 bonded carbons and various amounts of hydrogen. They are generally termed diamondlike carbon films because they have properties which can approach that of true crystalline diamond. Although these films are usually amorphous, some fine diamond crystals have been reported[4].

The third class of syntheses is based on chemical vapour deposition (CVD). World interest in diamond has been further increased by the much more recent discovery that it is possible to produce polycrystalline diamond films and diamondlike carbon films by a wide variety of chemical vapour deposition (CVD) techniques. Diamond is crystallized via a chemical reaction with the gas phase under low pressure condition, where it is the thermodynamically metastable form of carbon. Though last to gain commercial importance, synthesis of diamond in the laboratory, by CVD actually predates HPHT. CVD diamond has great potential for use in electronic packaging because it can be grown relatively inexpensively in thin films or thick slabs over large areas. Chemical vapour deposition (CVD) of diamond and diamond like carbon films has been widely investigated since the early 1990s to exploit the favourable mechanical and electrical properties of diamond in a large number of potential applications. As of these efforts, a host of techniques for the deposition of diamond films have evolved. These include hot filament CVD (HFCVD), microwave plasma CVD (MPCVD), thermal plasma CVD, direct current plasma CVD and the combustion flame method[1]. A summary of recent CVD and other related techniques for diamond and diamondlike carbon films deposition is given in Table 1.1:

No.	Researcher	System	Substrate	coating	Pretreatment	Gases	temperature	Year
1.	Yasushi Muranaka *et al.*[5]	Microwave PECVD	Silicon	Diamond films	Scratched with diamond powder	$CO/O_2/H_2$, CO_2/H_2, $CH_4/O_2/H_2$, $CO/CO_2/H_2$, CO/H_2 or CH_4/H_2	$750^{\circ}C$	1991
2.	Kazuhiro Aoyama *et al.*[6]	DC Plasma Jet	Molybdenum and niobium	Diamond films		$Ar/CO/H_2$		1992
3	Mansoor Alam *et al.*[7]	Hot filament CVD	silicon	Diamond films	Scratched with diamond powder	CH_4/H_2		1993
4	Mitsugu Hanabusa *et al.*[8]	Laser ablation		DLC films		Frozen acetylene	$<300^{\circ}C$	1995
5.	R. Manukonda *et al.*[9]	RFCVD		Diamond films		H_2O/CH_3OH	$915^{\circ}C$	1995
6.	J.B. Cui *et al.*[10]	Hot filament CVD	silicon	Diamond films	Scratched with diamond and silicon particle	CH_4/H_2	$750^{\circ}C$	1996
7.	A.N.Obraztsov *et al.*[11]	DC-arc discharge PECVD	silicon	Diamond films	Diamond particles implanted into silicon substrate by laser treatment	Carbon containing precursor		1996

No.	Researcher	System	Substrate	coating	Pretreatment	Gases	temperature	Year
8.	F.C.Chuang *et al.* [12]	Pulsed laser deposition(PLD)	molybdenum	DLC films		Carbon target	60-600 °C	1996
9.	Xiaoming He *et al.* [13]	Ion implantation and PVD /Ion beam assisted deposition (IBAD)	AISI52100 steel	DLC films		Ar/CH_4	Room temperature	1996
10	Z. Lj. Petrovic *et al.* [14]	RF plasma system	Optical fiber	DLC films		CH_4		1997
11.	C. Gomez – Aleixandre *et al.*[15]	Microwave CVD	silicon	Diamond films	Scratched with diamond paste	O_2/CH_4/H_2	900 °C	1997
12.	Yunjun Li *et al.* [16]	Microwave PECVD	molybdenum	Diamond films	Polished using diamond paste	CH_4/H_2		1997
13.	X. L. Peng *et al.* [17]	Hot filament CVD	Ti6Al-4V	Diamond films	Polished with diamond paste	CH_4/H_2	850°C	1997
14.	Mo Yaowu *et al.* [18]	Microwave PECVD	Alumina ceramic	Diamond films	Polished with SiC and diamond paste	Carbon contained precursor	1700°C	1997
15.	J.W.Lee *et al.*[19]	ECR system	Mn-Zn ferrite	DLC films		CH_4	100°C	1997
16.	P. C. Yang *et al* [20].	Hot filament PECVD	nickel	Diamond films	Seeding with diamond powder	CH_4/H_2	900 °C	1998

No.	Researcher	System	Substrate	coating	Pretreatment	Gases	temperature	Year
17.	Nita Dilawar *et al.* [21]	Hot filament CVD	Tungsten carbide	Diamond films	Fine scratched with diamond powder	$Ar/H_2/CH_4$	720-760^oC	1998
18.	Donald R. Gilbert *et al.* [22].	ECR with Microwave CVD	silicon	Diamond films	Diamond particles in ultrasonic bath	CH_3OH/H_2	700^oC	1998
19.	Dae-Hwan Kang *et al.* [23]	ECR with microwave and RF bias substrate	silicon	DLC films		Ar/CH_4		1998
20.	W.C. Chan *et al.* [24]	DC saddle field glow discharges techniques	silicon	DLC films		$CH_4/PH_3/B_2H_6$	200-400^oC	1998
21.	S. Barrat *et al.*[25]	Microwave PECVD	Silicon	Diamond films		$CH_4/H_2/Ar$		1998
22.	Fumio Sato *et al.* [26]	ECR with microwave and RF biased CVD	Silicon and nonalkaline glass	DLC films		CH_4/H_2	30-300^oC	1998
23.	D. Sarangi *et al.* [27]	Filtered saddle field fast atom beam deposition	Silicon and glass	DLC		CH_4/H_2		1998
24.	Jamal Bougdira *et al.* [28]	Microwave PECVD	Silicon	Diamond films	Ultrasonic bath with diamond particles	$CH_4/CO_2/N_2$	900^oC	1998

No.	Researcher	System	Substrate	coating	Pretreatment	gases	temperature	Year
25.	J. Schafer *et al.* [29]	RF capacitive	C-Si(III)	DLC		CH_4/Ar	300-400°C	1998
26.	T. Sato *et al.* [30]	Oxygen-acetylene combustion flame method	Titanium and iron	Diamond films	N_2-C_2H_2RF solenoid coil plasma deposition	O_2/C_2H_2	350-420°C	1998
27.	Y. Asakura *et al.* [31]	RF capacitive and DC	silicon	Diamond films		CH_4/H_2	900°C	1998
28.	P. Andreazza *et al.* [32]	Microwave PECVD	Titanium alloys	Diamond films		CO/H_2 and CH_4/H_2	600°C and 850°C	1998
29.	M.A. Vasaghi *et al.*[33]	DC plasma technique	Copper, steel and aluminium			Liquid gas (60% butane and 40% propane)	200°C	1998
30.	A.K.Sikder *et al.* [34]	Microwave PECVD	Nickel or Diamond coated nickel	Diamond films	Diamond particles suspended in the watt's batch	CH_4/H_2	925°C	1999

No.	Researcher	System	Substrate	coating	Pretreatment	gases	temperature	Year
31.	D.J. Kester *et al.* [35]	Hot filament CVD	Silicon	DL Non-composite (DLC and a-SiO network)		Siloxane precursor	150°C	1999
32.	Soonil Lee *et al.* [36]	Microwave PECVD	silicon	Defective diamond film	Scratching with diamond powder	CH_4/H_2	800°C	1999
33.	M.C.A Nono *et al.* [37]	Hot filament CVD	304 stainless steel	Diamond films	Plasma-immersed ion implantation (PIII)	CH_4/H_2	800°C	1999
34.	T. Grogler *et al.* [38]	Microwave CVD	Ti-6Al-4V	Diamond films	Fine blasted with diamond particles and ultrasonic bath	CH_4/H_2	750°C	1999
35.	S. Nijhawan *et al.* [39]	Microwave CVD	silicon	Diamond films	Scratching with diamond paste	CH_4/H_2	900°C	1999

Table 1.1: A summary of some Researches on CVD diamond or diamondlike carbon coating

1.3 Some applications of CVD diamond and diamondlike carbon films

1.3.1 Electronic packaging

Electronic devices generate heat. For some types of devices, removal of heat is a major engineering challenge and is the main barrier to improved device performance. CVD diamond can provide much better performance and longer device lifetime through better thermal management. This is true for both discrete devices and for integrated circuits such as microprocessors and digital signal processors.[1]

Diamond is the material with the highest Debye temperature (2220K), exceeding that of most other insulating materials by an order of magnitude and leading to the highest thermal conductivity of any material at room temperature (20-25W/cmK). Diamond is used in electronic packaging to promote heat transfer away from the microelectronic device. Typically, a hot device is soldered to a metallized diamond coupon. Diamond's exceptional thermal conductivity (500% greater than silver) allows heat to flow from the device into the bonded diamond heat spreader, which provides a lower thermal resistance pathway to the package's ultimate heat sink[40].

1.3.2 Cutting tools

CVD diamond is also finding applications as an abrasive and as a coating on cutting tool inserts[41]. CVD diamond is less costly than the natural diamond and can be made in larger size and more complex shape for added manufacturing flexibility. CVD diamond is being used increasingly in difficult commercial machining application like fiberboard sawing and high-volume wood molding manufacturing. Benefits include longer tool life, increased throughput, and better surface finish on the product. Coated CVD diamond cutting tools are now routinely available, and are sold as coated inserts, drills, mills, and other complex tooling shapes. These tools can be used in a wide variety of nonferrous machining work and typically operate at much higher speeds than conventional tooling, and give better machining performance with greatly extended tool life.

1.3.3 Surface Acoustic Wave devices

Surface Acoustic Wave (SAW) devices are critical components of many modern digital microwave and optical telecommunication systems. These devices perform complex signal processing functions through electroacoustic interactions in materials such as lithium niobate. Use of these devices in cellular telephones and other complex communications systems is increasingly portable, powerful, and affordable. As digital communications move to higher frequencies for more bandwidth, conventional SAW devices require more difficult, expensive lithography. Because diamond has the highest known speed of sound and other uniquely desirable acoustic properties, SAW devices built on CVD diamond provide operation at extremely high frequencies using existing low-cost lithography. Diamond SAW devices are currently in development at several major communications companies [42].

1.3.4 Radiation detectors

CVD diamond can be used to detect nuclear radiation, replacing silicon as the detector material. CVD diamond has much greater resistance to degradation in high radiation environments, and has been proposed as the detector material for particle accelerators. In commercial applications, diamond detectors have been proposed as dosimeters for radiation therapy systems. CVD diamond can provide more accurate dosage measurements and would allow physicians to achieve better therapeutic results with less risk to the patient of over-exposure. Achieving low-cost diamond manufacture is critical for successful development of diamond radiation detectors because most medical detectors require radiation sensing over large areas.

1.3.5 Effective negative electron affinity

Recently, diamond and diamondlike carbon has also been shown to be an effective negative electron affinity material. What this means is that if an electron is promoted to the conduction band, it can immediately be extracted at almost no power consumption. This could allow development of high speed vacuum microelectronics and flat e-beam displays (Cathode ray tubes). Working prototype displays have already been fabricated and several other consortia are working in this area [43, 44].

1.3.6 Protective coating

DLC films are chemically inert, making it a suitable protective coating for product which is required to be in contact with reactive chemical on the surface. As an example, medical guide wires are currently used to aid the insertion of medical devices into the human body. The wires are required to exhibit biocompatibility, a high degree of flexibility, low insertion and withdrawal forces and high chemical resistance. The DLC coating which is chemically inert is suitable for these applications [45].

1.3.7 Anti-stick coating

Treated moulds both for plastic injection and for metal forming have left out some plastic and metal stick on the surface after the process. By coating a layer of DLC on the mould surface, the combination of wear resistance and anti-stick behaviour of DLC coating provide longer lifetime, good scratch protection, improved corrosion resistance, a significant cycle time reduction and a simplified cleaning procedure [46].

1.4 Inductively coupled plasma (ICP) system

Plasma processing has been widely used in industry as well as for scientific and technology purposes. There are many ways to produce plasma such as inductively coupled plasma (ICP), magnetron system, microwave source, electron cyclotron resonance source and helicon source.

In the late 1980s, ICPs became popular because it is capable of producing uniform high density plasmas at low pressure with high efficiency and relatively low cost [47]. One type of ICPs is the radio frequency (RF) induction system, which has found many applications in a number of different disciplines; they are used in analytical chemistry as source of atomic excitations; spray coating of metals and ceramics; chemical vapor deposition of diamond films [48]; particle spheriodization; nucleation and growth of submicron powder; and, more recently, destruction of waste materials.

Generally, there are two types of RF ICP system namely the solenoid and the planar type. The first use of solenoid type system was in Japan and the first planar type system was invented by Coultas and Keller [49]. However, the planar configuration has attracted a lot of interest due to its ability to produce a disk like uniform plasma that can be scaled up easily. Inductive discharge for material processing is sometimes referred to as TCPs (transformer-coupled plasma), ICPs (inductively coupled plasma), or RFI plasma (RF inductive plasma) [50].

1.5 Planar coil configuration

The planar coil is flat spiral coil placed outside the process chamber with dielectric window in between them. RF power is coupled to the plasma across this dielectric window, by induction effect. This does not require substrate to be part of the plasma generation and enable us to bias it when necessary. The RF magnetic field lines near a planar inductive coil are shown in Figure 1.2.

In axisymmetric geometry, the coil generates an induction field having magnetic component H_r (r,z) and H_z (r,z) and an electric component E_θ(r,z). As shown in Figure 1.2(a) where plasma is formed at the top of the coil, from Faraday's law, an azimuthal electric field E_θ and an associated current density J_θ are induced within the plasma. In this case, the direction of the plasma current will be opposite to the coil current and is confined to a layer having a thickness of the order of skin depth δ near the surface. The total magnetic field, which is the sum of the fields due to the N turn exciting coil current and the 'single-turn' induced plasma current, is shown in Figure 1.2(b). The dominant magnetic field components within the plasma are H_z near the axis and H_r away from the axis, as shown in Figure 1.2. Near the axis, Faraday's law implies that both E_θ and J_θ vanish as E_θ, J_θ α r. This implies that the absorbed power density,

$$P_{abs} = \frac{1}{2} \mathrm{Re}\, J_\theta E_\theta$$

vanishes on axis, leading to a ring shaped profile for the absorbed power [50].

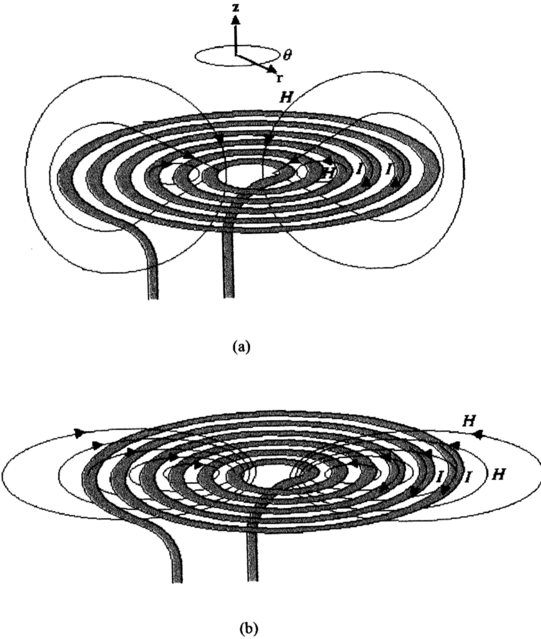


Figure 1.2: Schematic diagram of the RF magnetic field lines near a planar induction coil (a) without nearby plasma (b) with nearby plasma

1.6 Diamondlike carbon (DLC) thin film coating with RF ICPs

Most of the research on the plasma enhanced chemical vapour deposition (PECVD) of DLC film are using microwave plasma CVD (MPCVD), thermal plasma CVD or the combustion flame method. All these methods require higher power for the operation compared to inductively coupled plasma. In this project the deposition of DLC films with a low power RF ICP system will be investigated.

1.7 Objective and the organization of this thesis

The objective of this project is to construct and study the characteristics of the RF planar coil inductively coupled plasma (ICP) system and investigate the application of this system in plasma processing of material, particularly on plasma enhanced chemical vapour deposition of diamondlike carbon (DLC) film. The organization of this thesis is as follows: Chapter 2 gives an account of the system descriptions and instrumentations. Chapter 3 presents the study on the plasma characteristics of the ICP system. The theoretical background of PECVD technique and the observation of PECVD deposition of diamondlike carbon film deposition are presented in Chapter 4. Conclusions and suggestions for future work are presented in Chapter 5.