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ABSTRACT

PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF DIAMONDLIKE CARBON FILMS USING ACETYLENE

by

Sriram Vishwanathan

This study is focussed on the synthesis and characterization of diamondlike carbon (DLC) films deposited on silicon wafers and glass by plasma enhanced chemical vapor deposition (PECVD), using acetylene (C_2H_4) as a precursor. The process parameters, such as temperature, pressure, power and reactant gas flow rate have been systematically varied and their effects on the film growth rate and properties were investigated. The optimized deposition condition appeared to be at 150°C, 200mTorr, 200 Watts and flow rate = 25 sccm. For these conditions, the films were hard and found to have good adhesion to the substrate, and resistant to HF etching (49% HF diluted to 10% with distilled water). It was found that the adhesion of the DLC film to the substrate is good if the substrate is first etched with oxygen and CF_4 prior to the deposition.

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by
Sriram Vishwanathan

A Thesis
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August 1998

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PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF DIAMONDLIKE CARBON FILMS USING ACETYLENE

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This thesis is dedicated to
my beloved parents

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CHAPTER 1

INTRODUCTION

1.1 What is Diamondlike Carbon (DLC) ?

Diamondlike carbon or DLC is an amorphous, metastable material which may include a microcrystalline phase. DLC contains a mixture of sp^3, sp^2 and sp^1 hybridised carbon in a disordered network. DLC does not have a long range order but may contain a short range or medium range order. These disordered forms of carbon material are called 'diamondlike' due to their extreme hardness and significant optical gap, which are characteristics of diamond.

In most cases, DLC contains Hydrogen, which plays a very key role in determination of its properties especially the optical and electrical properties, as it passivates the dangling bonds in the amorphous structure [1]. This removes the midgap defect states, and stabilises the random network, preventing its collapse into a graphitic phase. Hydrogen also influences the ratio between the carbon atoms in the different co-ordinations. The films which contain Hydrogen are denoted as a:C-H, these are necessarily deposited using hydrocarbon precursors, while those films that do not contain Hydrogen are called a:C.

The main advantage of DLC over diamond is that smooth DLC films can be deposited over very large areas at relatively low temperatures [2] on virtually any substrate and thus opens a much wider range of applications in comparison to rough diamond films.

DLC films can be prepared by a variety of methods including DC or RF plasma-assisted chemical vapor deposition (CVD), sputtering, and ion beam deposition, using a variety of carbon bearing, solid or gaseous source materials [3]. DLC exhibits a wide range of properties between those of diamond, graphite and hydrocarbon polymers.

1.2 Comparison Between Diamond and DLC

The diamond films are polycrystalline materials, with crystallites up to tens of micrometers in size, having diamond's crystal structure. Although DLC films may crystallise under bombardment with high energy ions [4] and some degree of crystallinity was reported by several authors for films deposited at relatively high substrate bias [5], DLC films are essentially amorphous without any long range order. However short or medium range order may occur in these films [6]. Thus, although diamond and diamondlike carbon are both hard inert materials, the crystalline form of diamond and the amorphous structure of diamondlike carbon give them inherently different properties.

While diamond and diamond layers is a well defined material with fixed properties, the properties of DLC cover a wide range of values between those of diamond, graphite, and hydrocarbon polymers. The term diamondlike is used for these materials mainly because on average their properties are most similar to those of diamond. The wide interest in the deposition and characterization of DLC films stems from the fact that very smooth films can be deposited uniformly over wide areas on a large variety of substrates. This makes possible the possible the practical commercial use of DLC films in numerous applications, not yet possible with relatively rough diamond films. Further, DLC layers are fabricated at temperatures well below those employed in

diamond deposition, making this coating compatible with a wider range of substrate materials. Besides this, the cost of fabrication of DLC is low because relatively cheap precursors are used and deposition can be done at lower power densities of 0.1-0.3 W cm^{-2}. The following table shows the comparison between the different forms of Carbon in terms of some of their properties.

Table 1.1 Comparison between different forms of carbon in terms of some properties

	Density(g/cm^3)	Hardness(kg/mm^{-2})	% sp^3	At.% H	Gap (eV)	Ref.
Diamond	3.515	10^4	100	0	5.5	
Graphite	2.267	-	0	0	-0.04	
a-C:H	1.6-2.2	1000-2000	40-70	10-35	0.8-1.7	[7]
Polyethylene	0.95	1-4	100	67	6	

1.3 Applications and Properties of DLC

The unique properties of DLC films, such as high hardness and low friction coefficient, chemical inertness, infrared transparency, and high electrical resistivity, combined with smoothness and low deposition temperatures, make them suitable for a large number of applications. The various applications based on the corresponding property is shown in the table below.

Table 1.2 Applications and the corresponding requisite property of DLC

APPLICATIONS	PROPERTY REQUIREMENTS
TRIBOLOGY	
Wear resistant coatings for cutting tools [8].	Hard, corrosion resistant, wear resistant, and chemically inert.
Impact resistant coatings for high-density computer disks [8].	Thin films with high hardness, corrosion resistance, and chemical inertness.
Decorative coatings[8]	Hard, transparent in the visible range.
Protection of Magnetic storage disks [9], coatings for recording cylinder tapes[10].	Hard, corrosion resistant, and thin and nanosmooth, low coefficient of friction.
Coatings for metallic orthopedic pins[11], artificial heart valves[12].	Chemically inert, biocompatibility.
OPTICS	
Protective coatings for IR optics (windows and lenses of Ge, ZnS, or ZnSe) [8]	Hard, corrosion resistant and chemically inert, transparent in the IR region of the EMS spectrum.
Protective coatings for Aluminum mirrors in optical imaging, copper mirrors for CO_2 lasers. [8]	Hard, corrosion resistant and chemically inert
Anti-reflection coatings for Ge.[8]	Same as above and refractive index of ~ 2
Protective layer for solar cells used in space[8]	Low radiation damage, transparent in visible range of the spectrum.
X-ray windows[8]	Self-standing films with high transmission and low damage threshold for x-rays, smooth surface topography.

Table 1.2 (Continued)

APPLICATIONS	PROPERTY REQUIREMENTS
OPTO-ELECTRONIC	
Protective layer for electronic devices [8]	Hard, chemically inert, and corrosion resistant, insulating and high breakdown voltage.
Heat sinks for high power devices and PCB, electrical insulation of chip cooling devices in high performance computers [8]	Same as above and high thermal conductivity.
Schottky diodes , DLC - diamond / Silicon heterojunction diodes, transistors [13], barrier in electronic tunneling devices [14], for and for UV detectors.	High electrical resistivity, di-electric constant, charge mobility.
Diffusion barriers for optical fibres and optoelectronic devices [15].	Moisture resistant, resistant to oxygen, hard.
Protective coatings for photolithography masks [16] and optical disks.	Low sputtering yield.
Passivating layers in semiconductor applications	Thermal stability and electrical resistance.

1.4 Issues Related to Diamondlike Carbon

Issues related to DLC films: Although DLC films show promising properties, their thermal and mechanical instabilities restricted their use in many potential applications. Difficulties in obtaining high growth rate, limitations on obtaining thick films due to residual stresses in the films, and degradation of film properties at temperatures as low as 350 degrees C are some of the constraints [8].

However, it is possible to widen the properties of DLC and improve some of the difficulties by incorporation of different elements, such as metals [17], halogens [18], nitrogen .Addition of metals can reduce the stresses in the films and may also improve their behaviour for tribological applications; it can also increase the electrical conductivity of the films. Addition of other elements may allow tailoring the optical properties of DLC for specific applications and may improve the tribological properties.

1.5 Chemical Vapor Deposition Techniques

1.5.1 Fundamental Aspects of Chemical Vapor Deposition

Chemical vapor deposition (CVD) is one of the most popular techniques of growing a very thin film on various substances. The reason for its promising applications lies in its versatility for depositing a very large variety of materials at relatively low temperatures [19].

Chemical vapor deposition (CVD) is defined as the formation of a non-volatile solid film on a substrate by the reaction of vapor phase chemicals (reactants) that contain the required constituents. The reactant gases are introduced into a reaction chamber and are decomposed and reacted at a heated surface to form the thin film.

Thin films used in a host of different applications in VLSI fabrication must exhibit the following characteristics: 1) good thickness uniformity; 2) high purity and density; 3) controlled composition and stoichiometries; 4) high degree of structure perfection; 5) good electrical properties; 6) excellent adhesion; 7) good step coverage. CVD films synthesized under optimized conditions can satisfy these requirements.

The procedure of CVD involves flowing a reactive gas or gas mixture over a surface that catalyzes a chemical reaction to form a solid product [20]. CVD reactions can be homogeneous, heterogeneous or a combination of both. Homogeneous reactions nucleate in the gas phase and lead to particle formation, which can result in low density films, poorly adhering, or defects in the depositing films. In addition, such reactions also consume reactants and can cause a decrease in deposition rates [19]. Heterogeneous reactions are generally favored because they take place at the substrate surface rather than in the gas phase and form desirable good quality film deposit. One important characteristic of a chemical reaction for CVD application is the degree to which heterogeneous reactions are favored over gas phase reactions. A typical CVD process consists of at least the following steps [21]:

Arrival

1. bulk transport of the reactants and diluent inert gases into the reaction chamber;
2. gaseous diffusion of the reactants to the substrate surface;
3. adsorption of the reactants on the surface;

Surface reaction

4. surface diffusion of the reactants;
5. chemical reaction of the adsorbed reactant molecules;

Removal of reactant by-products

6. desorption of the reactant by-products;
7. gaseous diffusion of the reactant by-products;

8. bulk transport of the by-products and unreacted gases out of the reaction chamber.

Thermally-driven CVD reactions are dynamical equilibrium processes. There is a typical temperature dependence of deposition rate sketched in Figure 1.1[22]. At low temperature the reaction is generally surface reaction controlled, while at high temperature, it is usually limited by mass transfer.

If the process is controlled by the surface reaction, i.e. reaction rate is limited by the rate of surface reaction, the deposition mechanism of the solid film follows the empirical Arrhenius behavior [21,22]:

$$D.R. = A \exp(-E_a / RT) \tag{1.1}$$

where ,

D.R. is the deposition rate of the film;

E_a is the apparent activation energy of the chemical reaction;

R is the gas constant;

T is absolute temperature (K);

A is constant.

According to this equation, the reaction rate increases with the increasing temperature. There is a linear plot of ln(D.R) vs. 1/T.

When the temperature rises high enough and the reaction rate approaches the rate of the reactant species arriving at the surface, the reaction rate can not increase any more,

unless there is an increase in the rate at which the reactant species are supplied to the surface by diffusion and mass transport. In this case, the reaction is mass transport controlled. The reaction rate can then be expressed as below:

$$D.R. = s\, k_D / RT\, (P - P_0) \tag{1.2}$$

where,

s is surface area of the substrate;

k_D is mass transport coefficient;

P is partial pressure of the reactant;

P_0 is equilibrium partial pressure of the reactant at certain temperature;

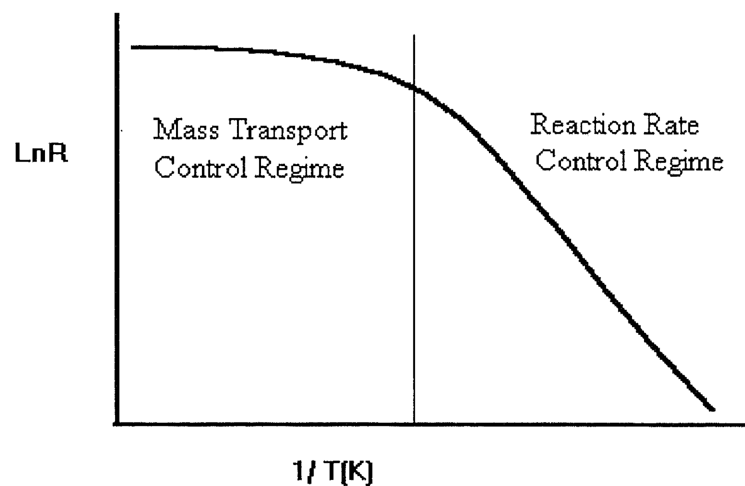

Figure1.1 Temperature dependence of deposition rate

The critical temperature at which the reaction mechanism is switched from one rate-controlling regime to another is associated with the activation energy and the gas

flow conditions. Adsorption of decomposition products on the surface of the substrate may be an additional factor retarding film growth.

For those processes in which heat is not the predominant energy source, such as plasma-enhanced CVD, the reactions are non-equilibrium. The mechanism of the reaction is complex, since there are many excited species, e.g., radicals, atoms, ions produced by electron impact and unexcited gas molecules as well. Upon being adsorbed on the substrate, these species are subjected to ion and electron bombardment, rearrangements, reactions with each other, new bond formations and film growth [19]. The relationship between deposition rate and temperature is not like that stated above. However, temperature is still an important factor affecting the CVD process and the properties of the deposits as well.

Consequently, the deposition rate and the properties of the CVD film depend on the deposition conditions, such as reaction temperature, pressure, reactant flow rates, power density (as in plasma-enhanced CVD process) and so on. Studies on the effects of such variables will result in good understanding of the CVD processes.

1.5.2 Categories of CVD

The energy to activate and drive the chemical processes can be thermal, supplied by an electric glow discharge plasma, or attained by electromagnetic radiation (usually ultraviolet or laser radiation). According to the type of energy supplied to initiate and sustain the reaction, CVD processes can be classified into following categories [23]:

1) Thermally activated reactions at various pressure ranges; which comprise the vast majority of CVD processes. Heat is applied by resistance heating, rf inducting heating , or infrared radiation heating techniques.

2) Plasma promoted reactions, where an rf or dc induced glow discharge is the source for most of the energy that initiates and enhances the rate of reaction, usually called plasma-enhanced CVD (PECVD).

3) Photo induced reactions, where a specific wavelength radiation triggers and sustains the reaction by direct photolysis or by an energy transfer agent .

The most important and widely used CVD processes are atmospheric pressure CVD (APCVD), low pressure CVD (LPCVD) and plasma enhanced CVD (PECVD). A general description of APCVD and LPCVD will be made below and PECVD as the technique employed in this study will be discussed in detail.

1.5.2.1: Atmospheric Pressure CVD (APCVD): Much of the early CVD development work was done by APCVD. It offered such advantages as operation without the need for a vacuum system, high dilution of toxic or flammable gases, and the potential for operation as continuous-feed belt systems. Disadvantages of APCVD operation included the need for large volumes of carrier gas, large size, and high levels of particulate contamination. In recent years, atmospheric operation have faded from popularity, with most significant developments occurring in the remaining two categories.

1.5.2.2. Low Pressure CVD (LPCVD): In low pressure CVD processes [24-30], the reduced gas pressure enhances the mass transfer rate relative to the surface reaction rate,

this makes it possible to deposit film uniformly in a relative highly economical close spaced positioning of the substrate wafers in a standup fashion [24]. The outstanding advantage of LPCVD technique lies in the thickness uniformity of the films and the step coverage which are substantially improved over those obtained in conventional atmospheric pressure CVD reactors. The films have fewer defects, such as particulate contaminants and pinholes, because of the inherently cleaner hot wall operations and the vertical wafer positioning that minimize the formation and co-deposition of homogeneously gas phase nucleated particles [30]. These considerations are especially important in VLSI processing where a very high device reliability and high product yield must be achieved.The drawbacks of the LPCVD is the need of relatively high temperature (550-850^{0}C) and relatively low deposition rate.

1.5.2.3. Plasma-Enhanced CVD (PECVD): Plasma deposition is a combination of a glow discharge process and low pressure chemical vapor deposition in which highly reactive chemical species are generated from gaseous reaction by a glow discharge and interact to form a thin solid film product on the substrate and electrode surface [23]. Since the plasma assists or enhances the CVD reaction, the process is denoted as Plasma-Enhanced CVD (PECVD).

Plasma-enhancement offers an alternative to thermal energy for initiating chemical reactions leading to film deposition. Use of plasma frequently allows deposition at a much lower temperature than could otherwise be achieved, and/or it permits the use of source gases that would ordinarily be considered non-reactive. This is the major advantage of PECVD. Radicals, which are predominant species in plasma field, tend to

have high sticking coefficients, and also appear to migrate easily along the surface after adsorption. These two factors can lead to excellent film conformality. Another benefit is very high growth rate, although, care must be taken to minimize stresses and contaminations [23]. Desirable film properties such as good adhesion, low pinhole density, good step coverage, adequate chemical properties can also be obtained by PECVD superior to those of APCVD or LPCVD films. Moreover, the mechanical strength of plasma deposited films is excellent due to their intrinsic compressive stress and high film density [31,32]. However, the complexity of reactions associated with PECVD makes the synthesis of stoichiometric composition difficult. And, as a consequence of the low temperature for film formation, gases are trapped in the films, which frequently causes thermal instability due to outgassing. Though sensitive MOS devices may be damaged by the radiation associated with the plasma discharge, the damage can usually be eliminated by a thermal anneal at the deposition temperature [20]. The main factors which affect the PECVD processes and the thin film properties include plasma power density, frequency as well as the substrate temperature and partial pressure of reactant gases, etc.

1.6 Objective of the Thesis

This work on the PECVD of DLC is focused on the film composition study, i.e., deposition parameters' effects on the film stoichiometry, impurities levels and its properties. In this study, Acetylene (C_2H_2) is used as the precursor of CVD DLC, using Plasma-enhanced CVD technique. The effects of deposition parameters on the growth rate and physical properties of the PECVD DLC films were investigated.

1.7 Precursors Used for the Process

Practically any organic hydrocarbon can be used for the deposition of Diamondlike carbon [33], however extensive works have been carried out using acetylene, ethylene, methane, ethane, propane, benzene, toluene, butane, butene etc. We used Acetylene for our experiments. Many times, these organic precursors were also diluted using Hydrogen or some inert gas like Argon.

1.8 Advantages and Disadvantages for Various Methods of Preparation of DLC

Various deposition techniques have been employed for the deposition of DLC, however for this thesis Plasma enhanced Chemical Vapor Deposition (parallel plate type) has been employed.

The following table shows the various methods of preparation of Diamondlike Carbon, and their salient features in terms of advantages and disadvantages.

Table 1.3 Various CVD techniques and their salient features

CHEMICAL VAPOUR DEPOSITION

PROCESS	TYPE AND QUALITY OF FILM PRODUCED	ADVANTAGES	LIMITATIONS
Hot wire CVD	Very thin films (1000-5000A°), Rough and opaque	Inexpensive and easy to operate	High susstrate temperatures, low rates (1mm/h), difficult to scale up,film quality is not suitable for most of the applications.
Electron assisted CVD	films are rough and opaque, showing agglomerations of sp3 sites.	Inexpensive, possible to obtain higher deposition rates.	Difficult to control, high deposition temperature, unlikely to be acceptable for most electronic and optical applications.

PLASMA ASSISTED CHEMICAL VAPOUR DEPOSITION

PROCESS	TYPE AND QUALITY OF FILM PRODUCED	ADVANTAGES	LIMITATIONS
Microwave assistedCVD	Thin transparent films, rough topography	Cleaner process, easier to control and optimise	High deposition temp, low deposition rates , rough surface topography may limit optical & electronic applications
Remote plasma assisted CVD	Limited data available	Clean process, low film damage	Difficult,very low deposition rate, substrate temperature requirements not known. Inadequate for production applications
PACVD using hollow cathode	Transparent films	Possible to obtain films at high rates, external heating during deposition not reqd.	Difficult to scale up for large area substrate, control / optimisation of the film properties is yet to be demonstrated.

PHYSICAL VAPOUR DEPOSITION

PROCESS	TYPE AND QUALITY OF FILM PRODUCED	ADVANTAGES	LIMITATIONS
Ion beam sputtering	Smooth, transparent i-C film	Extremely good operational control, low substrate temp. Possible	Very low deposition rate, usable only for small area substrate
Dual sputtering beam	Smooth, transparent i-C film	Same as above	Same as above
Laser ion beam technique	Limited data	High deposition rates are possible	Difficult to scale up to large area, control and optimisation of film properties and quality yet to be demonstrated.

CHAPTER 2

PLASMA ENHANCED CVD

Plasma CVD or plasma-enhanced CVD combines a radio frequency-induced glow discharge process and low pressure CVD in which the reaction is activated by a plasma. Glow discharge creates a highly reactive chemical species generated from gaseous reactants which subsequently interact to form a thin solid film on the substrate surface [34]. Plasma CVD processes were developed in the 1960's at first for semiconductor applications notably due to the desire to replace silicon dioxide metal protection layers with silicon nitride. These nitride layers requires a temperature of approximately 660°C for a thermally activated CVD. This temperature causes enough problems with the underlying aluminum layers as to be unusable [35]. Plasma CVD process has been expanding ever since and is now used in a wide variety of CVD applications.

2.1 Principles of Plasma CVD

If the energy of a gas is increased to a high enough level, all gas molecules will be dissociated into atoms that are increasingly ionized (stripped of their electrons) forming a plasma consisting of positive ions, electrons and unionized (neutral) atoms. However, this requires a temperature >5000K. Plasma generated by combustion flame has a temperature limit of 3700K which is insufficient for complete ionization (appx 10%).

A more efficient way to achieve the higher temperatures needed for more complete ionization is to apply either a high or low frequency electric field. When the electrical energy of a fixed amount of gas is increased complete ionization is achieved [34].

a) Low frequency (isothermal) plasma discharge- when a low frequency electric field is applied to a gas, both electrons and the positive ions acquire energy and have their temperatures raised almost equally, so the plasma is in equilibrium (isothermal). These isothermal plasmas are generated at relatively high pressures (100 torr - 1atm.). The high pressure reduces the mean free path between colliding molecules, increasing the frequency of collisions between ions and molecules which are heated readily. For a typical example of this type of discharge, the arc discharge, requires a large amount of power (in the MW range) and are extremely hot. Therefore their applications have been limited in CVD deposition with the exception of diamond deposition.

b) Non-equilibrium (non-isothermal) plasma (glow discharge)- In this process the plasma is generated by a high frequency electric field at a lower pressure than isothermal plasma (< 2 torr). In the high frequency electric field, the gas molecules are ionized into positive ions and electrons. The electrons have a much lighter mass and higher mobility than other species and are quickly accelerated to high energy levels (>5000K at an average energy between 1 and 10 eV.). Because of the very low mass they do not appreciably increase the temperature of the plasma as a whole. The heavier ions however cannot respond to the rapidly alternating electric field due to their inertia and do not have their energy and temperature raised, in contrast to the low frequency process. (electron temp./gas temp. 10 -100 [34].Thus the plasma is in non-equilibrium (non-isothermal). The energy of these heavier species is < .05 eV. The high energy electrons then collide with the gas molecules resulting in dissociation into highly reactive chemical species (free radicals, ions, atoms, metastable species, excited molecules, photons [34] which subsequently initiate the reaction. The efficiency of the ionization process is a function of the kinetic energy of the

electrons, with the efficiency rapidly increasing between 10 and 100 eV. The electrons acquire energy directly from the applied electric field. The concentration of positive and negative charge carriers are approximately equal, with an electron (and positive ion) density range of 109 -1012 /cm3. Glow discharge plasmas are weakly ionized with the ratio of neutral species to electrons or ions greater than 103. Due to this higher concentration of neutral species it is primarily these species responsible for film formation [34]. The high frequency currents can be generated by a radio frequency (rf), ac, dc or microwave source. The vast majority of research and development employs a rf field as the means of plasma excitation because many of the films deposited are dielectrics where a dc source is not feasible. An rf source typically operates at 450 KHz or 13.45 MHz and the microwave at 2.45 GHz. For the rf source the reactor configuration consists of a parallel plate, cold wall reactor with two parallel electrodes with the substrate(s) serving as one of the electrodes, usually the grounded one while the other is powered.

2.2 Characteristics of the Plasma CVD Process

In addition to the generation of chemically reactive species via breaking of chemical bonds through electron/gas molecule collisions, the other primary function of the plasma is to provide energetic radiation (primarily ions but also electrons and photons) for surface chemistry alteration [35]. Due to the difference in mobility between electrons and positive ions, the substrate surface initially assumes a negative potential with respect to the plasma. This in turn leads to a positive ion bombardment of the surface. The energy of the ions striking the surface is a function of the potential difference between the

plasma and substrate, the number of collisions (related to gas pressure) and the rf frequency. These energies are usually greater than most bond strengths (up to 1000 eV) and can modify surface chemistry during deposition. Resulting phenomena that can result from plasma surface interaction includes the following:

a) Surface cleaning and desorption of unwanted impurities during and/or after deposition due to ion bombardment. Sufficient particle energy will cause sputtering/etching of surface.

b) Creation of adsorption and nucleation sites is another development of impinging particles which can break chemical bonds. Finer-grained deposits will result, and the growth of unique phases is another possibility.

c) Increase in surface mobility of adsorbed species due to momentum transfer possibly resulting in increased step coverage

d) Implantation of bombarding particles or recoil implantation of adsorbed species resulting in impurity incorporation and subsequent modification of surface properties and composition.

e) Generation of defects (vacancies, dislocations, interstitials, stacking faults, etc.) by particle bombardment.

2.3 Advantages of PECVD

The major advantage of plasma CVD is the ability to produce deposition processes that would normally occur only at much higher temperatures with LPCVD [35]. As explained above, the generation of reactive chemical species is done at gas temperatures near ambient due to the non-isothermal nature of the plasma. Therefore many high

temperature reactions can be made on temperature-sensitive substrates at low temperatures. Examples are aluminum, which would melt at the required LPCVD temperature, organic polymers which would otherwise degrade and outgass, or metals and alloys which would undergo structural changes at higher temperatures. Dopants for semiconductors (boron, phosphorus) can readily diffuse between buried layers of the device if the temperature exceeds 800° C with damaging effects to the semiconductor properties [36]. Other advantages of the plasma process are that deposition rates are usually increased. With the low pressures used, the rate-controlling regime is surface kinetics leading to greater film uniformity. Low temperatures are more conducive to the growth of amorphous or fine-grained polycrystalline films. A number of deposition parameters necessary to alter film characteristics are available with PECVD for "tailoring" of these properties [35].

2.4 Limitations of PECVD

Deposits of pure materials are often difficult to achieve. Low temperatures during deposition in many cases results in incomplete desorption of byproducts and other gases, particularly hydrogen, resulting in unwanted inclusions and outgassing causing thermal instability. An example of this phenomenon is hydrogen given off from plasma nitride films that may cause damaging effects on the electronic properties of certain devices [35]. The complexity of reactions makes stoichiometric compounds difficult to achieve, as in the case with carbides, nitrides, silicides and oxides. While usually detrimental to film properties and lowering its resistance to chemical etching and radiation, such alterations can be beneficial in certain applications, i.e. improved opto-electronic properties of

amorphous silicon used in solar cells when hydrogen is present. Another disadvantage is potential damage to fragile substrates such as in ULSI and some III-V and II-VI semiconductor materials due to ion bombardment if the ion energy exceeds 20 eV. In addition, the plasma will react strongly to the surface as deposition takes place meaning that the deposition rate and many film properties will be a function of the plasma uniformity. More fully exposed areas of the substrate will therefore be affected by plasma interactions than less exposed, more sheltered regions. Reproducibility and deposition control is often inhibited by these complex gas phase and surface dynamics. Other disadvantages include the creation of undesirable compressive stresses particularly at lower frequencies and the generally more expensive and complicated nature of the equipment.

2.5 Applications of Plasma CVD

As mentioned above, the advantage of low deposition temperatures is particularly important for the fabrication of semiconductor materials due to the high possibility of inter-diffusion at film thickness of about 2000A° at high processing temperatures. For this reason semiconductor technology was the first major application for plasma CVD and remains its major application. Recently plasma has emerged as an application in deposition of films for cutting tools and wear and corrosion protection. The most important materials used in film products are the following [35,36]:

a) silicon nitrides and silicon oxy-nitrides: Si_3N_4 films are used to completely passivate and encapsulate microelectronic devices because it is somewhat elastic and does not crack. Other benefits of this material are it provides an effective barrier against water and

sodium and has good adhesion to aluminum and gold. However stoichiometry is difficult to control and hydrogen is often incorporated in the lattice structure where the material is then best described as $Si_xN_yH_z$. As much as 25% hydrogen can be incorporated into the film. While Si_3N_4 is denser, has higher resistivity and dielectric breakdown strength, and is more resistant to chemical attack, $Si_xN_yH_z$ can provide better step coverage.

b) silicon dioxides: plasma-processed SiO_2 is used as an insulator in semiconductor devices and more recently as a coating for fiber optics.

c) metals: PECVD has been used to synthesize transition metals, transition metal silicides and transition metal nitrides for the formation of conducting layers for barrier, contact, and interconnect applications which will be described in more detail as it pertains to tungsten deposition.

d) carbides and the elements carbon and boron have also been deposited using plasma CVD.

2.6 General Plasma Parameters

The key parameters effecting to plasma deposition result are gas operating pressure, rf power input, gas flow rate, loading quantity, and temperature. The followings are some significant characteristics of each parameter in plasma etching.

2.6.1 Plasma Condition

Low pressure plasma used in process apparatus are generally characterized by low degree of gas ionization, (typical 0.1-1 %) and an absence of thermal equilibrium between the ionized component, the free electrons and the neutral gas molecules. Thus one can

consider three separate temperatures (or separate energy distribution systems). The range of electron energies are between 1-20 eV and the ion densities are normally between 10^9 - 10^{12} cm^{-3}.

The mass difference between electrons and ions results in the electrons being accelerated to higher velocities than the ions, in the presence of electric field. In particular, in high frequency (hf) and radio frequency (rf) systems the electrons can reach much higher energies than the ions because of their smaller mass and the rapidity of the field change. Ions in the region of the space charge sheath are accelerated towards the electrode surface producing secondary electrons on impact. The secondary electrons are accelerated out into the plasma by the same space charge sheath and may all obtain considerable energy from the sheath.

Ions, because of their larger mass, and smaller mean free path, can more effectively transfer kinetic energy by elastic collision with gas molecules. The average fraction of an electron energy lost in an elastic collision with a gas molecule is $\cong m/2M$ where m is the mass of the electron and M is the mass of the molecule. Thus only 10^{-5} of the kinetic energy is lost by an elastic collision, and the electron energy may continue to rise between collision.

Typical ratios of ion energy and electron energy in the plasma region of the glow discharge are between 1:10 - 1:1000. This absence of thermal equilibrium makes it possible for the gas temperature (Tg) in the plasma zone to be near ambient, with the ion temperature (Ti) in the plasma region of the glow discharge only slightly higher than Tg, i.e. $Ti \cong Tg$.

However, some of the electrons have enough energy to excite, or ionize molecules or atoms and even rupture molecular bonds during inelastic collisions. Compounds exposed to high temperature (e.g. flames) are composed mainly of radicals and molecules that are incompletely dissociated. However, in glow discharge or plasma the larger average electron energy produces many more molecular and atomic fragments, which may also be ionized. It is such species produced in an rf discharge with an excitation frequency between 5 kHz and 5.6 GHz which are used in the fabrication of semiconductor devices.

However, as discussed here, an ion sheath may form adjacent to the wafer resting on the electrode surface. Ions from the plasma zone enter the ion sheath and are accelerated towards the electrode, gaining considerable energy. If an inert gas is used the ions are accelerated and bombard the wafer surface removing material by physical sputtering.

By careful choice of plasma chemistry and conditions a volatile compound is formed between the active gas and the substrate. This volatile compound can be removed from the reaction vessel by pumping.

This is the basis of the plasma deposition or etching process, which requires a chamber for plasma reaction, a flow meter to monitor the rate of gas flow into the chamber and a mechanical vacuum pump to maintain a vacuum in the chamber. The pump should rough out and maintain a pressure in the region 0.01-1.0 torr and at the same time remove the reacted compounds. The plasma can be sustained by dc or ac supplies, but it is more useful to use rf excitation because of the charging that occurs on dielectric films when depositing / etching is dc plasmas. At low rf frequencies the

coupling through insulated layers such as a quartz vessel starts to become difficult and electrodes have to be located with in the plasma volume. There may also be other advantages of using rf excitation, such as sustaining plasmas at lower pressure. A typical plasma process system layout is shown in Figure 2.1 [37].

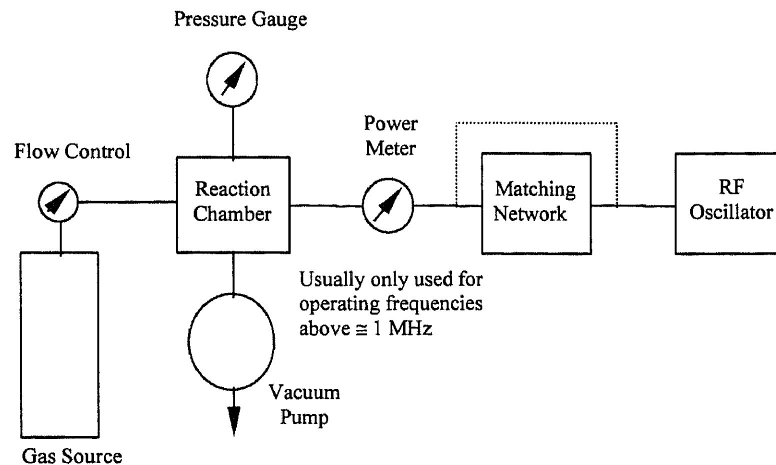

Figure 2.1 Typical plasma processing arrangement

2.6.2 Gas Pressure

The manner in which depositing depends on plasma pressure is complex as many effects occur simultaneously. As the gas pressure is raised there is generally a reduction in the mean free path of the plasma components producing more radicals and ions, (depending on the electron temperature and the species in the system). The increase in free radical and ion production can have several effects. For example it can increase the deposition rate on the wafer by raising the ion or free radical concentration at the surface of the wafer. On the other hand, free radicals can recombine with each other forming higher molecular weight species, called dimer.

The dimer can also fragment and recombine eventually forming high molecular weight condensed polymers on surfaces. Such an event is more probable at higher pressures, and with long resident times for free radicals of heavy mass.

When increasing the pressure, the ion concentration may initially increase and thus the impedance of the plasma may fall thereby resulting in a lower applied potential at a given power input. At the ion sheath, the ion bombardment energy will fall with the decrease in sheath potential caused by the reduction of applied potential to the plasma. Thus polymer may grow on an exposed surface as the ions arriving have lower energy. Also the ion energy may be too low to induce chemical reactions which need ion bombardment.

The increase in ion density at a given power input with a rise in pressure is due to the increase in collision rates between the electrons and gas molecules and between ions and neutrals. The pressure rise will also increase the ionization events and recombination events in the plasma. It may also increase the collisions between ions and neutrals whilst traversing the dark space, thus reducing the ion energy on impact with the electrode surface. Increasing the operating pressures of plasmas may also increase the rate and type of species that could physically or chemically absorb on the wafer surface. This could then change the rate-controlling step in wafer deposition or etching processes.

2.6.3 RF Power Input

At constant pressure the plasma density can be raised by increasing the power input into the plasma. This increase in power will cause a rise in the applied potential particularly at the lower pressures [39]. It will also increase the potential across the ion sheath, thus

raising the ion bombardment energy. Any increase in power will also increase the rate of formation of other plasma products such as free radicals. However, any polymer condensation from heavy free radicals will be offset by the higher ion bombardment energy.

The increase in ion bombardment energy by increasing rf power input could make the ion bombardment, at the surface, a more probable reaction for inducing chemical change by bond rupture or damage. There will also be an increase in ion density, which will increase the rate of material being deposited on the surface. Alternatively, if the reaction rate is limited by a free radical process, an increase in ion energy or density alone may not be significant. Thus, deposition will be enhanced by a rise in free radical concentration in the plasma. An increase in ion bombardment energy may also have an effect on surrounding atoms in the area of bombardment which could lower the activation energy and increase the rate of reaction thus increasing the deposition rate.

2.6.4 Gas Flow Rate

The dependence of gas flow rate on the deposition rate of specific wafer surface material varies from plasma reactor to plasma reactor. However, below a critical flow rate, there is an inadequate supply of reactant to deposit the wafer material and thus a small increase in flow rate can rapidly increase the wafer deposit rate.

As the flow rate is raised, the product species are flushed away and thus subjected to less dissociation and recombination reaction in the plasma but at the same time the initial reactant gas is less utilized [40]. Use of the precursor will increase as the rf power input is increased [40]. If the flow rate is further increased with accompanying increase in

pumping speed to maintain a constant pressure of operation, then it is possible that the active species produced in plasma can be pumped away before they have the opportunity to react.

2.7 RF Glow Discharges (Plasmas)

A plasma is a partially ionized gas composed of ions, electrons, and a host of neutral species in both ground and in excited states. In addition, a plasma has approximately equal concentrations of positive and negative charge carriers. Usually, it is formed by applying a large electric field to a volume of gas. Numerous plasma types exist [41]; they differ primarily in electron concentration (n_e) and in average electron energy (kT_e).

A quantity that is useful in characterizing the average electron energy in a plasma is the ratio of the electric field to the pressure, E/p [41]. As the electric field increases, free electrons, whose velocities increase as a result of acceleration by the field, gain energy. However, they lose this energy by collision processes, so that an increase in pressure, which decrease the mean free path of the electrons, decrease the electron energy.

In thin film processes for micro electronic applications, radio-frequency (rf) glow discharges are used almost exclusively. Typical properties of these plasma are indicated in Table 2.1.

Table 2.1 Properties of glow discharge used for plasma process

Properties	Magnitude
F	50 kHz - 40 MHz
P	0.02 - 10 Torr
n_e	10^8 - 10^{12} cm^{-3}
N_N	10^{15} cm^{-3}
Kte	1-10 eV
kT_i	0.04 eV

Since the plasma is essentially electrically neutral, the positive ion density is approximately equal to the electron density. However, the neutral species concentration (n_N) is many orders of magnitude higher than the charged particle density. Thus, these plasmas are only weakly ionized. As a result of this concentration difference, the neutral species (atoms, molecules, radicals, etc.) are primarily responsible for etching or deposition. In addition, electron energies are high in such systems (1-10 eV, corresponding to temperature of 10^4 - 10^5 °K). Because the ion energy is much lower than the electron energy, glow discharges are called non-equilibrium plasmas.

The above characteristics impart glow discharge plasma with unique and useful properties. Energetic electrons are capable of breaking chemical bonds via collisions with gas molecules. In this way, highly reactive chemical species are produced for etching (or deposition) reactions. Since the gas temperature remains near ambient, temperature sensitive materials can be processed in this environment. Also, the surface chemistry occurring in glow discharges is generally modified by the impingement of ions and electrons onto the film being etched. The combination of these physical processes with the strictly chemical reactions (due to atoms or molecules) results in etch / deposit rates

and etch profiles unattainable with either process individually. Thus the role of the plasma in deposit / etching processes is two fold [42]: create chemically reactive species, and provide energetic radiation (principally ions and electrons, but also photons) for alteration of surface chemistry.

Essentially all plasma etching and deposition processes in thin film technology utilize rf rather than dc glow discharges. The reasons for this are severalfold [35]. Electrons gain sufficient energy during oscillation in the alternating field to ionize molecules during impact collisions. Therefore, unlike dc plasmas, the discharge can be sustained even with low secondary electron yield. Electron oscillations also enhance ionization efficiency so that low pressures can be invoked. Finally, since surfaces in contact with plasma are bombarded with electrons and positive ions on alternate half cycles of the rf, insulators can be used as electrode materials.

2.8 The Planar Reactor

The planar reactor, now widely used for depositing / etching, is one type of plasma reactors for which this study used. The system using parallel plate electrodes was an important development because it provided the capability under some conditions for anisotropic etching. A typical reactor consists of a top electrode connected via an insulated feed through to a rf supply and a bottom electrode which is normally grounded, as shown in Figure 2.2 The wafers rest on the ground electrode and are immersed in the plasma. The top electrode is normally capacitively coupled via a blocking capacitor to the rf supply. In this system each electrode is negatively biased to the plasma and generally the negative bias is higher on the top electrode, as shown in the experimental studies.

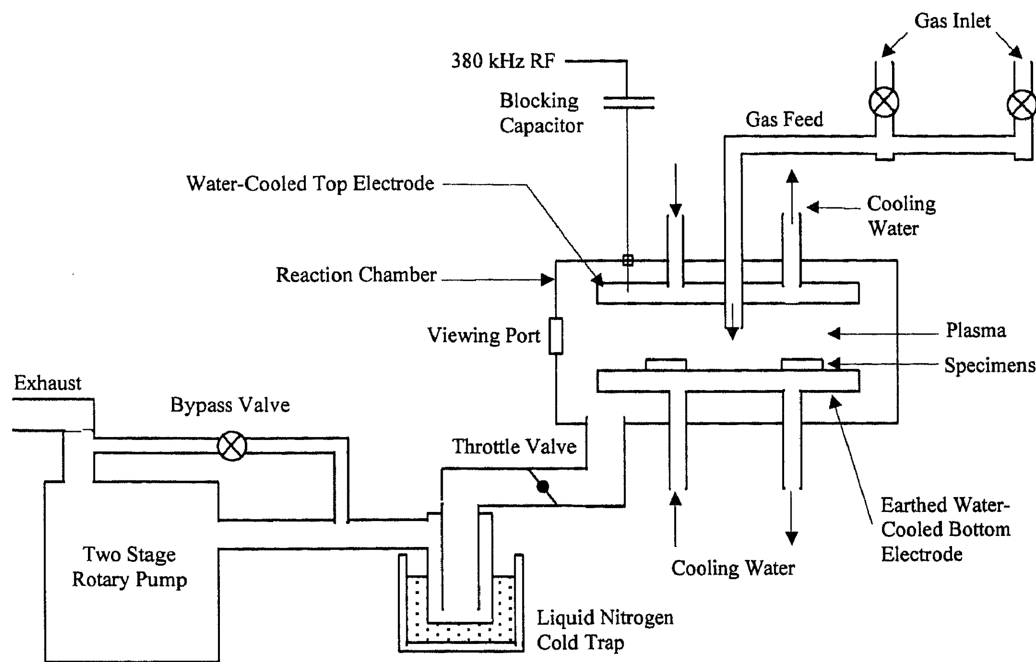

Figure 2.2 A typical planar reactor system

It is noted here that a planar reactor will etch wafers located on either electrode surface and in some cases will etch wafers faster on the top rf electrode due to the larger negative bias developed on the top electrode.

In the planar system considered here, the work surface is the grounded electrode which forms an adjacent ion sheath because of the negative bias developed with respect to the plasma potential. Thus the wafers placed on the ground electrode are bombarded by atomic and molecular ions which have been accelerated in the ion sheath as well as low energy electrons. The wafers are also exposed to free radicals and molecular fragments produced in the plasma volume.

Planar reactors have some disadvantages such as high cost, low selectivity, and small wafer throughput. The poor selectivity is because of physical sputtering from the ion bombardment contribution which also produces heating effects that can result in poor

etching uniformity, rapid removal of photoresist, and resist flow if heating is too excessive. However, to improve the uniformity, the planar reactor electrodes have been designed to have water cooling.

A problem arising in the large planar reactors is obtaining uniform etching. Thus, if the etching selectivity in a particular process is poor, then serious etching can occur in the substrate of some wafers before others have had the layer to be etched removed. For this reason, some manufacturers have made a planar machine for production use holding and etching a single wafer at a time. This is true for deposition also. These machines have a fast pump down and fast deposit or etch rates because the chamber is small and the power density can be high. Although the throughput of these machines is obviously smaller than that of the large capacity plants, they give better uniformity. End point detectors are used on plasma etching machines to avoid over-etching. End point systems work particularly well on single wafer machines since there is a smaller volume for observation.

With all plasma process machines, it is necessary to precondition the reaction chamber by running the process before the wafers are processed, thus improving uniformity and reproducibility. The preconditioning of the chamber (before wafers are placed in the chamber) warms the chamber and reduces the wafer contamination. Water vapor is considered one of the contaminants. Prevention of water vapor or atmospheric contamination in the plasma reaction chamber can improve the uniformity and reproducibility of the process.[38]

CHAPTER 3

EXPERIMENTAL SET-UP AND PROCEDURE

3.1 Set-up of the PECVD Apparatus

The synthesis of diamondlike carbon films was carried out in the Applied Materials AMP 3300IIA PECVD system with an external flow control equipment. The scheme of the reactor is given in Figure 3.1. The reaction chamber is an aluminum cylinder with aluminum plates on both the top and the bottom, as upper electrode and susceptor, respectively. The diameter of the electrode and the susceptor are about 26 inches and the distance between the upper electrode and the susceptor is 2 inches. There are heater elements beneath the susceptor to heat it up. The reactant gas was introduced into the reaction chamber before the rf power was supplied. The flow rate of acetylene was controlled and measured by the built-in flow controller and can be obtained from the flow rate read-out and multiplied by the calibration factor of acetylene vs. nitrogen, which was 0.55 which was calibrated before the experiments.

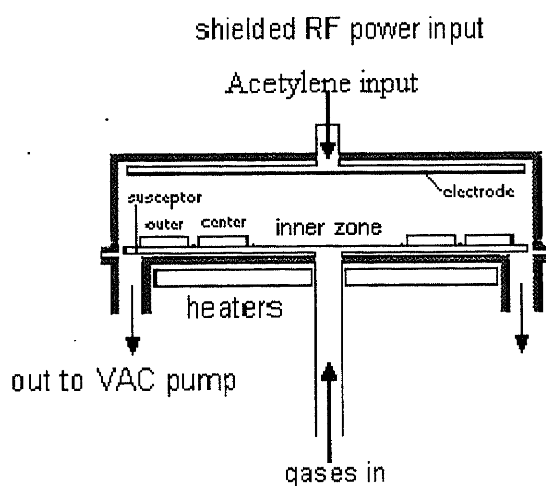

Figure 3.1 Schematic Diagram of PECVD Set-up

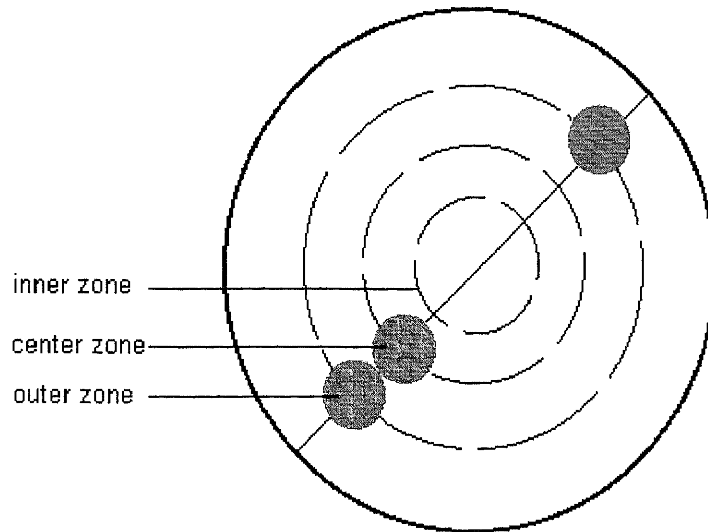

Figure 3.2 Schematic Diagram of the Susceptor

3.2 Pre-experiments

3.2.1 Susceptor Temperature Calibration

The temperature of the substrate is an essential parameter for deposition. But in the plasma reactor, there is no means to determine the absolute temperature under the deposition conditions. Therefore, susceptor temperature was used as a process variable. The susceptor which holds the substrate wafer is divided into three zones (Figure 3.1, Figure 3.2): inner zone, which has one heater element, center zone, which has three, and outer zone, which has two. Since the susceptor is heated through conduction of a metallic plate from the heater, there must be difference between the real susceptor temperature and the set point. So a temperature calibration was necessary before the experiments.

A J-type thermal couple was put in different position beneath the susceptor to monitor the temperature of each zone (see Figure 3.1, Figure 3.2). Measurement was

done under the half-open-chamber condition. About one hour and a half was taken for the susceptor temperature to increase from one point to another and to become constant.

The temperatures of the outer zone and the inner zone were several degrees lower than those of the center zone, and the higher the temperature, the larger the difference. This can be attributed to the cooling effect of the surrounding air. (There is a gas inlet in the center of the susceptor). Thus it can be assumed that the temperature will be uniform when the chamber is completely closed. It is more reasonable to take the temperature of the center zone as the susceptor (substrate) temperature.

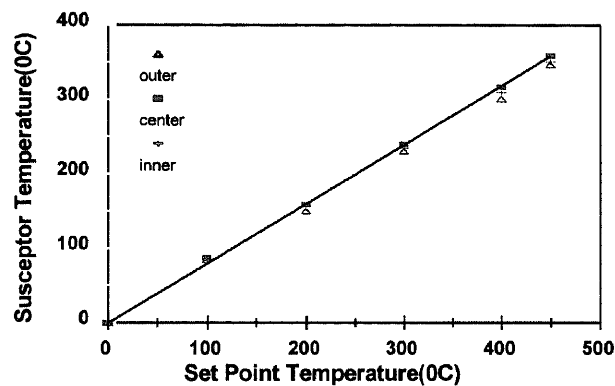

Figure 3.3 Temperature Calibration Curve

Figure 3.3 shows a linear relationship between the susceptor temperature and the set point. The function is:

$$Y = 0.7977\,X \tag{3.1}$$

where Y is susceptor temperature (^{0}C);

X is set point temperature (^{0}C).

Then for the required substrate temperature of T (^{0}C), the heater should be set at 1.25T (^{0}C).

3.2.2 Flow Rate Calibration

An AFC automatic N_2 mass flow controller MFC (Applied Materials) was used to control and measure the Acetylene flow rate.

The N_2 calibration of the MFC was checked by delivering a fix volume of gas (product of the metered flow rate and the time) into the known reaction chamber volume. The pressure increase was measured and used to calculate the volume of the gas corrected to the standard condition (0^{0}C, 1atm). This process was repeated with Acetylene to find out the correction factor. According to the gas law, the flow rate corrected to STP (sccm) is given by the formula below:

$$F.R. = 60(\Delta P/\Delta t)(T_0 V/P_0 T) \tag{3.2}$$

where ΔP = pressure increase, Torr

T_0 = 273 K

P_0 = 760 Torr

V = volume of the chamber; cm^3

Δt = time of delivering gas, sec.

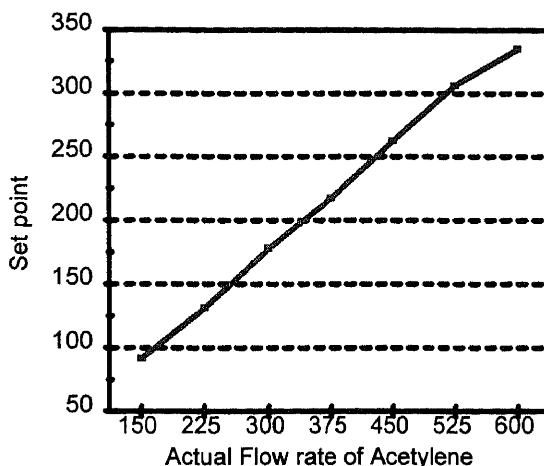

Figure 3.4 Flow Rate Calibration for Acetylene

Figure 3.4 gives the calibration curve of acetylene flow rate, which was employed to obtain the actual flow rate of acetylene from the set point.

3.2.3 Leak Check

Routine leak checks were conducted everyday. After evacuating the chamber with valves and flow controller fully open, close the valves and calculate the leak rate from the chamber pressure rise. Typically the leakage is less than 6 mtorr/min.

3.3 Experimental Procedures for Deposition

3.3.1 Wafer Loading

P-type single crystal silicon wafers, of orientation <100>, polished on one side, 10 cm in diameter, 525 um thick, marked and weighed with an accuracy of 0.1mg, were placed horizontally on the susceptor. At the beginning, three wafers were mounted separately in the outer and center zones (see Figure 3.2). Those two placed in the symmetric position

of the center zone are comparable, and the two along the radius are used to monitor the radical depletion effect. After the great depletion effect was observed, only two wafers were loaded in each run without the one posited in the outer zone. Along with this, glass pieces were also placed on the susceptor.

We also prepared samples for carrying out thickness measurement, by using scotch-tape to hide some portion of the wafer, with the intention of getting a step profile, abd then employing Dektak method. Besides this, a sample for step coverage determination was also kept in the initial runs.

3.3.2 Wafer Cleaning and Etching

Prior to loading the wafers, they were properly cleaned with methanol and subsequently with acetone to remove surface contamination. Then the samples were blown dry with dry air. This process was carried 2-3 times.

The wafers were then etched in a mixture of CF_4 and O_2 in the ratio of 4:1 (in terms of the set points, the conversion for CF_4 is 0.42 and that for O_2 is 0.985).

3.3.3 Setting Deposition Conditions

After the substrates' loading, the reaction chamber and the reactant delivery lines were evacuated. The temperature controller was set to the desired point, and the susceptor was heated for an hour under the vacuum to ensure an uniform temperature. At the same time, the cooling water was turned on. The flow rate of Acetylene was set at its flow rate controller, and the total pressure, deposition time, plasma power and frequency were set at the engineering panel.

3.3.4 Film Deposition

When a constant temperature was reached, the deposition was started by pressing the START button in MANUAL state, ETCH-DEPOSITION MODE. The chamber was pumped down to the base pressure. The sequential steps included: high purging, prepurging and processing gas (with the indicator lights on). The Acetylene flow controller was opened manually since it was not controlled by the machine. The gases were processed into the reaction chamber at the set flow rate automatically controlled by the system. The total pressure was also adjusted to the set value at the PROCESS GASES stage, by manipulating the speed of the blower. After that, the flow rate of reactant gases and the system pressure were maintained at the desired level, the rf power was applied and the deposition started.

3.3.5 Post-deposition Procedure

When the deposition was advanced to the set time, the rf power would shut off automatically. The chamber was pumped down and cooled down under the vacuum to below 100^0C with the cooling water on to avoid any undesired reactions. The chamber was back-filled with nitrogen, the wafers were then taken out and weighed. As soon as the wafers were removed, the chamber was evacuated and kept under vacuum. The deposit properties were then determined by the characterization techniques.

3.3.6 Reactor Etching

During the deposition reactions, films also have been deposited on the upper electrode and the susceptor. The reactor must be cleaned in order to remove the deposits in the

reactor chamber, which may peel and affect the deposition process. As suggested by the Applied Materials AMP-3300IIA PECVD system user's manual, the chamber was etched after every 5 microns(50,000Å) deposit, and the etching are performed under the following conditions for 45 minutes: chamber pressure = 0.3 Torr, oxygen flow rate = 200 sccm, Freon flow rate = 300 sccm, plasma power = 800 W (power density = 0.24 W/cm^2), with the heater off (typically about 100 ^0C).

CHAPTER 4

CHARACTERIZATION OF DLC THIN FILMS

4.1 Thickness

Film thickness was measured by Nanospec Interferometer which bases its estimation on the monochromatic light interface fringes formed within a zone limited by the sample surface and a semi-transparent mirror. The device consists of Nanometrics NanoSpec/AFT microarea gauge and SDP-2000T film thickness computer. The thickness of the film deposited on the wafer was measured at five different points, as shown in Figure 4.1. The average value was taken as the film thickness. Uniformity in radial distribution of the deposits was estimated from the relationship:

$(T_{max} - T_{min})/(T_{max} + T_{min}) \times 100$.

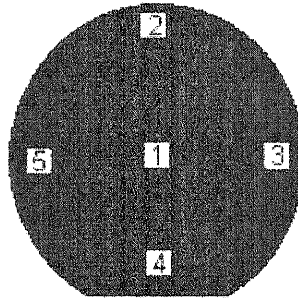

Figure 4.1 Wafer Image Showing the Points of Thickness Measurement

Deposition rate was determined as the film thickness over the deposition time, i.e., $D.R. = \Delta T/\Delta t$. The instrument used to measure the thickness of the films has an error which varies from ± 0.05% to 0.1%.

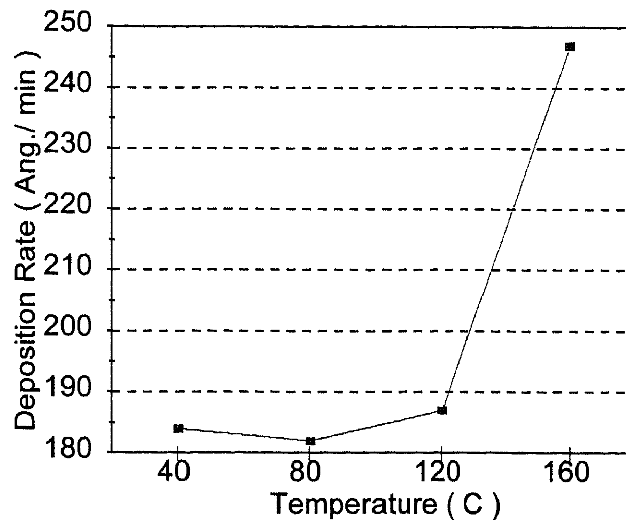

Figure 4.2 Deposition rate versus temperature

4.2 Refractive Index

The refractive index of the deposits was determined by a Rudolph Research AutoEL ellipsometer, which consists of a polarizer and a compensator. Plane (45^0) polarized light from the polarizer is elliptically polarized when it passes through the compensator. It is then reflected by the sample surface, collected by a detector, analyzed for its intensity and finally quantified by a set of delta psi values. But the refractive index data may not be accurate because the ellipsometer used also takes into account the thickness of the films. The error of the instrument varies from ±0.05% to 0.08% within a thickness of 3000A.

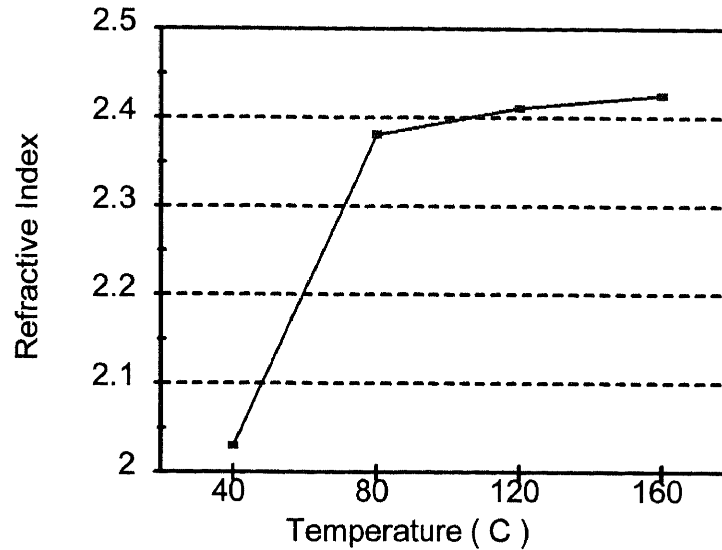

Figure 4.3 Refractive index versus temperature

4.3 Stress

The stress of the film was determined by an in-house-developed device, employing a laser beam equipment which measures change in the radius of curvature of the wafer resulting from the film deposited on one side. Two fixed and parallel He-Ne laser beams were incident on the wafer surface before and after deposition. The reflected beams from the two surfaces were then projected by an angled plane mirror as two points onto a scale in a certain distance thus their separation could be measured more accurately. The change in the separation of these two points was then fed into Stony's Equation to obtain actual stress value. The calculation formula is:

$$\delta = 12.3D/T \tag{4.1}$$

Where D = distance difference between the two image points before and after the deposition (mm);

T = thickness of the film (μm);

δ = stress of the film (MPa), negative value indicates compressive stress.

It should be noted however that the error associated with the instrument varies from ±0.05% to 0.09%.

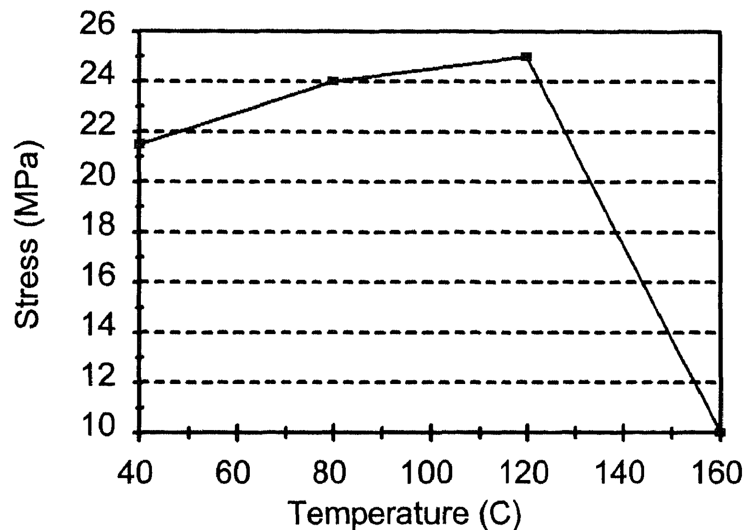

Figure 4.4 Stress versus temperature

4.4 Etch Rate

An HF etch process was selected to measure the etch rate of the PECVD DLC film. The etch solution consists of 1 part HF (49%) and 9 parts distilled water to make 250 ml of the mixture. A piece of the wafer was immersed in etch solution at room temperature (about 25 ^{0}C) for 30 seconds, then the thickness of the remained film was measured. However, it was observed that there was no appreciable change in the appearance of the film and there was no reduction in the weight of the wafer.

4.5 Raman Spectroscopy

Raman Spectroscopy, a probe of the optically active vibrational modes of a material, is one of the most convenient and powerful tools for characterization of DLC. It is apparent from the graph that the major features of the DLC Raman spectrum are derived from those of graphite. The two peaks are situated at 1580 cm^{-1} and 1150 cm^{-1}, which are very similar to the main peaks of the microcrystalline graphite. Therefore, following the nomenclature of graphite Raman spectra, we designate these peaks as the G-band (near 1580 cm^{-1}) and D-band (near 1150 cm^{-1}) respectively [43].

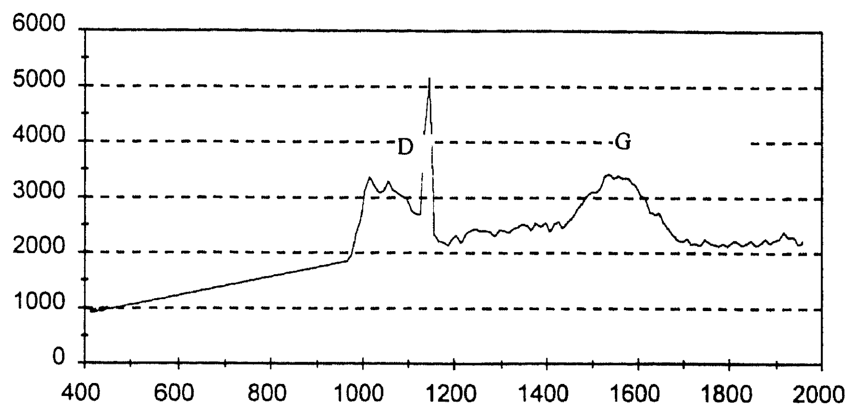

Figure 4.5 Raman Spectrum of a DLC film deposited at 200C, 200W, 250 mtorr,25sccm and 30 min

Thus the deposition rate, refractive index and stress were determined for the films as a function of temperatures.

The following table gives the summary of the results obtained.

Table 4.1 The various characterization results for the DLC films for deposition of 30 min

Deposition Temperature (°C)	**Deposition Rate (Å/min)**	**Stress (Mpa)**	**Refractive Index**
200	247	10	2.030
150	187	25	2.381
100	182	24	2.411
50	184	21.5	2.425

CHAPTER 5

OBSERVATIONS, RESULTS AND DISCUSSIONS

A lot of experimental runs were carried out by varying each of the variables namely power, temperature, pressure, time and flow rate. However, it is difficult to prove any co-relation between the quality of films and these variables at this stage, a complex relationship seems to exist between them. An initial run was carried out using the conditions given below

Table 5.1 Initial run conditions

Power Watts	Temperature C (set pt.)	Pressure mTorr	Flow-rate sccm	Time min	Comments / Observations
200	200	400	100	30	A lot of black powder was formed on the plates of the reactor.

The black powder is supposedly carbon particles formed due to gas phase nucleation. After this initial run, all the plasma variables were fine tuned with a view to achieve optimum deposition conditions.

It was suggested that gas phase nucleation could be mimimised by reducing the flow rate, which evidently was too high. Control of the reactor pressure at such a high flow rate was also difficult. Besides, the reduction in pressure could also minimise the gas phase nucleation. Runs were then carried out by varying the flow rate of the precursor and pressure of the reactor.

Table 5.2 Runs carried out by varying the Flow rate and temperature

Power Watts	Temperature C(set pt.)	Pressure mTorr	Flow-rate sccm	Time min	Comments / Observations
200	200	400	50	20	A lot of black powder was formed on the plates of the reactor.
200	250	250	25	30	This condition was very close to ideal, the film was of good quality and it sustained the HF etch.

It was observed that the gas phase nucleation was reduced with lowering flow rates of the precursor. The optimum flow rate was found to be somewhere in the range of 10 to 25 sccm. The film deposition rate was seen to increase with the flow rate.

DLC could open to a whole world of new applications, if room temperature deposition could be made possible. With this view in mind, a run was carried out at room temperature.

Power, which is expected to play a lead role in the film properties was varied and some studies were conducted.

Most of the films which we obtained had some typical color, ranging from purple to green. It was proposed that higher power would give the characteristic black color to the DLC films, as the acetylene would break completely to carbon and hydrogen atoms,

and carbon being of higher density than hydrogen, would only be selectively deposited, thus giving black color to the film. It was proposed, that hydrogen is responsible for the colors in the DLC films, and in order to minimise the hydrogen content, higher powers were necessary. The runs were carried out for 90 minutes with a view to obtaining thick films for carrying out Hardness measurements.

Table 5.3 Runs carried out by varying the Power and time at different temperatures

Power Watts	Temperature C(set pt.)	Pressure mTorr	Flow-rate sccm	Time min	Comments / Observations
200	25	200	10	30	The films peeled out as soon as they were removed out from the reactor.
700	25	200	10	30	The films were covered with particles, giving somewhat irregular surface, possibly due to gas phase nucleation.
700	300	200	10	90	The reactor tripped at overload.
400	300	200	10	90	The reactor tripped overload.

The reactor tripped at overload at typically higher temperatures and powers. We then carried out the same runs at elevated pressures in order to counter act this. Besides, the films peeled off due to insufficient adhesion at the surface. Peeling may arise due to a

very large compressive stress. It was suggested that etching the substrate surface prior to carrying out deposition could solve the problem, as loose bonds would be created which would enhance the adhesion of the deposited film on the substrate. The adhesion was seen to be good at elevated temperatures.

Table 5.4 Runs carried out after carrying out etching of the substrate

Power Watts	Temperature C(set pt.)	Pressure mTorr	Flow-rate sccm	Time min	Comments / Observations
400	300	500	10	90	The films peeled out eventually, some sort of structure was also observed.
800	300	500	10	90	The films peeled out.
300	100	200	10	90	The films showed signs of peeling out.
300	200	200	10	90	The films peeled out.

A number of runs were then carried out to obtain an optimum condition, by varying all the variables available, that we thought were the cause of the problems. Typical problems faced were the peeling out of films, formation of the powdery stuff on the reactor and films, formation of some kind of structure on the film surface. This problem was proposed due to gas phase nucleation, which causes particles to form, thus covering the substrate surface randomly and thus prevents further deposition of the film at the surface. However, such films showed very good hardness and adhesion to the

surface. Hardness tests were carried out by scraping the films with tweezers and by Scotch-tape test. Some of the unsuccessful run conditions are cited below.

Table 5.5 Some of the unsuccessful runs

Power Watts	Temperature C(set pt.)	Pressure mTorr	Flow-rate sccm	Time min	Comments / Observations
300	375	200	10	90	Reactor tripped at overload.
200	200	200	10	90	The films peeled out.
300	300	200	10	90	The wafers were not coated with DLC, even at the reactor there was selective deposition only.
200	200	250	20	30	The films peeled out immediately.

The subsequent runs were carried out with the substrate being etched prior to deposition, in a mixture of CF4 and O2 for a period of 3 minutes. This series of runs were carried out as a function of the temperature. The etch conditions are given in the table below.

Table 5.6 Conditions for the prior etch of the substrate

Power Watts	Temperature C(set pt.)	Pressure Mtorr	Flow-rate CF4 sccm	Flow-rate O2 Sccm	Time min
600	same as the corresponding deposition temperature	300	571	63	3

Table 5.7 Runs carried out by varying the temperature

Power Watts	Temperature C(set pt.)	Pressure mTorr	Flow-rate sccm	Time min	Comments / Observations
200	200	200	25	30	A few pinholes were observed.
200	150	200	25	30	Good hard films, signs of some kind of structure on the films.
200	100	200	25	30	Good hard films, signs of some kind of structure on the films.
200	50	200	25	30	Good hard films, signs of some kind of structure on the films.

CHAPTER 6

CONCLUSIONS

An attempt was made to carry out the synthesis and characterization of diamondlike carbon (DLC) films deposited on silicon wafers and glass by plasma enhanced chemical vapor deposition (PECVD), using acetylene (C_2H_4) as a precursor. The process parameters, such as temperature, pressure, power and reactant gas flow rate were systematically varied and their effects on the film growth rate and properties were investigated. The optimized deposition condition appeared to be at 150°C, 200mTorr, 200 Watts and flow rate = 25 sccm. For these conditions, the films were hard and found to have good adhesion to the substrate, and resistance to HF etching (49% HF diluted to 10%). It was found that the adhesion of the DLC film to the substrate is good if the substrate is first etched with oxygen and CF_4 prior to the deposition of the films. It is proposed that the etching creates loose bonds on the surface of the substrate and thus better bonding of the DLC films is possible. Further studies can be carried out by introducing some diluent along with the precursor in order to reduce the gas phase nucleation that was a major problem in the study.

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