Synthesis diamond films from low pressure chemical vapor deposition

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SYNTHESIZING DIAMOND FILMS FROM LOW PRESSURE CHEMICAL VAPOR DEPOSITION

MATHIEU JON FREEMAN

AUGUST, 1990

THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

David Harding
Project Advisor

Gerald A. Takacs
Department Head

Library

Rochester Institute of Technology
Rochester, New York 14623
Department of Chemistry
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ABSTRACT

Experiments were performed on the deposition of both diamond crystals and films from hydrogen and methane gas mixtures on silicon and polymer substrates by various plasma enhanced chemical vapor deposition techniques (PECVD). Microwave, arc, and dc plasmas to assist the deposition of the diamond metastable phase of carbon were used. Discussed in the following thesis are the plasma configurations used together with experimental parameters such as gas composition, flow rate, chamber pressure, and power. The crystallinity of the films, which can be controlled and changed from polycrystalline to amorphous, was ascertained by scanning electron microscopy (SEM). Other characterization techniques employed were profilometry to indicate uniformity, depth profiles and growth rates, and Raman spectroscopy which depicted chemical structure.
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The unique properties of diamond permit applications that range from wear-resistant coatings for bearings and cutting tools, to freestanding windows and lens coatings for visible and infrared (IR) transmission, to thin films for high-temperature, high-power semiconductor devices. Applications requiring advanced materials can uniquely utilize diamond because it: (1) is the hardest known material; (2) has the highest room-temperature thermal conductivity of any material (10 W/cm·K); (3) is resistant to heat, acids, and radiation; (4) is a good electrical insulator which can be doped to produce either p-type or n-type semiconductors (B,Na and P,N, respectively); (5) has a low dielectric constant; (6) has a high electron and hole mobility (2000 and 18000 cm²/V·s @ 300 K); and (7) is transparent over a wide range of the UV, visible, and IR spectra (220 to 2500 nm and from 6000 nm and over) [1].

The high-pressure high-temperature (HPHT) synthetic diamonds developed by General Electric in the 1950s are now commonplace in cutting, grinding, and polishing [2,3]. Many potential applications of diamond require thin films or coatings which cannot be produced from either natural or HPHT synthetic diamonds.

The diamond coating process which has received recent intense investigation utilizes temperature and pressure conditions under which graphite is clearly the thermodynamically stable form of carbon. However, under these same conditions the formation of crystalline diamond is kinetically favored over the formation of graphite in the net chemical reaction:

\[
\text{CH}_4(g) \rightarrow\text{C(diamond)} + 2\text{H}_2(g)
\]

In addition to methane, a wide variety of carbon-containing reactant gases can be used. The typical process in the
vapor deposition growth of crystalline diamond consists of a reactant gas at pressures lower than atmospheric pressure, and containing greater than 95% hydrogen. The gas mixture is activated by a microwave plasma or in the vicinity of a 2000 °C heated filament located above the growth surface on which the diamond is to be deposited.

1.1 History of Vapor-Deposited Diamond

The production of synthetic diamonds from low-pressure gases was first reported in 1911 by von Bolton [4]. He claimed to have achieved growth on diamond seed crystals by illuminating gas (acetylene) decomposition at 100 °C in the presence of mercury vapor. However, little attention was given to these claims. Systematic studies of diamond vapor deposition techniques began primarily in the late 1950s in the Soviet Union and the United States. The major Japanese effort began in the 1970s.

The early Soviet research primarily involved the thermal decomposition of hydrocarbons and hydrogen with no additional activation of the gas. Similar research was also being conducted in the United States during this early time period. In 1958, Eversole [5] filed a patent for the low-pressure vapor synthesis process, but the growth rates of tens of angstroms per hour were very low and non-diamond graphitic carbons were simultaneously deposited. These deposits are termed "diamond-like carbon" (DLC) films and are different from crystalline diamond coatings grown from low-pressure gases. The term DLC is often used to indicate a variety of noncrystalline carbon materials, ranging from a few to about 50 at. % hydrogen. A thorough review of noncrystalline carbon coatings has been given by Angus, Koidl, and Domitz [6]. These early synthetic processes required many cycles of growth followed by hydrogen etching.
to remove excessive graphitic deposits. Angus and co-workers [7,8] continued to pursue these techniques during the 1960s and early 1970s and obtained results similar to those of Eversole.

As in the early 1900s and given the poor quality of results and less sensitive analysis procedures as compared to those used today, most of the scientific community viewed the results of the 1950s through the mid-1970s with great skepticism. However, these results began laying the groundwork for our scientific understanding of vapor processes leading to diamond growth. Deryagin's group reported the use of gas activation techniques which resulted in dramatic increases in diamond growth rates while eliminating much of the graphite codeposition [9,10,11].

Starting in the early 1980s, Japanese researchers began reporting dramatic successes in low-pressure diamond growth using a variety of new gas activation techniques. The successful use of a microwave-plasma-assisted method (MPACVD) to activate the gas for growing crystalline diamond was reported by Kamo and co-workers [12].

A thorough review of previous investigations on the "Synthesis of Diamond Under Metastable Conditions," including the history of vapor-deposited diamond, was recently written by DeVries [13]. This review and a paper by Badzian et al. [14] also include patent literature on this topic. A major increase in diamond research around the world on both the science and the technology of vapor-deposited diamond is quite apparent today from the number of scientific publications and conferences. This activity is a result of a combination of industrial demands for new super materials, decades of unheralded research on low-pressure diamond growth long held as an elixir, and the breakthroughs of the 1970s which dramatically increased
diamond growth rates while decreasing the codeposition of graphite.

1.2 Thin Film Deposition

A general definition of thin film deposition processes would be the placing of a solid layer onto a substrate, usually from the gas phase under a partial vacuum. This determines the amount of impurities deposited from the atmosphere. Processes used in thin film depositions can be separated into two classes; physical and chemical vapor deposition.

Physical vapor deposition (PVD) involves physically sputtering solid material from a target source with positive ions that are generated at a cathode connected to a voltage supply (ac or dc). The atoms removed from the target vaporize in the glow discharge region, which is between the biased target and the substrate holder, before condensing into thin films onto a substrate that faces the target. Another variation of PVD includes ion-plating where the negative potential is applied to the substrate holder [15].

Chemical vapor deposition (CVD) is a materials synthesis method in which the constituents of the vapor phase react to form a solid film on a substrate. The chemical reaction is critical. Fundamental aspects of CVD include reaction chemistry, thermodynamics, kinetics, transport phenomena, temperature, pressure, mass flow rates, and film growth [15].

A variation of CVD is plasma assisted chemical vapor deposition (PACVD) where a plasma is needed to dissociate unreactive precursor gases into reactive ions or radicals. Factors influencing plasma deposition are the reactor design, the electrical energy, and the substrate. The
reactor design governs the uniformity modes of the microwave field or the rf field, the existence of laminar or turbulent flow of gases, and hence the reaction time of reactive species, and the ease of operation of the system. The electrical energy applied controls the temperature of the substrate, the energy, and surface mobility of adsorbed atoms (ability of atoms with sufficient energy to move around the substrate after impinging on the substrate [1]), and the diffusion of gases into and out of the plasma region. The substrate material (insulating or conducting) is important when determining the position of the substrate with respect to the plasma which ultimately affects substrate temperature.

1.3 Chemistry of the CVD Diamond Growth Process

A generally accepted understanding of chemical mechanisms which lead to low-pressure growth of either diamond-like carbon or crystalline diamond is still lacking, but kinetic data on the processes have been reported. Deryagin, Fedoseev, Spitsyn, and their co-workers [16,17,18] reported an extensive experimental base of chemical and kinetic information and proposed global kinetic theories for diamond growth based on nucleation theory, Langmuir adsorption-desorption kinetics and equilibrium. Chauhan, Angus, and Gardner [19] reported detailed kinetic data on diamond deposition from thermally activated methane and methane-hydrogen mixtures.

The following facts appear to be prominent in the low-pressure CVD growth of diamond films:

(i) Activation of the gas; PACVD is required for achieving appreciable CVD diamond growth rates.

(ii) Independence of the method of activation. UV-, rf-, laser-, microwave-, electron assisted, and hot
filament-activated gas mixtures have produced good quality diamond films.

(iii) Independence of starting material. Crystalline diamond has been grown using aliphatic and aromatic hydrocarbons as well as alcohols and ketones as the precursor.

(iv) Hydrogen is required for efficient growth. Fedoseev et al. proposed that it is atomic hydrogen that has to be present in the gas phase in superequilibrium concentration [11]. Activated hydrogen etches graphite at a much higher rate than it does diamond.

(v) Small amounts of O$_2$ added to the precursor gas accelerate the growth rate of diamond films through the formation of OH radicals that assist in H radical desorption off the surface. However, these OH radicals also have been observed to inhibit the initial formation of nucleation sites on the substrate.

(vi) Spectroscopic studies of activated gas environments indicate the predominance of acetylene (C$_2$H$_2$) and methyl radical (CH$_3$·) growth species.

(vii) Formation of graphite usually accompanies the growth of diamond although the conditions employed enable the conversion of most sp$^2$ hybridization to sp$^3$ hybridization.

(viii) The temperature dependence of the rate of diamond growth exhibits a maximum; that is, it initially increases with temperature and then decreases. This behaviour is a manifestation of the competition between the growth of diamond and graphite.

.ix) Various substrate surface treatments such as scratching, seeding, and etching affect primarily the induction time (nucleation rate), but not the rate of subsequent growth.
(x) \{111\} and \{100\} surfaces dominate and depend upon initial CH$_4$ relative composition of the gas. Cubo-octahedral crystals composed of both of these surfaces are common. Twinning (lattice stacking faults) frequently occurs on \{111\} surfaces. Proposed mechanisms must be consistent with these experimental observations.

A major breakthrough in developing both the science and the technology of low-pressure diamond growth occurred when Deryagin et al. experimentally determined the importance of atomic hydrogen for enhancing the rates of diamond growth and reducing or eliminating codeposition of graphite. They found that the addition of excess hydrogen to the hydrocarbon precursor gas led to less graphite codeposition, but they also discovered that "activating" the gas prior to deposition increased the diamond growth rates from A/h to µm/h. Two mechanisms were used to activate the gas: an electric discharge in the system and a hot 2000 °C tungsten filament over which the gas flows before encountering the lower-temperature deposition region. They argued that atomic hydrogen behaves like a "solvent" for graphite and their studies of the relative etching rates of diamond and graphite showed that the removal of graphite by activated hydrogen was orders of magnitude faster than that for diamond. Setaka [20] has recently reported etching rates of graphite, glassy carbon, and diamond in a hydrogen plasma under typical activated growth conditions for diamond to be 0.13, 0.11, and 0.006 mg/(cm$^2$.h), respectively.

Another experimental observation of Deryagin et al. [9] was that the nature of the precursor hydrocarbon gas had little effect on the deposition behaviour. Sato et al. [21] have grown diamond from gaseous mixtures of various hydrocarbons and hydrogen by PACVD, and found similar results. Both saturated and unsaturated hydrocarbons were
used and similar growth features were noted for all the hydrocarbons when comparisons were made as a function of the C/H ratio in the input gas. The density of nucleation and the growth rates were found to be essentially the same as those observed with the more commonly used methane in previous studies.

This relative independence of diamond growth on the nature of the input hydrocarbon species is consistent with the fact that most hydrocarbon sources tend to chemically transform to common product species (such as acetylene, one of the most stable of such gaseous products) under harsh environments such as those found in high-temperature pyrolysis, combustion, and plasmas [22,23,24]. Supporting this is the observation that approximately the same growth conditions (temperature, pressure, concentrations of precursors) are needed for crystalline diamond growth, regardless of the method of activation. The method of activation influences the rate of diamond growth, but not the general structure of the deposited crystallites. This also supports the conclusion that the same critical growth species are produced by all activation methods that produce crystalline diamond.

Recent in situ measurements of species concentrations in activated methane-hydrogen gas mixtures above diamond growth surfaces have been made [25,26]. Although many species have been detected, indications are that the primary species are methyl radicals and acetylene. Such diagnostic measurements are needed as a function of growth conditions and activation method. The results then need to be correlated with growth rates, crystallite morphology, and the relative amounts of codeposited diamond and non-diamond carbon.

Emission spectroscopy has been performed, but species such as CH₃ radicals and C₂H₂ can not be detected [27].
Matsumoto [28] examined a hydrogen plasma with no hydrocarbon in the gas and no substrate. As expected, only the molecular and atomic hydrogen emissions were observed. Upon placing a graphite substrate in the hydrogen plasma, CH, C₂, and H emissions were all observed. Mass spectroscopy measurements of the plasma showed C₂H₂ to be the main product of the chemical etching of the carbon.

IR diode laser absorption spectroscopy was employed by Celii et al. [29], as an in situ method to examine gas-phase species present during filament-assisted deposition of diamond films. From a reactant gas mixture of 0.5 mol% methane in hydrogen, C₂H₂, CH₃ radical, and ethylene (C₂H₄) were detected above the growing surface, while ethane (C₂H₆), and various C₃Hₓ hydrocarbons were below their sensitivity levels. These authors noted that their findings were consistent with the Frenklach-Spear mechanistic growth model [30] for propagating (111) planes through the addition of acetylene to activated surface sites.

Kawato and Kondo [31] examined gas mixtures of CH₄-H₂ and CH₄-H₂-O₂ in growing CVD diamond by the heated-filament activation technique. They examined the exhaust gas by gas chromatography and found the major content of this gas to be CH₄, C₂H₄, C₂H₂, H₂, and carbon monoxide (CO). The addition of oxygen caused the growth rate of diamond to increase over the oxygen-free system, particularly at higher CH₄ percentages. The addition of oxygen also decreased the quantity of non-diamond carbon as determined by Raman spectroscopy. At the same time, the addition of oxygen caused a larger decrease in the C₂H₂ than in the CH₄ concentration in the exhaust gas. The authors reached the following conclusions from these results:
(1) The addition of oxygen reduces the concentration of acetylene, which is probably produced by the pyrolysis of methane or hydrogenation of non-diamond carbon.

(2) The deposition of graphitic or amorphous carbon is suppressed by a reduction of the acetylene concentration or the oxidation of non-diamond carbon, so that the quality of the deposited diamond is improved.

(3) With the addition of oxygen the growth rate of diamond increases and the total pressure for diamond synthesis can be extended.

The morphology of vapor-deposited faceted diamond crystallites is dominated by cubic (100) and octahedral (111) surfaces and (111) twin planes (stacking faults of the (111) planes). Cubo-octahedral crystals exhibiting both (100) and (111) surfaces are common. Very rarely are (110) surfaces observed. Dangling sp³ bonds exist on all three surfaces; one for each surface carbon on the (111) and (110) faces, and two for each carbon on the (100) face. Figure 1 shows a (111) surface with C-H bonds satisfying the dangling bonds of the surface carbons; stabilizing the diamond surface structure.

Diamond has been vapor deposited on a wide variety of substrate materials, though the dominant substrate has been single-crystal silicon. Examples of substrate materials are Si, Ta, Mo, W, SiC, WC, and diamond [32]; graphite, SiO₂, and Ni [33]. The diamond nucleation rates and adhesions vary with the tendency to form intermediate carbide layers such as SiC.

1.4 Phases and Crystal Structures of Carbon

Diamond and graphite are both pure carbon with well-known crystalline forms, but with quite different properties. Other crystalline forms of pure carbon which
Figure 1. The hydrogen atoms bonded to the surface carbons depict their role in stabilizing the diamond surface structure.
are not as common include lonsdaleite (sometimes called hexagonal diamond because its structure and properties are similar to those of diamond) and the carbynes (cross-linked linear carbon polytypes of which at least six forms have been reported) [34].

The ideal structures of diamond and lonsdaleite are formed completely from tetrahedrally bonded sp\(^3\) carbons. Graphite is formed completely from trigonally bonded sp\(^2\) hybridized carbons. The carbynes are formed primarily from linearly bonded sp hybridized carbons, but the cross linking which is critical to their structure requires sp\(^2\) and/or sp\(^3\) carbons.

The atomic arrangements in graphite, lonsdaleite, and diamond are depicted in Figure 2, which clearly indicates the similarities and differences expected in the properties of these materials. The planar graphitic bonding is similar to that in benzene, and it creates strongly bonded two-dimensional planes, but weak bonding between the planes. Alternatively, the four equivalent sp\(^3\) bonds in diamond and lonsdaleite form strong, uniform three-dimensional frameworks. The \{111\} planes of diamond are composed of puckered hexagonal rings of carbon atoms which have the chair form. The \{001\} planes in lonsdaleite are identical to the diamond \{111\} planes. The difference in the two structures is in the stacking of these planes and is similar to the difference between cubic-close-packed and hexagonal-close-packed metal structures.

1.5 Energetics of Gas-Solid Growth Interface

The pressure versus temperature phase diagram for carbon given in Figure 3 clearly shows that graphite is the stable form under the conditions used in vapor-depositing crystalline diamond. Why is it then possible to grow
Figure 2. Schematic drawings of the atomic arrangements in hexagonal graphite, hexagonal lonsdaleite, and cubic diamond. Note the shaded hexagonal rings of carbons in these three structures: planar (graphite), boat-form (lonsdaleite), and chair-form (diamond).
Vapor deposition produces diamond at low pressure

Figure 3. Phase diagram of carbon [1].
diamond at less than atmospheric pressure in the temperature range indicated?

The heart of the hypothesis on "metastable" diamond growth rests on the fact that the diamond growth process occurs at the gas-solid interface in the carbon-hydrogen system. The vapor growth process does not involve just elemental carbon, the one component which is represented on the phase diagram, but it also involves hydrogen. A diamond carbon surface saturated with sp$^3$ C-H bonds is more stable than a carbon surface free of hydrogen. Once a surface carbon is covered by another diamond growth layer, then that covered carbon possessing four sp$^3$ C-C bonds is metastable with respect to a graphitic carbon. Thus, an upper temperature limit for the vapor growth of diamond is determined by the kinetics of the diamond-to-graphite solid-state transformation (and how these kinetics are influenced by structural imperfections).

The question then arises as to why earlier thermal CVD studies utilizing hydrogen-methane mixtures for epitaxial growth on diamond surfaces were of very limited success. The pressure-temperature-composition conditions used by these researchers were quite similar to those used in later successful activated vapor growth of crystalline diamond, but growth rates were in the range of several angstroms per hour, and without periodically etching away of the codeposited graphitic carbon, diamond growth would cease [8]. The net saturation of a C=C double bond with hydrogen has a

$$\Delta H^\circ_{\text{reac}} = -126 \text{ kJ}$$

favorable negative enthalpy change. However, an activation energy to produce either a carbon or a hydrogen radical
exists and additional energy supplied by the plasma will be required for the net reaction to proceed at a significant rate. Likely mechanistic radical reactions are

\[ \text{C} = \text{C} \quad + \quad \text{H} \quad \rightarrow \quad \text{H}-\text{C} = \text{C} \]

\[ \text{H}-\text{C} = \text{C} \quad + \quad \text{H-H} \quad \rightarrow \quad \text{H}-\text{C} = \text{C} + \text{H} \quad . \]

where a hydrogen atom attacks the C=C double bond to produce a carbon radical, which then reacts with a hydrogen molecule to complete the saturation and regenerate a hydrogen atom. This is in agreement with the observation that only when gas-activated vapor deposition methods were first employed in the 1970s did the growth rates of crystalline diamond become large enough to be of technological interest.

The thermodynamics of the deposition process may place a lower limit on the deposition temperature for given total pressures and gas concentrations. Without some type of surface activation, such as bombardment, the surface reactions for deposition may not approach their equilibrium limits. The fact that faceted diamond crystals are produced during deposition is an indication that surface mobilities are large enough for surface reactions to reach equilibrium [35]. Two plots of the output of equilibrium calculations are shown in Figure 4 to illustrate how the deposition limits depend on experimental parameters [36,37]. The fraction of carbon deposited from methane-hydrogen mixtures is plotted versus temperature for several total pressures and compositions. The following
Figure 4. Equilibrium plots of the fraction carbon deposited from methane-hydrogen mixtures as a function of temperature: (A) constant total pressure, varying CH₄ content in reactant gas and (B) constant CH₄ content, varying total pressure. [1].
observations can be made:

(i) The fraction of carbon deposited changes from practically zero at lower temperatures to close to 100% over 200 °C.

(ii) High pressures and/or low methane concentrations increase the lower temperature limit required to obtain any deposit.

Thus, thermodynamic considerations set a lower temperature on diamond growth of about 400 ° to 600 °C, depending on specific pressure-composition conditions, unless "nonequilibrium" bombardment techniques are used. These techniques always produce some DLC along with crystalline or microcrystalline diamond [38]. Even small quantities of a defective form of carbon could render the deposited film useless for electronic applications.

1.6 Mechanisms of Growth

Spitsyn et al. argue [10], based on their experimental studies, that the growth of diamond is controlled by kinetic factors. For example, Varnin et al. [39] wrote that, "if the condensate as a whole under the regular conditions of crystallization mostly reveals properties close to those of graphite, then this is a consequence of not the energetic advantage of graphite (which is quite insignificant), but the kinetic preferences in the growth of the graphite structure." Thus, Varnin et al. proposed that the formation of diamond competes kinetically with the formation of graphite. Although the Russian school developed kinetic arguments using macroscopic concepts, such as classical nucleation theory, they did not make specific suggestions regarding the elementary chemical reactions and/or species involved in either gas-phase or surface processes.
Tsuda et al. [40, 41] conducted quantum chemical computations in order to determine the lowest energy path for a proposed mechanism of diamond growth on \{111\} surfaces. They initially assumed [40] that only \textit{CH}_1-3 radicals and ions can be the growth species in \textit{CH}_4-\textit{H}_2 plasmas and reported the following two-step reaction sequence. In the first step, the \{111\} plane of the diamond surface is covered by the methyl groups via either methylene insertion or hydrogen abstraction followed by methyl radical addition. In the second step, following the attack of a methyl cation and the loss of three \textit{H}_2 molecules, three neighboring methyl groups on the \{111\} plane are bound together to form the diamond structure. In the subsequent publications, they extended their analysis and concluded that the epitaxial growth of a diamond film is sustained, provided that the surface maintains a positive charge and that there is a supply of methyl radicals [41]. This mechanism does not explain the critical effect of hydrogen atoms on the growth and relies on maintaining a positively charged surface or a precursor of \textit{CH}_3\textsuperscript{+} cations, whose abundance in a plasma is questionable.

A paper by Frenklach and Spear [30] proposes an alternative mechanism for the growth of \{111\} diamond surfaces. It consists of two alternating steps where the first step is the surface activation by H-atom removal of a surface-bonded hydrogen.

\[
\text{H}^- + \text{C-H} \rightarrow \text{H}_2 + \text{C}^-. 
\]

In the second step, this surface-activated carbon radical
then acts as a site for adding more carbons to the structure by reacting with acetylene (or other carbon-hydrogen species in gas/plasma).

\[
\begin{align*}
\text{C} & + \text{H-C≡C-H} \rightarrow \text{C=C=C}.
\end{align*}
\]

The additional radical reactions for the mechanism of propagating a growth step on the \{111\} plane of diamond are given in the paper by Frenklach and Spear [30]. The propagation results in the addition of two acetylene molecules for one hydrogen abstraction step, with the resulting regeneration of the hydrogen which was consumed in forming the activated surface site.

Although the mechanism is described by Frenklach and Spear [30] for the addition of acetylene molecules, it is possible for other carbon-hydrogen species to enter into the reaction sequences. The mechanism is in general agreement with the macroscopic views of Deryagin, Fedoseev, Spitsyn, and Varnin and is consistent with experimental observations, such as the importance of atomic hydrogen and the independence of the diamond growth on the chemical nature of the input hydrocarbon species.
The initial and generally favored technique employed here is the use of a microwave plasma to enhance the deposition of the diamond metastable phase of carbon. Initially an Evenson cavity was used to couple the microwave energy (up to 200 W) into a 1/2" diameter quartz tube that constituted the plasma chamber. This chamber contained the substrate upon which diamond growth was to occur. Despite following the procedures described in previous scientific literature this experimental configuration was unable to produce an appreciable, easily identifiable diamond growth [42]. The problem was believed to be the inability of the microwave applicator to couple sufficient energy into the plasma chamber to achieve surface temperatures and electron densities sufficiently high for the diamond phase to stabilize. Consequently, the microwave plasma applicator was replaced and a second, additional, experimental configuration was designed that could use either an arc discharge or a dc discharge to form the plasma.

2.1 Plasma Deposition Systems

Two different plasma design configurations were constructed. The bell-jar plasma configuration consisted of six components: 1.) a glass-pipe reactor chamber, 2.) two power sources, 3.) a vacuum pump, 4.) a gas flow readout unit, 5.) two mass flow controllers, and 6.) two pressure gauges. The microwave plasma system was also composed of six components: 1.) a tubular reactor chamber, 2.) cavity equipment and a power generator, 3.) a vacuum pump, 4.) a gas flow readout unit, 5.) two mass flow controllers, and 6.) three pressure gauges. The two plasma
systems could not operate simultaneously because they each utilized the same pump, readout unit, flow controllers, and pressure gauges. Details about each component are described below.

2.1.1 AC Reactor Chamber and Power Source

The advantage of using an arc discharge to establish a plasma is that the plasma can be readily confined within a container without special restrictions being placed upon the dimensions of the container, as is the case with a microwave powered plasma where health concerns are paramount. Consequently, all that is required is a vacuum chamber capable of sustaining pressures in the millitorr range, the appropriate vacuum-tight electrical feedthrough connectors, a power supply, and a cathode/anode configuration where both cathode and anode can be electrically isolated from the chamber. A schematic of the system is presented in Figure 5.

Vacuum chamber:

The vacuum chamber used to investigate the deposition of diamond particles and films was composed of a 6" i.d. Pyrex glass-pipe that extended 12" in height. It had grooves and used Viton o-rings and greased rubber seals to connect a baseplate and a top-plate, and base pressures below 150 mtorr could be maintained. The top-plate was made of stainless steel with a 2" aperture that was connected to a 2-3/4" two-conductor electrical feedthrough conflat flange that was fastened with bolts and a greased Viton o-ring. Occasionally, a discharge between the two electrodes, which were only 1/2" apart, occurred, indicating a need for teflon sleeves that could slide over the electrical feedthroughs and serve as a better dielectric than the ambient pressure conditions.
Figure 5. Schematic of the equipment used on the arc plasma powered plasma enhanced chemical vapor deposition (PECVD) experiment.
Within the baseplate of the glass-pipe were five vacuum feedthroughs that allowed two Tylan FC-260 mass flow controllers to be connected to regulate the flow of gas through the system. Since the gas inlet and pump outlet were both located in close proximity in the baseplate it was necessary to fasten a 1/4" × 4" curved piece of stainless steel tubing directly to the baseplate with epoxy. This assured a direct flow of gas from the inlet to the plasma region. In addition, two MKS Baratron type 221A capacitance manometer pressure transducers were used to monitor the pressure (the ranges on the pressure transducers were: 0 --> 10 torr and 0 --> 1000 torr). Also, present was a feedthrough to a D-30-A Leybold Dual-Stage rotary pump and an 1/8" NPT (National Pipe Thread) plug for an unused opening that is available for later grounding on the anode. A 1/8" × 12" grounded thermocouple wire (Omega Corporation, K-type, -200 to 1250 °C) was incorporated through the ceramic material of the anode to the base of the substrate to enable the temperature of the substrate to be monitored on a readout unit. Finally, a small wooden chamber support table with a hole in the middle to permit access to the vacuum lines in the baseplate of the glass-pipe was constructed. All NPT connections used an anaerobic pipe sealant with TFE (tetrafluoroethylene), Swak T.M., whereas all swagelok connections utilized a cap, ferrule, and nut that was permanently secured onto the tubing when tightened. By contrast, cajon connections use a rubber o-ring and a ferrule that is more interchangeable and easily removed for rapid access and modification while maintaining vacuum integrity afterwards.

Electrode Configuration:

The cathode was a 99.9 % pure 3/16" diameter solid tungsten rod that was positioned at the end of a mount with
access to a screw which could change the electrode height. The other end of the mount was connected by 10-24 UNC threaded rod to a piece of teflon. Another piece of threaded rod was required to connect the bottom of the teflon to the base of the mount. The base of the mount was fastened by an epoxy resin to the baseplate. The cathode was electrically isolated by using a 3/4" diameter solid teflon rod, drilled, and tapped to the threaded rod specifications. A 2-1/2" diameter aluminum disk with a 3/8" hole in the center was supported by a series of three ceramic disks with similar dimensions as the disk below the electrode. A graphite cylinder with a 3/8" inner diameter completed the base of the anode and was fastened with an epoxy resin to the baseplate directly over a vacuum feedthrough. That feedthrough accommodated a thermocouple wire that measured the substrate temperature. A hollow stainless steel rod which had a 3/8" o.d. and a 1/4" i.d., 2" in length was used to accommodate the thermocouple wire and connect the anode base to one of the two conductor feedthroughs by soldering electrical wire to the stainless steel rod. The anode was electrically isolated from the base of the bell-jar by ceramic supports. The thermocouple was electrically isolated by using a 1/4" solid teflon rod and drilling an 1/8" hole to accommodate the thermocouple wire and prevent discharging from the wire to the stainless steel rod.

A Cenco, 115 volt-60 cycle power supply with a 5000 V output at low current and a 60 Hz ripple on the signal, was used to generate the plasma arc. Electrical wire, connectors, nuts, and alligator clips were utilized to complete the circuitry between the power supply and the electrical feedthroughs. By switching the bias on the electrodes within the bell-jar and grounding first the electrode upon which the electrode was based, and then the
cathode, it was possible to compare the effect of having the substrate initially on the powered electrode (where ion bombardment occurred) and secondarily on the grounded electrode. The disadvantage of an arc plasma is that there is no cathode and anode since the powered electrode is constantly alternating, but when one electrode is grounded then the other electrode becomes the powered electrode. This procedure was attempted to determine whether this simulation of a high voltage dc power supply was feasible.

2.1.2 DC Reactor Chamber and Power Source

The same vacuum chamber, top-plate, and baseplate were employed in this configuration, but a number of modifications from the earlier experiments were required here because of the higher temperatures achievable. The two-conductor electrical feedthrough was replaced by a single high voltage conductor feedthrough inserted through a 2-3/4" conflat flange. This could be fastened with bolts and a greased o-ring to the top-plate. Unlike the previous experiments there was no need for a teflon sleeve for the feedthrough, which was connected to the cathode.

Preliminary experiments revealed that the cathode had to be slightly altered as excessive heat was generated. The excessive heat caused the materials supporting the tungsten electrode to expand, and finally melt which resulted in the electrode shorting. An alternative constructed mechanism replaced the supporting set screw that had supported the electrode and excessive heating of the electrode assembly no longer became an issue. Initially, the base of the electrode stand was electrically isolated by a piece of teflon in the arc plasma experiments. Due to excessive heat generated by the dc plasma, the teflon would soften causing the electrode mount
to tilt and the electrode to touch the substrate. A solid 3/4" \* 2-1/2" piece of ceramic rod was drilled and tapped to the specifications of the threaded rod to replace the teflon. This material could withstand the heat as well as electrically isolate the baseplate. The aluminum disk that in the previous set-up constituted the anode was discarded as it is possible to contaminate growing films at the elevated temperatures due to high power densities, and the ceramic slices became the substrate holder. The electrical wire that was soldered to the anode base for ac experiments and connected to one of the two conductor feedthroughs was eliminated for dc experiments. In the baseplate, the 1/8" NPT plug was replaced by a 1/8" NPT \* 1/16" swagelok adapter that permitted a 1/16" diameter solid piece of stainless steel to act as a ground. A base with a mounting screw supported the threaded rod, the isolating ceramic cylinder, and the steel bar that extended the electrode to just above the surface of the substrate and in close proximity to the anode. With an electrical spade connector the ground wire was attached to the base.

A DC-1000 Energy Research Associates power supply generated the direct current plasma arc with a maximum output of 1500 volts and 1.5 amperes. The 600 volt rated electrical wire used in the ac experiments had to be replaced with a heavier gauge (12 gauge) and better insulated wire. The negative line from the power supply was attached in series to a 130 ohm resistor (four 500 ohm resistors in parallel), and to the electrical feedthrough with 30 kV rated wiring, connectors, screws, and nuts. Finally, the positive end was connected with a vacuum tight electrical feedthrough to the anode. A schematic of the configuration is shown in Figure 6.
Figure 6. Schematic of the equipment used on the dc plasma powered PECVD experiment.
2.1.3 Microwave Reactor Chamber, Equipment, and Generator

The first experimental design used a microwave generator to initiate the plasma and an Evenson cavity to couple the microwave energy into the plasma chamber. This has been described in Section 2.0. The inability of that configuration to reproduce earlier experiments resulted in a totally different experimental configuration, and it is this latest generation of equipment that yielded the positive results that are described in this report.

A 500 W Micro-Now Model 420B Microwave Generator supplies radiation at 2.45 GHz to a WR 284 transition component by means of an N-type coaxial cable. This permits power flow to continue from one type of transmission line to another without reflection. This rectangular waveguide converter is bolted to the microwave waveguide ensemble which consists of a 4-stub tuner waveguide, the applicator (microwave chamber containing the substrate to be coated), and a dummy load (Figure 7).

The role of the tuner waveguide component is to develop an impedance in the waveguide which is the reciprocal of the impedance of the applicator. The sum of the two impedences is then seen by the power source as a matched load. A Gerling Laboratories 404 stub tuner was utilized for low power usages with no side cooling necessary. The brass stubs consisted of a cap screw and nut that was adjusted manually; it took four stubs, separated by an eighth of the width of a waveguide apart, to be able to generate an impedance of any value at any phase.

Following the tuner was a variable Q waveguide applicator which was one-half of a guide wavelength long. The GL 518 applicator has a 2-1/8" diameter aperture with 12" perforated tubes on either side of the hole; these arms
Figure 7. Schematic of the equipment used in the microwave powered PECVD experiment.
attenuate the microwave energy that is diffracted radiation from the aperture in the cavity. The primary purpose of the perforations was to allow observation and also direct air cooling to the plasma tube. The aperture in the cavity permits a 2" o.d. mullite tube (a silica/alumina ceramic tube) to pass through the cavity. It is within this tube that the substrate is placed, and a plasma is generated from the hydrogen and methane gases that flow through the tube. A Simpson model 380m microwave tester indicated the level of microwave energy escaping from the system in units of mW/cm². Usually the most sensitive scale was employed to detect the small amounts of microwave leakage in the vicinity of the cavity during experiments.

The Q of a cavity is a measure of the efficiency, or the ability, to store energy within the applicator. The electric field strength within the material being heated is higher when the applicator becomes resonant than it would otherwise have been. Reducing the Q reduces the tendency to arc and increases the operating bandwidth making the interaction between the applicator, tuner, and the power source easier to manage. The Q of the cavity can be varied by using one of several variable size irises which separate the applicator from the dummy load that absorbs the power coupled out of the resonant chamber; dissipating it as heat. All experiments could be performed using a blank iris to maximize the Q of the cavity so as to heat the sample to the maximum. Also, the Q was sufficiently high when a blank iris was employed so the low VSWR tuning cavity could be efficiently utilized.

Unfortunately, the power coupled to the dummy load represents a loss of efficiency since the power can not be applied to the product being heated. However, the loss of efficiency can be compensated far more economically than can some of the operational problems imposed by more
efficient (higher Q) applicators. All four waveguide components had 5.31" o.d. flanges that were connected by three sets of eight cap screw bolts and nuts [43].

The reactor chamber used to investigate the deposition of diamonds in a microwave plasma system was a 1-3/4" i.d. x 30" sillimanite (mullite) tube made by Coors Ceramics Co. The opaque tube is composed of approximately 60% Al₂O₃ and 40% SiO₂ with a maximum usage operating temperature of 1700 °C. Air cooling was employed near the plasma region to reduce the possibility of stress at elevated temperatures. Periodically, the tube was annealed in the 600-1100 °C range to relieve stress that may occur due to repetitive thermal shock as temperature ramps in excess of 150 °C/hr increase in the microwave cavity.

To maintain vacuum integrity a series of compression fittings, copper flange gaskets, and conflat flanges were used. The top fitting was comprised of a 2-3/4" flange size, 1-3/8" view area zero length conflat viewport made of boro-silicate glass followed by a 2-3/4" double-edged conflat flange with the same dimensions except no viewport and two 1/8" NPT x 1/4" cajon adapters on the side of the conflat. A 3-3/8" x 2-3/4" conflat reducing flange was connected to a 3-3/8" conflat flange with a 2" i.d. that was silver brazed to a 2" i.d. o-ring compression seal that contained the mullite tube. Copper gaskets of the appropriate size were between each flange and cap screws were utilized to bind the flanges together.

The other end of the mullite was contained in another silver brazed compression fitting that was connected to a 2-3/4" double-sided conflat flange and an 1/8" NPT occupied by a thermocouple gauge opposite a back-to-air valve. Finally, a 2-3/4" flanged baseplate with a 1/16" NPT x 1/8" swagelok adapter in the center accommodated a 1/8" o.d. Omega Corp. chromel-alumel inconel sheth K-type (-200-1250
°C) thermocouple wire that was 24" in length. The same readout unit for the thermocouple wire was used for these experiments. The 1-1/2" diameter ceramic substrate holder was 14" in length, and contained the thermocouple so that it was in contact with the substrate.
2.1.4 Gas Flow Readout Unit and Mass Flow Controllers

The gases used in all experiments were H₂ and CH₄. The gas composition for diamond deposition varied from 0.5 to 5% CH₄ with the balance being H₂. These percentages by volume were chosen because they were known from the literature to generate diamond films of varying purity and morphology [44]. The total flow rate was 100 sccm (standard cubic centimeters per minute) in all experiments.

Gas flow rates were controlled by Tylan FC-260 mass flow controllers. The temperature rise of a gas is a function of the amount of heat added, the mass flow rate, and properties of the gas being used. Mass flow control is a means of measuring and automatically controlling the weight flow rate of a gas. To measure gas flow rate each instrument uses two externally heated resistance thermometers wound around a small, stainless-steel sensor tube. A bridge circuit exists between these two thermometers and senses a temperature differential, thereby producing an output signal of 0 to 5 dc volts proportional to the gas flow rate. This signal is compared to a command voltage from a potentiometer and an error signal is generated, which adjusts the valve power, thus changing the flow rate until the setpoint is reached. During these experiments, the setpoints were controlled and monitored by a Tylan RO-20-A unit. It features a digital setpoint command signal, a digital readout scaled in sccm units, and PC Board mounted components for up to four mass flowmeters [45]. The two mass flow controllers (one for each gas) were connected to 1/4" plastic tubing from the gas cylinders using swagelok fittings. Two throttle valves were positioned so as to supply gas flow to all three systems. The bell-jar system utilized a 1/4" swagelok connection to the throttle valve, more polyethylene tubing,
and a 1/8" NPT x 1/4" swagelok adapter to the chamber. The microwave system utilized a 1/4" swagelok connector with tubing from the throttle valve to a 1/8" NPT x 1/4" cajon adapter to the chamber.

2.1.5 Pressure Gauges

A MKS Baratron type 221A capacitance manometer pressure gauge was used to measure the reactor chamber pressure which varied from 20 to 80 torr in all experiments [46]. These pressures were chosen because they were known from the literature to generate diamond films [44]. The voltage signal from the transducer is displayed on an automatically ranging MKS Baratron type PDR-A combination power supply/readout unit with a 15 Volt output from each of five channels. A Potentiometer is built into the transducer power supply and the readout allows zero adjustment to calibrate the transducer [47]. The pressure sensor is a recent development of the diaphragm gauge where the tightly tensioned diaphragm constitutes one plate of an electrical capacitor. As the pressure changes the displacement between the two plates of the capacitor varies, which changes the output signal. One side is evacuated to 10⁻⁷ torr and sealed to provide a zero reference pressure, while the gaseous media whose pressure is to be measured is exposed to the other side. Sensor electronics amplify the signal that is produced by the change in capacitance between the electrode and the diaphragm [48]. The MKS Baratron capacitance manometer is accurate to ±5% at 10⁻⁴ torr.

Two transducers were utilized to gauge chamber pressures in all experiments. One transducer ranged from 0-1000 torr while the other transducer ranged from 0-10 torr, and were connected to a 1/4" cajon tee via 1/4"
flexible tubing. The third opening on the tee went to the chamber with more flexible tubing which was interchangeable depending upon the system being employed. The microwave experiments used a zero length doublesided conflat with two 1/8" NPT holes through which 1/4" tubing was connected to the pressure gauges and the gas inlet. The bell-jar experiments made use of a 1/8" NPT \& 1/4" swagelok fitting to connect the tubing to the bottom of the chamber.

In order to assist measuring the pressure in the range from 1 to 10^{-3} torr, a type 0531 Varian 1/8" NPT thermocouple gauge was employed in the side of a conflat with a back-to-air valve at the base of the microwave chamber. A Varian NRC 802 vacuum gauge controller was connected to the thermocouple gauge for the readout. A thermocouple gauge was not used for the bell-jar based experiments.

A change in temperature is used as a measure of pressure in the thermocouple gauge, and is based on the known thermal conductivity of the gas. A low-temperature filament is heated by a constant current that depends upon the rate of heat loss to the surrounding gas. The temperature is determined from the emf produced by a thermocouple in contact with the filament; therefore it depends upon the thermoconductivity of the air [48]. The accuracy was adequate for it only determined whether the base pressure in the system was sufficiently low to begin the experiments.

2.1.6 Vacuum System

The vacuum system consisted of a D30A Trivac dual stage rotary vane pump which was used to reduce the pressure in the enclosed vessel for rough vacuums (760 to 10^{-3} torr). The direct drive mechanism was composed of a
motor that turns the pump shaft which is connected by a coupling and elastic element to absorb shock and vibration. The pumping mechanism was comprised of two stage pump cylinders. The primary, high vacuum stage pump cylinder sits below the pump intake tube, diminishes the chamber pressure and compresses a gas upon rotation of the vanes. The gas is forced out through an opening in the center bearing plate and into the second stage pump cylinder which further compresses the gas through the exhaust port. The gas ballast mechanism is just below the exhaust port and prevents water vapor from condensing in the pump possibly ruining seals and degrading pump fluid [49]. VWR Scientific pump oil 19 was utilized in the mechanical pump.

The pump intake was connected to both systems with a 1-1/2" × 40" stainless steel flexible tubing followed by a 1-1/2" slip insert by 1/4" NPT female adapter fastened with snap joint connectors. A 1/4" NPT × 1/4" swagelok was screwed in followed by a 1/4" tee with the other two aperatures connecting each system. For the bell-jar system, 30" of 1/4" diameter plastic tubing with a throttle valve to alter the pressure was employed, while only 10" was utilized for the microwave system. A 1/8" × 1/4" swagelok adapter connected the tubing to the chamber; a 3/8" cajon adapter with 1/4" × 3/8" slip cajon adapter connected the throttle valve and tubing to the microwave system.

The ability of a tube to transmit gas is characterized by its conductance which is analogous to Ohm's Law for electrical circuitry [48].

\[ C = \frac{12\pi D^3}{L} \]

where diameter and length are measured in centimeters. The master equation relates the net speed of a system \( S \) to the capacity of the pump \( S_p \) and the conductance leading to the pump is given by:
\[
1/S = 1/S_p + 1/C
\]

with the capacity of the pump being 12.67 l/sec. The microwave system had a conductance of 7.41 l/sec and a net speed of 4.67 l/sec, while the bell-jar system's conductance was 6.55 l/sec with a net speed of 4.31 l/sec.
2.2 Substrate Analysis

2.2.1 Scanning Electron Microscopy

An ISI-40 International Scientific Instrument scanning electron microscope (SEM) was used to analyze the surface morphology of various silicon and polymeric substrates which had been exposed to experimental conditions [50]. Using double-stick tape, the bottom side of samples were fixed onto an SEM sample stud. Photomicrographs of the samples were taken using Polaroid Type 53 film where magnification varied from 0.1 kx to 6 kx and the filament voltage was kept constant at 15 kV. The physical sputtering process was performed in a Polaron Instruments Inc. E 5000 SEM coating unit to make the films conducting so that secondary electrons could be scattered off the substrate surface. A scintillator disk converts those electrons into photons where they are detected as an image by a photomultiplier tube. Before the films were placed into the stage of the vacuum chamber of the SEM, a Au/Pd film was sputtered onto the samples. After the sputtering process was completed, argon was allowed to flow into the chamber for two to three minutes preventing the oxidation of the newly sputtered coating. An oxidized coating will decrease the resolution of a photomicrograph.

2.2.2 Profilometry

Precise knowledge of the surface microtopography in microelectronics is critical especially for determining the surface profiles, the roughness characteristics, and the waviness and bow of deposited thin films or etched wafers. All surface profiles and estimated deposition rates were performed with a Sloan Dektak capable of measuring the
surface elevation differences from 25 Å to 100 μm accurately. It has an additional provision for magnifying horizontal dimensions of a profile from 2X to 5000X with a microscope.

Contact with the sample is made by a diamond stylus at the forward end of the arm which swings on jeweled pivots, and is suspended by a coil spring used for tracking force adjustment. The sample stage can be tilted, to accommodate samples whose surfaces are not parallel, with a leveling thumbwheel. Vertical magnification is selected from seven levels (1 kÅ-1 MÅ) and three profile scanning speeds regulated at 0.01, 0.1, and 1 cm/min. The sensing head is a differential transformer that can sense electrically the relative differences in elevation as the sample is moved horizontally under the stylus. These differences in elevation are displayed visually by a Sloan chart recorder which has a full scale sensitivity of 100 MV with full span zero adjustment and chart speeds regulated at 2, 10, and 50 cm/min [51].

Before a substrate was analyzed, a calibration was performed using a 10 kÅ measuring standard (9.11 ±5%). Only silicon substrates were analyzed because the polymers are not sufficiently rigid to resist deformation under the weight of the stylus head.

2.2.3 Laser Raman Spectroscopy

Since the discovery of the Raman Effect in 1928, Raman spectroscopy has been important for the determination of molecular structure, especially in locating various functional groups or chemical bonds in molecules. A unique feature of Raman scattering is that each line has a characteristic polarization which can provide additional information about the molecular structure.
A highly collimated and intensely monochromatic beam of light passing through a nonabsorbing medium is invariably found to undergo a change in molecular polarizability as the molecules vibrate. If a portion of the scattered light is passed through a spectrometer the bulk of scattered energy will be at the frequency of the incident beam; a process known as Rayleigh scattering. This is when the energy of the photons before and after scattering off the sample is the same.

However, a small fraction of light will be found at different frequencies, both higher and lower than that of the incident beam. The Raman effect refers to the production of these altered frequencies not initially present in the monochromatic incident light and is characteristic of the material being investigated. It should be emphasized that the shapes and positions of Raman bands do not depend on the frequency of the exciting radiation since the numbers derived from the spectra are the differences between incident and shifted frequencies. This scattering process involves no intrinsic absorption of radiation, therefore, the scattering system is never in an electronic excited state. The whole process takes place in less than $10^{-12}$ sec.

A molecule placed in an electromagnetic field has its charge distribution periodically disturbed by the field. The induced resultant, the alternating dipole moment is generally expressed as the dipole moment per unit volume, and is called the polarization. The polarization is proportional to the inducing field:

$$P = \alpha E$$

and the constant $\alpha$, the polarizability, is of central importance in the theory of the Raman effect. Although the description of the details of the Raman effect requires quantum theory, the existence of the effect is easily
predicted from classical electromagnetic theory [52].

The inducing electromagnetic field is given by

\[ E = E_0 \cos 2\pi ft \]  

We then expect a polarization:

\[ P = \kappa E_0 \cos 2\pi ft \]  

The polarizability consists of two parts. The first is a constant, \( \kappa_0 \), which represents the static polarizability. The second is a sum of terms having the periodic time dependence of the normal frequencies of the system under consideration. The polarizability may then be written as:

\[ \kappa = \kappa_0 + \sum \kappa_n \cos 2\pi \nu_n t \]

The normal frequencies \( \nu_n \) may be rotational or vibrational frequencies of a molecule, lattice frequencies of a crystal or vibrational modes of a glass, and so on. If (2) and (4) are set into (1), we get:

\[ P = E_0 \kappa_0 \cos 2\pi ft + E_0 \sum \kappa_n \cos 2\pi \nu_n t \cos 2\pi \nu_n t \]

\[ = E_0 \kappa_0 \cos 2\pi ft + 1/2 \sum \kappa_n \{ \cos 2\pi (\nu_+ \nu_n) t + \cos 2\pi (\nu_+ \nu_n) t \} \]

Equation (5) correctly predicts the major qualitative features of the Raman effect. First, there is the leading term, which represents the component of the polarization having the frequency of the exciting field. This accounts for Rayleigh scattering. Second, each variable component of the polarizability, \( \kappa_n \), gives rise to components of the polarization having frequencies \( (\nu+\nu_n) \) and \( (\nu-\nu_n) \). These account for the Stokes and anti-Stokes Raman bands.

Usually incident radiation is scattered by a molecule in the lowest vibrational state. If the molecule reemits by returning to an excited vibrational state of the ground electronic state, the radiation is of lower energy than the incident radiation. The difference in frequency is equivalent to an integral mode of vibrational frequency of the molecules ground electronic state, known in this case
as Stokes lines.

A few molecules will scatter radiation while they are in the excited vibrational state and will decay to a lower energy level. Their Raman scattered light will have a higher frequency than the incident radiation. These are called anti-Stokes lines. For chemical analysis, only Stokes lines are normally considered because they are more intense since most molecules are initially in the lowest vibrational level.

The Raman Spectrometer consisted of a laser with a power supply, an illuminating stage with optics, a spectrometer with a control drive unit, a photomultiplier chamber with power supply, a photomultiplier tube with high voltage power supply, a photon counter with data converter, and a chart recorder. See Figure 8 for spectrometer set-up.

The Spectra-Physics Model 164 Argon Ion Laser System consists of the Model 164 Laser Head and the Model 265 Power Supply connected by an umbilical cord containing power cables and water cooling lines. It had an output capacity of 1 W at 488.0 nm excitation wavelength which is ideal for Raman Spectroscopy [53]. The Model 155 Spectra-Physics 0.5 mW Helium-Neon Laser was used for simple alignment applications for it is a reliable and dependable source of coherent light.

The blue output light is bent around two mirrors to the base of the illuminator which was 90° from the incident light where a 45° aluminum block was situated on a track. The beam was reflected up through a focusing lens with positioning knobs to the substrate holder. The substrate was placed between two microscope slides of glass and fastened to two brass 45° angle supports with adhesive tape. The focused beam was reflected from the substrate into the spectrometer.
Figure 8. Block diagram of a laser Raman spectrometer.
The Spex 1403 CompAct Double Monochromator-Spectrometer consists of the 1301 1/2-meter double spectrometer whose drive is linear in wavenumber and a Compudrive control unit to operate the stepping motor in the spectrometer [54]. From shutter widths up to 3 mm and heights to 20 mm, the beam was directed through the entrance slit towards a mirror followed by a grating fixture to another mirror through the intermediate slit into the second half of the spectrometer. The beam went through the same sequence of mirrors and gratings to the exit slit into the photomultiplier tube. Care was taken to make sure the beam was focused onto the sample and directed to the intermediate slit by visual inspection.

A "Products for Research" TE-104-RF shielded water cooled thermoelectric refrigerated photomultiplier tube chamber with power supply by the same name accepted any 2" photomultiplier tube socket [55]. Water was circulated through the chamber for one hour before the power supply was turned on.

The "Products for Research Model" RF TSA interchangeable tube socket assembly contains the tube socket [55], the quick connect cathode to the Keithly Instruments 244 High Voltage Supply, and the anode connecting the Model 1120 "Princeton Applied Research Corp." photon counter [56]. The photomultiplier tube chamber power supply was on for one hour before the high voltage power supply was operated. The Model 1105 Data Converter used low voltage levels to power twelve linear full scale ranges which we used 10,000 cts/sec, and two log ranges covering seven decades of count where we used the 1-10^4 cts/sec scale [56].
2.3 Sample Preparation

2.3.1 Silicon

2.25" silicon wafers were used in the bell-jar discharge systems but had to be sheared into squares or triangles to fit in the 1.75 i.d. mullite tube for microwave experiments. All wafers were cleaned with hot water followed by a reagent grade acetone or a reagent grade methanol rinse to dispose of grease, grime, and fingerprints. After drying, the silicon surface was scratched by hand using 1/4 μ synthetic diamond powder from the "Industrial Diamond Powders Inc." to provide additional nucleation sites upon which diamond crystallization could occur. The residue was polished off with Kim Wipes and blown off with compressed air to remove the diamond powder.

2.3.2 Kapton H (a brandname of Polyimide)

Kapton H was obtained from DuPont and the thickness of the film was 40 micrometers. The Kapton H film was pressed between two aluminum rings until it was taut. The sample was scratched with diamond powder and blown with compressed air to remove any dust or diamond residue before being placed on the substrate holder.

2.3.3 Upilex-S

Upilex-S was obtained from IBM and the thickness of the film was 50 micrometers. The film was prepared exactly as the Kapton H film.
This section consists of a description of the conditions under which thin films were deposited on the substrates together with those diagnostics performed on the material to determine the topology, morphology, and the purity of the films. The diamond and diamond-like films deposited on the substrates were subjected to the following analytical techniques: profilometry to determine the magnitude, uniformity, and rate of deposition, laser Raman spectroscopy to identify the diamond metastable phase, and scanning electron microscopy to ascertain the morphology of the surfaces obtained.

3.1 Results of Different Deposition Configurations

3.1.1 Arc Plasma Configuration

The arc plasma experiments were intended to provide complementary information on diamond growth conditions while the microwave plasma system was reconstructed. Eight experiments were conducted using the arc plasma: In each experiment silicon wafers were initially treated as described in Section 2.3.1, and a tabulation of experimental conditions together with observations on surface texture is provided in Table 1. A more complete visual description of the deposition is contained following Table 1.

The conditions that were varied in the experiment using the arc plasma were: the overall pressure, the biasing of the electrodes, the ratio of hydrogen gas to
Table 1

Arc Plasma Experimental Results

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>% Gas Comp.</th>
<th>Pressure (torr)</th>
<th>Duration (minutes)</th>
<th>Elec Vis.</th>
<th>Sep. Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5/95</td>
<td>50</td>
<td>170</td>
<td></td>
<td>1 mm diamond and graphite + C dust deposit from gas</td>
</tr>
<tr>
<td>2</td>
<td>5/95</td>
<td>100</td>
<td>180</td>
<td></td>
<td>1 mm localized plasma, no C dust good growth</td>
</tr>
<tr>
<td>3</td>
<td>1/99</td>
<td>100</td>
<td>225</td>
<td></td>
<td>5 mm polycrystal-line growth</td>
</tr>
<tr>
<td>4</td>
<td>5/95</td>
<td>100</td>
<td>240</td>
<td></td>
<td>5 mm same as #1 but no C dust</td>
</tr>
<tr>
<td>5</td>
<td>2.5/97.5</td>
<td>100</td>
<td>180</td>
<td></td>
<td>5 mm same as #4</td>
</tr>
<tr>
<td>6</td>
<td>2/98</td>
<td>100</td>
<td>75</td>
<td></td>
<td>5 mm same as #4</td>
</tr>
<tr>
<td>7</td>
<td>2/98</td>
<td>30</td>
<td>420</td>
<td></td>
<td>5 mm same as #3</td>
</tr>
<tr>
<td>8</td>
<td>5/95</td>
<td>30</td>
<td>420</td>
<td></td>
<td>3 mm same as #1</td>
</tr>
<tr>
<td>9</td>
<td>0.5/99.5</td>
<td>30</td>
<td>420</td>
<td></td>
<td>5 mm same as #3</td>
</tr>
<tr>
<td>10</td>
<td>5/95</td>
<td>30</td>
<td>420</td>
<td></td>
<td>5 mm same as #1</td>
</tr>
</tbody>
</table>

methane gas, and the duration the 2.25" substrate was exposed to the plasma.

At higher pressures the reddish-purple discharge became more localized with an arc forming between the two
electrodes, while striking the surface of the substrate. This was possible since one electrode was below the substrate and the powered electrode was above the surface of the substrate. As the overall pressure in the bell-jar was lowered, a sheath was formed around the substrate.

From temperature measurements made on the base of the substrate using a thermocouple it was determined that the average temperature of the base was 120 °C. Even allowing for poor thermal conductivity through the substrate from the top to the base, it seems unlikely that the surface could reach the temperatures of ca. 800 °C usually believed to be necessary for diamond formation. The magnitude of the electrode separation did not appear to affect the surface temperature.

From visual inspection, films that were produced from higher methane concentrations had poorer adhesion and rougher textures while lower methane concentrations had good adhesion to the silicon substrates. In addition, the presence of black carbon grit was observed at higher methane concentrations while a smooth tan colored deposition predominated at lower methane concentrations.

In addition to using a 60 cycle arc discharge to initiate the plasma, by grounding the anode upon which the substrate is based, it is possible to consider the effect of a dc plasma and ion bombardment in experiments #9 and #10. The depositions looked similar to experiments #3 and #1 respectively with the exceptions of a decreased amount of carbon dust on both substrate and electrode in experiment #10 and lower deposition temperatures averaging 70 °C. These results were quite promising as an alternative to the low frequency ac power supply.
3.1.2 DC Plasma Configuration

A 1.5 Ampere dc power supply with 1500 V provided the high voltage necessary for the plasma. With this power supply, there was a greater potential for a uniform deposition since the plasma was not striking the substrate. It was also an opportunity to attempt depositions on polymeric films which to our knowledge has not been attempted before.

Twenty-five experiments were conducted using the dc plasma: In each experiment the substrates were treated as described in Section 2.3.1, 2,3, and a tabulation of experimental conditions is contained in Table 2. The conditions that were varied in the dc experiments were: the overall pressure, the ratio of H$_2$ gas to CH$_4$ gas, the substrate material, the duration of plasma exposure to the substrate, the electrode height, and the amount of power introduced into the system.

The dc plasma did not strike the surface of the substrate as in arc plasma experiments, therefore the substrate surface was not ablated. Instead, there was a glow discharge between the hot electrode and the grounding electrode which were situated just above the substrate.

From the previous arc experiments shown above it was determined that better crystallinity can be achieved with lower CH$_4$ concentrations, thus most dc experiments were conducted with 0.5 or 1% CH$_4$. In order to achieve the substrate temperatures at which diamond growth is generally believed to occur; the overall pressure (80 to 100 torr) was increased, the electrode separation (1 to 3 mm) was decreased, and the power (700 watts) was increased.

The optimum dc experiments (#20 to #25) produced more translucent films on silicon substrates than previous dc or
Table 2
DC Plasma Experimental Results

<table>
<thead>
<tr>
<th>Expt</th>
<th>Gas</th>
<th>Pres</th>
<th>Duration</th>
<th>Elec</th>
<th>Substrate</th>
<th>Power</th>
<th>Thermo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_4$/H$_2$ (torr) (minutes) Sep (watts) (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2/98</td>
<td>30</td>
<td>60</td>
<td>8 mm</td>
<td>Si</td>
<td>200</td>
<td>210</td>
</tr>
<tr>
<td>2</td>
<td>1/99</td>
<td>30</td>
<td>15</td>
<td>9 mm</td>
<td>Si</td>
<td>600</td>
<td>245</td>
</tr>
<tr>
<td>3</td>
<td>1/99</td>
<td>30</td>
<td>20</td>
<td>9 mm</td>
<td>Si</td>
<td>600</td>
<td>247</td>
</tr>
<tr>
<td>4</td>
<td>1/99</td>
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<td>30</td>
<td>5 mm</td>
<td>Si</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>0.5/99.5</td>
<td>30</td>
<td>60</td>
<td>5 mm</td>
<td>Si</td>
<td>540</td>
<td>472</td>
</tr>
<tr>
<td>6</td>
<td>0.5/99.5</td>
<td>30</td>
<td>90</td>
<td>2 mm</td>
<td>Si</td>
<td>300</td>
<td>465</td>
</tr>
<tr>
<td>7</td>
<td>1/99</td>
<td>40</td>
<td>270</td>
<td>7 mm</td>
<td>Si</td>
<td>300</td>
<td>370</td>
</tr>
<tr>
<td>8</td>
<td>1/99</td>
<td>30</td>
<td>90</td>
<td>3 mm</td>
<td>PI</td>
<td>300</td>
<td>411</td>
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<td>1/99</td>
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<td>150</td>
<td>7 mm</td>
<td>Si</td>
<td>300</td>
<td>278</td>
</tr>
<tr>
<td>10</td>
<td>1/99</td>
<td>30</td>
<td>180</td>
<td>4 mm</td>
<td>Si</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>11</td>
<td>2/98</td>
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<td>240</td>
<td>3 mm</td>
<td>Si</td>
<td>350</td>
<td>320</td>
</tr>
<tr>
<td>12</td>
<td>3/97</td>
<td>30</td>
<td>180</td>
<td>4 mm</td>
<td>Si</td>
<td>350</td>
<td>330</td>
</tr>
<tr>
<td>13</td>
<td>1/99</td>
<td>30</td>
<td>210</td>
<td>7 mm</td>
<td>PI</td>
<td>350</td>
<td>234</td>
</tr>
<tr>
<td>14</td>
<td>1/99</td>
<td>30</td>
<td>255</td>
<td>5 mm</td>
<td>Upilex-S</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>15</td>
<td>1/99</td>
<td>30</td>
<td>210</td>
<td>4 mm</td>
<td>Upilex-S</td>
<td>300</td>
<td>345</td>
</tr>
<tr>
<td>16</td>
<td>1/99</td>
<td>30</td>
<td>120</td>
<td>5 mm</td>
<td>Upilex-S</td>
<td>350</td>
<td>360</td>
</tr>
<tr>
<td>17</td>
<td>1/99</td>
<td>20</td>
<td>540</td>
<td>7 mm</td>
<td>Upilex-S</td>
<td>300</td>
<td>290</td>
</tr>
<tr>
<td>18</td>
<td>5/95</td>
<td>20</td>
<td>1080</td>
<td>7 mm</td>
<td>Upilex-S</td>
<td>300</td>
<td>290</td>
</tr>
<tr>
<td>19</td>
<td>1/99</td>
<td>40</td>
<td>480</td>
<td>6 mm</td>
<td>Si</td>
<td>490</td>
<td>420</td>
</tr>
<tr>
<td>20</td>
<td>1.5/98.5</td>
<td>50</td>
<td>60</td>
<td>2 mm</td>
<td>Si</td>
<td>700</td>
<td>602</td>
</tr>
<tr>
<td>21</td>
<td>1.5/98.5</td>
<td>50</td>
<td>315</td>
<td>4 mm</td>
<td>Si</td>
<td>700</td>
<td>520</td>
</tr>
<tr>
<td>22</td>
<td>1/99</td>
<td>50</td>
<td>150</td>
<td>2 mm</td>
<td>Si</td>
<td>700</td>
<td>612</td>
</tr>
<tr>
<td>23</td>
<td>0.5/99.5</td>
<td>50</td>
<td>150</td>
<td>3 mm</td>
<td>Si</td>
<td>700</td>
<td>580</td>
</tr>
<tr>
<td>24</td>
<td>1/99</td>
<td>80</td>
<td>190</td>
<td>3 mm</td>
<td>Si</td>
<td>700</td>
<td>712</td>
</tr>
<tr>
<td>25</td>
<td>0.5/99.5</td>
<td>80</td>
<td>185</td>
<td>3 mm</td>
<td>Si</td>
<td>700</td>
<td>722</td>
</tr>
</tbody>
</table>
arc plasma experiments with deposition temperatures of more than 700 °C. The adhesion to the substrate was good for it was necessary to use a razor blade to remove material from the substrate. Before analysis compressed air was blown over the deposited surface, and very little carbon grit or other loose material was seen above deposition temperatures of 250 °C.

Finally, polymer films were incorporated into the system as substrates replacing silicon. In experiment #8, the portion of the polyimide substrate exposed to the hottest region of the plasma was thermally degraded at a deposition temperature maximum of 411 °C. The deposition was tan in color with poor adhesion when compressed air was blown over the deposition surface. In experiments #14-16, it was determined that a deposition temperature maximum of over 300 °C would degrade the polymer. Experiment #17, using the Upilex-S substrate produced a silver colored deposition at a 1% CH₄ concentration with better adhesion than the polyimide substrate. The maximum deposition temperature was 290 °C with no polymer degradation. At 5% CH₄ concentration, the deposition was similar in appearance to the arc experiments at that concentration.

3.1.3 Microwave Plasma Configuration

The work performed using an arc plasma or dc plasma to dissociate the precursors for the thin film deposition is intended to provide complementary information on diamond growth conditions, however it is the use of the microwave applicator that is the preferred experimental method. In each experiment substrates were initially treated as described in Section 2.3.1,2,3, and a tabulation of experimental conditions is contained in Table 3.

Important variables are: the absolute gas flow through
the applicator, the relative gas composition of methane and hydrogen, the microwave power, the substrate material, the duration of plasma exposure to the substrate, and the displacement of the substrate from the center of the plasma (which directly affects the temperature of the substrate).

Table 3

Microwave Plasma Experimental Results

<table>
<thead>
<tr>
<th>Expt.</th>
<th>CH(_4)/H(_2)</th>
<th>Pres. (torr)</th>
<th>Duration (minutes)</th>
<th>Substrate</th>
<th>Separation of Substrate (in.)</th>
<th>Power (watt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/99</td>
<td>30</td>
<td>60</td>
<td>Si</td>
<td>1.25</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>1/99</td>
<td>50</td>
<td>60</td>
<td>Si</td>
<td>1.25</td>
<td>325</td>
</tr>
<tr>
<td>3</td>
<td>1/99</td>
<td>60</td>
<td>90</td>
<td>Si</td>
<td>1.00</td>
<td>350</td>
</tr>
<tr>
<td>4</td>
<td>1/99</td>
<td>20</td>
<td>200</td>
<td>Si</td>
<td>1.00</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>1/99</td>
<td>20</td>
<td>100</td>
<td>Si</td>
<td>0.75</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>5/95</td>
<td>60</td>
<td>300</td>
<td>PI</td>
<td>0.75</td>
<td>300</td>
</tr>
<tr>
<td>7</td>
<td>2/98</td>
<td>30</td>
<td>180</td>
<td>PI</td>
<td>0.50</td>
<td>300</td>
</tr>
<tr>
<td>8</td>
<td>1.5/98.5</td>
<td>40</td>
<td>180</td>
<td>Upilex-S</td>
<td>0.50</td>
<td>300</td>
</tr>
</tbody>
</table>

The most visibly intense region of the plasma was contained against the wall of the mullite tube where the edge of the substrate was in close proximity to the wall. At pressures higher than 50 torr, the reddish-purple color
of the plasma was quenched.

Experiment #1 produced a translucent film on the edge of a silicon substrate near the reactor wall, while a clear crystalline-like material was synthesized on the center of a silicon substrate at a different power level in experiment #2 at a 1% CH₄ concentration. The adhesion of these two materials was good with no excess material blown off by compressed air. Observation of the film surface through a reflectant light microscope reveals a surface covered by many microcrystallites with multiple grain orientations. Although temperature measurements made on the base of the substrate using a thermocouple averaged 90 °C, the thermocouple was located opposite the plasma region, and the temperature is believed to be higher closer to the plasma.

3.4 Scanning Electron Microscope Investigations

A series of surface morphology investigations of the diamond and diamond-like depositions were completed using an SEM described in Section 2.2.1 on silicon, polyimide, and Upilex-S substrates for all deposition configurations. See Table 4 below for the Magnification Coding System for the SEM in the following micrographs.

Table 4
Magnification Coding System for SEM

1. The ubar represents 100 μm when followed by three dots.
2. The ubar represents 10 μm when followed by two dots.
3. The ubar represents 1 μm when followed by one dot.
4. The ubar represents 0.1 μm when followed by no dots.

Magnification can be calculated from the micron bar by
using the following relationships:

\[10X = 1 \text{ mm when the } \text{ubar} \text{ represents } 100 \mu\text{m}\]
\[100X = 1 \text{ mm when the } \text{ubar} \text{ represents } 10 \mu\text{m}\]
\[1000X = 1 \text{ mm when the } \text{ubar} \text{ represents } 1 \mu\text{m}\]
\[10000X = 1 \text{ mm when the } \text{ubar} \text{ represents } 0.1 \mu\text{m}\]

Figures 9 and 10 are micrographs of a treated silicon wafer without scratches and with scratches, respectively. The unscratched wafer has no surface features as opposed to the wafer scratched with diamond powder. In Figure 11 the progression of the covering of a silicon substrate by a hard carbon film is shown. Initially there is sparse coverage of the surface with the predominance of nucleation sites being located in the vicinity of a scratch on the surface (Figure 11A). The coverage of the surface is then extended almost uniformly (Figure 11B), although isolated pinhole defects in the surface can be observed. Finally, complete coverage of the surface is achieved (Figure 11C).

Electron micrographs (Figure 12) of the surface indicate the region of ablation on the growing film, as indicated by the arrows, where the arc discharged to the silicon substrate, however such an area is small. Two separate surface morphologies on silicon substrates in the arc plasma depositions in Figure 13 were noted: (a) an undulating surface texture with good adhesion to the silicon substrate could be obtained at lower CH\(_4\) to H\(_2\) ratios (Figure 13A), or (b) higher growth rates, but with poorer adhesion and rougher textures could be obtained at the higher methane ratio of 5% (Figure 13B).

The dc experiments produced three separate types of morphology on a silicon substrate. Figure 14 represents a large growth region in the center with small amounts of
Figure 9. SEM micrograph of a treated, unscratched silicon wafer.
Figure 10. SEM micrograph of a treated, scratched silicon wafer.
Figure 11: SEM micrographs of the progression of covering on a silicon surface by a thin film. Conditions were those of experiment #1 in the microwave.
Figure 12. SEM micrographs of silicon surface ablation by an arc discharge. Conditions were those of experiment #7.
Figure 13. SEM micrographs of deposition material grown on silicon substrates. Conditions were those of experiment #3 for Figure 13A and of experiment #4 for Figure 13B in an arc plasma.
Figure 14. SEM micrographs of an amorphous morphology on a silicon substrate. Conditions were those of experiment #24 in a dc plasma.
nucleation occurring on the outskirts of the growth. Upon closer inspection the deposition appears quite amorphous possibly polyaromatic. There were holes and voids in the deposition as well. Figure 15 looks to have more structure to it. This deposition could be classified as polycrystalline with some amorphous character to it. In Figure 16 there are definite edges adhered to the surface. This deposition is the most crystalline of the dc experiments. The amorphous deposition was photographed further away from the hottest part of the plasma where the most crystalline was viewed.

Figure 17 showed individual crystals in two different depositions on a silicon substrate in a microwave plasma. Figure 17A photographed single crystals within a growing film, while Figure 17B photographed a lone crystal without a film surrounding it.

Figure 18 is a scratched PI surface with diamond powder. Notice that the abrasions do not show up as the more brittle silicon wafers do. Figure 19 shows an amorphous deposition followed abruptly by the PI surface. This micrograph was taken away from the plasma region. The bottom figure shows a close-up of holes as indicated by arrows in the deposition. Figure 20 is photographed at the center of the film where the plasma was hottest. The polymer was degraded in the black region, but just outside this area a deposition was adhered to the surface. Figure 21 was photographed between the hottest and coldest areas viewed. There is an indication of some crystalline form.

Figure 22 is a scratched Upilex-S surface with diamond powder. As with polyimide, the scratches do not appear on the Upilex-S surface either. Figure 23 is a deposition viewed at the edge of the Upilex-S surface where an overview shows cracking on the surface and adhered nucleation sites to the left of the deposition. Upon
Figure 15. SEM micrograph of a polycrystalline morphology on a silicon substrate. Conditions were those of experiment #9 in a dc plasma.
Figure 16. SEM micrographs of crystalline depositions on a silicon substrate. Conditions were those of experiment #24 in a dc plasma.
Figure 17. SEM micrographs of individual crystals deposited on silicon substrates. Conditions were those of experiment #1 in Figure 17A and of experiment #2 in Figure 17B in a microwave plasma.
Figure 18. SEM micrograph of a scratched polyimide surface.
Figure 19. SEM micrographs of an amorphous deposition along with holes on a polyimide surface. Conditions were those of experiment #8 in a dc plasma.
Figure 20. SEM micrograph of a deposition at the hottest region of the plasma on a polyimide surface. Conditions were those of experiment #8 in a dc plasma.
Figure 21. SEM micrograph of a more crystalline deposition on a polyimide surface. Conditions were those of experiment #8 in a dc plasma.
Figure 22. SEM micrograph of a scratched Upilex-S surface.
Figure 23. SEM micrograph of an amorphous deposition with nucleation on a Upilex-S surface. Conditions were those of experiment #17 in a dc plasma.
closer inspection, the deposition looks amorphous. Figure 24 was photographed away from the deposition and shows a spider-web morphology.

3.5 Profilometry Investigations

Typical growth rates of 0.5 \( \mu \text{m/hr} \) for an arc plasma deposition are achieved over a surface covering ca. 1 cm in diameter. A profilometry trace over the surface of a deposited film displayed the texture (Figure 25) and was consistent with the approximate dimensions observed in the electron micrographs.

Growth rates for the microwave depositions were typically 1.5 \( \mu \text{m/hr} \) with the two different types of diamond deposition noted. A profilometry scan of the surface indicates significant non-uniformity (Figure 26).

3.6 Laser Raman Spectroscopy Investigations

Of all characterization techniques, the Raman spectrum is the most sensitive for identifying the presence of crystalline diamond in mixtures of various forms of carbon [1]. Figure 27 shows three typical Raman spectra for diamond films deposited on silicon substrates. The peak at 519 cm\(^{-1}\) (wave number) is from the silicon substrate, whereas the peak at 1332.5 \( \pm \) 0.5 cm\(^{-1}\) is characteristic of diamond. The broad peaks occurring in the 1500 to 1600 wave number range are characteristic of disordered sp\(^2\)-type carbons in the deposit [1]. The Raman scattering efficiency for the sp\(^2\)-bonded graphite is more than 50 times greater than that for the sp\(^3\)-bonded diamond; therefore, small amounts of sp\(^2\)-bonded carbon in the diamond deposits can be readily detected. The Raman spectra labeled (A) is a typical pattern for a highly
Figure 24. SEM micrograph of holes on a Upilex-S surface. Conditions were those of experiment #17 in a dc plasma.
Distance Traversed along silicon wafer

Figure 25. Profilometry scan of experiment #3 in the arc plasma.
Figure 26. Profilometry scan of experiment #1 in the microwave plasma.
Figure 27. Raman spectra for three typical diamond samples vapor-deposited on single-crystal silicon.
perfect diamond film. The pattern labeled (C) is typical for an imperfect film of crystalline diamond with appreciable amounts of sp$^2$ carbon present as defects or in a separate phase. The pattern labeled (B) is for a film of intermediate perfection. Noncrystalline carbon such as DLC would not show the 1332 wave number peak. Given the extremely thin nature of the films obtained it is unlikely that x-ray diffraction or electron diffraction would indicate any evidence other than that the films are amorphous. Under these circumstances Raman spectroscopy becomes a preferred method for determining the purity of the films.

Knight and White [57] have written a comprehensive paper and review on the Raman spectroscopy of vapor-deposited diamond films and of other forms of carbons. In addition to the various vapor-deposited films, they have included spectra for natural diamond, a General Electric HPHT diamond, lonsdaleite, carbonado (natural polycrystalline diamond), three forms of graphite (polycrystalline, highly orientated pyrolytic, and a natural graphite crystal), glassy carbon, diamond-like carbon, coke, and charcoal. Additional information about the degree of lattice distortion, strain, and disorder can be determined from the half-width of the 1333 cm$^{-1}$ line (natural diamond = 1.65 cm$^{-1}$; polycrystalline 5 -> 16 cm$^{-1}$ depending on the silicon contamination), the frequency shift of the 1333 cm$^{-1}$ line, and the intensity ratio of the 1333 cm$^{-1}$ line to the background, respectively.

To ascertain the purity of the diamond films that we produced, a Laser Raman scan of the surface was performed using the 488.0 nm excitation line of the Ar ion laser in all spectra. By virtue of the ability to focus the laser to a spot of less than 1 mm diameter it is possible to obtain a Raman spectrum of the surface composition of the
thin film as a function of position of the thin film within the plasma. In this manner the uniformity of the purity, which is dependent upon the gas flow dynamics (important at the relatively high pressures employed here), mass transport phenomena of the radical species across the boundary layer of the surface, and also the temperature of the surface can be investigated.

Figure 28 is a Raman scan of a silicon wafer that has only one band characteristic to it in the wavelength region of interest. An example of a Raman spectrum obtained for our sample (Figure 29) shows a narrow well defined scattering peak at 1332.6 cm\(^{-1}\) and another at about 796 cm\(^{-1}\).

The former peak is well known to be due to the presence of sp\(^3\)-hybridization (which is the tetrahedral configuration associated with a diamond phase) while the latter peak is due to the presence of crystalline B-SiC, a material believed to be formed at the interface of the silicon substrate and the carbon film. Figure 30 is probably a strained polycrystalline diamond-like film (1355 cm\(^{-1}\)). Figure 31 should be considered "graphite-like" material with peaks at 1555 cm\(^{-1}\) and 1570 cm\(^{-1}\). Graphite is an extremely efficient scatterer of incident light and is characterized by a broad band peak with a double maxima at 1560 cm\(^{-1}\) and 1600 cm\(^{-1}\). The 1302 cm\(^{-1}\) could be a strained and disordered sp\(^3\)-hybridized diamond-like material grown along with the graphite.

Figure 32 is a Raman scan of a Upilex-S substrate. There is a large scattering after 1800 cm\(^{-1}\) and 1604 cm\(^{-1}\), indicative of the molecular structure of the polymer surface. Figure 33 shows the Raman spectrum of a film deposited on the polymer substrate. The huge scattering at 1800 cm\(^{-1}\) and 1604 cm\(^{-1}\) is probably due from the substrate, but the broad peak extending from 1100-1400 cm\(^{-1}\) could be
Figure 28. Raman spectrum of a silicon substrate.
Figure 29. Raman spectrum of diamond material grown on a silicon substrate. Conditions were those of experiment #3 of the arc plasma.
Figure 30. Raman spectrum of strained sp³-hybridized polycrystalline diamond material grown on a silicon substrate. Conditions were those of experiment #9 of the dc plasma.
Figure 31. Raman spectrum of sp²-hybridized graphite-like material mixed with strained and disordered sp³-hybridized diamond-like material grown on a silicon substrate. Conditions were those of experiment #1 of the microwave plasma.
Figure 32. Raman spectrum of a Upilex-S substrate.
Figure 33. Raman spectrum of strained and disordered sp$^3$-hybridized diamond-like material grown on a Upilex-S substrate. Conditions were those of experiment #17 of the dc plasma.
due to highly strained and disordered diamond-like material. The broad peak at 1003 cm⁻¹ is not reported in the literature, but between 990-1007 cm⁻¹ is characteristic of substituted polyaromatics [52].
DISCUSSION

Three different plasma configurations were operated to produce diamond films and crystals on silicon, PI, and Upilex-S. The conclusion is that while graphite is present, definitive evidence for the deposition of diamond and diamond-like material exists. The name diamond-like films implies that they possess properties similar to but not quite as desirable as the properties of diamond.

Substrate surface ablation occurred in the ac plasma due to an arc forming between the two electrodes, which struck the surface of the substrate. It is generally held [15] that the presence of ion bombardment that results from placing the silicon substrate on the electrode helps stabilize the metastable diamond phase in PVD. The desired operating conditions exist when ionization beneath the sheath of the plasma generates the desired free radicals and ions that propagate the formation of the carbon chain and ensures the crystalline structure of the film. It is beneath the sheath around the cathode that the greatest changes in ion density, electron density, space-charge effects, electric field, and potential gradient exist. The effects of the ion bombardment more than compensate for the relatively minor ablative effects of the discharge giving a net deposition.

The arc plasma depositions on silicon showed optimum methane concentrations to be 1% or less. This is in good agreement with other work [12]. Lower methane concentrations produced films with good adhesion. Higher methane concentrations gave poorer adhesion and rougher surfaces with a cabbage-like morphology (Figure 13). In addition, the presence of carbon grit was observed at higher methane concentrations: this is presumably a product of gas phase nucleation forming carbon clusters.
with a variable hydrogen concentration. The Laser Raman scan (Figure 29) shows evidence of an appreciable Si content in those diamond films that have good adhesion properties and a complete covering of the surface (uniformity). This is due to nucleation that occurs on the B-SiC microcrystals that are formed by etching of the quartz reactor vessel, or any silicon present. There is a lattice matching of the B-SiC and C lattice planes in most atomic positions. In this manner, an increased Si content in the reaction process produces an increased density of B-SiC crystals, which acts to improve the adhesion, depth and growth rate of diamond thin films. However, B-SiC is also associated with increased planar defects, lattice disorder, and strain in the diamond phase [57].

The substrate was not ablated in the dc experiments. The glow discharge between the powered electrode and the grounding electrode, situated just above the substrate is the area where the gas mixture is partially dissociated and ion bombardment occurs. High substrate temperatures believed necessary for diamond growth to occur were attributed to the following three factors. First, the overall pressure was increased so that ions and radicals are not whisked away to the pump as at lower pressures thus keeping the ions and radicals in the plasma region longer and creating an ion bombardment environment abundant with diamond growth species. Second, the electrode separation was decreased which means that the plasma region is closer to the substrate creating a warming effect. Third the power was raised to increase the amount of radicals and ions that may attack the growing carbon chain.

The dc experiments were promising in that they were able to deposit amorphous carbons on polymer surfaces. The experiments with the polymer substrates determined the temperature at which the polymers degraded, the nature of
the surfaces that could be deposited at temperatures below degrading temperatures, and the adhesion between the polymer and the growing film. Polyimide and Upilex-S were chosen because they thermally degrade at higher temperatures than most polymers and because of their extensive use in the fabrication of chips in the microelectronics industry. Polyimide was used first but more emphasis was placed on Upilex-S because its thermal expansion and thermal resistance coefficients were closer to that of diamond than polyimide. A better match in thermal expansion coefficients would favor better adhesion of the deposited thin film to the substrate.

There is uncertainty whether nucleation occurs in the gas phase, or on the substrate surface. However, the weight of experimental evidence suggests surface effects predominate with silicon influencing competing crystalline and graphitic nucleation. If the surface chemistry of the growing film is controlled, the stabilization of the diamond phase is achieved with only one crystal grain phase. An unscratched substrate has no surface features, therefore any species that impinges onto a featureless surface has excess energy utilized for surface mobility. The role of the abrasions (Figure 10) are to create vacancies for nucleation sites on the microscopic level. These scratches inhibit surface mobility and help growth. The polymer surfaces studied did not exhibit abrasions when scratched with diamond powder. This could explain why nucleation sites were difficult to find on the polymer surfaces as opposed to the abundant amount of sites on the silicon substrate.

The holes or voids indicated in Figure #14 could be the preferential etching of graphite over diamond that occurs simultaneously with the deposition. Figure #16, which was much more crystalline than the amorphous
deposition of Figure #14, was photographed closer to the plasma region. This indicates the elevated temperature limit required for crystalline depositions.

It appears from the polyimide surfaces that at the plasma region, the polymer was degraded (Figure #20). It also seems that away from the plasma region, where deposition temperatures are lower, an amorphous deposition can result along with etching of graphite as shown by Figure #19. There was some indication of crystalline character in Figure #21 which was between the hottest and coldest regions of the deposition.

Figure #23 viewed the edge of a Upilex-S substrate with an amorphous deposition probably due to low surface temperatures, and cracks on the Upilex-S substrate due to the plasma heat. Graphite etching is believed to be shown in Figure #24 by the looks of the presence of the spider-web morphology. Figure #33 of the diamond-like film grown on Upilex-S is an indication that diamond films can be grown on polymers. The appearance of shifted and grossly wide diamond peaks suggests strain and lattice distortion at the interface. If a polymer could be found which better simulates silicon (similar thermal expansion coefficients and thermal resistance) less strain and lattice distortion might be expected in depositions on this substrate. As it stands the major difficulties in deposition on polymer substrates lie with the low thermal stability of the polymers, initially nucleating the surfaces, and producing sufficient adherance to that surface once nucleated.

The most noteworthy results from the microwave experiments were the ability to produce two morphologies at the same methane concentrations. A diamond-like film (experiment #1) was produced as well as a single crystal (experiment #2). The film however was not very uniform as
shown by the profilometry scan (Figure 26). The uniformity of the deposition can be related to the uniformity of the plasma. The electromagnetic mode known to predominate in the microwave applicator is TM_{01}. The TM_{01} mode for a cylindrical cavity has an electric field one-third and two-thirds the diameter of the cylinder. The electric field is located above the substrate accelerating ions cylindrically. The magnetic field, which is perpendicular to the electric field, affects radicals towards the center and the walls of the substrate due to the symmetry of the cylindrical cavity. The film morphology noted in experiment #1 was grown near the wall of the cylindrical cavity for it was deposited on the edge of the substrate. The crystalline morphology (experiment #2) was grown on the center of the substrate, the other node of the magnetic field. Consequently, the predominant growth mechanism would be through the initial formation of many nucleation sites where the greater density of nucleation sites would presumably cause an initial "island formation" of material followed by a coagulation of the many sites until complete coverage of the surface occurs if at all.

The substrate surface of experiment #1 in the microwave discharge was covered by many microcrystallites with multiple grain orientations that was observed with a reflectant light microscope. This condition is believed to be directly related to lower surface temperatures and hence lower surface mobility for the physisorbed radicals and ions from the plasma. Due to the fact that the microwave cavity had a low Q, the amount of energy stored was low. This could explain the relatively low surface temperature readings as well as the fact that the thermocouple was situated away from the plasma region. The mullite tube is a refractory material that absorbs large amounts of heat. This loss of heat to the substrate could explain the lower
surface temperatures experienced in the microwave experiments.
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