CHAPTER II

THEORY BACKGROUND

2.1 Alumina

Aluminium oxide (Al_2O_3) is commonly known as alumina in the ceramic community. Alumina has been considered as one of the most promising advance materials used for varieties of application such as media ball, wear-resistance material, cutting tool and orthopaedic implant due to its distinctive chemical, mechanical and thermal properties [22].

2.1.1 Crystal structure

The most common form of crystalline alumina (Fig. 2.1) is known as corundum (α-aluminium oxide). Al_2O_3 has an internal structure where oxygen ions are positioned in the closely-packed hexagonal (cph) arrangement and stacked with Al^{+3} ions, occupying two-thirds of octahedral interstices. The lattice parameter of the hexagonal crystallographic cell is a = 0.475 nm and c = 1.297 nm, which differ entirely from the diamond structure. As a result, the diamond nuclei cannot grow from an α- Al_2O_3 directly. The details on adhesion of diamond film on alumina are described in 2.1.4 [7, 22].

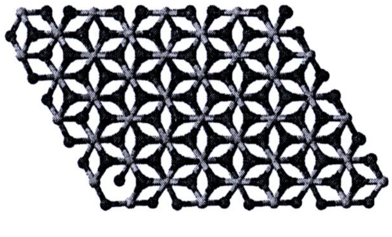

Figure 2.1 Crystal structure of α-aluminium oxide [22].

2.1.2 Processing method

Alumina is the most widely used as inorganic chemical for ceramics and is produced from the mineral bauxite using the Bayer process. Bauxite is a mixture of hydrated aluminium oxide with iron oxide (FeO_2), silica (SiO_2), and titania (TiO_2) impurities. The Bayer process produces a nominal 99.5% Al_2O_3 product. The alumina can be prepared in a range of grades to suit specific applications, where the grades differ by the size and shape of the crystals and the impurity content [7, 22].

The steps in the Bayer process are as follow [7]:

Digestion: The roughly bauxite is treated with a sodium hydroxide (NaOH) solution. Most of the hydrated alumina goes into solution as sodium aluminate:

$$Al(OH)_3(s) + NaOH(aq) \longrightarrow Na^+(aq) + Al(OH)_4^-(aq)$$

Filtration: The solid impurities, mainly SiO_2, TiO_2, and FeO_2, remain undissolved and are separated by filtration.

Precipitation: After cooling, the filtered sodium aluminate solution is seeded with very fine and at a lower temperature that the aluminium hydroxide reforms as the stable phase. Having reduced the pH by bubbling CO_2 through the solution encouraged the precipitation.

Washing: The precipitation is filtered and washed to reduce the sodium content.

Calcination: The powder is calcined at temperature ranging between 1100-1200 °C to convert the hydroxide to the oxide:

$$2Al(OH)_3(s) \longrightarrow Al_2O_3(s) + H_2O(g)$$

At this stage the alumina is in the form of agglomerates of small grains.

Milling: The powder is then milled to give the desired particle size and particle size distribution. The alumina produced in this way contains $\geq$99.5% of Al_2O_3.

2.1.3 Forming techniques

There are numbers of techniques used to shape ceramics. The selection of shaping operation for a particular product is very dependent on the size and dimensional tolerances of the product, the levels of required reproducibility, economic considerations, and most importantly, the required shape. Each of the techniques can be described as followed [7, 23]:

2.1.3.1 Dry pressing

Dry pressing is ideally suited to the formation of simple solid shapes and it consists of three basic steps: filling the die, compacting the contents and ejecting the pressed solid. Because the dry pressing process is simple and involves low capital equipment costs; it is the most widely and commonly used as high-volume forming process for ceramics. Production rates depend on the size and shape of the part and the type of press used.

2.1.3.2 Hot pressing

Pressing can also be performed at high temperatures in which a process is known as hot pressing. The die assembly used for hot pressing is very similar to dry pressing. The main difference is that the die assembly is contained within a high-temperature furnace in hot pressing. During hot pressing, the ceramic powders may sinter together to form a high-density component. Hot pressing, like dry pressing, is limited to simple solid shapes, such as flat plates, blocks, and cylinders. More complex or large shapes are difficult and often impossible to be produced by hot pressing.

Isostatic pressing involves the application of hydrostatic pressure to a powder in a flexible container. The advantage of applying pressure in all directions is that there is more uniform compaction of the powder and more complex shapes can be produced than with uniaxial pressing. Isostatic pressing can be performed either with or without applying heat.

2.1.3.3 Cold isostatic pressing

Powder is weighted and put into a rubber bag then a metal mandrel is inserted to seal the mouth of the rubber bag. The sealed bag is placed inside a high-pressure chamber filled with a fluid and it is hydrostatically pressed. Once pressuring is completed, the pressure is released slowly until the mold is removed from the pressure chamber and the pressed component is removed from the mold.

2.1.3.4 Hot isostatic pressing

The hot isostatic press (HIP) requires heat and pressure simultaneously. A furnace is constructed within a high-pressure vessel and the pressed objects are placed inside. Fig. 2.2 shows a typical HIP arrangement. Temperature can be up to 2000 °C and pressures are typically in the range of 30-100 MPa in which a gas is used as the medium pressure. Argon is a gas most commonly used for HIPing, but oxidizing and reactive gaseous can be also used. Now HIPing is used for a wide variety of ceramic components, such as alumina-based tool bits and the silicon nitride nozzles used in flue-gas desulphurization plants by the utility industry. The advantages of the HIPing process are becoming more important as the interest in structural ceramics.

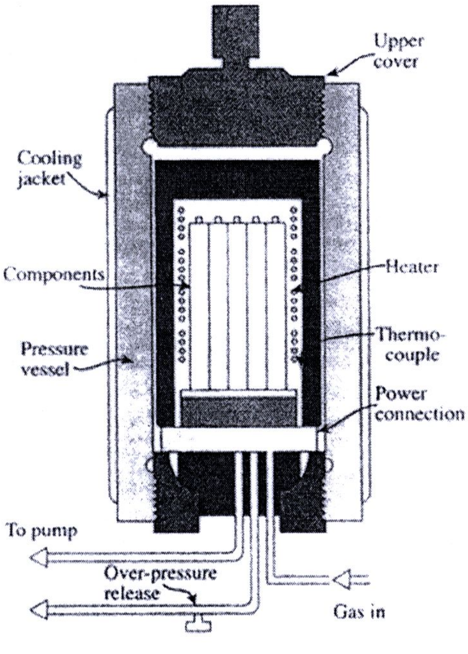

Figure 2.2 Schematic of a hot isostatic pressing apparatus [23].

2.1.3.5 Injection molding

Injection molding can be applied to shape and form ceramic components if the ceramic powder is added to a thermoplastic polymer. The ceramic powder is added to the binder and is usually mixed with several other organic materials to provide a mass that has the desired rheological properties. Firstly, the plastic mass is heated in order to indentify thermoplastic polymer, which becomes soft then it is forced into a mold cavity. The heated mixture becomes a fluid and is not self-supporting. The mixture is allowed to cool in the mold when the thermoplastic polymer hardens. Because of the large volume fraction of organic material used in the mixture, there is a high degree of shrinkage of injection-molded components during sintering. However, complex shapes are retained with very little distortion during sintering.

2.1.4 Properties and applications of alumina

Alumina is the most cost effective and widely used material in the ceramic community. The raw materials from which this high performance technical grade ceramic is made are readily available at reasonably priced, resulting to a reasonable cost of fabricated alumina shapes. With an excellent combination of properties and an attractive price, it is widely used in ranges of applications [7, 24]. Alumina properties and applications are given in Table 2.1.

Table 2.1 Typical properties and applications of alumina [25].

Properties	Applications
Hard (7-9 GPa), wear-resistant and high strength (2100 MPa)	Grinding media, cutting tool and mechanical parts
Resists strong acid and alkali attack	Laboratory instrument tubes and sample holders
Good thermal conductivity (18 W/m•K) and thermal expansion coefficient ($8.1x10^{-6}K^{-1}$)	Furnace liner tubes and Thermometry sensors

However, alumina could wear after a certain period of time. Hence, this work aims to improve an alumina surface by diamond coating and as a result, its hardness of alumina increase.

2.1.5 Adhesion of diamond film on alumina

The alumina structure is very different from the diamond structure, therefore the diamond nuclei cannot grow from an α- Al_2O_3 directly. It is easy to form a non-diamond carbon on the alumina surface, and the diamond nuclei can be formed preferentially on the surface with a diamond-like or amorphous carbon phase. In process of diamond deposition on the alumina substrate, the initial deposited positions are porosity, grain boundaries and vacancies on the surface of the substrate, in which encourage high carbon diffusion into the substrate during the process [13]. This process can be described in three parts: (1) non-diamond carbon deposited on the substrate at the grain boundaries and vacancies of the surface, (2) diamond nuclei formed on the non-diamond surface and (3) diamond nuclei grew up and formed stable nuclei [21, 26]. However, alumina substrates without surface pre-treatment have coarse morphologies, large number of grain boundaries and a hole existed in the surface. Therefore, surface pre-treatment can induce a number of small diamond particles, reduce the roughness of the alumina surface, but generate a large number of scratches with small size in the surface. Diamond films can grow directly on the diamond particles reserved on the surface. Moreover, scratches will increase the surface energy of the substrate and reduce the contact angle and the barrier potential of nucleation [13, 21].

2.2 Carbon Atom and Diamond Structure

Diamond and graphite are crystal forms of carbon. The ideal structure of graphite is a close-packed hexagonal crystal with the carbon in sp^2 hybridization as shown in Fig. 2.3, representing the infinite layers of carbon atom. The carbon atoms form three σ bonds due to the overlap of three sp^2 superimposed orbital, and a π bond form the interaction of p orbital. The in-plane C-C distance is 0.14 nm and the inter-plane C-C distance is 0.34 nm. The carbon atoms form strong covalent bonds in plane and weak Van der Waals bond between the planes. Carbon atoms have four free electrons, where one carbon atom is linked to three carbons so only three free electrons are paired and it is left with one free electron. Thus carbon atoms in graphite only utilize three of the four valence electrons for the covalent bonds formation. The fourth electron is free to move from one carbon to another, hence it can conduct heat and electricity [27].

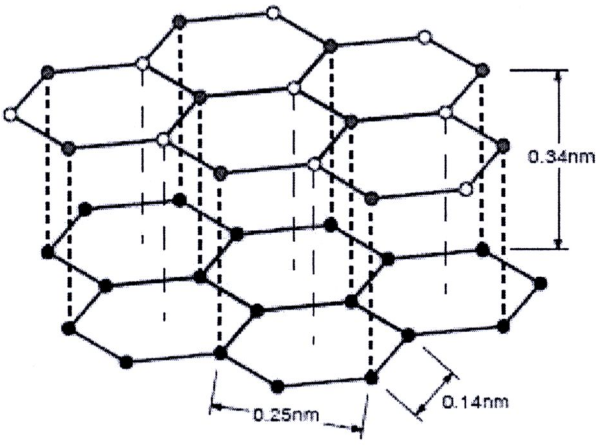

Figure 2.3 Crystal structure of graphite [28].

The diamond structure (Fig.2.4) shows a three-dimensional network of strong covalent bonds. The diamond structure is cubic with cube edge length of a_0 is 0.3567 nm. The diamond structure can be defined as two interpenetrating face-centered cubic (FCC) structure with interatomic distances of 0.154 nm. Each atom is covalently bonded to four other carbon atoms in a form of a tetrahedron. Although the structure is simple, there are lots of consequences for understanding the exceptional properties of diamond. The most common and most utilized implication of the structure is the fact that the carbon crystals are top ranked in hardness and exhibit exceptional tribological properties [8, 29].

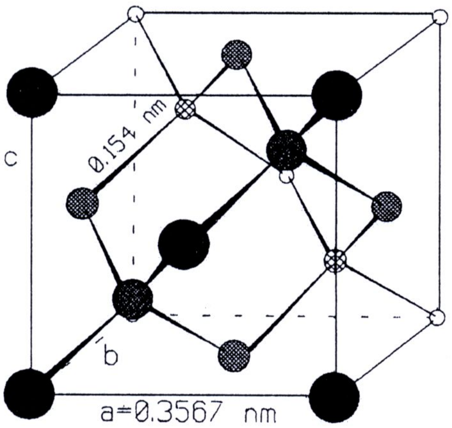

Figure 2.4 The cubic unit cell of diamond structure [29].

Many forms of solid carbon can be produced by CVD process because of the hybrid sp, sp^2 and sp^3 carbon orbitals that are readily available for bonding. A mechanism of diamond nucleation and growth process requires a structural knowledge of the competing crystalline and amorphous phases. Cubic diamond containing only sp^3 carbons and graphite containing only sp^2 carbons are most widely known as phases of crystalline carbon [29]. However, the structure of diamond formed by sp^3 hybridization carbon atoms is unique in nature. Its unique properties make it suitable for a variety of commercial applications. Table 2.2 represents the properties and applications of diamond.

Table 2.2 Properties and applications of diamond [8].

Properties		**Applications**
Hardness (GPa)	85-100	Drill bits, polishing materials, cutting tools, coating materials
Coefficient of friction	0.05-0.15	Wear resistance coating on lenses, bearings, tools or hard disk, sliding parts
Chemical inertness	Inert	Coating for reactor vessels, sample containers for analytical instruments
Thermal conductivity ($W\cdot m^{-1}\cdot K^{-1}$)	2000	Insulating heat sinks for high power electronics
Thermal expansion coefficient ($\times 10^{-6}\cdot K^{-1}$)	1.2	

2.3 Diamond-like carbon (DLC) film

Diamond-like carbon films are metastable amorphous materials, which may include a microcrystalline phase. Diamond-like carbon can also be known as an amorphous carbon material, which composed mainly of carbon and hydrogen and a simple random network of covalently bonded carbon as shown in Fig. 2.5. DLC films contain sp^3, sp^2, and even sp^1 in coordination with carbon atoms in a disordered network. DLC films are amorphous with a significant fraction of sp^3 hybridized carbon atoms, which can contain a significant amount of hydrogen. Depending on the deposition conditions, these films can be fully amorphous or contain diamond crystallites. The differences in both structures and chemical bonds between sp^2 and sp^3 hybridized carbon produce the variety of the DLC film properties [29-30]. The properties of DLC films, listed in Table 2.3, cover a wide range of values between those of diamond and graphite.

Table 2.3 Properties and applications of diamond-like carbon films [30].

Properties	**Applications**
transparency in visible and infrared	optical coatings, both antireflective and wear resistant
chemical inertness in acids, alkalis, and organic solvents	chemically passivating coating, corrosion-protective coatings of magnetic media
high hardness (5-80 GPa) and low friction coefficient (<0.01-0.7)	tribological and wear-resistant coatings
wide range of electrical resistivities (10^2-10^{16} Ω/cm)	insulating coatings

The term 'diamond-like carbon' is used mainly for these materials because their properties are most similar to those diamonds. High hardness and the chemical resistance of DLC films make them good candidates for the use as wear-resistant coatings on metals and on optical and electronic components [29].

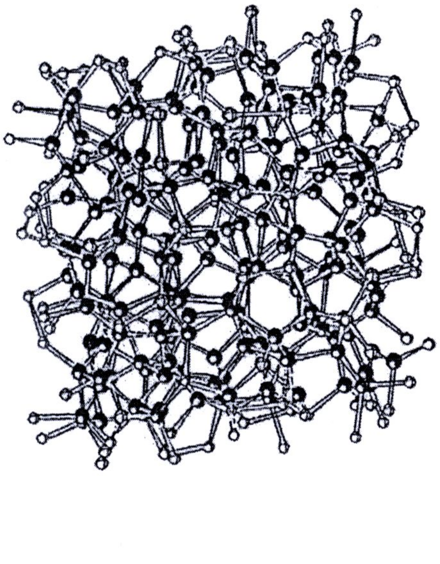

Figure 2.5 Schematic representation of DLC structure [31].

2.4 Plasma

Plasma is a kind of ionized gas. When a solid is heated so sufficiently that the thermal motion of the atoms breaks the crystal lattice structure apart, usually liquid is formed and when a liquid is heated enough for atoms to vaporize off the surface faster than they recondense, the gas is formed. When the gas is heated enough that the atoms collide with each other and knock their electrons off in the process, plasma is formed, known as 'fourth state of matter' (Fig. 2.6). In most materials the dynamics of motion are determined by forces between near-neighbor regions of the material. Typically in the laboratory, a small amount of gas is heated and ionized by driving through an electric current. The thermal capacity of the container is used to keep it from getting hot enough to melt, resulting alone ionize.

Generally, these means of plasma formation give energy to free electrons in the plasma directly, and then electron-atom collisions liberate more electrons and the process cascades until the desired degree of ionization is achieved [32]. Collision processes in the gas phase can be broadly divided into elastic and inelastic collisions, depending on whether the internal energies of the colliding particles are converted. Neutral particles usually have two types of energy, kinetic energy and potential energy, which may be a form of electronic excitation, ionization, dissociation, etc. An elastic collision is one in which there is an interchange of kinetic energy only; it is also called a collision of the first kind. An inelastic collision is one in which the internal energy changes. The simplest collisions are elastic, so the kinetic energy is conserved. But since the electron and any atom have greatly different masses, so the electron only changes its momentum without significantly changing its kinetic energy. When the electron is moving in an electric field, elastic collisions generally have the effect of restricting its velocity in the direction of the field. The charge particles collide incessantly with on another and with the neutral particles in the plasma. The distance traveled by a given particle between two successive collisions is called its free path. The magnitude and direction of free path are distributed at random. The mean free path is the average of the free paths traveled by charged particle collisions with neutral particles. Therefore, it is inversely proportional to the gas density and the gas pressure at a given gas temperature [33].

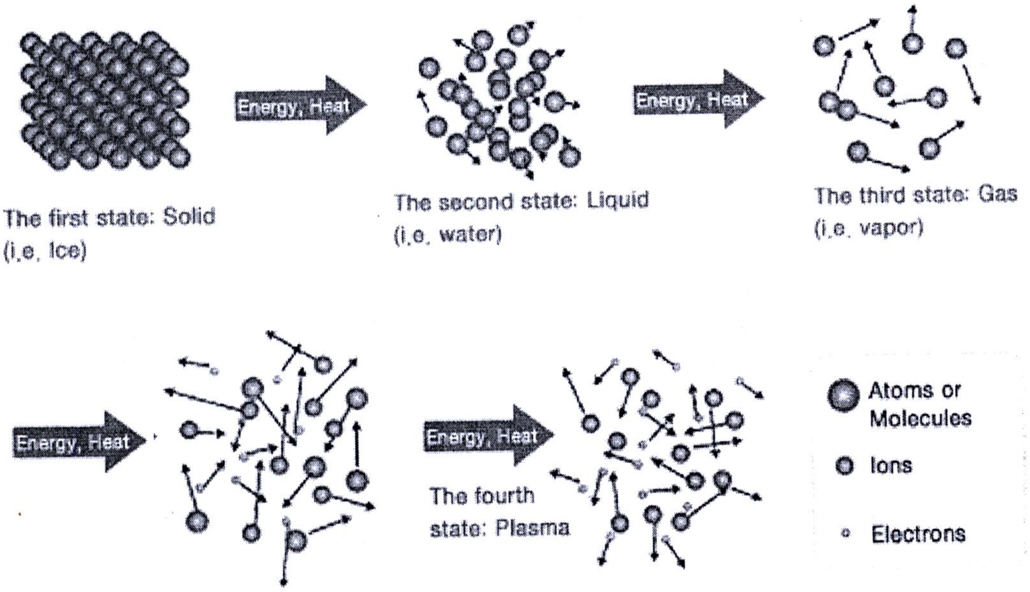

Figure 2.6 The four states of matter [34].

2.5 Chemical vapor deposition (CVD) technique

Chemical vapor deposition is the technique of modifying properties of material surface by depositing a compound layer through chemical reactions in the gaseous medium surrounding the material. CVD may be defined as a technique in which a mixture of gaseous interacts with the surface of a substrate at a relative high temperature, resulting in the decomposition of some constituents of the gas mixture and the formation of a solid coating film of a compound on the substrate [35].

The growth of diamonds from the vapor phase is basically a chemical reaction in which the formation of the diamond structure (carbon with sp^3 bond hybridization) and the graphitic structure (carbon with sp^2 bond hybridization) compete. This process occurs either in the solid-gas interface or at the vapor phase. The precursor gas is initially diluted with excess hydrogen. Energy is needed to activate the gas phase in order to produce diamond films. This gas phase contains a mixture of molecules, radicals, ions, and electrons that oscillate randomly in three dimensions. These energies could come from many variety of sources such as hot filament, electrical discharge (DC, RF or MW), or even from a combustion flame [8, 36].

The fundamental sequential steps that occur in every CVD process are sketched in Fig. 2.7 include [37]:

1. The total gas flows from gas inlet lines to the reaction zone
2. Chemical reactions in the gas phase will produce reactive radicals, atom ions and electrons
3. The initial reactants and reactive species are transported to the substrate surface
4. Adsorption (chemical and physical) and diffusion of reactive species on the substrate surface
5. The reactive species will react on and diffuse close to the substrate surface
6. Diamond nucleation forms on the substrate surface and starts to grow
7. The by-products of surface reactions will be desorbed back into the gas phase.
8. The reaction by-products will be transfer to main flow.

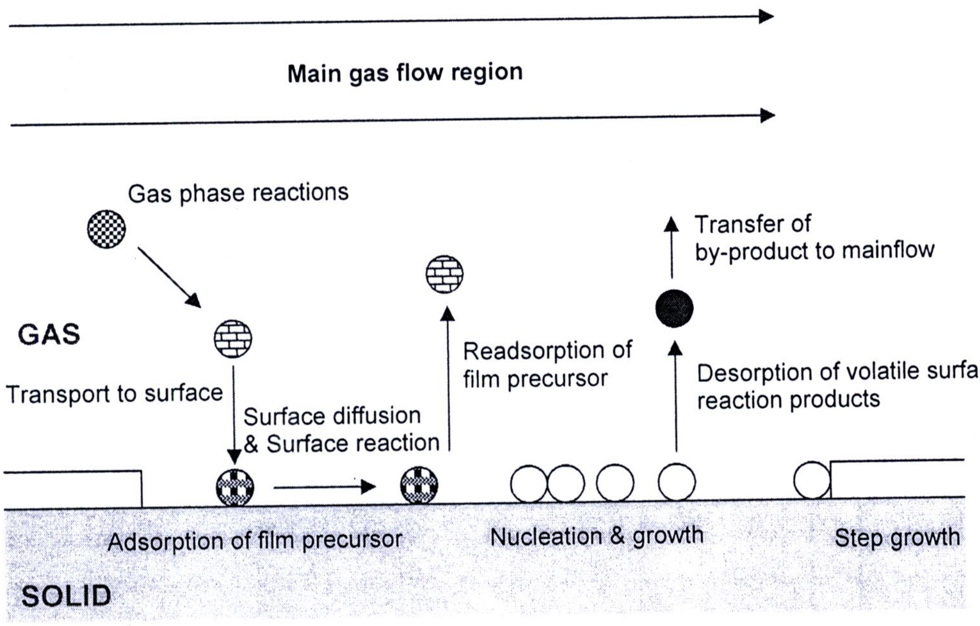

Figure 2.7 Sequence of gas transport and reaction processes contributing to CVD film growth [38].

The influence of diamond nucleation and growth processes requires knowledge of its complex deposition chemistry. This chemistry is complex in comparison to most deposition system because of the competition for deposition among sp^2 and sp^3 types of carbon and because of many possible chemical reactions resulting from the complexity of CVD systems. There are several reactions or important precursor species for deposition, of which importance depends on experimental parameters, such as pressure, temperature, composition, activation mode and reactor geometry. An understanding of the competitive molecular processes, resulting in carbon deposition is needed if the simultaneous deposition of diamond is controlled.

Fig. 2.8 schematically shows the complexity of the competitive processes occurred during diamond growth. The competitive rates of deposition of sp^2 and sp^3 carbon, the conversion of sp^2 and sp^3 carbon and the reverse, etching of the various forms of carbon, and other such processes determine the net deposition quality. It is known that these processes do not only increase gas phase processes which may alter concentrations of hydrocarbon precursors, but also site-specific chemical reactions occurred on surfaces [9, 29].

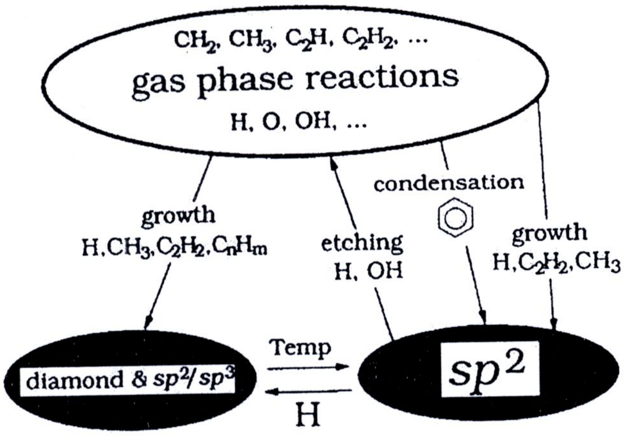

Figure 2.8 Schematic diagram of chemical species and reactions pathways leading to various forms of deposition carbon [29].

2.5.1 Microwave plasma enhanced chemical vapor deposition

In the plasma enhanced CVD (PECVD) technique, the heating of the gas mixture is attained by creating high energy plasma that activates the chemical reactions at considerably reduced temperature as compared to the conventional CVD [35]. A PECVD system is illustrated schematically in Fig. 2.9. A combination of gaseous is fed into the vacuum system and forms active species in the plasma, including precursors or monomers that are deposited in a thin film on the substrate. Different reactors are designed in order to get only the desired process. For this purpose, there are many operating parameters (external variables) such as pressure, substrate temperature, gas composition, gas flow rate, electrical power and frequency, and reactor geometry. The internal variables are electron and ion densities and fluxes, electron and ion temperature, neutral gas molecules and the free radicals produced in the reactor. The understanding and the control of the relationship between the external and internal variables are important due to the large number of above parameters involved and the complexity of any plasma medium have become important for advancement of plasma aided manufacturing [39-41].

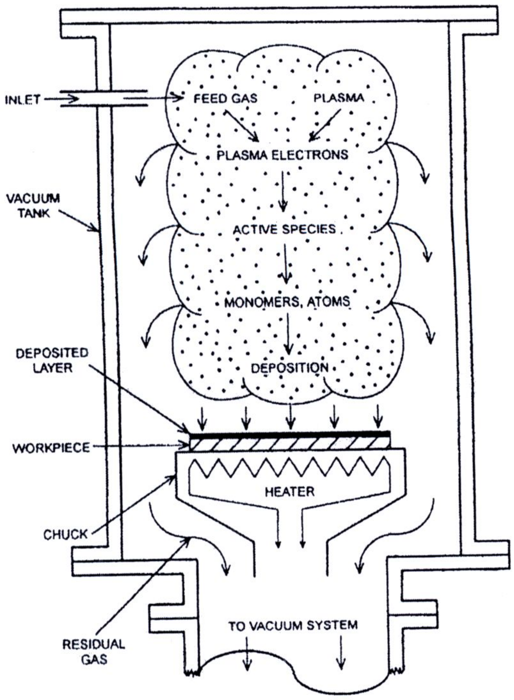

Figure 2.9 Schematic illustration of reactor for plasma enhanced chemical vapor deposition (PECVD) [39].

In a microwave plasma CVD (MWCVD) reactor, microwave power is coupled into the vacuum chamber via quartz window in order to create a discharge. The microwaves couple energy into gas phase electrons caused the electrons to move very quickly. When they collide with the molecules of gas inside the chamber, they dissociate the molecules of the gas into atoms. Further collisions between the electrons and the atoms result in ionization, forming ions and free radicals. Finally, diamond is deposited onto a substrate, which is immersed in the plasma [1, 41].

The two common types of MWCVD reactor are the NIRIM-type and the ASTEX-type reactor as shown in Fig. 2.10. In ASTEX-type reactor, microwaves are coupled into a cavity through a quartz window using an attenna. Microwave plasma CVD (MWCVD) techniques have been used much more extensively than any other techniques for the growth of diamond films. This technique has a number of advantages over the other techniques of film growth such as an electrodeless process avoiding contamination of the films due to electrode erosion. Furthermore, the microwave discharge at 2.45 GHz, being a high frequency process, produces high plasma density with high energy electrons. This could result in high concentration of atomic hydrogen and hydrocarbon radicals [9].

It is generally well known that the CH_4 molecules are decomposed into some hydrocarbon neutral radicals (CH, CH_2, CH_3), ionic radical (CH^+, CH_3^+, $C_2H_5^+$), and atomic or ionic hydrogen (H, H^+). The hydrocarbons etch into the substrate surface and create the dangling bonds on it, the neutral hydrocarbon radicals are adsorbed at the dangling bonds. At the same time, more of graphite-like sp^2 bonded phases are etched by atomic or ionic hydrogen and the diamond films are formed [29]. Therefore, the hydrocarbon and hydrogen ions density and the ion energy have great influence on the characteristics of DLC films.

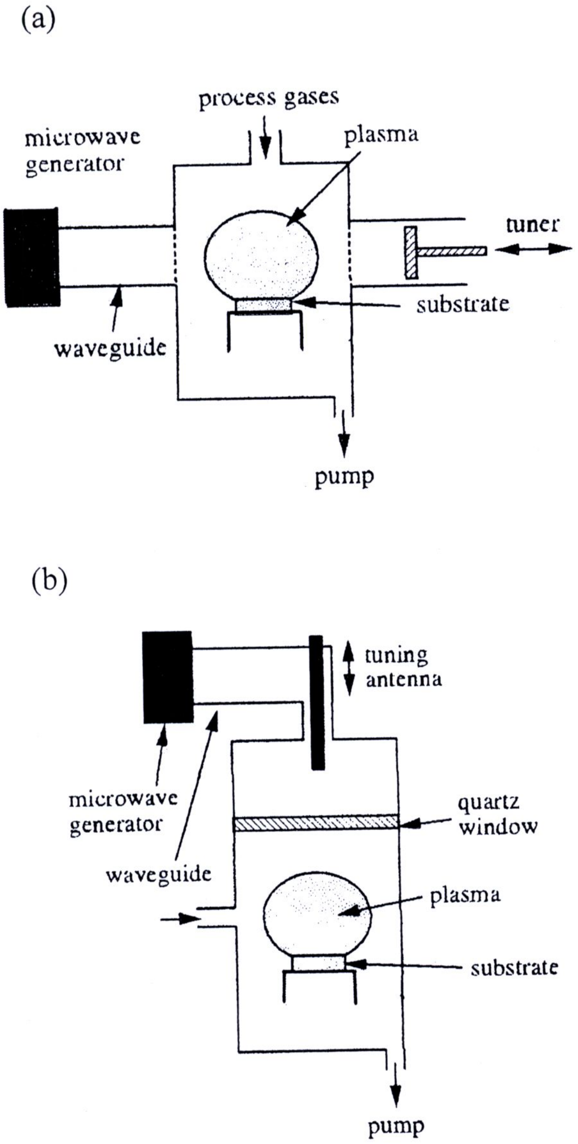

Figure 2.10 Example of the common types of microwave plasma reactor. (a) NIRIM-type and (b) ASTEX-type [1].

2.6 Nucleation growth of diamond film

Substrate pretreatment played an important role to control the nucleation, morphology, orientation and the surface roughness. Surface scratching with diamond powder [42-44] and substrate biasing [45-46] are the common techniques used to increase the nucleation density and decreasing incubation time. The most commonly used method of substrate pretreatment to increase the nucleation density is scratching with diamond powder. Ion implantation [47-48] and chemical etching [49-50] of substrate surfaces are one of the other treatments used to increase the nucleation density and adhesion of the film to the substrate. Nucleation density and surface damage of the substrate strongly depend on the size of the diamond particles used for the pretreatment method. In the substrate pretreatment process, small fragments of diamond particles are embedded in the substrate materials and directly acted as the nucleation center of diamond growth. Scratching the substrate causes serious surface damage and hence the application of the coating for optical and electronic materials needs alternative nucleation techniques [8, 9].

According to Linjun Wang *et al.* [20], the research showed that the surface pretreatment of the substrate was commonly needed to obtain a continuous film. Based on their experiment, alumina substrates were ultrasonically cleaned with diamond powder suspended in acetone. Then, the microwave plasma CVD technique using a gaseous of methane and hydrogen was applied to deposit diamond films on substrate. It is proven by SEM, XRD and Raman measurements that diamond films were in good quality.

Wang *et al.* [45] studied the nucleation growth of diamond on molybdenum using hot filament CVD technique. The process was performed with negative bias of -300V in order to remove any contaminants on the surface and to activate the surface. They found that the negatively biased pretreatment greatly enhanced the nucleation density of diamond films on molybdenum, which were investigated by scanning electron microscopy.

Based on Chattopadhyay *et al.* [49], they studied the synthesis of diamond on cemented carbide substrate by hot filament CVD technique. The experiment showed that the substrate was etched with $HCl+HNO_3+H_2O$ (1:1:1) solution for 15 minutes at room temperature. From the SEM results, the etching pretreatment also increased the surface roughness of the substrate surface, in which it helped to hold the diamond coating to the substrate.

2.7 The CVD diamond growth conditions

In the CVD process, the optimization of diamond growth parameter space is very large and complex. The influences of the important parameter, controlling the films quality, including the substrate material, substrate temperature, concentration of gas methane, and deposition pressure are described as below.

2.7.1 Substrate materials

The influences of substrate materials are found to affect the growth properties of diamond films. The thermal expansion of substrate material should be comparable with diamond. This is because the high growth temperature in currently processes, a substrate will be expanded and thus the diamond coating will be grown upon and bonded directly to an expanded substrate. For this reason, the diamond film will have significant compressive stresses from the shrinking of the substrate and causes bowing of the sample, cracking and flaking or delamination of the film. The based substrate for vapor phase of growth diamond film is various, such as Mo, WC, Co, Pt, Cu, Fe, Ti, Ti alloy, TiC, Si, SiC, Si_3N_4, Al_2O_3, etc. [8].

Ristic *et al.* [50] studied that diamond films grown on different substrates (Cu, Si, WC-Co, Mo) by hot filament CVD technique. In all their experiment, the working gaseous mixture was 1% methane in hydrogen. The total gas pressure was 30 mbar. The position time was around 30 hr. The surface morphology of growth diamond films are given in SEM micrographs. They found that a well-faceted diamond crystals continuous coating were deposited on Cu, WC-Co and Mo substrates, whereas the morphology of diamond films grown on Si substrates were obtained a fine-grained. From the results on XRD and Raman measurements presented crystalline phase and high-quality diamond films on these substrates.

In this work, the DLC thin films are grown on alumina substrate. Deposition of diamond coating is utilized the ability of the material to increase hardness and wear resistance. However, the properties of diamond growth films are also upon to other parameters such as substrate temperature, methane gas concentration and deposition pressure.

2.7.2 Substrate temperature

The influences of substrate temperature are found to affect on the growth diamond films. In various CVD methods, diamond growth takes place at substrate temperature between 300 and 1200 °C. At low temperature, the formation of active sites is slow because it is limited by the low rate of reaction. With the increase of temperature, this rate is increased. However, at high temperature (>1200 °C), the number density of active species decreases due to their thermal decomposition and subsequent graphitization. The sp^2 carbon formed at these high temperatures is rapidly etched away by hydrogen atom. These phenomena explain the maximum in diamond growth rate with substrate temperature. At higher temperature than this maximum, the increasing density of surface radical enhanced sp^2 formation; while at lower substrate temperature, the condensation of aromatics can lead to a possibly amorphous sp^2 and sp^3 carbonaceous network [29]. Therefore, the substrate temperature of diamond growth in this work was kept in the range of 300-350 °C. In this experimental set up, he substrate is heated predominantly by heat transfer from the plasma gas rather than by direct microwave absorption [36].

Kulisch *et al.* [42] studied the influence of substrate temperature on the growth of nanocrystalline diamond films on silicon substrate in the range of 520-770 °C. They found that the growth process was thermally activated, leading to increasing growth rates with increasing temperature and the properties of crystalline (e.g. the grain size) of the films were almost not affected by the temperature in the range.

Study by Tyagi *et al.* [51] showed that the crystalline nature of the films deposited on molybdenum substrate change from polycrystalline to single crystal as they increase substrate temperature and for a certain set of parameters the growth of the diamond single crystals can be seen. The films were polycrystalline in the range of substrate temperature 850–900 °C, as the substrate temperature increasing.

Yan *et al.* [19] studied the effect of substrate temperature ranging from 750 to 950 °C on microstructure and the quality of diamond films deposited by DC arc plasma jet CVD technique. The results indicated that the covered crystalline planes on film surfaces changed from {220} to {111} planes as the temperature increased from 750 °C to 930 °C. For the diamond film deposited at 870 °C, there were still a few interspaces, but for the films deposited at 930 °C and 935 °C, the films were very dense. It indicated that the temperature had a significant effect on the film density. In addition, the purity of the film increased with increasing temperature in the range of 750-900 °C, and when the temperature exceed 900 °C, the purity decreased.

2.7.3 Methane gas concentration

Diamond films have been grown from a variety of carbon-containing species mixed in certain concentrations with other reactive and inert gaseous. A large variety of carbon-containing species have been employed to synthesize diamond using CVD technique. These include methane, propane, butane, ethylene acethylene and carbon monoxide. In addition to carbon-containing carrier, the gas phase must usually contain nondiamond carbon etchings and diamond phase stabilizing agents, such as hydrogen, oxygen, chlorine, and fluorine atoms [8, 36]. The main factor affecting to the deposition characteristics with the increase in the initial hydrocarbon concentration are higher concentrations of growth species and therefore it is a larger deposition rate; increased formation of graphitic, which reduced film quality; and lower hydrogen atom concentrations [29]. The growth of diamond thin films normally requires the methane gas diluted in the hydrogen gas. In this work, methane gas concentration is varied between 0.5-5% in order to examine the film quality.

Askari *et al.* [43] reported that a low value of methane concentration is chosen in order to obtain a well-faceted good polycrystalline diamond films grown on titanium substrate, whereas a high value of methane concentration was preferred to achieve a smooth and fine-grained nanocrystalline diamond films with a surface roughness.

Buhlmann *et al.* [44] studied the influence of the methane/hydrogen gas ratio between 1-12.5%. They found that at low methane concentrations, faceted diamond deposits were formed on silicon substrate, whereas at higher methane contents, ballas or cauliflower-like morphology was observed. The methane content necessary for the faceted-to-ballas or cauliflower-like transition decreased with increasing temperature.

Regarding to Li *et al.* [18], the research was based on the effect of methane gas concentration on diamond films deposited on molybdenum substrate by DC-plasma jet CVD technique. It was reported that at the beginning of diamond nucleation, diamond crystallites orientation was random, and the influence of CH_4 concentration was negligible. At a low CH_4 concentration (1%) and the substrate temperature of 850 °C, a high quality diamond film was prepared. The film structure was polycrystalline and (111) face was observed. When increasing CH_4 concentration, diamond film has more local clusters, amorphous graphite. Thus, higher CH_4 concentration had negative influence on preparing high quality diamond film. In addition, CH_4 concentration had significant affects on film uniformity, growth rate and crystal sizes.

2.7.4 Deposition pressure

The total pressure of hydrogen-hydrocarbon gaseous mixture determines the recombination length, the lifetime, and the drift distance of atomic hydrogen. In the condition of low pressure, the electrons and molecules are not in thermal equilibrium. Due to the difference in mass between electrons and ions, the electrons accelerate rapidly in an electric field, while the ions move slowly. However, there is no redistribution of energy between electrons and molecules and the gas temperature remains relatively cool due to the large electron mean free path. Thus, atomic hydrogen and neutral carbon-containing radicals, needed for the growth of diamond, are primarily generated by the high energy electrons of which concentration is relatively small. In addition, the growth rate in low pressure plasma is expected to be small. In the condition of high pressure, it causes the electron mean free path is small which could result to the redistribution of energy between electrons and molecules. So, the gas temperature is as near as the temperature of the electron, and both temperature can cause the generation of atomic hydrogen and neutral carbon-containing radicals. Consequently, the expectation of the growth rate in the high-pressure will increase [29]. Thus, the deposition pressure in this work is varied between 10-50 torr in order to investigate the influence of pressure on the formation of DLC thin films.

Liang *et al.* [14] studied the effect of pressure on the deposition of nanocrystalline diamond (NCD) films on silicon substrate in a hot filament chemical vapor deposition (HFCVD) system was investigated employing a 1% CH_4 in H_2 gas mixture. They found that diamond films as the growth pressure decreasing from 5.0 to

0.125 kPa, showed a gradual reduction of the diamond grain sizes from sub-micrometer to nanometer scale. In addition, the surface roughness of the deposited diamond films also decreased with the reduction of the growth pressure.

2.8 Film characterizing technique

The DLC films quality have been investigated by a variety of techniques. The characterizations of surface morphology are examined by scanning electron microscopy (SEM). Raman spectroscopy is the most widely used techniques to characterize carbon bonding in DLC thin films. Finally, the investigations of mechanical properties are evaluated by nanoindentation testing.

2.8.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is one of the most widely used techniques to characterize thin film surface morphology. It operates by scanning a focused electron beam over a surface and sensing the secondary electrons emitted from the surface. The electron beam can be focused on a very small and the beam size is the detrimental factor of the microscopy resolution. It is often necessary to coat a diamond film surface with a thin layer of gold or carbon for avoiding charging effects. Working at low electron voltage is always useful for avoiding the charging effect while working with insulating films. It has been recognized that diamond films produced on nondiamond substrates are comprised of different surface morphologies depending on the deposition conditions and substrate chemical nature [8].

A basic diagram of an SEM is shown in Fig. 2.11. The electron gun produces a beam of electrons that is attracted through the anode and condensed by the condenser lens and then focused as a very fine point on the substrate by the objective lens. A set of small coils are energized by a varying voltage produced by the scan generator and created a magnetic field that deflects the beam of electrons back and forth in a controlled pattern. When the beam of electrons strikes the substrate, a complex series of interactions occurs, resulting in the production of secondary electrons from the sample, which are collected by the detector, converted to a voltage, and amplified. The amplified voltage is then applied to the grid of the cathode-ray tube (CRT) and changes the intensity of the spot of light on the surface [52].

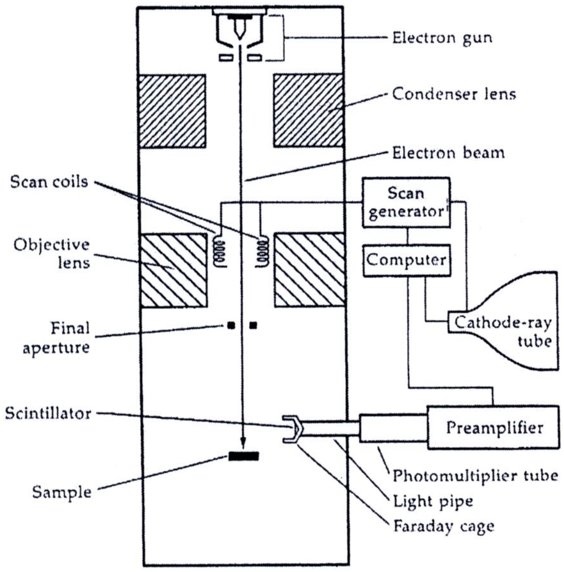

Figure 2.11 Schematic of a scanning electron microscope [52].

Based on Rujisamphan's research [53], he studied the growth of diamond thin film on silicon substrate by MW-PECVD technique. According to SEM, he found that the diameter of individual diamond nuclei was increased as deposition time increased. The film surface morphology changed from scatter well-faceted to cauliflower-like continuous film with increasing CH_4 concentration. Moreover, he observed that the surface roughness and grain size decreased with increasing in CH_4 concentration.

Askari *et al.* [43] presented that the surface morphology of growth diamond film on titanium substrate at low CH_4 concentration was well-faceted and polycrystalline morphology. The average grain size was less than 1 μm and exhibited [111] orientation. The average surface roughness of this film was approximately about 95 nm. Furthermore, the surface morphology of the grown nanocrystalline diamond film (high CH_4 concentration) showed that the film consisted of nanocrystals with average grain size of 30 nm or less. The surface roughness of nanocrystalline diamond film was approximately 35 nm.

2.8.2 Raman spectroscopy

Raman spectroscopy has been the most widely used tool for the examination of the types of bonding present in carbon films. It is a complementary technique to IR spectroscopy. A modern Raman spectrometer is designed for ultraviolet excitation. Radiation from a laser is focused on the substrate surface. The reflected and scattered radiations are collected normally to the substrate surface by a high-power microscope objective and, after reflection by a beam splitter, transferred to a grating monochromator through a Rayleigh-line rejection filter, and detected by an array detector. The filter separates the elastically scattered (Rayleigh) radiation from the inelastically scattered Raman radiation. Because the former is a general order of magnitude more intense than the latter, the development of such a notch filter constitutes a major advance of modern commercial Raman spectrophotometers. The beam splitter also directs light from an illuminator, which had been reflected by a second beam splitter, to impinge on the substrate surface. This light makes it possible to see the Raman-analyzed surface and detect inhomogeneities. Both the impinging excitation and the reflected and scattered Raman radiations are distributed over a wide solid angle. Raman spectra are plotted as frequency shifts from the exciting frequency against intensity [30, 54].

There are three types of signal in a typical Raman experiment as illustrated in Fig. 2.12. In Rayleigh scattering, a molecular is excited by the incident photon to a virtual energy level. This energy level is caused by a distortion of the electron distribution of a covalent bond. The molecular returns to the vibrational ground state by emitting the same energy. Rayleigh scattering is an elastic process. Vibration excitations can be created, and causes a decrease in the frequency of the scattered light, which causes an increase. The decrease in frequency is called Stoke scattering and the increase is called anti-Stoke scattering. Stokes scattering is the normal Raman effect and Raman spectroscopy generally uses Stokes radiation [7].

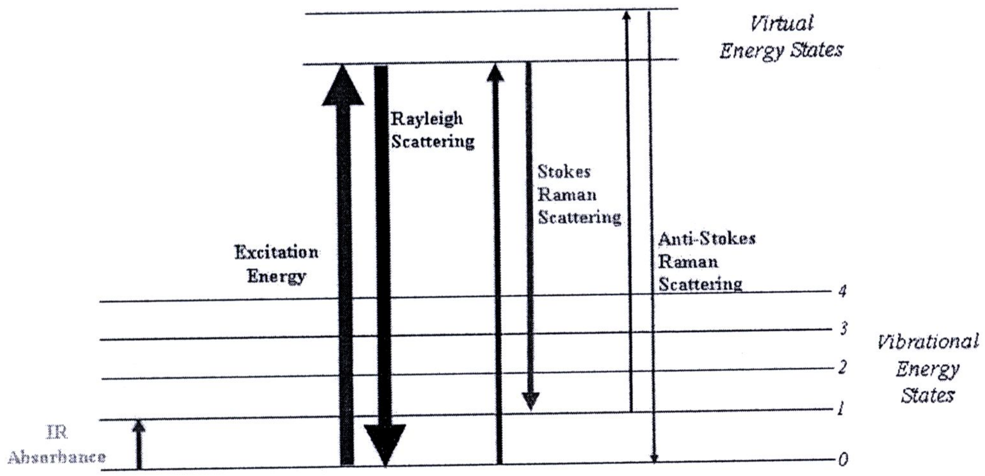

Figure 2.12 Schematic of transitions occurring in Raman spectroscopy [54].

Using the Raman spectroscopy technique with diamond, which has a phonon density of states and it has a very different form from other carbon phases. The Raman signal is very sensitive to short range disorder and subsequently it can reveal different forms of amorphous carbon and graphite. The position of various Raman bands observed in CVD diamond films, and their corresponding assignments and descriptions are given in Table 2.4.

Table 2.4 Raman bands in CVD diamond films [8].

Position (cm^{-1})	**Assignments**	**Descriptions**
~1140	Nanocrystalline (sizes of 1-100 nm) diamond	occasionally observed in diamond films small grain sizes
1332	Cubic diamond	first order peak with FWHM of 1.9 cm^{-1} for natural diamond
1345	Amorphous carbon	broad band
~1550	Amorphous or diamond-like carbon	broad band
~1580	Graphitic	first order peak

Askari *et al.* [43] reported that the Raman spectrum of nanocrystalline diamond film deposited on titanium substrate clearly showed the characteristic diamond and graphite phase. There was a peak at about 1334 cm^{-1}, which corresponded to the diamond peak. Raman bands around 1475-1550 cm^{-1} could be attributed to sp^2-bonded carbon. Raman peak at approximately 1130 cm^{-1} was caused by a size effect of nanoscale diamond.

Wang *et al.* [20] studied the effect of substrate temperature on the quality of diamond films, and they worked the Raman measurements on diamond films deposited on alumina substrate under 700, 780, 830 and 900 °C. They found that the films were mainly composed of the diamond phase at 1334 cm^{-1}. An obvious intensity decreased with the weak broad band around 1580 cm^{-1} (related to sp^2 bonding).

2.8.3 Nanoindentation test

Nanoindentation technique is one of the most popular applications for determination the mechanical properties of material surface. This nanoindenter can be used to characterize organic, inorganic, soft or hard materials and coatings. Examples are thin films and multilayer PVD, CVD, PECVD, and many other types of films and coatings. In the nanoindentation tests, the properties of thin films maybe measured without removing the films from the substrate as it done in other of testing. The nanoindentation tester has been designed to provide surface mechanical characterization data by indenting to depths at the nanometer-micron scales [7].

In nanoindentation tester, an indenter tip is driven into a specific site of the sample to be tested by applying an increased normal load. Indenter displacement is measured using a capacitive transducer. Using the partial-unload technique, the contact hardness of the sample can be calculated as a function of depth of penetration into the sample. The instrument applies load via calibrated electromagnetic coil and displacement of the indenter is measured using a capacitive sensor. A schematic of the instrument is shown in Fig. 2.13. A particular feature of this instrument is the use of a sapphire ring that remains in contact with the sample surface during the indentation. The ring provided a differential measurement of penetration depth and thus the load frame compliance and the thermal drift are automatically compensated [55].

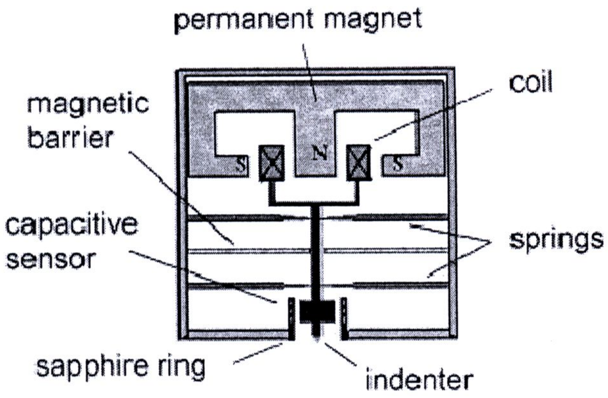

Figure 2.13 Schematic of a nanoindentation tester [56].

Based on Martinez *et al.* [57], their research studied the effects of substrate temperature on the hardness and adhesion of DLC thin films deposited on silicon substrate by radio frequency plasma CVD technique using CH_4 and H_2 gaseous mixture. In their experiment, nanoindentation system was used to evaluate the hardness of the films. The hardness and Young's modulus of the films were calculated form the load-displacement curves. These curves were obtained with a diamond Berkovich indenter and a lading and unloading rate of 0.1 mNs^{-1} up to maximum load of 5 mN, which gave contacts penetration depths lower than 20% of the films thickness. The films as a function of deposition temperatures presented hardness value in the range of 12-14 GPa. Furthermore, they found that the hardness of the films was similar in samples deposited at temperatures from 20 to 300 °C and decreased at higher deposition temperature to 9.5 GPa.

Regarding to Kulish *et al.* [58], their research studied the mechanical properties of nanocrystalline diamond/ amorphous carbon composite films grown on silicon substrate by microwave plasma CVD technique from CH_4 and H_2 gaseous mixture. They presented the results of the investigation of the films mechnical by nanoindentation measurements. They found that the average indentation hardness of the film at 17% CH_4 is 39.7 ± 2.2 GPa. A typical nanoindentation load-displacement curve of the film is shown in Fig. 2.14.

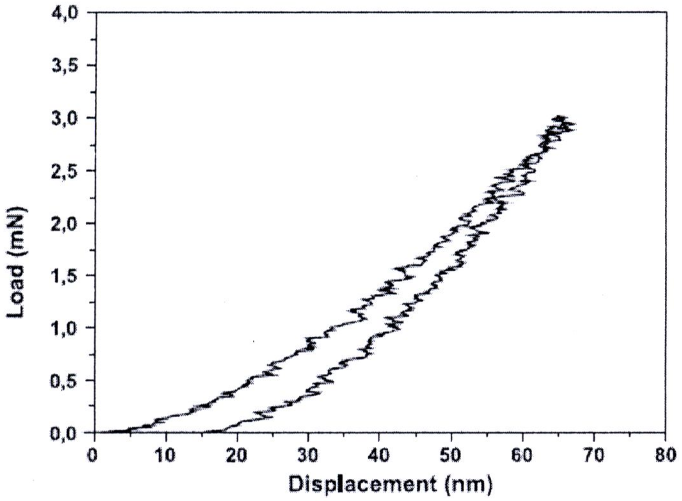

Figure 2.14 Load-displacement curve of nanocrystalline/amorphous carbon films prepared with 17% CH_4 [58].

2.8.4 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) has been extensively used to investigate the surface morphology, roughness, and initial stage of nucleation [8]. AFM is an electron microscope; instead of using a beam of electrons to image the sample, a very fine mechanical probe scans the surface of sample. The instrument uses a piezoelectric device for scanning. The piezoelectric effect occurs because certain crystals increase in size when a voltage is applied. By combining crystals, movement in x, y, z directions is possible. In an AFM, the sample is mounted on the piezo device and moved. A very fine tip is mounted on a triangular piece of metal foil called the cantilever (Fig. 2.15). The piezoelectric device moves the sample under the tip. The variation in attractive forces between the electrons in the orbital shells of the tip and those of the sample causes movement of the foil. The reflected beam of the laser is detected by a photodiode. Movement of the foil causes variation in the current in the photodiode. This variation in current is then used to produce an image on cathode-ray tube (CRT). Alternatively, a feedback mechanism can be used to move the tip in order to keep the photodiode current constant, and the variation in voltage applied to the piezoelectric device can be used to produce the image. One major advantage of the AFM is that samples do not need to be conductive [52].

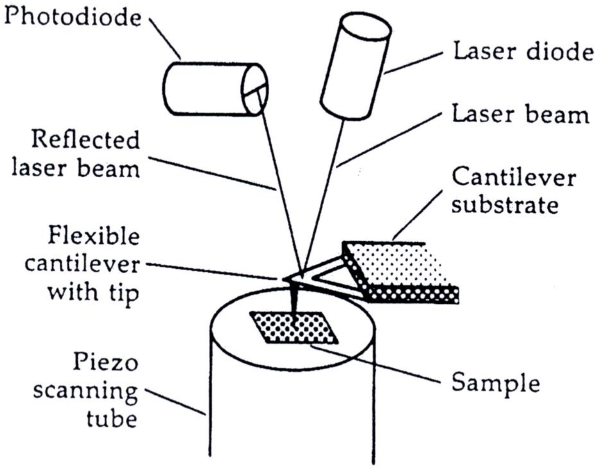

Figure 2.15 Schematic of an atomic force microscope [52].

Based on Cho *et al.* [59], their research studied the deposition of DLC films on silicon substrate by MW-PECVD technique with various DC bias voltages and by RF-PECVD technique with various RF powers. According to AFM, the surface roughness of the DLC films deposited by the MW-PECVD decreased with increasing the negative DC bias voltage due to the heat dissipation of impinging ions, which could help the surface smoothing. In case the films deposited by the RF-PECVD, the surface produced at a RF power of 25W was rough and it became smoother as the RF power increased except at a RF power of 200W.

Regarding to Liang *et al.* [14], their research studied the effect of pressure on nanocrystalline diamond films grown on silicon substrate by hot filament CVD technique from CH_4/H_2 gaseous mixture. From the results on AFM, they found that the size of most grains distribute in the range of 40-80 nm. Furthermore, the surface roughness of the films increased with decreasing the grain sizes. The root-mean-square (rms) roughness of the films was found to decrease from 16 nm to 8 nm as deposition pressure was decreased from 4 kPa to 0.125 kPa. The films deposited at pressure in between lies presented the rms roughness value in the range of 10-15 nm.