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This document details a study of the fundamental physical and chemical processes occuring in hot filament and laser assisted synthetic diamond CVD processes. The chemical model developed in this program permits a detailed analysis of previous investigations. This model suggests that several factors will limit the attainable purity and utility of synthetic diamonds grown by plasma or hot filament CVD techniques. A diamond deposition process based upon selective laser production of the chemical species which give rise to the films is described. This technique holds the promise of growing essentially pure diamond at rates comparable to existing schemes, and should permit co-deposition of selected dopant species to make novel new optic and electro-optic devices.

An experimental diamond CVD reactor has been designed, developed and tested to provide experimental verification of the model. The reactor has been run in two modes of operation; a hot filament CVD mode, and a laser-assisted hot filament mode. Films

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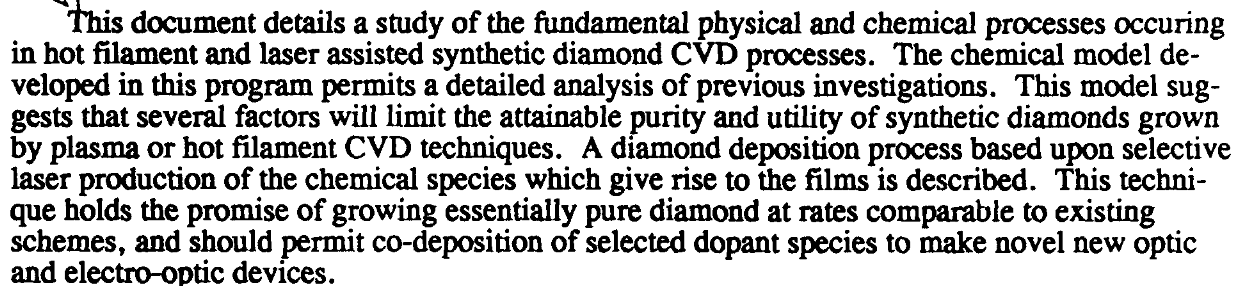
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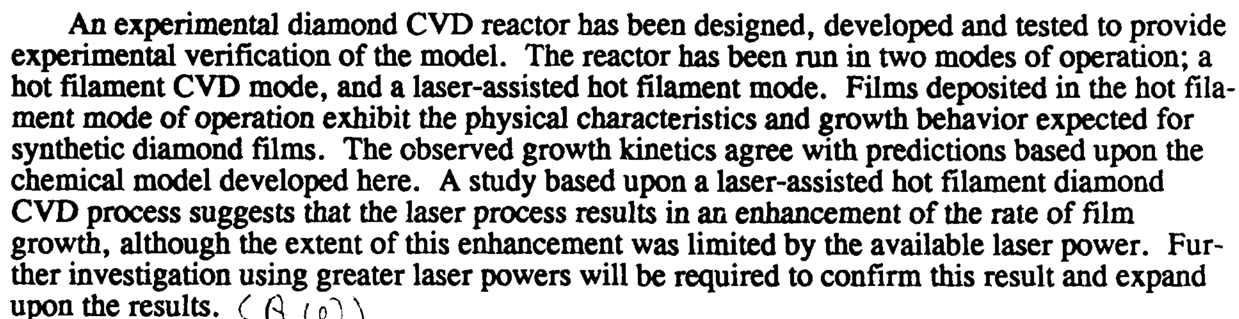
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I. INTRODUCTION

One of the most promising potential applications of synthetic CVD deposited diamond lies in the selective trace-doping of high purity, single crystals of a size suitable for laser and opto-electronic device construction. This goal has not yet been achieved due to a set of interrelated problems including the low purity of the films and the effects of the high deposition temperature on the lattice matched substrate. Since diamond is a slightly higher energy form of carbon than graphite, the issue of film purity in diamond refers primarily to the presence of graphite inclusions (double bonded carbon), which can easily dominate over the diamond if the deposition conditions are not right. The graphite inclusions disrupt the long range crystalline order because they act as seeds for new diamond crystallites which grow on top of the graphite patches but with altered orientations. A low density of graphite inclusions can result in the growth of a polycrystalline film even if the substrate is perfectly matched to the diamond lattice. This is probably the central obstacle to the opto-electronic development of synthetic diamond technology. A prerequisite for the growth of single crystal films is therefore a process which produces a minimum amount of double bonded carbon. Our photochemical approach, which produces a specific, well defined reactant (the methyl radical) is distinguished from the competing approaches principally by the absence of any double bonded reactant incident on the growing diamond surface. It is therefore uniquely suited to the CVD production of high purity, single crystal diamond.

Our laser selective approach gives us a complete understanding (and partial control) of the gas phase chemistry of the reactants incident on the growing diamond film. Although the surface processes involved in the diamond formation process are still unknown, we are in an excellent position to initiate studies of selected dopant co-deposition using a laser CVD process. An understanding of the interations which occur between the dopant atom and the diamond substrate can be acquired through the spectroscopic analysis of doped films.

As part of our Phase I effort we developed a basic chemical model of the gas chemistry responsible for diamond CVD growth, focusing upon the primary reactant species such as the CH_3 radical. The result has been the development of a photochemical scheme which allows these species to be selectively created and which should permit operation at lower reactor temperatures. In addition we have considered the impact of such a selective reactant production process on the overall reactor chemistry, specifically the need for excess hydrogen in the system. A recent theoretical study [1] of the role played by hydrogen in the diamond CVD process concludes that one of its roles is to scavange unwanted aromatic hydrocarbons and radicals in the gas phase, preventing the growth of graphitic material on the substrate. Since no undesirable radicals are formed using the technique we propose, and since the hydrogen termination of the surface bonds can be maintained from the hydrogen released by the methyl groups, excess hydrogen may not be required in the laser-CVD process.

We have constructed and demonstrated a diamond film CVD cell employing the hot filament technique, and have developed a simple chemical model of the process which predicts film growth rates for different chemical conditions. We have deposited diamond and diamond-like films on 1-2 cm^2 silicon wafer substrates to provide films for comparison with those formed in the laser assisted process. The reactor being used in these depositions was slightly modified and used in proof of principle laser assisted depositions. The results of these experiments (described below) are encouraging. A more sophisticated apparatus is described which will determine the potential for doping synthetic diamond films (and subsequently, single crystal synthetic diamond) by growing such films in the presence of trace concentrations of a dopant metal vapor and using spectroscopic absorption and emission techniques to characterize the resultant films.

BACKGROUND

The long standing interest in the development of synthetic diamond and diamond-like materials is the result of the unique properties of this material. These properties include its hardness, optical transparency, high electrical resistivity, chemical resistance, and high thermal conductivity. Diamond, being the higher energy lattice structure of carbon, can be formed from the lower energy graphite configuration if enough external energy is supplied. In an effort to duplicate the conditions believed to be responsible for its natural formation, early synthetic diamonds were formed by application of extreme pressure (10^5 Kg/cm^2) and high temperature (2500 K). Such processes do not lend themselves to general application.

Since about 1970, however, several techniques have been described which result in the formation of so-called "diamondlike" films which have many properties similar to those of diamond, and more recently, techniques producing diamond films of fairly high purity. These techniques have utilized ion beam deposition as well as thermal, plasma, and laser assisted chemical vapor deposition (CVD). The attraction of the CVD approach stems from its technical simplicity and its relatively mild processing environment. The real potential of the CVD process is the possibility of fabricating and modifying materials and devices without subjecting the substrate to the harsh conditions used in the classical synthetic approach. The most obvious anticipated applications are in the production of diamond coatings for optical and electronic materials. Diamond is the most efficient conductor of heat known and so has the potential for use as heat sink strips in large scale electronic circuits. Transparent surface coatings applied to laser mirrors could increase the damage threshold by dissipating thermal energy build-up and could protect the mirror coatings in harsh environments. Another application, with great potential, is the actual production of semiconductor material.

The diamondlike films, although they are not strictly diamond films, can be tailored to suit many applications. Examples of such applications would include the production of abrasion and corrosion resistant coatings for magnetic and optical information storage devices and the development of pitting resistant infrared windows for high speed airborne sensors. The technology for producing such films is fairly well established and commercial applications are being developed in both Japan and the U.S. The production of semiconductor quality diamond material will, however, require high purity films so much recent attention has been focused upon the vapor deposition processes which hold this potential.

EXPERIMENTAL TECHNIQUES

A variety of approaches have been employed in the production of diamondlike films yielding materials with a wide variety of useful properties [2-10]. In many of these studies the film produced had some, but not all of the properties of the natural diamond. For example, of the films produced in a study by Jansen et al [7], those which had a high transmission in the ultraviolet were reported to be soft, while films which were opaque were reported to be hard. In the following we review the techniques which have been used to deposit diamond films.

ION BEAM DEPOSITION

The techniques employing ion beam deposition are generally similar to those of Aisenberg et al. [2], Spencer et al. [3], and, more recently, Robertson et al.[11]. In these approaches a rare gas discharge plasma sputters small carbon ions from solid graphite loaded in the ion source

chamber. These ions are extracted from the source, accelerated to 50 - 100 eV, and targeted on the deposition surface. The target surfaces studied included polycrystalline and single crystal metals and ceramics such as Si, SiO_2, and Ni. In these studies the films developed over the exposed areas at a typical rate of 5 nm/sec (18 microns/hr) and consisted of a polycrystalline mix of cubic diamond with a single crystal particle size of up to 5 microns in diameter. Analysis using transmission electron beam diffraction has been used to identify the crystalline structures produced.

The ion beam techniques offer excellent spatial control of the deposition although the film quality is difficult to control or improve. It is, in fact, surprising that such techniques can produce diamond films of such quality since a carbon lattice energized by ion impact should form a significant amount of the lower energy graphite structure as it relaxes. It is quite possible that the graphite so formed is preferentially etched away by the ion impact since it has a two dimensional layered structure which cannot strongly bind to a surface. If this is occurring then lowering the ion beam energy will probably result in an increased retention of the graphite while a significant rise in ion energy will certainly give way to surface sputtering resulting in no film deposition.

CHEMICAL VAPOR DEPOSITION

The development of thermal and plasma deposition processes represented a significant advance in that these techniques are suitable for processing large surface areas. One of the first reports of high purity diamond film growth using a CVD approach was the work of Spitsyn et al. [4]. In this study a hot hydrogen plasma flow was passed over a graphite source where some of the atomic hydrogen reacted by etching carbon from the surface. This flow containing the carbon radicals was then passed over a heated substrate where diamond deposition occurred. The authors suggested the small hydrocarbon radicals formed in the chemical etching process were responsible for the film growth. The chemical etching environment was also cited as important in reducing the build up of graphite on the diamond surface. Such a cleansing environment would be important under the conditions employed since graphite impurities could easily develop. Much of the heated graphite sublimes as the triatomic species C_3 which has the same multiple carbon-carbon bond structure characteristic of graphite. The deposition of such species would probably lead to the growth of graphite rather than diamond. Essentially the same rate of film growth was realized whether the atomic Hydrogen was produced by thermal methods (1% concentration) or by electric discharge methods (10% concentration) suggesting that some unspecified process was limiting the rate of deposition.

Because of the complex nature of the chemical environment, both in the gas phase and on the surfaces, the actual concentrations of the reactive species were not determined nor were the identities of the hydrocarbon radicals and molecules ascertained. The films were grown on several different substrates such as diamond, copper, silicon and tungsten where nucleation was observed mostly on defects such as scratches and edge boundaries. This observation strongly suggests that the chemistry leading to diamond growth is occurring on the surface rather than in the gas phase. Without the reactant concentration profiles it is, however, impossible to estimate the deposition efficiency. The authors noted that the rate of formation varied greatly for different substrates and was found to be one to two orders of magnitude larger for those which form stable carbides (Mo and W) than for those which do not (Cu and Au). While such a correlation can clearly be made it provides little physical insight into the physics of the nucleation and bonding processes. It is interesting to note, however, that the metals promoting high growth rates both have high oxidation numbers (6) while those of the growth inhibiting metals

are low (2). This may be an indication of their ability to accommodate a newly adsorbed species. The resolution of such questions awaits a controlled deposition study.

A similar approach has been used by several Japanese groups with good results. Matsumoto et al. [5] modified the approach somewhat by eliminating the graphite carbon source and seeding methane gas (CH_4) directly into a hydrogen flow. The gas mixture was thermally activated above a hot substrate surface where deposition occurred. The films were analyzed using scanning electron microscopy and Raman spectroscopy which indicated the presence of both graphite and diamond in relative amounts which varied with the methane concentration and furnace temperature. For this experimental configuration the optimum methane fraction was found to be about 1%. In another study, Kamo et al. [6] replaced the thermal dissociation furnace with a microwave plasma discharge to provide the reactive radicals for the deposition. Similar results with respect to film quality were obtained and growth rates of 1-5 microns/hr were attained. More recently, Hirose and Terasawa [8] have demonstrated the thermal deposition of diamond films using a variety of organic hydrocarbon precursors. On the basis of their studies they have suggested that the methyl radical and the H atom play important roles in the process although the chemistry was not specifically investigated.

LASER ASSISTED CVD

There have been several reports of diamond and diamond like material deposition by a CVD process initiated by focused laser radiation [9,10]. In one study acetylene gas was used as the trace organic in a hydrogen flow and the output of an Argon-Fluoride laser focused into the gas above a hot surface. The acetylene gas, C_2H_2, has a weak molecular absorption at the output energy of the ArF laser (193 nm) and so can be excited specifically. With unfocused radiation the authors observed the formation of a brown film on the substrate which had the characteristics of a polymeric hydrocarbon material. With focused laser irradiation, however, a diamond-like film grew upon the substrate for temperatures between 40 and 800 C. The authors noted a strong nonlinear dependence of the film growth rate upon the laser power which indicates a multiphoton process is involved in the gas phase activation process. Recently [9-a], the authors have identified the film as a hard graphite material rather than a true diamond-like material. This suggests that the laser approach used did not add to the selectivity of the process but simply deposited energy into the molecules (probably through a multi-photon excitation).

The spectroscopy and photochemistry of the acetylene molecule are fairly well known [12,13]. In its ground electronic state, C_2H_2 is known to be linear in geometry. The bond dissociation energy, E, for the process

$$\text{H-C-C-H} + E \quad \text{H-C-C} + \text{H} \qquad (1)$$

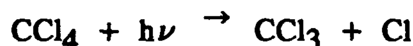
is E = 5.4 eV [12], while that for the process

$$\text{H-C-C-H} + E \quad \text{H-C} + \text{C-H} \qquad (2)$$

is E = 9.9 eV [13]. The output of the ArF laser, at 193 nm, corresponds to an energy of 6.4 eV which is sufficient to induce process (1) with a single photon transition but not process (2). The C_2H formed by (1) reacts with molecular hydrogen and with the C_2H_2 precursor to produce large organic chains and polymers [14,15] of the type deposited in the study using unfocused laser irradiation. When the laser power density is increased, by focusing the beam over the sub-

strate, the probability for inducing multiphoton processes increases and process (2) can occur via a two photon excitation. The CH radical produced in this process will react in the hydrogen flow through a three body interaction to yield CH_3, which is unreactive in hydrogen and acetylene. The CH_3 radicals are believed to be responsible for the growth of diamond film however the chemical mix produced by this photoprocess would be expected to result in a very impure diamond (or hard graphite).

Another, more recent, report [10] describes how diamond films are produced when the output of an ArF laser (193 nm) is passed through a mixture of CCl_4 and H_2 above a hot (800 C) surface. The CCl_4 molecule has a broad absorption in this wavelength range with a cross section of $\sim 10^{-18}$ cm^2 [13]. At these wavelengths the molecule is dissociated and can react in the hydrogen flow to produce other species. One likely sequence of events is the loss of a single Cl atom during each laser pulse;



$$CCl_4 + h\nu \rightarrow CCl_3 + Cl$$

followed by rapid reaction with hydrogen

$$CCl_3 + H_2 \rightarrow CCl_3H + H.$$

The new product, CCl_3H, can absorb a photon from the following laser pulse, losing another Cl atom and reacting to add another H atom. This chain of events will continue until the last Cl atom is lost producing the CH_3 radical, which does not react with molecular hydrogen at these temperatures. Based upon this model of events, no diamond film growth would be predicted if the gas flow rate were to be increased such that photodissociation products were removed from the deposition area in the time between laser pulses.

CHEMICAL MECHANISMS

The methyl radical, CH_3, is generally believed to be the basic building block for the diamond films. In a recent theoretical investigation, [16], it has been shown to react by sequential displacement of hydrogen atoms on the surface. The methyl radical, with sp^3 hybridized bonds, can undergo such sequential displacements and maintain a four-point bond structure characteristic of diamond. This suggestion is consistent with experimental observations in that most of the small mono-carbon species formed, either in a discharge or by (two photon) photodissociation, will react in a hydrogen rich environment, building up to the methyl radical which is unreactive in hydrogen at moderate temperatures. Larger carbon radicals with multiple bonds between carbon atoms (such as C_2H) would generally react to produce other species, often retaining the multi-bond character. Because the electronic structure of these radicals is similar to that of solid graphite, these species may seed the growth of graphite inclusions. The synthesis of ultra-high purity diamond films will require precise control of these chemical species. The attraction of our approach is based upon the great selectivity provided by the photochemical production of methyl radicals from acetone.

4. PHASE I TECHNICAL OBJECTIVES

The technical objectives of our Phase I program were to;

1) design and construct an apparatus consisting of; a) a gas flow cell containing a temperature controlled deposition surface and, b) an optical system to stimulate photodissociation and laser assisted CVD;

2) use this system to photodissociate acetone vapor at a wavelength near 300 nm. and measure the rate of diamond film deposition on wire mesh substrates;

3) analyze the deposited film quality using Raman scattering spectroscopy and use a mass analysis to determine the rate of deposition;

4) compare these findings with the predictions made using a model (outlined in this proposal) which assumes the film growth results from methyl radical adsorption on the substrate surface;

5) evaluate the potential of laser assisted CVD to making pure diamond films and develop a Phase II program to produce diamond films based upon the most promising configuration of this technique.

II. TECHNICAL

Much of the published work described above indicates that the methyl radical, CH_3, plays an important role in the formation of diamond films. The work discussed here seeks to determine just what this role is and whether the more selective control of CVD chemistry possible with a truly selective laser activation process will make high purity diamond film growth possible at a rate suitable for electronic device application. In this section we present a technical discussion of the laser CVD production of methyl radical and show that it will address these questions. To do this we must examine the photophysics of the laser CVD production, model the kinetic process, calculate the expected film growth rate, and devise an experimental configuration. We first examine the technique proposed for methyl generation to determine if it can be produced in sufficient amounts and purity. For several reasons the acetone molecule represents an attractive source for the generation of methyl radicals. Both the molecular spectroscopy and the reaction kinetics of this species are well known making an evaluation of its utility easy.

PHOTOCHEMISTRY OF ACETONE

The absorption spectrum and photochemical decomposition of acetone have been the subject of several studies. The absorption profile of acetone was first measured by Porter and Iddings [17] who determined the absorption coefficient as a function of wavelength in the spectral range of interest (250 - 350 nm). Much of the detailed spectroscopy of this molecule has been summarized by Herzberg [12]. A list of the relevant molecular constants as well as the appropriate thermochemistry is presented in TABLE I.

TABLE I MOLECULAR ACETONE

MOLECULAR FORMULA	CH_3COCH_3
MOLECULAR WEIGHT	58 amu
DISSOCIATION ENERGY (CH_3CO---CH_3)	3.3 eV
DISSOCIATION ENERGY (CH_3COCH_2---H)	4.2 eV
FIRST EXCITED STATE	3.8 eV
VAPOR PRESSURE (273 K)	60 Torr

The photochemistry of acetone has been detailed by Noyes et al. [18] and by Okabe [13]. Above a temperature of about 100 C, optical excitation of acetone with light of wavelength below 313 nm results in photodissociation in which the primary process yields two methyl radicals and a molecular CO fragment. Since the energetic threshold for photodissociation producing H atoms is 4.2 eV (corresponding to a wavelength of 295 nm) photodissociation energies should

not exceed this value to ensure that the production of methyl radicals is not accompanied by that of unwanted species.

The exact concentration of methyl radicals produced via UV photodissociation can be calculated using the absorption coefficients measured by Porter and Iddings [17] since the dissociation quantum yield below 310 nm and above 100 C is essentially unity. This measurement was based upon a Beer's Law approach

$$I_t = I_o 10^{-ecd} \qquad (3)$$

where I_t is the transmitted light intensity, I_o is the incident light intensity, e is the measured extinction coefficient, c is the concentration in moles/liter, and d is the traversed thickness in cm. For a 3 torr partial pressure of acetone the molecular concentration is about $2*10^{-4}$ moles/liter and at 296 nm the measured value of e is 9. For an effective optical path length of 2 cm (over the heated substrate) the fraction absorbed is

$$\text{FRACTION ABS.} = 1 - 10^{-(.0036)} \qquad (4)$$

or about 1%. An input laser pulse energy of 60 μJ at 296 nm (photon energy = 4.2 eV = $6.7*10^{-19}$ Joules) is comprised of about 9×10^{13} photons and so about 9×10^{11} molecules would undergo photodissociation producing 1.8×10^{12} methyl radicals (two for each absorption). This methyl concentration could give rise to a maximum film growth rate of 1.8×10^{12} atoms/pulse or, for 50 Hz operation, about 3.25×10^{17} atoms/hr. This deposition rate corresponds to a film growth rate of 0.025 μ/hr.

It will be shown in the next section that methyl concentrations of up to 10^{14}/cc can be efficiently utilized in the production of diamond films (significantly higher concentrations are difficult to maintain due to reactive loss mechanisms). It will be possible to achieve these concentration levels by increasing the acetone concentration (×3-5), and by using more intense excimer laser outputs (XeCl laser with 10 - 20 mJ energy per pulse at 308 nm.).

KINETIC SCHEME AND GAS CHEMISTRY

Before any diamond deposition technique can be fully developed it will be necessary to examine the gas phase reaction kinetics describing the chemistry occurring over the surface to determine what limitations may exist. Under low intensity irradiation, the gas phase methyl concentration will be low. Under these conditions the only gas phase reaction involving the methyl radical is that with the acetone precursor:

$$CH_3 + CH_3COCH_3 \quad CH_4 + CH_2COCH_3 \qquad (5)$$

For conditions of high intensity irradiation where the methyl radical concentration becomes high a second reaction could become important:

$$CH_3 + CH_3 + M \quad CH_3CH_3 + M \qquad (6)$$

Both of these reactions result in the undesirable loss of the methyl radical and the production of an unwanted side-product. The first order rate constant for reaction (5) has been determined [19] to be small, less than 10^{-19} cc molec^{-1} sec^{-1}. This means that for an acetone concentration of [illegible]10^{16} molec/cc (corresponding to a 1 torr pressure), and a reactant residence

time of a few milliseconds, the methyl fraction lost by reaction (5) would be only a few parts per million. While the production of methane should not have a detrimental effect upon the deposition chemistry the CH_2COCH_3 radical is likely to undergo further reactions. It is not clear whether such other products would have an effect upon the deposition purity at these low concentrations but for optimum results conditions should be controlled so as to minimize their impact (reduced acetone pressures and fast flows).

Recombination rates for processes such as (6) depend upon several factors, specifically; a) the methyl radical density, b) the total gas density, and c) the temperature of the system. The first factor simply represents the need to bring two radicals together for reaction. The second factor results from the need to deactivate the recombination product before it can re-dissociate and is related to the third factor in that a cool bath gas is more efficient at removing energy than a hot one. The second-order rate constant for reaction (6) has been measured to be about $3*10^{-11}$ cc $molec^{-1}$ sec^{-1} at a temperature of 50 C [20] and decreases to a value of $5*10^{-13}$ cc $molec^{-1}$ sec^{-1} at a temperature of 800 C [21]. This rate constant is large enough for this reaction to be the overall rate limiting process in the film deposition process. The observation that diamond film growth rates increase with temperature supports this suggestion since the greater methyl radical densities needed for increased deposition rates can be reached only if the loss to gas phase reaction is slowed. The recombination process, which at moderate densities (10^{12}/cc) will be the dominant mechanism for loss of methyl radicals, has a strong negative temperature dependence as noted above. For this reason an increase in system temperature will result in a decrease in the rate of this reaction, leaving a greater number of methyl radicals available for film deposition. While this reaction will occur to some extent at any methyl concentration of practical interest, the production of ethane should not feed the growth of graphite inclusions and, overall, simply represents a loss of potential reactant. Such a limitation would have important implications for the development of more efficient processes.

We have modeled the species concentration profiles for methyl radicals entrained in a 10 torr acetone flow for a range of conditions. This model assumes an experimental configuration in which the laser beam is passed over the hot deposition substrate and the photo-product reactants carried to the surface by the gas flow and through diffusion. The calculations described below have been carried out to provide a greater understanding of this chemical system and to suggest an optimum set of conditions for the deposition process. The model takes into account only the chemistry of the methyl radicals and the parent acetone molecules. The presence of hydrogen atoms (formed by hot wire atomization processes) is assumed but is not specifically treated in the chemical reaction equations. The radical-radical reaction;

$$CH_3 + H + M \text{ --- } CH_4 + M$$

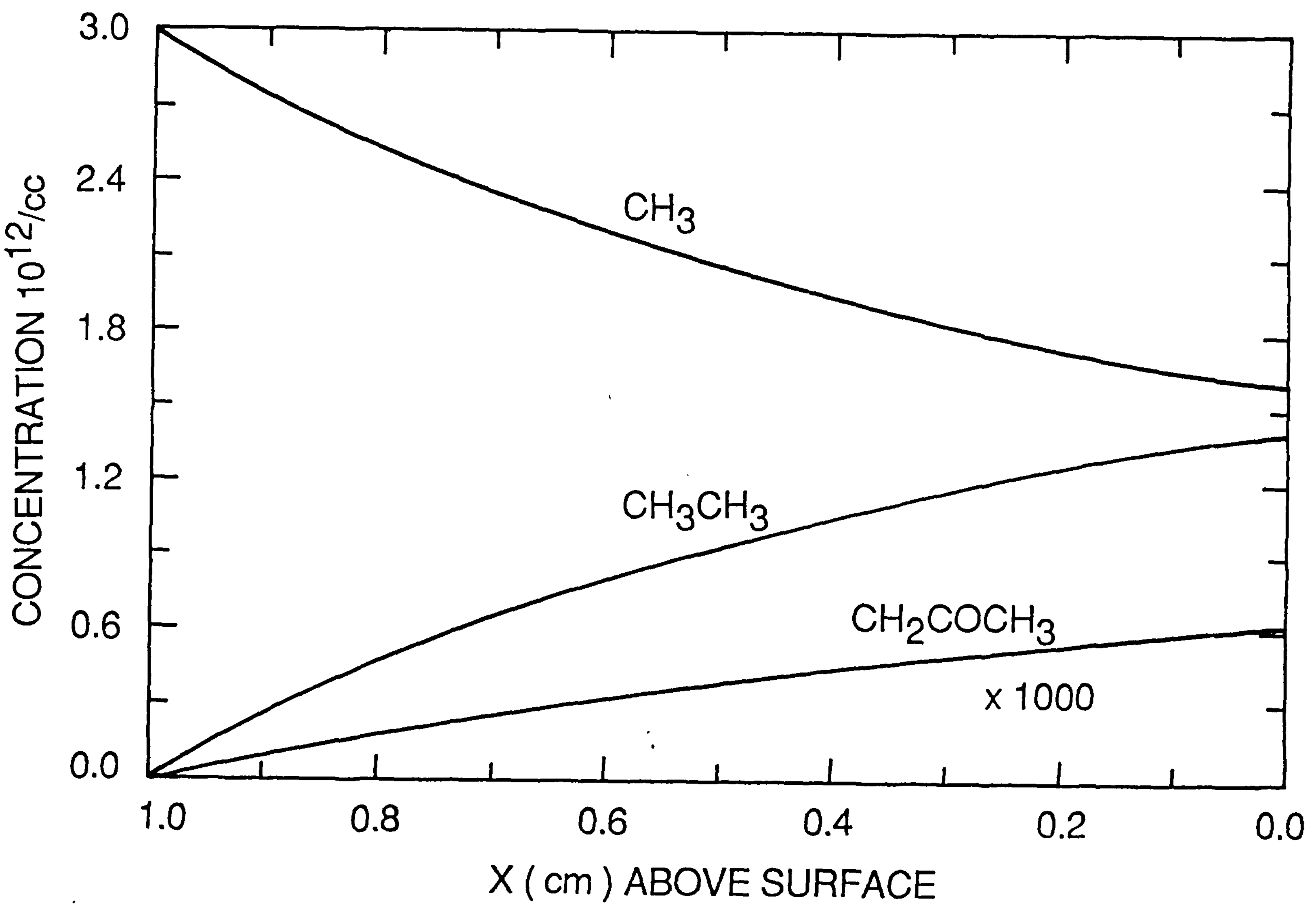
is believed to be very slow at the high temperatures used in the deposition processes. The model assumes that a 1 cc volume of acetone gas located 1 cm above a substrate is irradiated so as to form methyl radicals in a concentration ranging from 10^{11}/cc to 10^{15}/cc. These radicals are carried along in the flow (the speed of which is varied from 1 m/sec to 10 m/sec) and undergo the reactions discussed above. The effective temperature of the model system is varied from 300 to 800 K by changing the three body methyl recombination rate using the temperature dependence given by Van Den Bergh [21]. Results of these calculations are shown in Figures 1 through 3. In these figures the density of the methyl radical is plotted against the distance from the substrate surface to which the flow is moving. In such a flow system the x-axis is equivalent to a time axis with time increasing with decreasing distance.

Since the rate constant for reaction (5) is very small fairly high concentrations of acetone can be used. While this permits greater initial methyl concentrations to be formed for a given laser power this advantage is offset somewhat by the rapid loss of methyl radicals through recombination. This effect can be seen in Figure 1 where the decrease in methyl concentration is mirrored by the rising concentration of ethane. The reaction product growth curves for CH_3CH_3 and CH_2COCH_3 are not explicitly shown in Figures 2 and 3 however it should be understood that the dominant product is ethane.

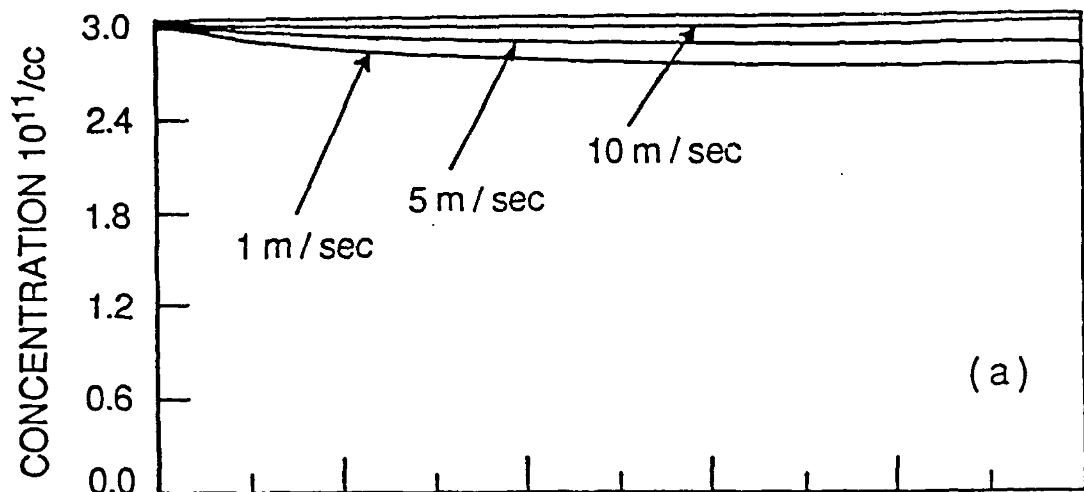
FIGURE 1 Concentration profiles for methyl radical and the recombination reaction products as a function of height over the film deposition substrate. The initial methyl concentration at a height of 1.0 cm. above the surface is $3*10^{12}$ radicals/cc. The system temperature and flow speed used for this calculation were 300 K and 5 m/sec respectively. The concentration of the CH_2COCH_3 radical has been multiplied by 1000 to be seen on this scale.

FIGURE 2 Concentration profiles for methyl radicals as a function of height above the deposition substrate for three initial methyl concentrations of; a) 10^{11}/cc, b) 10^{13}/cc, and c) 10^{15}/cc. Three flow rates are shown for each initial concentration and all correspond to a temperature of 300 K. The curves shown in c) have been multiplied by 10 to retain the same scale as Figure 3-c.

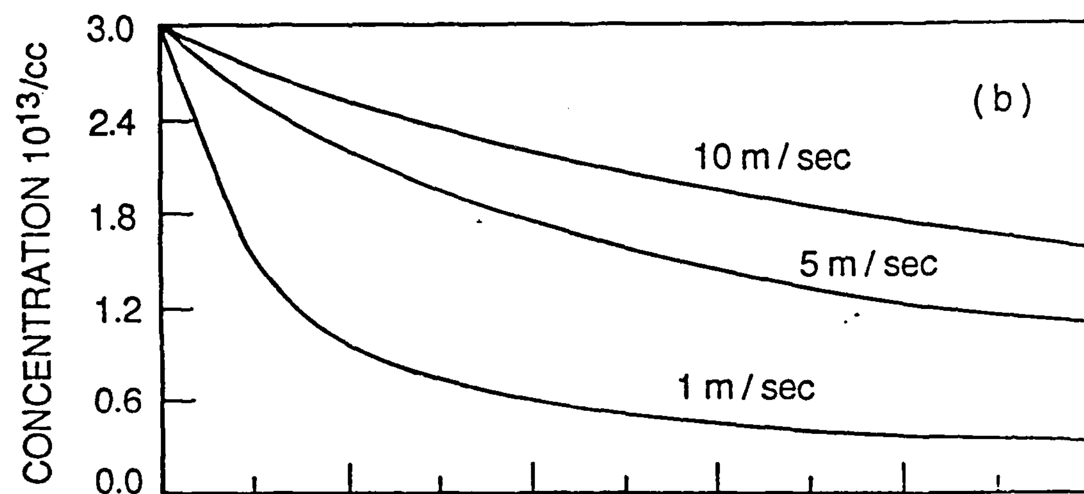
FIGURE 3 Same as Figure 2 but the flow rate has been fixed to a value of 5 m/sec and three temperatures shown for each initial concentration. Note that the curves corresponding to the two highest temperatures in a) have been omitted. Very little change is seen in either case.



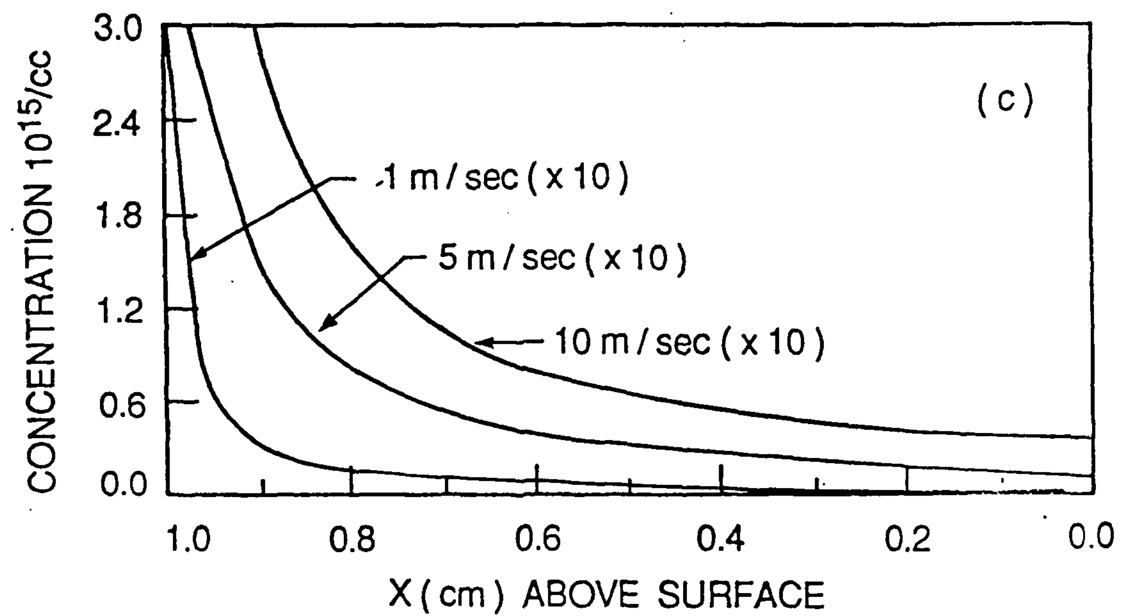
CONCENTRATION 10^{12}/cc
3.0
2.4
1.8
1.2
0.6
0.0
CH_3
CH_3CH_3
CH_2COCH_3
x 1000
1.0
0.8
0.6
0.4
0.2
0.0
X (cm) ABOVE SURFACE



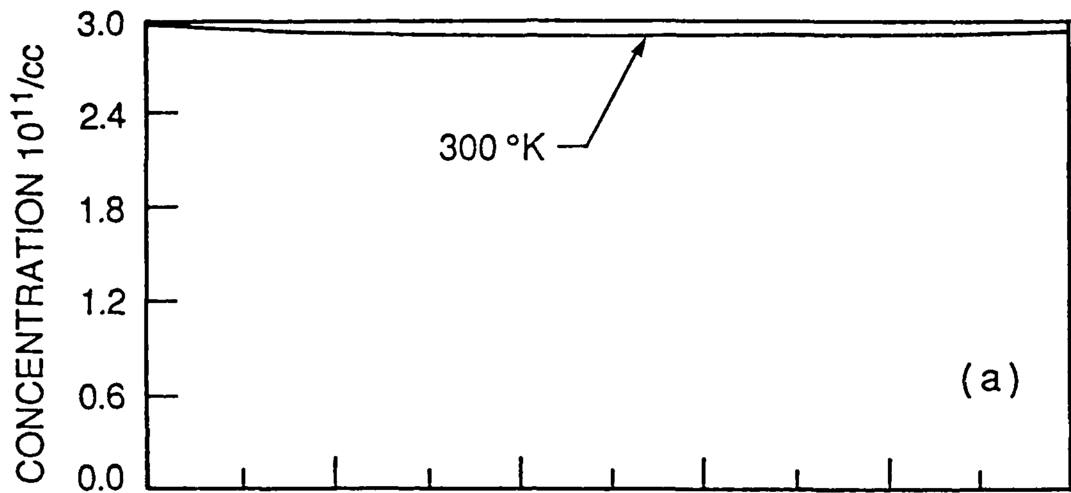
3.0
2.4
1.8
1.2
0.6
0.0
CONCENTRATION 10^{11}/cc
1 m / sec
5 m / sec
10 m / sec
(a)



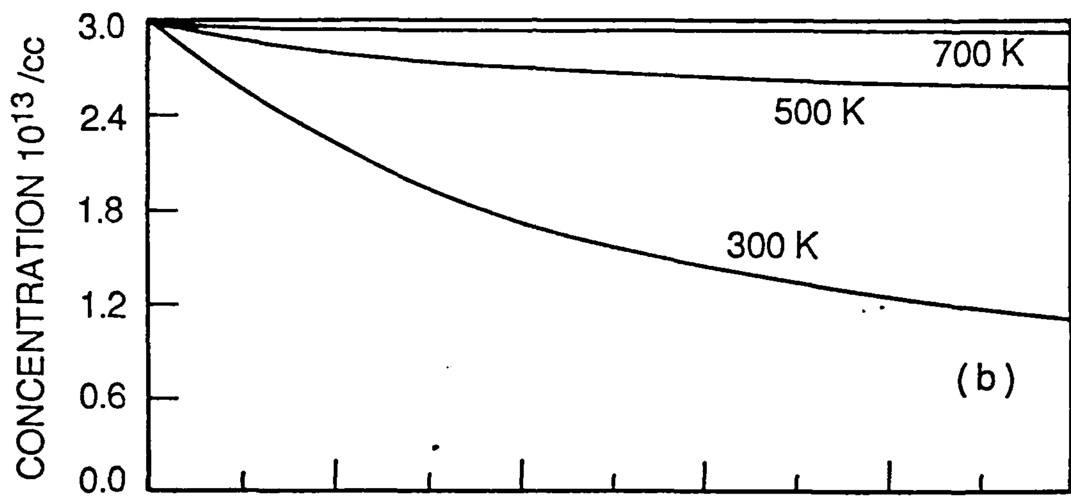
3.0
2.4
1.8
1.2
0.6
0.0
CONCENTRATION 10^{13}/cc
(b)
10 m / sec
5 m / sec
1 m / sec



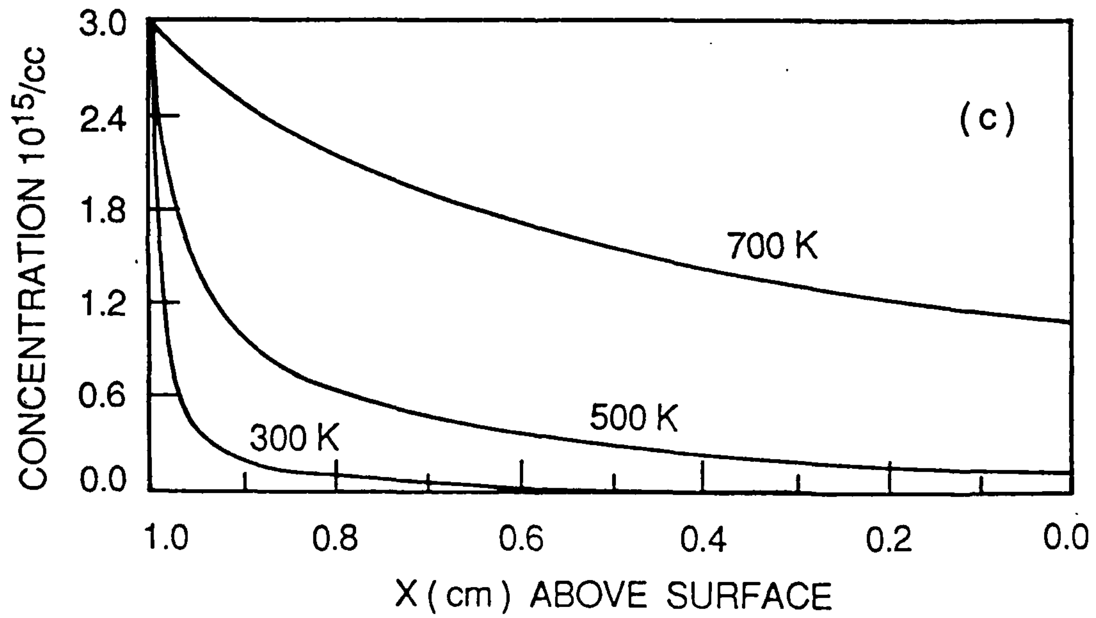
3.0
2.4
1.8
1.2
0.6
0.0
CONCENTRATION 10^{15}/cc
(c)
1 m / sec (x 10)
5 m / sec (x 10)
10 m / sec (x 10)
1.0
0.8
0.6
0.4
0.2
0.0
X (cm) ABOVE SURFACE



CONCENTRATION 10^11/cc
3.0
2.4
1.8
1.2
0.6
0.0
300 °K
(a)



CONCENTRATION 10^13/cc
3.0
2.4
1.8
1.2
0.6
0.0
700 K
500 K
300 K
(b)



CONCENTRATION 10^15/cc
3.0
2.4
1.8
1.2
0.6
0.0
(c)
700 K
500 K
300 K
1.0
0.8
0.6
0.4
0.2
0.0
X (cm) ABOVE SURFACE

A rapid loss of reactant radical is seen in Figure 2 for the flows with high initial methyl concentrations (b and c). Under these conditions the radical concentration downstream is insensitive to moderate increases in the initial density. For example, an increase in the initial methyl concentration of 100 fold in going from Figure 2b to 2c results in only a factor of two increase in the radical density at the surface even for the fastest flows. For a fixed initial concentration, however, a higher flow rate increases the radical concentration reaching the surface since the species undergoes reaction for a shorter period of time.

Using a fixed flow rate of 5m/sec, the effect of system temperature is demonstrated in Figure 3 for the same range of initial radical concentrations of Figure 2. For initial methyl concentrations of 10^{13} and 10^{15} per cc, which suffered substantial reaction loss at 300 K, the effect of increased temperature is dramatic. A comparison of the data presented in Figures 2 and 3 suggest a possible trade-off of temperature and flow rate which may be useful for some coating applications. While the data clearly suggests that the use of both high flow and high temperature will maximize the film deposition rate, certain substrates do not allow for the use of very high temperatures. By increasing the gas flow rate, however, it should be possible to maintain a high deposition rate at a reduced temperature.

FILM GROWTH RATE

The actual film growth rate for a CVD based process is dependent upon not only the chemical content of the vapor but the molecular transport properties of the flow constituents. The transport question is basically one of diffusion and can be modeled as a random walk process. As such, a diffusion range can be defined which will grow as the square-root of the product of temperature, elapsed time, and the inverse of the pressure. The present case is more complex since the diffusing species, (CH_3), is also undergoing self-reaction (recombination) at a rate which is concentration dependent. In addition to the flow movement of the bulk carrier gas in the cell, the reactants formed will undergo diffusion which results in a lower limit to the net transport rate. This effect can be estimated by calculating the time required to diffuse over a specified range. The diffusion range can be calculated if the system temperature, total pressure and species of interest are specified. The system temperature will determine the molecular velocity. For the methyl radical at a temperature of 700 K (a temperature intermediate between the hot substrate and the reaction chamber walls) the mean velocity is

$$v = 9.2 \times 10^4 \text{ cm/sec}.$$

Since diffusion is a random process the mean position (or center of mass) of a population consisting of many molecules will not shift in time however, the dispersion, which will be a measure of the spread, will grow. The mean displacement per step (or collision in a molecular model) can be used to determine this dispersion. The pressure dependence is usually expressed in terms of a time factor representing the mean time between collisions. For a total pressure of 50 torr and a temperature of 700 K, the mean time between collisions for a species such as the methyl radical is

$$t = 10^{-7} \text{ sec}.$$

The diffusion range is then defined as the root-mean-square displacement for a molecule after an elapsed time, T, and can be expressed as

$$R = v \times (2/3 \times t \times T)^{1/2}.$$

During a 1 msec time period the radicals will have diffused over a range of

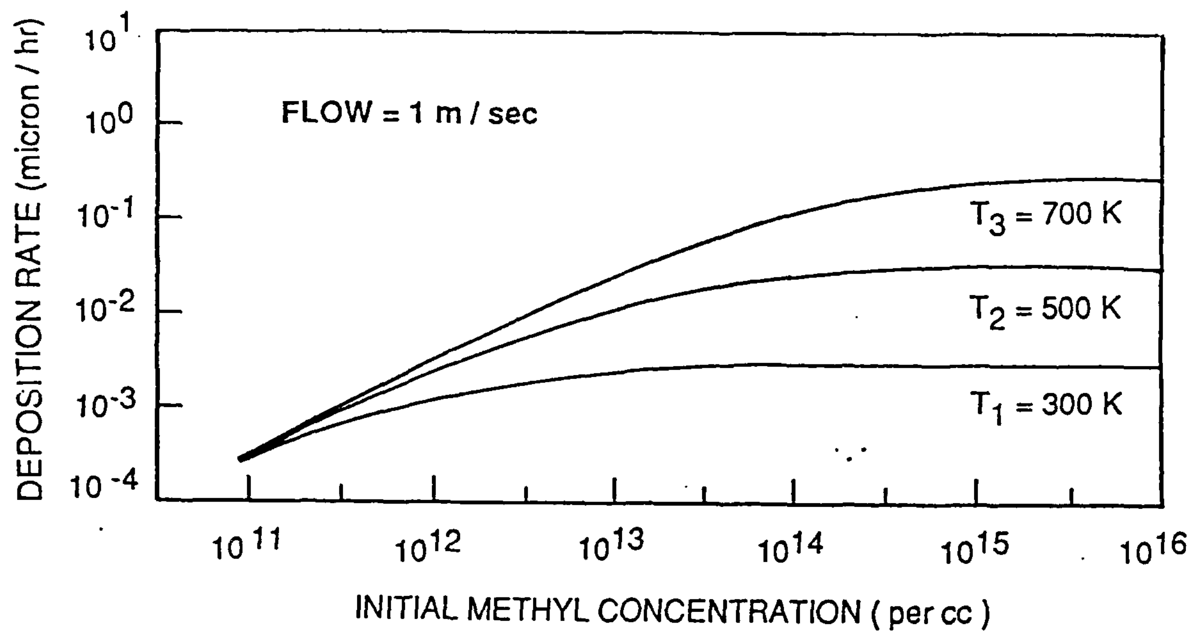
$$R = 7.5 \text{ mm},$$

a rate of travel which can be compared to a flow velocity of 7.5 m/sec. In order to ensure proper transport of the reactant radicals to the deposition surface the bulk gas flows should be less than this characteristic velocity.

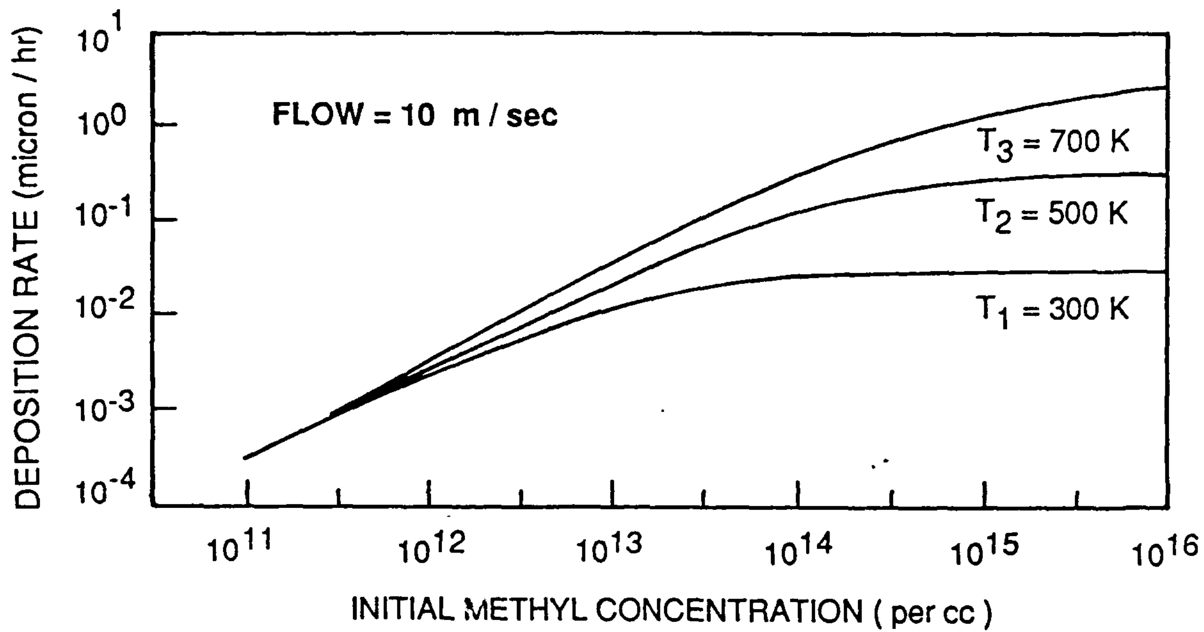
The species concentration profiles presented in Figures 1 - 3 can be used to determine the reactant flux reaching the film substrate. Within the framework of this model we can calculate the diamond film deposition rate expected for a given set of conditions. Assuming a sticking coefficient of 0.1, the calculated deposition rates for a 1 cm^2 surface are presented in Figures 4 and 5 for gas flow rates of 1 m/sec and 10 m/sec. These calculated rates assume a 1 cc volume of methyl radicals formed in the concentrations given on the x-axis, at a height of 1 cm above the substrate and at a repetition rate of 50 Hz. These parameters correspond to those anticipated for the proposed study. The rapid loss of methyl radicals at high concentrations results in a leveling off of the deposition rate as seen in both plots. Based upon these calculations a deposition rate of several microns per day could be achieved at moderate temperatures (500 K) and flow rates of a few m/sec).

FIGURE 4 Diamond film deposition rate for three temperatures calculated as a function of initial methyl concentration assuming the experimental geometry and conditions described in the text for a gas flow rate of 1 m/sec. The surface reaction efficiency is assumed to be 0.1.

FIGURE 5 Same as Figure 4 but for a gas flow rate of 10 m/sec.



DEPOSITION RATE (micron / hr)
10^1
10^0
10^-1
10^-2
10^-3
10^-4
FLOW = 1 m / sec
T3 = 700 K
T2 = 500 K
T1 = 300 K
10^11
10^12
10^13
10^14
10^15
10^16
INITIAL METHYL CONCENTRATION (per cc)



DEPOSITION RATE (micron / hr)
10^1
10^0
10^-1
10^-2
10^-3
10^-4
FLOW = 10 m / sec
T3 = 700 K
T2 = 500 K
T1 = 300 K
10^11
10^12
10^13
10^14
10^15
10^16
INITIAL METHYL CONCENTRATION (per cc)

III. EXPERIMENTAL FEASIBILITY EXPERIMENTS

The lack of a credible and comprehensive chemical model for the processes leading to the growth of diamond films makes any simple model, such as that presented here, subject to uncertainty. Some experimental testing of the ideas or verification of the predictions would permit refinement or extension of this model and may result in the formulation of a comprehensive mechanistic understanding. There are two possible approaches to such experimental testing;

i. develop and operate a laser-CVD system to grow diamond films using only a laser to form reactants over a hot deposition surface;

ii. operate a laser assisted-CVD system in conjunction with a proven deposition process and look for laser enhanced deposition.

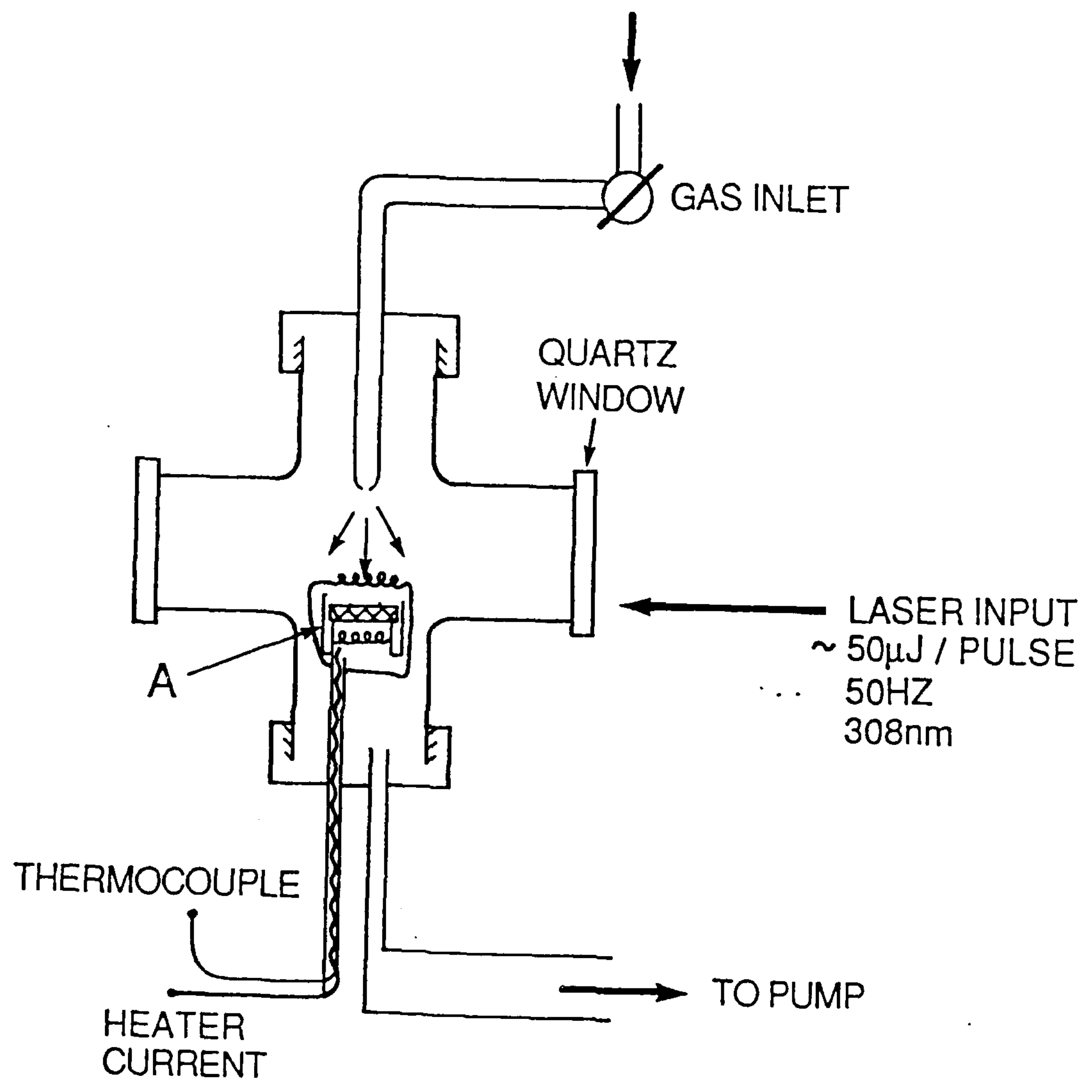
Since the specific roles played by species such as H atoms have not been determined it is possible that the first approach may fail for reasons unrelated to the role that the methyl radical may play. The second approach offers the best test of the chemical model presented here, however it requires that the degree of enhancement in the deposition rate or purity be great enough to be discerned above that of the normal deposition process. Using an existing laser system based upon a nitrogen laser and frequency doubled pulsed dye laser we can generate $\sim 60\ \mu J$ per pulse at 296 nm. From the discussion in Section II this can result in an additional growth rate of $\sim 0.025\ \mu m/hr$.

The experimental program proposed here can be broken down into; 1) the deposition stage, and 2) the film analysis stage. In the deposition stage the diamond CVD process will be carried out over the range of conditions covered in the model discussed above using a small gas flow/deposition cell. The deposition characteristics will be measured for both the standard approach as well as the laser assisted CVD process. The range of conditions will include gas flow rates between 1 and 10 m/sec, temperatures between 300 and 1000 K, and gas pressures and laser intensities sufficient for the photodissociation process to yield reactant methyl radicals in concentrations of about 10^{12} /cc. The film analysis will be performed using optical microscopic and scanning electron microscope analysis to determine the film growth rate and crystalline nature of the deposits produced.

HOT WIRE DIAMOND CVD SYSTEM CONFIGURATION

We have used the hot filament approach as the deposition technique best suited to making an evaluation of the laser enhanced process. This technique uses a hot tungsten filament wire located a few mm above the deposition surface to provide the reactants for diamond film growth. In this approach hydrogen atoms are efficiently formed by dissociation of H_2 on the hot filament surface. In addition, the acetone molecules which strike the wire surface will also undergo dissociation to produce CH_3 radicals as well as other species which will diffuse away from the wire surface, either toward the heated deposition substrate surface, or to be lost to the chamber walls. The gas flow cell used in both the deposition studies is schematically illustrated in Figure 6.

FIGURE 6 Schematic representation of the gas flow film deposition cell used for the studies described here. The gas enters the cell through an inlet tube shown at the top, and is passed over the heated deposition substrate which sits above the pumping orifice. The laser beam (when used) is passed directly over the substrate surface, and impinges at the surface edge at an angle of ~30 degrees. The initial density of radicals formed by photodissociation is controlled by the intensity of the laser and the acetone pressure in the flow. Both the substrate temperature and gas flow rate are monitored.

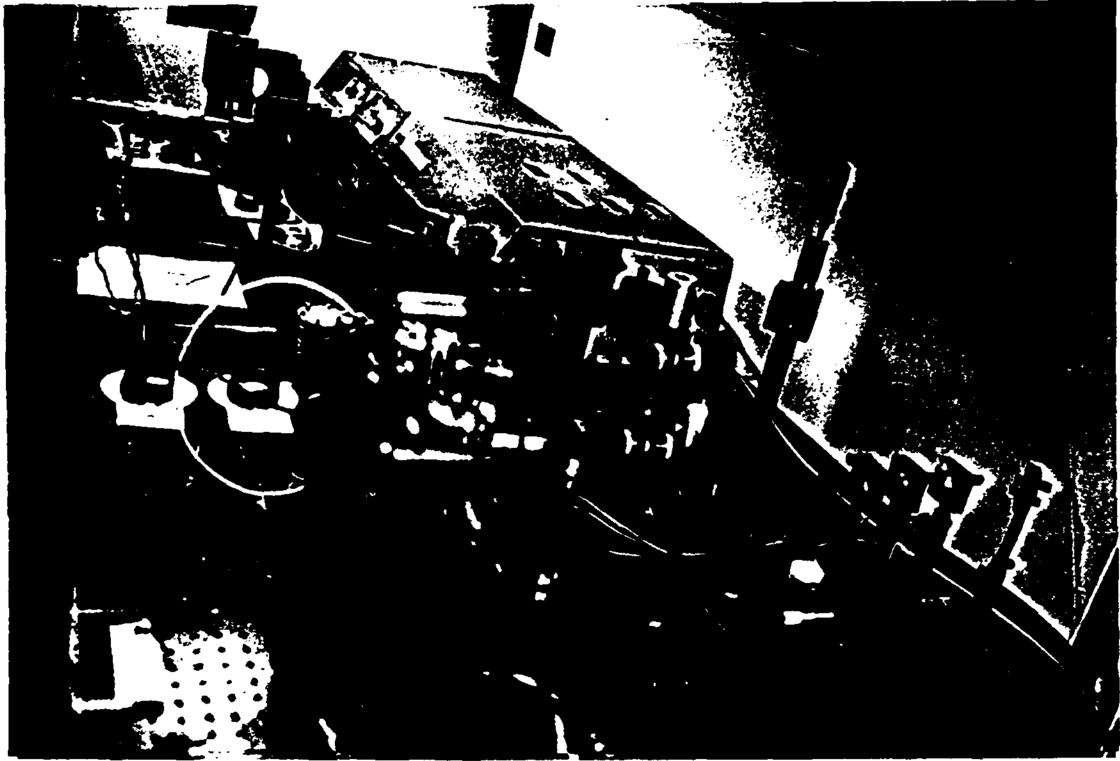

GAS INLET
QUARTZ WINDOW
LASER INPUT
~ 50µJ / PULSE
50HZ
308nm
A
THERMOCOUPLE
HEATER CURRENT
TO PUMP

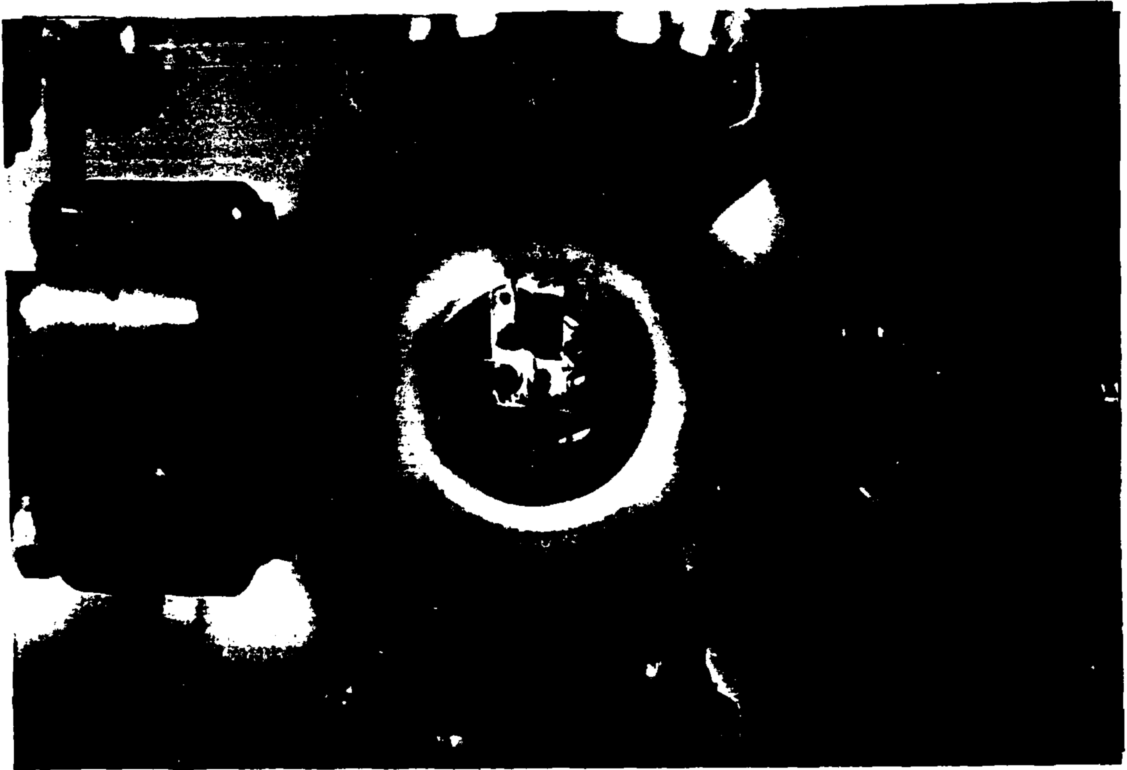
The CVD system consists of a small six-way cross fitted with fused-silica quartz windows on two ports, gas feedthroughs on two ports, substrate mounting lines and electrical feedthroughs on another and a vacuum pump orifice on the last port. Thin solid substrate samples were used instead of wire mesh substrates because the slow gas flow speeds and rapid diffusion rates made the flow-through geometry unnecessary. The use of solid wafer samples made the film analysis stage easier since fairly even coverage resulted. The film substrates used have been electronics grade silicon wafer pieces of $\sim 1\ cm^2$ size which have been roughened on the *surface by rubbing with a oil paste of fine* (10 micron) diamond dust for several seconds. The surfaces of the silicon samples are carefully cleaned after surface preparation and analysis by SEM reveals no significant residual of diamond on the surface. The temperature of the silicon substrate and the stainless steel mounting plate is controlled by a small heater assembly mounted below the substrate and monitored by a thermocouple wire. The flow speed would be controlled by throttling the pump and is typically 100 SCCM as measured using a Teledyne-Hastings flow meter. The total pressure in the deposition cell is set at 50 torr, with the acetone constituting 2-3 % of the total and H_2 accounting for the rest.

The laser system used in the deposition experiments was a frequency doubled dye laser pumped by a Molectron nitrogen laser. This laser system is capable of up to 50 Hz. operation and can deliver up to 0.06 mJ/pulse at a wavelength of 300 nm. From the discussion on the photochemistry of acetone, a pulse of this energy at 296 nm will produce about $4*10^{12}$ methyl radicals per cm pathlength in a 10 torr flow. A multipass optical arrangement could easily increase this number by an order of magnitude. The expected deposition rate for radical production in this range can be estimated from Figures 4 and 5 (these graphs refer to deposition on a $1.0\ cm^2$ substrate) to be up to 0.025 micron per hour at 500-700 K for gas flow speeds comparable to the diffusion speed (several m/sec). Photographs of the laser/deposition cell layout, as well as the glowing hot deposition substrate mount in operation are presented in Figures 7 and 8.

FIGURE 7 Photograph of the laser assisted CVD system constructed to study laser assisted diamond film deposition. The laser beam is directed from the pulsed dye laser at the top of the photo, through a telescope and frequency doubling crystal, in the foreground, and the optically filtered (to remove the $\sim$6000 Å light) output directed into the deposition cell seen in the center foreground.

FIGURE 8 Photograph of the heated substrate holder within the CVD cell. The glowing silicon substrate can be seen as the small square object over the white hot filament. A electrical connection wire passes in front of the substrate, partially obstructing this view.





CHEMICAL MODEL AND PREDICTED GROWTH RATE

To estimate the growth rate of diamond film on the hot substrate surface a simple chemical model must be assumed. We will assume that methyl radicals formed by dissociation on the hot wire surface diffuse to the substrate and result in film growth. A sufficient concentration of H atoms or any other species necessary for diamond formation will be assumed, making the methyl radical production rate and diffusion efficiency the limiting factors. The rate of methyl radical production by the hot wire can be determined by calculating the probability of thermal dissociation of an acetone molecule hitting the wire surface and the collision rate of acetone molecules with the surface.

The collision rate of gas molecules is given by the expression

$$\text{coll. rate} = n \times (v/4) \times A$$

where n is the number of acetone molecules per cm^3, v is the mean velocity of the radicals at the appropriate temperature, and A is the surface area of the wire. The appropriate temperature of the gas near the wire surface is lower than that of the hot wire (estimated to be ~2000 C) but higher than that of the deposition surface (650 - 700 C). We will use ~ 1000 C for this estimate. At this temperature the mean methyl velocity is $\sim 1.2 \times 10^5$ cm/sec, and the density is $\sim n = 7.5 \times 10^{15}/cm^3$. The surface area presented by the hot wire is $\sim 1\ cm^2$. From these the collision rate of acetone molecules with the wire is

$$\text{coll. rate} = n \times (v/4) \times A \simeq 2.25 \times 10^{20}\ sec^{-1}.$$

The probability of molecular dissociation can be estimated knowing the wire surface temperature and the dissociation energy of the acetone molecule. The energy needed to produce a single methyl radical from the molecule is (from Table I)

$$E_D = 3.3\ eV$$

The fraction of molecules on the hot surface with energies equal to or exceeding this value is given by

$$\text{Frac. Dissociated} = \exp\text{-}[E_D/kT].$$

Since the wire temperature is estimated (crudely) to be ~2000 C, and since $E_D \simeq 38000$ K,

$$\text{Frac. Dissociated} \simeq \exp\text{-}[16.5] \sim 6.7 \times 10^{-8}.$$

This result is very sensitive to the temperature of the hot wire; a change of -300 degrees results in a substantial decrease in the fraction dissociated;

$$\text{Frac. Dissociated} \simeq \exp\text{-}[19] \sim 5.6 \times 10^{-9}.$$

For a wire temperature of 3000 K the resulting number is;

$$\text{Frac. Dissociated} \simeq \exp\text{-}[12.6] \sim 3.2 \times 10^{-6}.$$

This strong dependence requires the use of the highest possible tungsten filament temperatures. The number of methyl radicals produced is the product of the number striking the surface per second and the fraction which are dissociated;

$$\#\ \text{methyls/sec} = 2.25\times10^{20} \times 6.7\times10^{-8} = 1.5\times10^{13}\ \text{sec}^{-1}.$$

This production rate corresponds to a radical density which is low enough that the radical-radical recombination reaction discussed in Section II will not be important and so most of the radicals which escape the hot wire will diffuse away to strike either the deposition substrate or the deposition chamber walls. The distance between the hot wire and the deposition surface is only a few mm and so the geometrical collection factor is about 0.2 to 0.25.

The film growth rate predicted using these numbers is in the range $\sim$3-4$\times10^{12}$ atoms/sec, which for a 1 cm^2 substrate results in a growth of 0.0005 μm/hr. The observed rate of deposition in our hot wire deposition experiments is about fifty times greater for the conditions used in this study. The discrepancy may be due to an error in the estimate of the tungsten wire temperature, or a dissociation energy at the surface which is lower than the thermodynamic free molecule value. The wire temperature required to account for the observed film growth rate is in the range $\sim$2600 C. Given the sensitivity of the estimate to the wire temperature, this agreement should be considered reasonable. Enhanced deposition resulting from other species in the reactor gas mixture is not likely since the other fragmentation processes which would be required are all of higher (thermodynamic) energy. This means that any other fragment species should be present in significantly lower concentrations.

DIAMOND FILM ANALYSIS

Once a film has been deposited for a given set of conditions the substrate is removed for optical and physical analysis. These analysis include an SEM analysis to determine the crystalline structure of the deposit as well as the size of the deposited crystals. This allows the rate of growth to be estimated at specific locations on the substrate. A determination of the mass of the substrate before and after the deposition process was originally planned to determine the rate of film growth, however the rate of growth suggested by the SEM analysis was below the sensitivity of this approach. A Raman scattering analysis was attempted on some of the film samples to provide a measure of the film purity. Since the diamond Raman frequency, 1334 cm^{-1}, is well separated from the graphite frequency at 1560 cm^{-1}, the relative amounts of each of these species could, in principle, be estimated. Unfortunately, the spotty coverage which characterized these depositions made such an analysis difficult and hard to reproduce. In addition, while this approach provides a qualitative measure of the film content there are serious problems concerning its use as a quantitative measure [22].

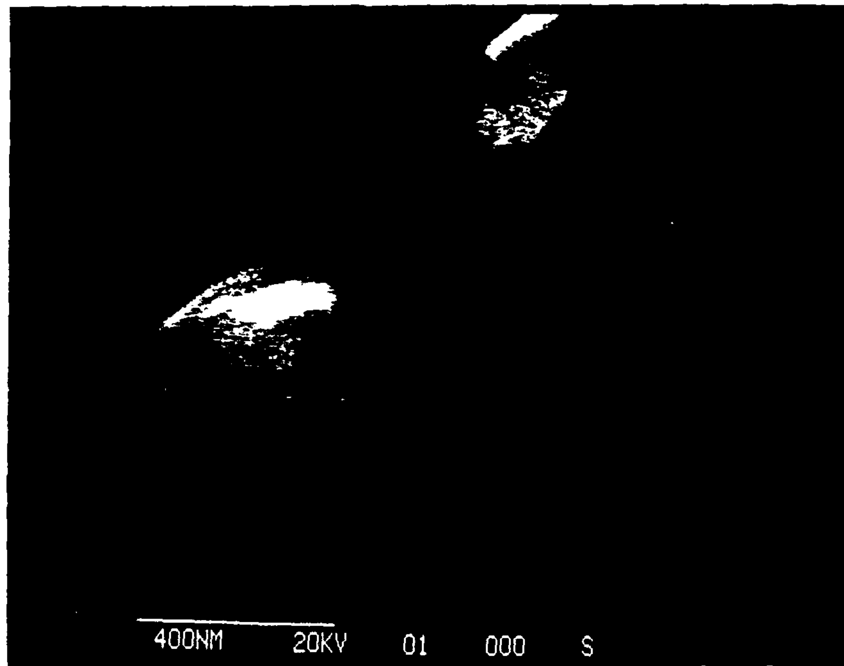
DEPOSITION RESULTS

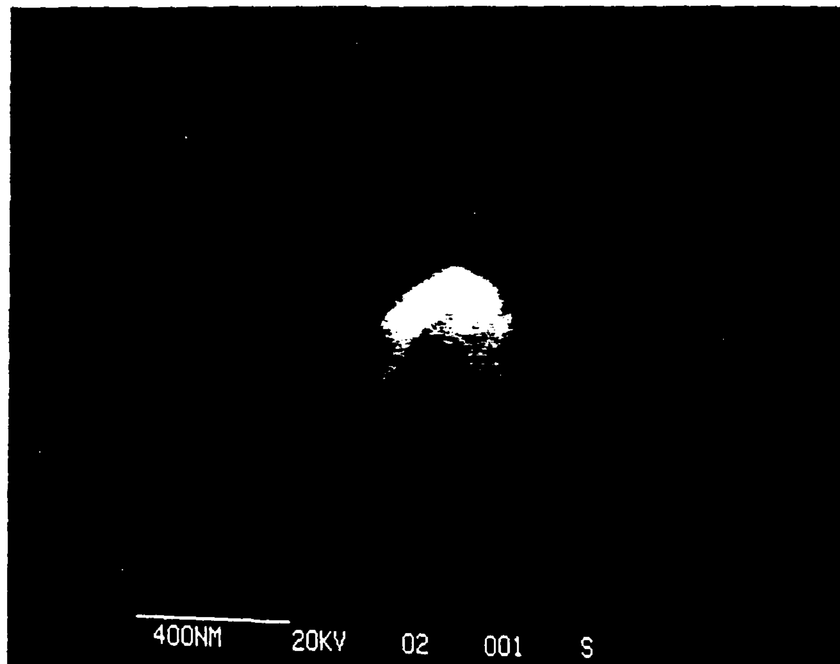
The deposition experiments carried out in this investigation can be broadly classified into two sets; those performed using only the hot wire/hot substrate technique, and those performed in the presence of laser radiation. A discussion of some of the results follows below. Not all of the experiments are presented since some are duplications of others and some failed to produce films for well understood reasons (too low a temperature, etc). A discussion of the information which may be drawn from these studies and some tentative conclusions follow in the next section.

1) In these experiments the silicon substrates, with surfaces roughened in the manner described above, were heated to a red glow (700 - 900 C) by a coiled tungsten heating wire located under the wafer piece. The hot tungsten wire used to create the reactant H atoms and methyl radicals was coiled (10 cm length in a 20 turn coil) and looped over the silicon at a distance of ~3 - 5 mm. The hot wire was heated by passing the 10 volt a.c. output of a variac through it. The wire glowed bright white hot, indicating a temperature in the range 2000 - 3000 C. Carbon monoxide gas, CO, was fed into the chamber through a flow meter (Teledyne Hastings model HFM-200) at a flow rate of ~1 standard cc per minute (SCCM) bringing the pressure within the deposition cell up to 100 microns. Hydrogen gas was then added to bring the total pressure up to 20 torr and the vacuum pump throttled closed until the total pressure reached 50 - 75 torr. These conditions were maintained for ~25 hours, after which the CO was shut off and the sample was allowed to cool to room temperature in the slow hydrogen gas flow. Scanning electron microscope analysis was performed at the facilities of Charles Evans and Associates (Redwood City, CA). No evidence was found for any species similar to diamond crystals on the surface.

2) These experiments were performed in the same fashion as those described in 1 above, except for the gas mixture ratio. The CO pressure was set to 1.0 torr and the hydrogen set to 10 torr. The pump was throttled to bring the total pressure up to ~50 torr and the sample and tungsten wire heated to the same temperatures used in 1. After a 25 hour deposition period the sample was unloaded (as above) and brought to Charles Evans and Assoc. for SEM analysis. The SEM images revealed a low density of small rounded or polyhedral objects on the surface which exhibited the charging effect expected for an insulator such as diamond. The objects had sizes ranging from 200 - 400 microns and appeared to be randomly located upon the silicon surface. While no definitive Raman analysis could be carried out, it seems likely that the deposited objects were a form of diamond or diamond-like material which had a very low growth rate under these conditions. Reproductions of two of the observed images are presented in Figure 9.

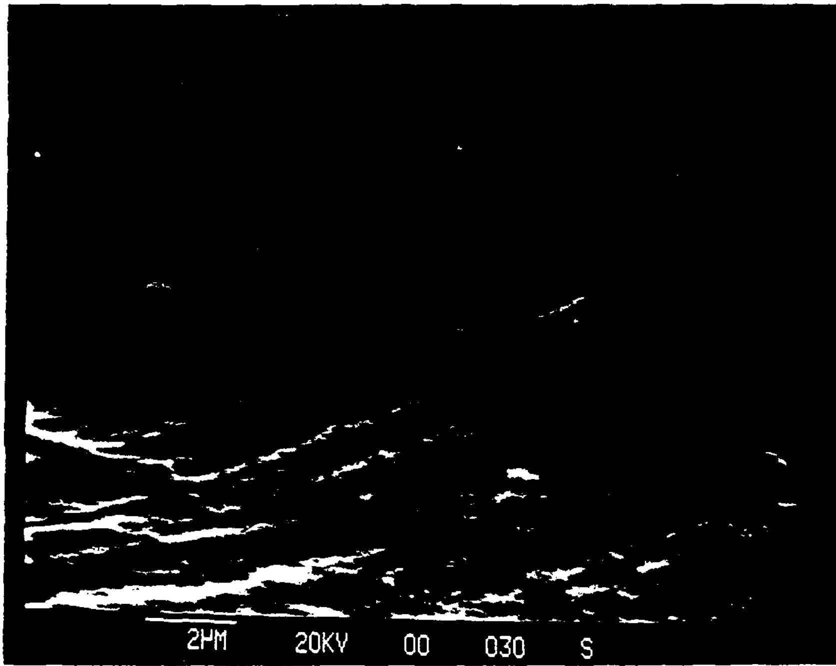
FIGURE 9 Representative images of small deposits left of the surface of an etched silicon substrate after 25 hours of hot wire CVD using 10% CO in 90% H_2. All of the objects exhibited electrical charging (and show up brightly) making precise focus impossible. The deposits ranged in size up to ~0.5 micron.


400NM 20KV 01 000 S

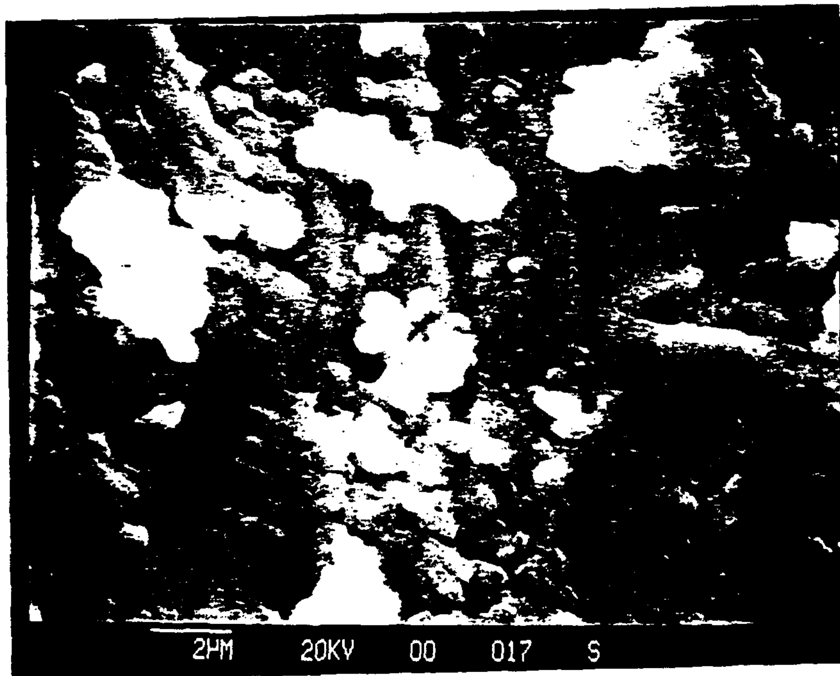

400NM 20KV 02 001 S

3) Several experiments were performed using a 1 cm^2 molybdenum foil substrate which was surface etched in the same fashion as were the silicon substrates. The experimental arrangement and conditions were the same as used above. Attempts at deposition using 1% flows of CO in hydrogen were unsuccessful in that no deposits were observed. When acetone was substituted for CO as the source of carbon in the reactor, small micro-crystals were deposited over the foil surface. These deposits had characteristics similar to the deposits found in 2, but were much more abundant and were frequently found to bind together in what appeared to be the initiation of film coverage. Representative images are shown in Figure 10.

FIGURE 10 SEM images of a molybdenum foil substrate. An area which was masked by a retaining screw is shown in (a), while typical deposits which formed on ex posed surfaces are seen in (b). The deposition technique was the hot filament approach using ~1% acetone (CH_3COCH_3) in 99% H_2. The substrate foil temperature was in the range 600-900 C.



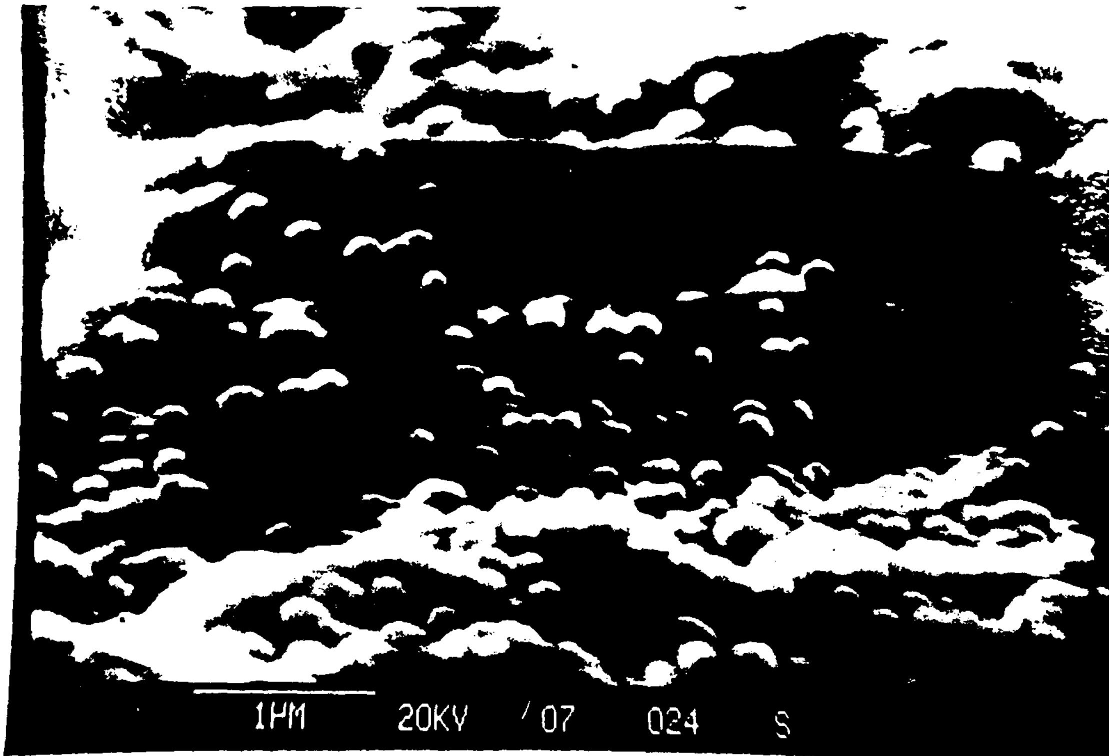
2µM 20KV 00 030 S

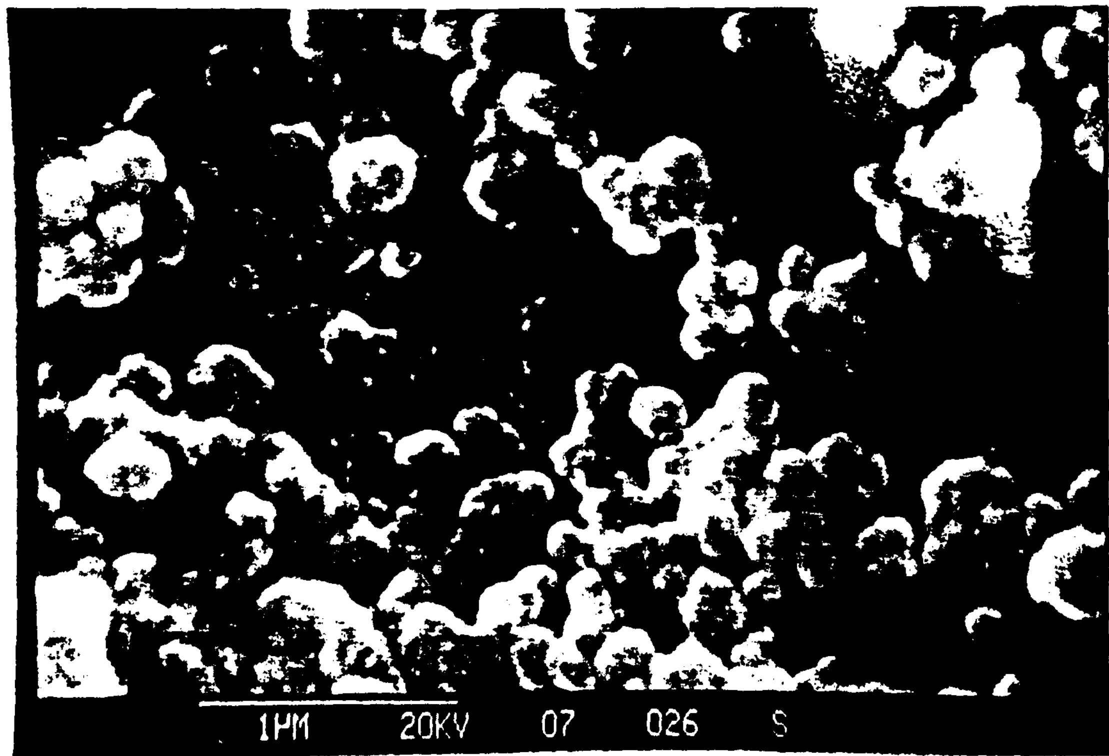


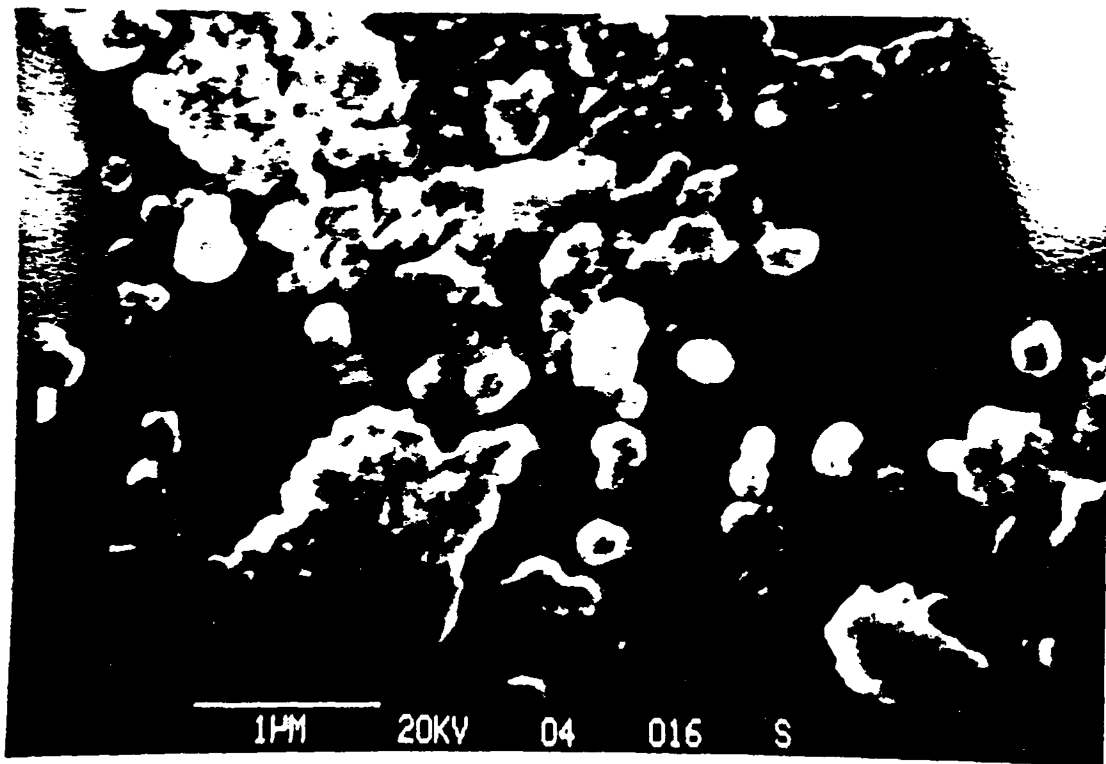
2µM 20KV 00 017 S

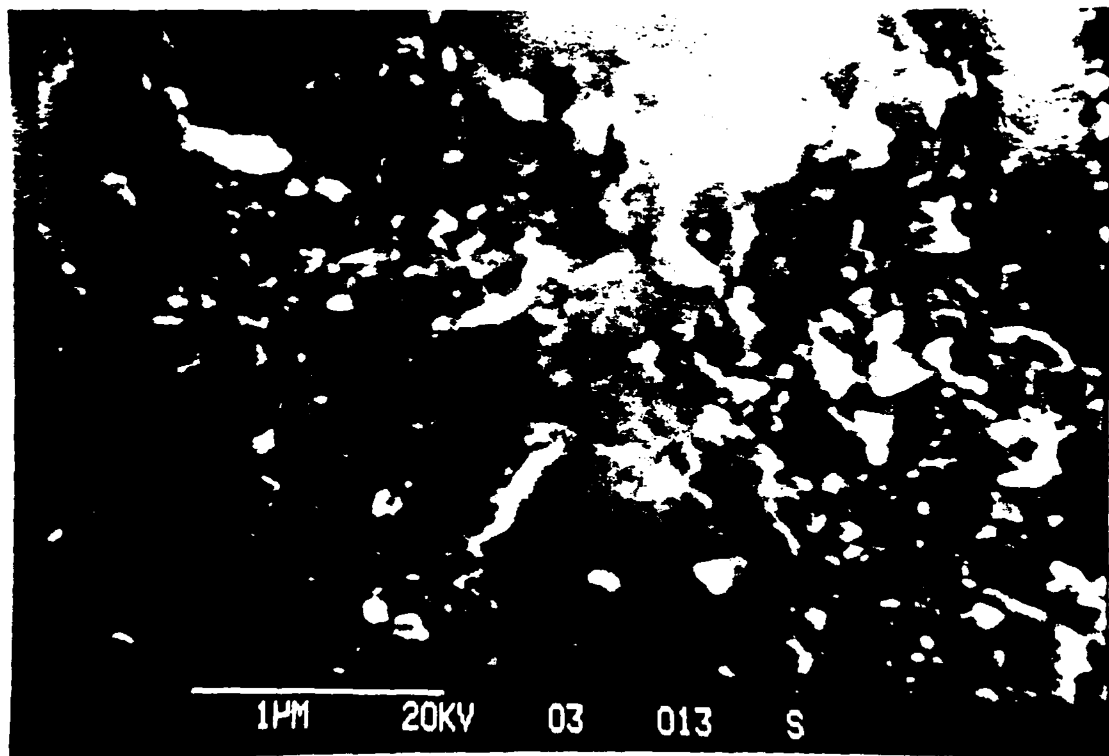
4) Similar experiments were carried out using acetone as the carbon source and silicon as the substrate. The depositions seen in these studies were present in high density and the "film" was evidenced by masking marks left by the screw head washers used to hold the substrate in place. The appearance of the film was similar to that of the treated silicon surface with a dull gray finish. The SEM images of the deposit were similar to those obtained from the metal sample used in 3. All of the micro-crystals were of size ~0.5 microns or less. Often the crystals bind together to form regions of near continuous coverage. Representative images are presented in Figure 11.

FIGURE 11 SEM images of depositions formed on etched silicon substrates after deposition treatment identical to that described in Figure 10. A view at ~30 degree angle is shown in (a); (b) and (c) show typical sites on the substrate indicating how the micro-crystals bind together to form essentially continuous coverage. An area which was masked by a retaining screw (and so is free of deposits) is shown in (d) for comparison. Bright areas are due to sharp edges.


1PM
20KV
07
024
S

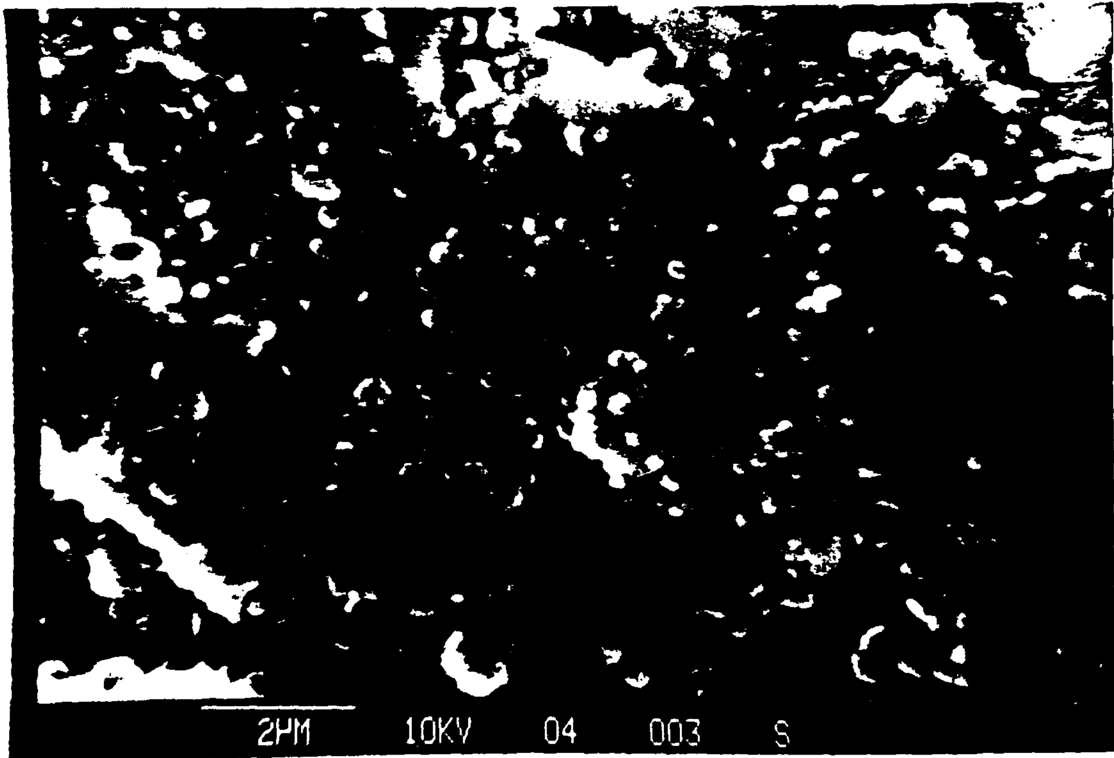

1PM
20KV
07
026
S


1μM 20KV 04 016 S


1μM 20KV 03 013 S

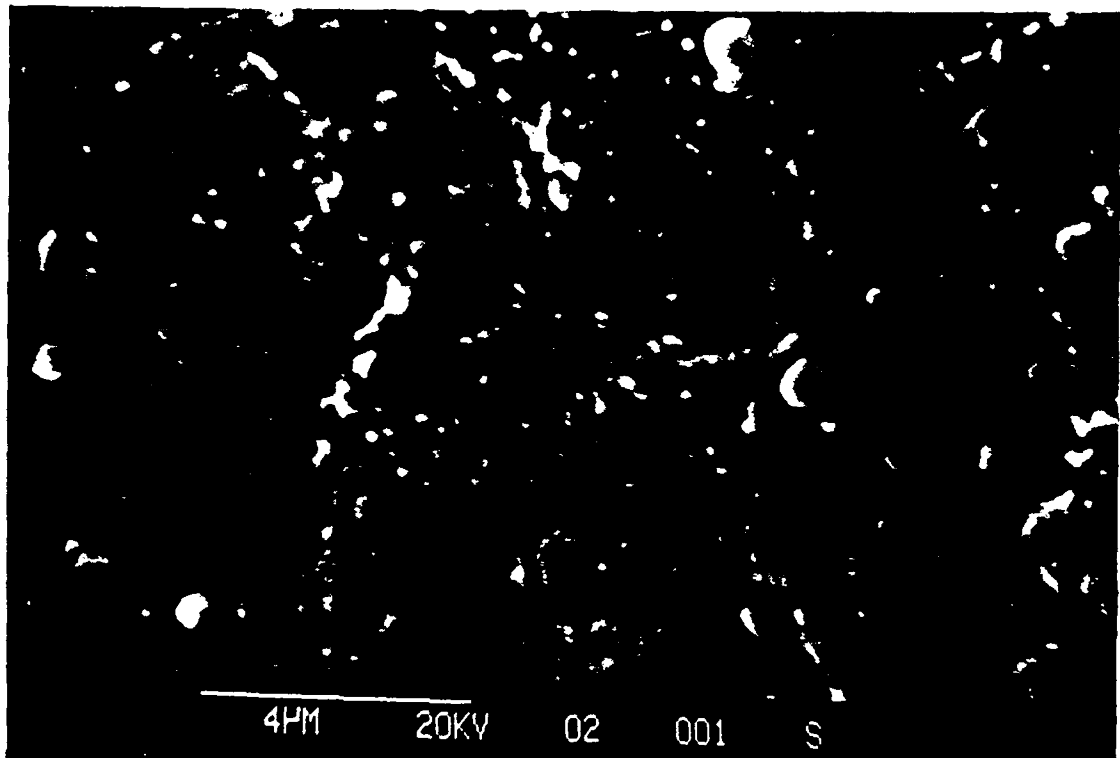
5) The same substrate used in 4. above was re-positioned (without re-etching) for a second deposition experiment involving a laser beam. The configuration of the experiment was identical to that used in 4. except the output from a frequency doubled dye laser was passed over the sample and impinged upon the sample at the edge at a low angle. The laser beam was at a wavelength of 296 nm and was run at 40 Hz producing ~40-60 micro-Joules/pulse energies. These conditions are essentially identical to those discussed in Section II and could result in an additional deposition rate of 0.025 micron/hr. This rate is comparable to that seen in the studies utilizing only the hot filament (above). The film deposited consisted of a complicated structure of micro-crystals and an underlying film of, what appears to be, diamond like amorphous carbon. This DLC film was deposited early in the run when the acetone pressure increased to ~10 torr for a period of approximately an hour due to poor leak valve seating. The pressures were re-set and the run allowed to run to completion. The presence of diamond and DLC film on the substrate is indicated by the bright images produced by charging in the SEM photos shown in Figure 12. The dark circular outline seen in 12-a is due to the shadowing of the surface by a securing screw. The DLC coating can be clearly seen in Figure 12-b and has a flakey structure with a characteristic size of 2-4 microns. The small diamond microcrystals can be seen covering most of the DLC film, and a magnification of one of the darker areas where there are no apparent microcrystals shows that it consists of many darker small microcrystals. These species may be lower purity crystals.

FIGURE 12 SEM images of deposits formed on top of the film produced in 4 and shown in Figure 11. A diamond like film was deposited early in the run as a result of an acetone pressure fluctuation. The presence of the film is indicated by the strong charging effect seen in (a), in which the bare silicon substrate which was masked to the deposition is seen at the top. The DLC film can be seen as an underlying flaky structure in (b) with a characteristic size of ~4-5 microns.


2μM 10KV 04 003 S

If the underlying DLC film completely masks the diamond microcrystals deposited earlier then all of the microcrystals seen in 12-b result from the laser enhanced deposition. The crystal densities for the hot filament deposition approach and the laser assisted hot filament approach are compared at the same magnification in Figure 13. While the coverage seen in the laser assisted deposition appears to be significantly greater than that generated using only the hot filament, a definitive conclusion can not be made. The ambiguity arises from two sources. The great sensitivity of the methyl radical production rate on the hot filament temperature can result in variations in growth rate due to slight variations in the heating current. Another problem in comparing the two depositions is that one occurs on a silicon surface and the other, in effect, on a carbon layer. The use of a larger laser system (with mJ pulse energies instead of μJ energies) for the acetone photodissociation process would make the predicted film growth rate much larger than the possible variations due to temperature fluctuations, etc.

FIGURE 13 Comparison of SEM images produced after diamond film CVD treatment. Deposition produced using only hot filament approach is shown in (a), while that found after laser assisted hot filament deposition is shown in (b). There is a noticable difference in the overall density of microcrystals deposited in the two processes, with the laser assisted deposition process apparently giving a higher yield.


4µM
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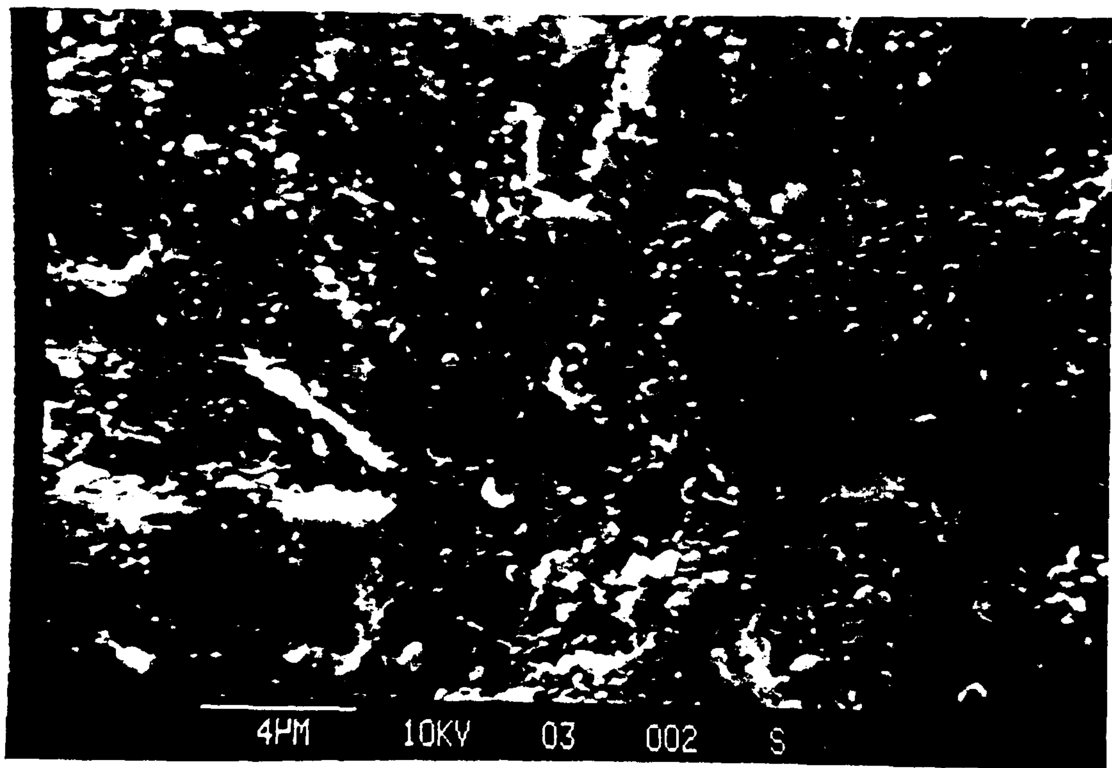
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SUMMARY OF EXPERIMENTAL RESULTS

The performance of the CVD system used in these experiments is essentially the same as that of similar systems described in previous works. For chemical gas mixes of 1-3% acetone in 99-97% hydrogen, in the presence of a white hot tungsten filament, and over a red hot (700-900 C) substrate, small microcrystals grow. These crystals exhibit the published characteristics of the diamond films produced in this fashion and, although we have not been able to perform either an x-ray diffraction or Raman scattering analysis, we believe these microcrystals to be diamond or diamond-like material. While a step-by-step systematic physical and chemical analysis of these films was beyond the scope of the Phase I study, a qualitative analysis of the trends seen in the microcrystal growth rates and morphology can be used as a guide to evaluating the potential of the proposed laser based CVD system. We can infer several conclusions from the set of experiments which have carried out using our CVD system.

Several observations warrant discussion. The source of the carbon in the gas phase (either carbon monoxide or acetone) had a great effect upon the rate of microcrystal growth. This is understood in terms of the chemical model derived for the hot filament process and described in Section III. The fraction of molecular CO which undergo dissociation on a hot filament to produce a free carbon atom (which would then react in the excess hydrogen gas to eventually produce a methyl radical) is much lower than the corresponding fraction of acetone molecules which will dissociate at the same temperature, producing methyl radicals directly. The fraction produced from CO is so small that it is possible the observed slow growth of microcrystals is, in fact, due to low level impurities in the vacuum system. The much greater growth rate realized using acetone supports the position that the methyl radical is the key reactant in diamond film growth. Overall, the growth rate observed when acetone is used as the methyl radical precursor is lower than what our model predicts however, given the uncertainty in the hot filament temperature as well as the possibility of surface catalyzed decomposition, the agreement is reasonable. The great sensitivity of the process to the hot filament temperature has been confirmed by the great variation of film quality with small temperature changes.

The temperature of the substrate and the acetone/hydrogen ratio were both important in determining the morphology of the deposited material. At too low a temperature, or too high an acetone concentration, the deposited film had a brownish appearance and, under SEM, had a flaky appearance with characteristic sizes of $\sim$4-5 microns, similar to the underlying film seen in Figure 12. This film exhibited electrical charging although not quite as much as that of the deposited microcrystals. We believe that this film constitutes a form of amorphous carbon or diamond-like carbon. Such a film is not expected to form under the conditions expected for a laser-CVD system. The aromatic carbon radicals which result in the formation of such films are not formed in the proposed photochemical process. We believe they are formed in these experiments due to the uncontrolled and undesirable chemistry occuring at the hot filament.

The results of the attempt to grow the microcrystals using a laser assisted hot-filament CVD process are somewhat obscured by the unintended deposition of a underlying film of DLC. The great enhancement in the density of nucleation sites seen in the laser-CVD process suggests that this technique does work well and that a system based only upon laser-CVD (i.e. no filament) should be developed. It should be emphasized that **there is no uncertainty surrounding the photochemistry of acetone and that methyl radicals can be selectively produced in quantities sufficient to produce good diamond film growth rates.**

DISCUSSION

We have described a chemical model which predicts the rate of diamond film growth for a laser assisted CVD process which is based upon the generally conceded idea that the basic building block of the diamond growth is the methyl radical. The attractive features of a laser CVD scheme are that the approach produces the required methyl radicals selectively and eliminates the need for electrical discharge, or high temperature (e.g. hot filament technique) processes to form the radical. Several observations can be made on the basis of these studies.

Several serious problems must be solved before the present state of diamond film CVD technology can be advanced to its full potential. The potential benefits include the growth of large high purity single crystal diamonds which may be used in laser and opto-electronic applications, and the growth of such crystals on novel substrates at low temperature to significantly broaden the range of electronic applications. The technical challenges which must be overcome to realize these benefits, film purity and single crystal growth, are interrelated and may be resolved with a single innovative solution. The purity of the crystals appears to suffer from the inclusion of hydrogen in the structure. As the microcrystals grow together the crystal defects which occur at the boundaries between different crystal faces become impurity sites. In the present technology, excess hydrogen is necessary to convert the various carbon fragments into methyl radicals, as discussed in our model. The growth of single crystal diamond could be accomplished in a MBE process using a suitable substrate. Such a substrate is the Nickel surface, however this material undergoes a phase change above $\sim$600 K and so cannot be utilized until the diamond deposition can be achieved at lower temperatures.

The approach that we propose may resolve both of these difficulties. Because the laser photodissociation creates the required methyl radicals selectively, there should be no need for the presence of excess hydrogen gas in the reactor system. Since the laser process can selectively put the needed dissociation energy directly into the acetone molecule the reaction gas flow should not require the high temperatures presently called for. As suggested in the hot-wire CVD model described in Section III, the need for high temperatures to efficiently decompose the parent molecule and form methyl radicals must be balanced against other factors (possibly the thermal decomposition of the diamond) resulting in observed optimum growth temperatures in the range 800-1000 C. The laser photodissociation process is capable of producing the methyl radicals efficiently at temperatures as low as 100 C, and as discussed in the model, requires only temperatures sufficient to reduce radical recombination reactions from depleting the species (100 -200 C). Successful deposition at such a low temperature would open the door to possible epitaxial growth of large single crystals.

We have built and demonstrated a hot filament diamond CVD reactor and have used it to make some tests of the models we have developed. In addition, we have configured the deposition reactor to permit the evaluation of a laser assisted hot filament diamond deposition process. Although the observed enhancement in the rate of film growth cannot be unambiguously attributed to the effects of laser photo-enhancement, the results are encouraging. **The photochemistry of the acetone molecule which gives rise to the production of the methyl radical is well established and there is no uncertainty involved in producing radical densities (or fluxes) comparable to, or greater than, those attained using present techniques.** In addition, work at other laboratories, as well as some of the results presented here leave little doubt that the methyl radical does, in fact, lead to the growth of diamond. Given these facts, and the results of the chemical models presented here, it is assured that a laser CVD deposition system would produce synthetic diamond in quantities sufficient to answer the remaining questions involving crystal purity and the growth of large single crystals.

IV. DETAILED WORK PLAN

The objectives of a continuing Phase II program would be to develop a new technology which will permit the growth of ultra-high purity, and selectively doped diamond on selected lattice matched substrates such as Ni. The work plan described here is structured so as to permit rapid advancement towards this goal while ensuring sufficient safeguards at each step to avoid unneccesary effort.

The first step in the Phase II effort is to identify the laser source best suited for carrying out the photo-induced depositions. As discussed in Section II, the optimum laser source should have output near 3000 Å but not shorter than 2953 Å (the energetic threshold for production of CH_3COCH_2 radical). The laser system may be either continuous or pulsed, but must be capable of providing sufficient photon flux to produce the methyl radicals in managable densities. We have determined that the use of a pulsed XeCl excimer laser with pulse energies in the 50-150 mJ range and capable of operation at high repetition rates (100 Hz) represents the optimum choice, both in terms of performance and of cost. This laser system will be coupled with a deposition chamber which will be designed and constructed at the Deacon Research facilities.

The general design features of the laser-CVD cell will be similar to those utilized in the prototype developed for the Phase I experiments, but with much greater flexibility. The system to be developed must permit the deposition experiments to be carried out under a wide range of temperatures, gas species and concentrations. Because it will be of interest to look at the effect of hydrogen atom concentration on the deposition process (either in a continuous flow or simply pre-treatment of the substrate) a remote source of H atom must be included in the design. The approach we will take to do this will be to employ several gas introduction ports, one of which will draw the desired atoms from a isolated hydrogen plasma. Other ports may be used to introduce the acetone flow, buffer gas (e.g. He or Ar), or low temperature H_2 gas. The walls of these introduction ports will be coated with a teflon layer (or a coating of dried boric acid) which is known to greatly reduce the rate of radical loss to wall recombination processes. The larger reactor cell walls will not require such treatment since the slow rate of molecular diffusion at the pressures to be used (in the Torr range) dictates that methyl radicals which diffuse more than a few cm from the substrate will likely be lost to reaction before returning.

The substrate mount will be a fairly massive metal block which will have electrical coil heaters mounted within it. The substrates themselves will be attached to the heater mount assembly in the same fashion employed for the Phase I work. The heater power supplies will incorporate a temperature feedback control the type of fluctuations which were encountered in the Phase I work. The substrates will face into the slow gas flow and will present an unobstructed view to a quartz window port to permit the determination of temperature by means of optical pyrometry (backed up by thermocouples in and on the heater block). The substrate and heater assembly will be positioned such that the output of the excimer laser can be passed directly over the substrate surface. This optical beam may be reflected back over the substrate several times, if desired, to increase the density of methyl radicals.

The vacuum system will be constructed of ultra-high vacuum components using copper gasket seals to eliminate possible contamination by organic impurities which can be produced by o-ring seals. The gas flow valves to be used will be grease free, UHV leak valves to ensure reproducible setting and oil contaminant free operation. This is important when controlling acetone flows, which can result in o-ring decomposition. The vacuum pumping system will employ an oil-free turbo pump.

The next stage in the work plan will be to demonstrate successful deposition of diamond films at temperatures characteristic of current processes. These experiments may be carried out using the remote hydrogen atom source described above to remove chemical ambiguity. These initial experiments will proceed by eliminating the constant H atom flow and substituting a flash cleaning by H atoms just before laser deposition is initiated. After each deposition run, the rate and quality of diamond film deposition will be determined (as outlined below) and the deposition system performance determined. This performance will be largely characterized by the efficiency of conversion - the fraction of methyl radicals produced by the laser which add to the growing film. This efficiency will be determined as a function of deposition time in an attempt to separate the efficiency of nucleation on a clean surface from the efficiency of growth on a diamond surface.

Once the deposition system has been demonstrated and the performance at elevated temperature characterized, the system will be dedicated to making a series of systematic measurements over a parameter space which is defined by the substrate temperature, the precursor acetone pressure, hydrogen concentration, gas temperature, and total pressure. The measurement grid defined by this space will be formidable, even for a modest partitioning of variables. Consider the following data grid: six substrate temperatures (200-700 C); six acetone concentrations (1%-100%); two H atom concentrations (on and off); two gas temperatures (heated and not heated); and three total pressures (50, 100, and 500 Torr). To make a complete spanning of this parameter space would require 432 measurements. Given the time required for each measurement this is very inefficient, and so the approach which will be adapted will be a much coarser stepping of parameters originally with more detailed measurements focusing upon the areas of interest as the data accumulates.

As these measurements are being made we will analyze the measured deposition efficiency (including rate and purity) so as to determine which conditions are most favorable for low temperature growth of diamond films. It is unlikely that the mechanisms which give rise to diamond film growth will suddenly cease beyond a fixed point (e.g. some lowest temperature) and so this evaluation will entail an evaluation of potential system trade-offs. Examples of such trade-offs include the toleration of reduced deposition rates (perhaps due to lower organic concentration) to produce high purity films at low temperatures.

The analysis of the films produced in this program will be carried out through both in-house and outside analysis. The diamond film characteristics which must be determined include the film growth rate and the film purity and quality. The rate of growth for the diamond deposits can be qualitatively evaluated using images obtained from scanning electron micrograph analysis. Such analysis also permits the quality of the microcrystals to be evaluated quickly over a broad area of the substrate surface. For depositions which will result in the growth of significant amounts of diamond, a sensitive mass balance can be used to determine the total growth. From the density of diamond ($\sim$3.5 gm/cc) the mass per micron deposited for a 1 cm^2 substrate is $\sim$0.35 mgm. This is certainly within the sensitivities of laboratory balances and indicates that average coverage determinations can be made in this fashion with a resolution better than 1 micron.

Once a diamond film has been produced for a given set of conditions the substrate will be first subjected to an optical analysis using a microprobe Raman spectrophotometer. Such an analysis can provide valuable information about the content and purity of the sample deposit with a spatial resolution sufficient to resolve local impurity inclusions if present. As discussed

in Section II, the Raman scattering signal produced from a natural diamond cantains an intense line at an energy difference of $\sim 1332\ cm^{-1}$. A sample of film containing what has been refered to as "disordered carbon" produces a easily resolved shift of $1350\ cm^{-1}$. The presence of graphite or graphitic deposits would be characterized by a Raman shift at $\sim 1580\ cm^{-1}$. While the absolute intensities of these signals cannot be easily interpreted as a measure of the relative abundances of each component, the signals can be used to provide a qualitative indication of the net change in film quality. This diagnostic represents an important step in the evaluation of the diamond film processing technique since it provides a resolved image of the deposition composition.

The important Raman analysis and the total deposition mass analysis will be carried out as in-house determinations, using equipment to be purchased for this program (see budget section equipment breakdown). The SEM analysis will be performed by outside sources. We have made extensive use of the services of Charles Evans and Assoc. analytical SEM services during the experiments and analysis performed during Phase I. The capabilities offered by this establishment are sufficient for any projected application within this proposed program.

When we have completed the evaluation of deposition performance over the parameter range of interest we will review the data and select the best set of conditions for growth of high purity diamond. Based upon these conditions we will design a reactor system which represents the most promising approach to the co-deposition of selected species in diamond films.

Finally, based upon these design considerations, we will attempt to initiate growth of selectively doped diamond films and will evaluate the potential for the doping of large synthetic single crystal diamond. This step represents the ultimate goal in the program described here.

We can summarize the approach we propose to follow in developing the technology for growing single crystal diamond on low temperature substrates:

1) simplify the existing process chemistry and selectively generate only reactants of interest using laser photo-production;

2) using this chemical control, map out the diamond growth characteristics over a wide range of chemical conditions and temperatures to document (and later understand and model) the process limitations;

3) use this chemical mapping to guide the design and optimization of a dopant co-deposition process to be carried out at a temperature which can support the presence of an identified epitaxy substrate;

4) attempt the growth of doped diamond upon a potential epitaxial substrate.

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VI. KEY PERSONNEL

Deacon Research was founded in 1981 based on the idea of applying the results of basic research to novel instrument development. We have worked with industrial, academic and government clients to help solve a variety of problems in the areas of lasers, optics and solid state physics. To date we have received five SBIR Phase I contracts from the Department of Defense, three of which are in the Phase II stage. Deacon Research has close contacts with the high performance optics community through our sales and measurement service of the Cavity Lossmeter.

Dr. Anthony O'Keefe has more than ten years in laser related research in the fields of chemical Physics and excimer laser development. He has held principal investigator positions at the Naval Research Laboratory in Washington, D.C. where he focused upon gas phase plasma and ion photochemistry and the interactions of high intensity laser beams with materials. These responsibilities included the active supervision of research staff, including two professional (Ph.D.) level scientists. While there he developed a research program to study the reactions and behavior of large molecular cluster ions formed by laser vaporization of various materials. This work was the first to reveal the existence of multiple geometrical structures for large carbon clusters and has led to the development of a theoretical description of these structures. He has also held the position of senior scientist with Western Research Corporation where he helped develop techniques to modify high energy laser beams using non-linear optical wave mixing processes. As a senior staff scientist his responsibilities included staff management as well as contract procurement. Dr. O'Keefe is Principal Investigator for four current research programs at Deacon Research. Two of these programs, funded through NASA, involve the development of laser based remote sensors for the analysis of gas flows. The other two programs involve the study of the basic processes leading to the growth of synthetic diamond films by chemical vapor deposition.

Dr. O'Keefe received his B.S. Degree in Chemistry from Beloit College in 1977 and his M.S. and Ph.D. in physical chemistry from the University of California, Berkeley in 1979 and 1981 respectively. He was awarded a National Research Council Postdoctoral Fellowship in 1981 to work at the NBS/NOAA labs in Boulder, CO. He is the author of more than twenty-five papers in scientific and technical journals.

Dr. Mira Bakshi received her Ph.D in physics from the University of Illinois at Champaign-Urbana in 1984 and has a strong background in metallic and semiconductor material science. Her doctoral studies focused upon the optical properties of metalic alloy films produced in high vacuum environments and probed using the technique of polarization modulation ellipsometry. From 1984 until 1987 Dr. Bakshi was a postdoctoral physicist at the University of Wisconsin Synchrotron Radiation Center and was responsible for experimental development as well as execution. This work included angle-resolved photoemission studies of magnetic film overlayers, radiation induced ion desorption measurements, and photoemission analysis of the catalytic oxidation of semiconductor materials. This later work was the first to demonstrate the rapid, catalytic oxidation and nitridation of semiconductor materials using an easily removed catalyst overlayer. Dr. Bakshi has authored more than fifteen articles in scientific and technical journals.

In her position as research physicist at Deacon Research Dr. Bakshi is responsible, as Principal Investigator, for managing a SBIR Phase II research program. Funded by ONR, this pro-

gram involves the study of UV catalyzed carbon deposition and contamination of optical elements within synchrotron and FEL optical beamlines.

Dr. David A.G. Deacon has thirteen years of experience in optics and instrumentation. He is currently Principal Investigator of a number of programs including the generation of UV harmonics in free electron lasers and the UV damage of optical materials. His other interests include the physics of free electron laser devices, UV photo-induced absorption in dielectric materials, and the development of novel techniques for the measurement of low level optical losses. He has been engaged in free electron laser (FEL) research and development programs since 1975. He was project leader of the Stanford-Orsay experiment which, in 1984, obtained the first visible FEL oscillation. In collaboration with researchers at Stanford University, he is designing a storage ring based FEL to be operated in the XUV wavelength range. His experience includes technical management, measurement techniques of very low optical signals, and laser systems. He is the inventor and the principal designer of the Cavity Lossmeter now marketed by Deacon Research.

Dr. Deacon received B.S. Degrees in Physics and in Electrical Engineering from MIT in 1975, and a Ph.D. degree in Physics from Stanford University in 1979. He is the author of more than fifty technical articles, the editor of a volume of papers on free electron lasers, holds two patents in FEL technology, and has one outstanding patent application.