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Hot filament assisted deposition of diamond films

Gat, Roy, Ph.D.

Case Western Reserve University, 1992

U.M.I
300 N. Zeeb Rd.
Ann Arbor, MI 48106
HOT FILAMENT ASSISTED DEPOSITION OF DIAMOND FILMS

by

ROY GAT

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Materials Science and Engineering
CASE WESTERN RESERVE UNIVERSITY

May 1992
We hereby approve the thesis of

[Name]

candidate for the Ph.D.
degree.*

Signed: [Signature]

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HOT FILAMENT ASSISTED DEPOSITION OF DIAMOND FILMS

Abstract

by

ROY GAT

A novel hot filament assisted chemical vapor deposition reactor for diamond was designed and built. The substrate is an independently heated, isothermal wire. This provides for the decoupling and independent control of substrate and hot filament temperatures, which is not possible in conventional diamond reactors. The reactor was used for: 1) the measurement of energy flows during diamond deposition, 2) estimation of hydrogen recombination rates on the substrate and 3) study of deposition of diamond and other forms of carbon outside of the normal parameter space for diamond deposition.

The recombination rate of atomic hydrogen on the substrate was measured as a function of substrate temperature and methane concentration. The gas phase concentration of atomic hydrogen at the substrate was estimated. A detailed analysis of the energy transport to the substrate was performed showing that atomic hydrogen recombination on the substrate is a major mechanism of energy transport. The conditions under which the transport of atomic hydrogen to the substrate is diffusion limited were found. This reactor also permitted broad investigation of the experimental parameter space. It was discovered that graphite fibers can be deposited by the vapor-liquid-solid mechanism by making modest variations in the diamond growth conditions. Diamond can be deposited on these fibers resulting in a new composite material which may have numerous technological applications.
This work is dedicated to my
Mother, Father and Sister.
Acknowledgements

Much credit is due to Prof. John Angus for his many significant contributions to the work, and for providing a very pleasant and professional working environment. It is a great pleasure to acknowledge Mr. C. C. Hayman for sharing his vast knowledge in many inspiring discussions. I am very grateful to Mr. W. Schmidt for his excellent suggestions about the design of the reactor, and Dr. W. Jennings for expert Auger work.
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List of Symbols

A - Substrate area.

C_H - concentration of atomic hydrogen.

C_{H,s} - concentration of atomic hydrogen near the substrate.

C_{H,af} - concentration of atomic hydrogen near the hot filament.

c_m - total concentration of molecules.

D - atomic hydrogen diffusion coefficient in hydrogen.

f - atomic hydrogen recombination rate.

F - Flow rate.

J - flux.

k - homogenous recombination rate constant for atomic hydrogen.

k - thermal conductivity.

l - substrate length.

l - minimum separation between substrate and hot filament.

m - mass of atomic hydrogen.

n - Number of moles.

P - Reactor pressure.

P - Power.

P_A - Partial pressure of A

Q_{elec} - Electrical power supplied to the substrate.

Q_{gen} - Power lost from the substrate to atomic hydrogen generation.

Q_{rec} - Power gained by atomic hydrogen recombination.

Q_{cd} - Power lost by conduction to the electrodes.

Q_{ce} - Power lost by conduction through the gas to the walls.

Q_{rad,af} - Power gained by radiation from the hot filament.

Q_{rad} - Power lost by radiation.
R - gas constant.
S - sticking coefficient.
t - time.
T - temperature.
T_s - substrate temperature.
v - average kinetic velocity.
v - voltage across reference resistor.
V - reactor volume.
V - voltage across substrate filament.
V_m - molar volume.
\( x \) - distance.
Y_{eth} - mole fraction of ethanol.
\( \alpha \) - thermal accommodation coefficient.
\( \beta \) - recombination coefficient, the ratio of the rate of recombination to the rate of collision.
\( \gamma \) - geometrical constant for heat conduction.
\( \Delta H \) - formation enthalpy of atomic hydrogen.
\( \mu \) - viscosity.
\( \lambda \) - mean free path for collisions.
\( \rho \) - density.
\( \tau \) - characteristic time for diffusion.
\( {'} \) - primed quantities are measured when the hot filament is off.
Chapter 1

Introduction

In the last decade, the scientific community has developed widespread interest in synthetic diamond produced by low pressure techniques. This interest is in response to exciting results reported by the Japanese in which they demonstrated methods for achieving high rate growth of diamond by chemical vapor deposition \([1, 4]\).

Today, polycrystalline diamond films of micron thickness (see figure 1) are routinely grown by a variety of techniques. The common denominator of these techniques is some means of gas excitation providing a large excess of atomic hydrogen together with carbon containing free radicals. The deposition systems are essentially CVD systems that are typically assisted by one or more of the following methods: micro-wave, radio-frequency, DC plasma, hot-filament, ion and electron beams. Diamond is also grown by flame synthesis using an off-the-shelf welder’s oxy-acetylene torch or in low pressure flames. The substrate temperature for all methods is typically \(800-1000^\circ C\). Much lower temperatures e.g., \(300^\circ C\), have recently been reported \([2]\).

Diamonds can also be made at low pressures from water, alcohol and acetic acid in a radio-frequency plasma at 1 torr \([2]\), and from \(CF_4\) in \(F_2\) gas mixtures by unassisted CVD \([3]\).

Diamonds and diamond films possess some extreme properties. The poten-
ential for engineering applications of diamond films is large and has sparked widespread interest. Diamonds have long been used as jewelry and abrasives, but the recent production of continuous diamond films makes feasible the application of diamond as a wear resistant and chemically protective hard coating. Its semiconductivity and excellent heat conductivity make it useful in high power density devices and heat dissipators (commonly referred to as heat sinks). Its low cross-section for interaction with radiation makes it useful in high radiation environments such as devices in nuclear missiles. Finally, diamond's optical transparency (band gap 5.6eV) in the visible and infrared regions make diamond an ideal instrument window. Table 1.1 summarizes the properties of diamond and table 1.2 relates them to potential applications.

Although each system has very different parameters, there is remarkable similarity in the final morphology of the diamond polycrystals. This similarity indicates that general and fundamental principles are at work in all the processes used. However, understanding of the nucleation and growth mechanisms is conspicuously lacking.

For comprehensive reviews of the state of the art of diamond formation see references [4,5,6].

The substrates used so far for diamond growth include metals, oxides, carbides, and nitrides. However, no diamond has been successfully grown directly on iron (including steels) and cobalt and only some researchers have grown diamond on nickel. A common finding is that scratching the substrate with diamond powder prior to the deposition step greatly enhances the diamond nucleation rate. Therefore, it is hypothesized that the diamond nucleation is heterogeneous. A group in the former USSR has demonstrated homogeneous diamond nucleation using focused laser beams [7]. The carbon carrying gas used most frequently is methane, but diamond has been produced from many other carbon containing cases including: acetylene, acetone, alcohols, CO, Scotch whisky, and sake.

Diamond films occur in very distinctive morphologies. These depend on
<table>
<thead>
<tr>
<th>Property</th>
<th>Diamond Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical reactivity</td>
<td>Extremely Low</td>
</tr>
<tr>
<td>Hardness</td>
<td>$9 \times 10^9$ kg m$^{-2}$</td>
</tr>
<tr>
<td>Heat Conductivity</td>
<td>2000 W/m K at 30° C</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>$3.5 \times 10^8$ kg m$^{-2}$</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>$9.8 \times 10^9$ kg m$^{-2}$</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient</td>
<td>$0.8 \times 10^{-6}$/K</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.41 at 590 nm</td>
</tr>
<tr>
<td>Friction Coefficient</td>
<td>0.05 (dry)</td>
</tr>
<tr>
<td>Band Gap</td>
<td>5.4 eV</td>
</tr>
<tr>
<td>Resistivity</td>
<td>$&gt; 10^{18}$ ohm m (natural)</td>
</tr>
<tr>
<td>Young Modulus</td>
<td>$10.5 \times 10^{11}$ Nm$^{-2}$</td>
</tr>
<tr>
<td>Density</td>
<td>$3.515 \times 10^3$ kg m$^{-3}$</td>
</tr>
</tbody>
</table>

Table 1.1: Properties of diamond.
Table 1.2: Relationship between the properties and the potential applications of diamond.
Figure 1.1: Diamonds grown by low pressure CVD on a TEM grid.
the experimental parameters, but seem to be independent of the hydrocarbon or type of gas activation used. The observed morphologies may be divided into two classes: rounded or faceted crystallites. Faceted crystals typically yield a single Raman shift at 1332 cm\(^{-1}\), which is characteristic of natural diamond, whereas the un faceted kind shows additional features from graphite and amorphous carbon.

1.1 Growth Mechanisms

The theoretical understanding of diamond nucleation and growth is very limited. Some of it is outlined below. The gas specie or species responsible for diamond growth are unknown and contradictory models are offered. Tsuda [12] considers that the candidate growth species are \(CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, CH_5, CH_3, CH_2, CH\) and \(C\). The justification for considering only these species is that due to the dilution of hydrocarbon species in \(H_2\) only reactions between hydrocarbons and hydrogen are important. His quantum mechanical computations show \(CH_3\) as the growth species on (111) diamond surfaces. The sequence of steps is: surface hydrogen abstraction, attachment of \(CH_3\)'s and subsequent \(CH_3 - CH_3\) bonding along the surface. The latter step is activated by the \(CH_3^+\) cation.

This differs from a later model [19] in which a two step mechanism for diamond growth on (111) surfaces is postulated. Here, hydrogen abstraction from a surface adsorbed layer is followed by the addition of acetylenic molecules \((C_2H_2, C_2H_3, C_2H_4)\). The latter are presumed to be the basic building blocks for diamond growth.

Matsumoto [11] finds that the deposited diamond crystals have symmetries identical to that of some higher hydrocarbon cage compounds such as \(C_{10}H_{16}, C_8H_{14}, C_{12}H_{18}, C_{15}H_2,\) and \(C_{20}H_{22}\). He suggests that these compounds, which may be produced in the plasma discharge, form a gas phase precursor or embryo for the diamond crystals.
Sunkara and Angus [8] showed that the symmetrical morphologies of the diamond crystal can be accounted for by sequential growth errors. The complex molecular structures that form at the center of the crystallites arise from subsequent growth and are not present as initial seeds. A varied assortment of diamond morphologies was explained in this way including octahedral, cubic, cubo-octahedral, decahedral and even (twinned) icosahedral crystallites and hexagonal platelets. Often the boundaries between facets have re-entrant surfaces. Such features were observed in the crystallization of silicon from amorphous silicon, and are associated in both the silicon and the diamond cases with faster growth [9,8].

The idea that the complex diamond morphologies arises from growth twins and not by complex initial nuclei is supported by a landmark experiment by Martin and Hill from Aerospace Corp. [14]. In this experiment, pure hydrogen was excited by microwaves. Methane was introduced down-stream from the excitation region inside a fast gas flow tube. Diamond nucleation occurred at a distance along the tube that corresponds to 1 millisecond after the mixing of methane and excited hydrogen. The short time interval and the fact that the hydrocarbons were not subjected to the microwave discharge severely limits the probability of formation of complex hydrocarbons in the gas. Hence, it appears that initial condensation into large molecular weight species occurred on the surface. A related observation is that the growth rate peaks with hydrocarbon to hydrogen ratio. Natural diamond crystals were used as substrate material [15]. Thus, this effect appears to be related to growth rather then nucleation. A possible explanation is that growth proceeds by the competitive adsorption of at least two species and their subsequent reaction on the surface.

The Soviet group has applied classical nucleation theory and Langmuir isotherms [7] to study diamond homoepitaxy. They propose that diamond and graphite
are simultaneously deposited, but that films containing mostly diamond remain due to the relative inertness of the \( sp^3 \) bonds to gasification by oxygen and hydrogen as well as their lower sputtering yield. Fedoseev et al. present a semi-empirical model of diamond nucleation on diamond seed based on competitive Langmuir isotherm coverage of the substrate by diamond and graphite [7]. At low temperatures graphite grows by reaction of surface adsorbed species (Langmuir mechanism), while at high temperatures by reaction between adsorbed and gaseous species (Rideal mechanism).

Perhaps the most successful model to date for diamond growth on the \{100\} and \{111\} surfaces is due to Harris et al. [22]. The reaction steps are hydrogen abstraction, methyl addition, subsequent hydrogen abstraction and reaction between adsorbed methyls. Using experimental values of the gas concentration of methyls and hydrogen and assuming the gas to surface reactions of both atomic hydrogen and methyl are at equilibrium, his model gives good agreement for the growth rate on diamond \{100\} but not on \{111\}.

1.2 Surface Structure.

Since each surface has a different atomic scale geometry, the growth kinetics may be a function of the surface type. In the following, the surface structure is analyzed in terms of its relevance to growth kinetics, defects, and final crystal morphology.

An unreconstructed \{111\} diamond surface has a single dangling bond per atom. The bond is aligned along the surface normal. Single \( CH_3 \) molecules (for example) could bond to a \{111\} surface (see Tsuda's theory). Bonding between adjacent bound \( CH_3 \)'s occurs by bonding to a third atom in a third atomic layer. The latter bond can assume one of two conformations: a boat - forming an ABA sequence, or a chair - forming an ABC sequence. Since the difference involves only second nearest neighbor interactions, the energy difference is small and such growth errors occur
readily.

A three-atom nucleus with the ABA sequence may continue to grow across the surface and will then constitute a planar defect such as a stacking fault or twin (depending on subsequent layer sequences). Thus, growth from a planar \{111\} surface leads to the easy formation of planar growth defects in the crystal and to the final crystal morphology [8].

Considering only planar unreconstructed surfaces, the following information on growth from the vapor phase can be deduced from the surface structures:

- \{111\} - There is one dangling bond per surface atom. A nucleus of three bonded atoms, two on the surface and one bonding between them constitute the smallest surface step. The step can then grow into a layer by sequential additions of methyls, each forming a single bond to the surface, and hydrogen abstraction reactions. Stacking errors are easily generated.

- \{001\} - There are two dangling bonds per surface atom. Growth may proceed by single C atom additions each forming two bonds to the surface. No stacking errors can occur.

- \{011\} - This surface is 'intrinsically' faceted. There are atomically deep valleys running in the \{1\bar{1}0\} direction, which lies in the \{110\} plane. The slopes of the valley are \{112\} type surfaces. There is one dangling bond per surface atom. Growth may proceed by addition of C-C units forming two surface bonds, or, once a single C-C unit has bonded, by sequential single carbon atom additions in the two nearest neighbour positions to the C-C unit along the \{1\bar{1}0\} valley. Once the initial C-C unit has deposited, sequential deposition of single or double carbon units is possible. However, each \{1\bar{1}0\} valley requires its own C-C nucleation event before single carbon atoms can find sites for 2 of their bonds. Growth on a \{011\} surface does not lead to stacking errors but a partially growing \{1\bar{1}0\} valley and
its virgin neighbor together constitute a small (111) surface. Hence in practice, (011) surfaces may lead to the growth defects seen in (111) growth.

Higher index surfaces are more complex. The {311} surface for example is, like the {110} surface, intrinsically stepped. The surface atoms have either a single or a double dangling bond. The {100} or {111} surfaces are by far the most common found in CVD diamond.

In fact, surfaces are rarely planar and growth is usually controlled by the migration of steps and kinks. Terraces are regions of low index separated by ledges of atomic dimensions. Kinks are displacement of the ledges by one or more atomic distances (see figure 1.2). Steps and kinks are formed either geometrically – due to a mis-orientation between the local and average surface planes (see angles $\alpha$ and $\theta$ in figure 1.2), or thermally – due to the effect of entropy. On a stepped surface growth proceeds by the lateral migration of the steps and kinks. At low undercoolings the growth rate increases linearly with undercooling but peaks due to diffusion limits at the low temperature end. This growth mechanism leads to a faceted morphology for the final crystal. Another complication to the growth mechanisms is surface reconstruction. On a [100] diamond surface, surface reconstruction leads to a 2 x 1 structure where surface bonds form between adjacent carbon atoms thus eliminating the dangling bonds that are necessary for fast growth. One of the proposed roles for atomic hydrogen in diamond growth is the prevention of surface reconstruction.

1.3 Thermodynamic Analysis

1.3.1 Thermochemical Calculations

In order to gain some insight into the chemistry of diamond CVD, a series of equilibrium thermodynamic calculations was performed. For a given number of moles of hydrogen
Figure 1.2: The geometrical interpretation of terraces (T), kinks (K), ledges (L). A surface vacancy, and adatom are also shown.
and methane a computer code\(^1\) was used to calculate the equilibrium mole fractions of all the possible product species, both gaseous and solid, at various temperatures and pressures. The calculation is based on minimization of the Gibbs free energy of the system and relies on an extensive database of thermochemical data.

In assessing the applicability of equilibrium thermodynamics to chemical vapor deposition (CVD) of diamond, it should be noted that the metastability of diamond with respect to graphite is not an important factor. This is because the difference in Gibbs free energy for diamond and graphite is less than \(kT\) at typical deposition temperatures.

The non-equilibrium nature of diamond deposition is manifested primarily through the existence of super-equilibrium concentrations of radicals (in the HFCVD system these are mainly atomic hydrogen, electrons and some hydrocarbon radicals and possibly ions), and the existence of large temperature and concentration gradients. Wherever actual species concentrations were measured \([34]\) it was found that they differed from those predicted by thermodynamics. Nevertheless, several trends seem to follow thermodynamic predictions.

Figure 1.3 shows the solubility of carbon in the gas phase vs. temperature for typical diamond growth conditions \([13]\). The carbon mole fraction calculated from a feed methane concentration of 1\% is indicated by the horizontal line. The carbon solubility exhibits a minimum at about 1500K. The curve is independent of the feed C/H ratio and the hydrocarbon used. The temperature and carbon fraction defined by points on the high temperature side of the solubility curve are reported to be the best diamond growth conditions, where the temperature refers to the hot filament. This experimental result can be understood in terms of figure 1.3.

Figure 1.3: The solubility of carbon in hydrogen gas.
The figure can be read as a phase diagram for the filament as a function of T, P and carbon fraction. Graphite\(^2\) will form on the filament if the gas feed carbon fraction exceeds the gas solubility at the filament temperature. Graphite will gasify in other regions. The above behavior of graphite overlayer on a tungsten filament has been verified experimentally [16] and has been shown to influence the atomic hydrogen generation by the filament [18]. The latter effect is important for diamond formation.

Also seen in figure 1.3 is the region in the experimental parameter space where graphite will exist on the substrate as a stable phase. If graphite is not stable then diamond is even more unstable. Hence, the figure describes outer bounds for the diamond deposition window. The supersaturation of carbon as a function of gas temperature in the system can be read off the figure. It is proportional to the difference between the feed carbon fraction and the solubility. Hence, for the indicated inlet gas concentration of 1%, there is a thermodynamic driving force for carbon precipitation from the gas phase at gas temperatures less than about 2000K.

Figure 1.4 shows equilibrium mole fractions of \(H, CH_4, C_2H_2\), and graphite as a function of temperature. Initial mole fractions were: 0.96 \(H_2\), 0.01 \(CH_4\), 0.02 \(H_2O\), 0.01 graphite. The pressure was 50 torr. It can be seen that different species dominate at different temperatures. At 1000K to 1500K, methane mole fraction decreases and the mole fraction of graphite increases. On further heating the graphite re-gasifies to form acetylene. This trend has been verified experimentally for a variety of hydrocarbon-hydrogen mixtures.

Atomic hydrogen is thought to play a major role in diamond formation. It is known that atomic hydrogen preferentially etches graphite over diamond, and hence may enhance the diamond content of the deposit. Atomic hydrogen terminates the diamond surface thus maintaining the \(sp^3\) bond character needed for diamond growth.

\(^2\)Typically at 1000K only ungraphitized carbon or lamp black will form. Accurate free energies of such highly defective material is unavailable.
Figure 1.4: The equilibrium mole fractions of some of the species present in the gas phase as a function of temperature.
and preventing reconstruction of the surface. Associative desorption or desorption of hydrogen by reaction with gaseous hydrogen can lead to surface dangling bonds that promote the growth of the diamond lattice. The present work shows that atomic hydrogen recombination on the substrate surface is an important mechanism of heat transport to the substrate. Figure 1.5 shows thermodynamic calculations for atomic hydrogen mole fraction dependence on temperature and pressure. The atomic hydrogen concentration increases with decreasing pressure and increasing temperature. The increase in atomic hydrogen with temperature was confirmed experimentally [18].

Figure 1.6 shows thermodynamic predictions for the mole fraction of graphite as a function of temperature and pressure. It can be seen that the stability region for graphite extends to very low temperatures at low pressures. This suggests the potential for diamond deposition at lower temperatures provided that the pressure is lowered too. Recently, diamond deposition at 300°C was reported at 0.5-1 torr [2].

1.3.2 Summary of Thermodynamic Analysis

Some general aspects of diamond deposition at low pressure can be learned from equilibrium thermodynamic analysis. The region in P,T space in which graphite exists as a stable phase defines outer bounds for the diamond growth window for any given gas composition. This is a useful method for investigating potential new diamond forming chemistries. Atomic hydrogen mole fraction increases with hot filament temperature and decreases with pressure. In the carbon-hydrogen system, hydrogen, atomic hydrogen, methane, and acetylene are the dominant species in the diamond growth environment at equilibrium. The experimental evidence that graphite is codeposited with diamond and the small energy difference between the two phases indicates that the diamond forming region is very close to the stability region of graphite in the C-H system and partially explains the success of thermodynamic calculations.
Figure 1.5: The atomic hydrogen mole fraction dependence on temperature and pressure.
Figure 1.6: The stability region for graphite as a function of pressure.
Chapter 2

The Dual Filament Reactor

2.1 Introduction

In diamond growth systems utilizing plasmas, the complex hydrocarbon chemistry is further complicated by the electric fields and ions necessary to maintain the plasma and the reactions involving the molecular ions. Since plasmas are not necessary for diamond formation, we have chosen to use the simpler hot filament assisted CVD method (figure 2.1).

Even for the relatively simple hot filament chemical vapor deposition method (HFCVD) the list of experimental parameters is long. These are:

1. Filament temperature.
2. Substrate temperature.
3. Filament to substrate distance.
4. Gas pressure and composition.
5. Flow rates.
The importance of the last item is often underestimated. There are many ways that the geometry of the reactor can influence the deposition process. One of the most important effects of geometry is the influence on the relative contribution of the various mechanisms of energy and mass flux. For example, changes in geometry can change the mass flux from diffusion to reaction control or the heat flux from being dominated by radiation to conduction.

Over the past decade, a diamond deposition ‘window’ has been marked out by many researchers in the above parameter space. Virtually all of the work was done in systems where substrate heating is accomplished by energy transport from the excitation source. In effect, parameters 2 and 3 were coupled and could not be varied independently. Also, all the previous systems were limited in their substrate temperature range. The low end was limited by heating from the excitation source and the high end by the melting points of heating elements, housing, or substrate.

In the present system, the substrate is replaced by another filament positioned parallel to the flow direction and normal to the hot filament (see fig. 2.1). This geometry minimizes the radiation heating and decouples parameters 2 and 3 allowing independent substrate temperature control with a range of 300K - 2700K for a tungsten filament. Additionally, a single experimental run provides complete information on the effect of parameter 3 by observation of the deposit along the filament. Alternatively, by using a short filament as the substrate, conduction of heat at the filament ends becomes important and causes a large temperature gradient along the filament. Temperature differences of the order of 1000°C can be maintained. Hence, a single run can also yield information on a wide range of substrate temperatures. In addition, the reactor geometry is particularly easy to model. Extensive modelling of the mass and energy flux including the most important chemical reactions were performed [32].
Figure 2.1: Schematic drawing of the dual filament hot filament chemical vapor deposition reactor. AC are power supplies; OP is optical pyrometer; M are mass flow controllers; B is ethanol bubbler; HF is hot filament; SF is substrate filament; RGA is residual gas analyser and MP is mechanical pump.
2.2 Reactor Design

The reactor is constructed from a horizontal cylindrical quartz tube, 20" in length and 4" internal diameter. It is sealed at each end by steel flanges with 'O'-ring seals. The pump, throttle valve and residual gas analyser are connected to the downstream flange, and the gas feed, mass flow controllers, and electrodes are connected to the upstream flange. The electrodes are \( \frac{1}{4} \) inch molybdenum rods. They are used to supply power and act as mechanical supports for the substrate and hot filament. The rods are insulated from the flange by teflon sleeves that are tightened about the rods by bored-through \( \frac{3}{8} \) inch Swagelocs\textsuperscript{TM}. This construction satisfies the difficult requirements of mechanical stability, chemical inertness, electrical insulation, and leak resistance. The rods can be conveniently slid in and out of the reactor by loosening the Swagelocs\textsuperscript{TM}. The distance between hot filament and substrate and the length of each filament can be adjusted over wide ranges. One of the electrodes to the substrate filament is mounted on a motion feedthrough that permits in-situ position adjustments. Considerable flexibility in mounting the filaments with respect to the rods exists. This is accomplished, for each geometrical requirement, by putting together an assortment of short molybdenum rods, nuts and screws (not unlike a Leggo\textsuperscript{TM} set).

2.3 Ethanol Flow Rate Calculation and Measurement.

When ethanol is used as the carbon source in the hot filament reactor it is transported into the reactor by hydrogen bubbled through the liquid ethanol. The partial pressure of ethanol, \( P_{\text{eth}} \), in the bubbler is the vapor pressure, which is determined by the bubbler temperature. If \( P_{\text{H}_2} \) is the partial pressure of hydrogen in the bubbler, then the mole fraction of ethanol, \( Y_{\text{eth}} \), is given by:
\[ Y_{\text{eth}} = \frac{P_{\text{eth}}}{P_{\text{eth}} + P_{H_2}} \]

If \( F_{\text{eth}} \) and \( F_{H_2} \) are the flow rates of ethanol and hydrogen respectively, and assuming good mixing and ideality of the gases:

\[
\frac{F_{\text{eth}}}{F_{\text{eth}} + F_{H_2}} = \frac{P_{\text{eth}}}{P_{\text{eth}} + P_{H_2}}
\]

In a typical run \( P_{\text{eth}} + P_{H_2} = 811 \) torr as measured by a Bourdon mechanical pressure gauge. \( P_{\text{eth}} \) at room temperature is \( 56 \pm 10 \) [17] \( F_{\text{eth}} + F_{H_2} = 14 \) sccm as measured by a MKS mass flow meter. Hence \( F_{\text{eth}} \) can be determined from eq. 2.3:

\[ F_{\text{eth}} = 14 \times \frac{56}{811} = 0.97 \text{ sccm}. \]

The error introduced by ambient temperature variations was minimized by enclosing the bubbler in styrofoam.

### 2.4 Leak Rate Calculation and Measurement.

In this section, the apparent leak rate is calculated in standard cubic centimeters per minute (SCCM) from the rate of pressure change with time. Knowledge of the leak rate allows direct comparison with the feed gas flow rate and thus an assessment of the significance of the leak rate. In the present type of reactor the apparent leak rate is dominated by outgassing from the ‘O’ rings seals and not from permeation [23].

Differentiating the ideal gas law:

\[
\frac{dn}{dt} = \frac{dP}{dt} \cdot \frac{V}{RT} \tag{2.1}
\]

Let the flow rate of the leak be \( F \):

\[ F = (\text{no. of moles/min}) \times (\text{volume of 1 mole at STP}) \]
\[ F = \frac{dn}{dt} \cdot V_m \]

Multiplying both sides of eq. 2.1 by \( V_m \):

\[ F = \frac{dP}{dt} \cdot \frac{V}{RT} V_m \]  \hspace{1cm} (2.2)

Now, the reactor is a 20" by 4" diameter tube giving:

\[ V = 20 \cdot \pi D^2 / 4 = 20 \cdot \pi \cdot 4 = 240 \text{ in}^3 = 3933 \text{ cm}^3 \]

Also, there are 40" of 1" diameter tubing:

\[ 40 \cdot \pi \cdot 1/4 = 30 \text{ in}^3 = 670 \text{ cm}^3 \]

The total volume is 4.61.

The rate of change of pressure, \( \frac{dP}{dt} \), is measured by noting the pressure increase during one minute when the system is isolated from its pump. The pressure gauge is a MKS Pirani gauge type 385 Moducell. Its voltage output is converted to torr using calibration curves for N\(_2\), Ar or He supplied by the manufacturer. The curve for He was used since no calibration curve is available for H\(_2\). The units and values for the constants are RT=19188 l-torr, and \( V_m=22.41 \). Substituting in eq. 2.2:

\[ F = \frac{dP}{dt} \cdot \frac{4.6 \cdot 22.4}{19188} = 0.0054 \cdot \frac{dP}{dt} \text{l/min} = 5 \cdot \frac{dP}{dt} \text{ SCCM} \]  \hspace{1cm} (2.3)

F is in SCCM if \( \frac{dP}{dt} \) is in torr/min.

The measured leak rate was 0.007 SCCM. This is of the same order as the predicted outgassing rate for an elastomer 'O' ring sealed vacuum chamber [23]. Hence, no significant improvement in the apparent leak rate is possible for this kind of reactor.

The outgassing gas from 'O' rings is typically \( H_2 O \), \( CO \), and \( CO_2 \). Residual gas analysis showed that in the present reactor the outgassing is mainly \( H_2 O \). Assuming that the total outgassing rate is due to \( H_2 O \), the \( O_2 \) mole fraction in the reactor at
a hydrogen flow rate of 100 sccm is $7 \times 10^{-5}$. When the hot filaments are turned on, there may be transient outgassing of $H_2O$ that exceed this value.

2.5 Temperature and Power Measurements

In a HFCVD reactor, a 2300°C hot filament is positioned about $\frac{1}{2}$ cm away from a 1000°C substrate. Optical pyrometers are inaccurate when applied to a situation where there are large temperature gradients (as in this case) for two reasons: Their low spatial resolution implies that there will be averaging over significant regions, and light from a nearby hot surface may be reflected by a colder surface to cause the latter surface to appear hotter.

An important feature of the dual filament system is that the resistance and hence the temperature of the substrate filament can be measured in-situ. The resistance is a linear function of the average substrate temperature (see fig. 3.1). These data were used to determine the average substrate temperature in the experiments discussed below. The slope of a plot of the resistivity vs. temperature is a material property. The slope of fig. 3.1 is $1.4 \times 10^{-4}$ ohm/K. The value of the slope based on literature values for tungsten [10] is $1.6 \times 10^{-4}$ ohm/K. The literature value falls within 12% of the measured value. The discrepancy can be accounted for by inaccuracies in the measured length and area of the filament. The length and area of the filament necessarily enter the calculation when the slope of the resistance is calculated from the slope of the resistivity.

The resistance vs. temperature calibration was made with the hot filament off so that the pyrometer could be used more reliably. The measured resistance is an average over the length of the filament and therefore depends to some extent on the temperature distribution. The relationship shown in fig. 3.1 indicates that changes
in the temperature distribution as a function of substrate temperature do not strongly
effect the linearity of the resistance measurements.
Chapter 3

Transport Analysis

3.1 Introduction

Experimentally, it is known that when hydrogen is used as the carrier gas, atomic hydrogen is necessary for rapid diamond growth. It is thought that atomic hydrogen stabilizes $sp^3$ bonds, destroys $sp^2$ bonds, and creates surface dangling bonds by abstraction reactions [19,21].

We show that atomic hydrogen plays another important role during diamond deposition, namely that it transports much of the energy reaching the substrate. The heat is transferred to the substrate in the form of chemical energy, which is released by the strongly exothermic hydrogen recombination reaction, $H + H \rightarrow H_2$. This energy release is measured and used to compute the hydrogen recombination rate on the substrate, the atomic hydrogen concentration near the substrate and the concentration gradient in the reactor. The experimental conditions under which atomic hydrogen transport is diffusion limited are found.

Our experiments are based on power measurements to a heated substrate
wire held at a constant temperature. Such isothermal probes have been used to determine diffusion coefficients and concentrations of radicals [24,25], kinetics of heterogeneous hydrogen atom recombination [27], and homogenous hydrogen recombination rate [28]. Thermocouple junctions have similarly been used [29].

3.2 Experimental

A horizontal, fused-quartz tube hot filament chemical vapor deposition reactor was modified as follows: The tungsten hot filament was positioned perpendicular to the tube axis and the substrate was replaced by a tungsten filament positioned parallel to the tube axis. The latter filament was used as a substrate and could be independently heated electrically. The substrate filament and the hot filament were 0.25 mm diameter tungsten wires of length 14 mm and 90 mm respectively. The distance between the substrate and hot filament was 6 mm. Diamonds were deposited on the substrate filament under normal diamond growth conditions [4,5]. The reactor is shown in fig. 2.1, and is described in detail in section 2.1.

The resistance of the substrate filament was measured in-situ and is a linear function of its average temperature (see fig. 3.1). These data were used to determine the average substrate temperature in the experiments discussed below. The measured resistance is an average over the length of the filament and therefore depends to some extent on the temperature distribution. The relationship shown in fig. 3.1 indicates that changes in the temperature distribution as a function of substrate temperature do not strongly effect the linearity of the resistance measurements.

The resistance was measured by simultaneously measuring the voltage across the substrate filament, V, and the current through it. To measure the cur-
rent accurately, a 0.01Ω, fan-cooled, resistor was inserted in series with the substrate filament and the voltage across it, \( v \), was measured. The resistance, \( R \), is given by \( R = 0.01 \times \frac{V}{v} \). The power supplied to the substrate, \( P \), is given by \( P = \frac{Vv}{0.01} \).

Temperature control was implemented via two variable auto-transformers connected in a cascade for both the substrate and hot filaments (see fig. 3.2). This allowed reproducibility of the temperatures of each filament to within 2°C in the range 25-2500°C. The accuracy of the temperature measurements relies on pyrometer reading which is accurate to approximately ±100°C.

### 3.3 Experimental Procedure and Results

#### 3.3.1 Temperature Measurements

The experimental procedure was as follows:

1. A calibration curve of substrate temperature vs. substrate resistance was determined using a two color pyrometer (see fig. 3.1).

2. The substrate was electrically heated to 1316°C, and the substrate resistance was measured.

3. The hot filament was turned on and set to 2000°C.

4. The new value of the substrate temperature was now found by another measurement of the resistance and use of the calibration curve.

Figure 3.3 shows the substrate temperature increase when the hot filament is turned on vs. pressure and ambient gas.

#### 3.3.2 Power Measurements

The experimental procedure was as follows:
1. The substrate was electrically heated to a specified temperature, $T_s$, and the required electrical power, $Q'_{elec}$, and the substrate resistance were measured.

2. The hot filament was turned on and set to 2000°C.

3. The electrical power to the substrate was reduced until the substrate regained its original resistance (and therefore its original temperature, $T_s$) and the new electric power to the substrate, $Q_{elec}$, was measured.

The difference $Q'_{elec} - Q_{elec}$ was used to analyse the heat transport from the hot filament to the substrate at different substrate temperatures, reactor pressures, and ambient gases as described below.

Table 3.1 shows some representative substrate power measurements taken using helium and hydrogen. Figure 3.4 shows the power supplied to the substrate at 1485°C as a function of hot filament temperature for helium and hydrogen ambients. Figure 3.5 shows the effect of the addition of methane on the heat flow to the substrate. Figure 3.6 shows the difference in powers supplied to the substrate when the hot filament is off and on (at 2000°C). The substrate temperature was maintained the same in both cases. The results for tungsten and platinum substrates are shown. Figure 3.7 shows the effect of substrate to filament distance and substrate length on the heat flow to the substrate.

3.4 Analysis of Results.

3.4.1 Temperature Measurements

The change in substrate temperature when the hot filament was turned on is shown in figure 3.3 as a function of reactor pressure and ambient gas. Four different gases were used: Ar, N$_2$, He and H$_2$. A detailed quantitative analysis of substrate heating can be
found in the next section. Figure 3.3 is analysed qualitatively below.

The figure shows that for every ambient gas used, the change in substrate temperature approached zero when the pressure was reduced. This indicates that radiation contributes little to substrate heating.

An increase in heating is apparent for all gases in the pressure range 0.1 to 30 torr. This is due to an increase in the thermal conductivity of the gases as the flow regime changes from mixed mode of molecular and viscous to viscous only [42].

The substrate is positioned below the hot filament. Convective currents caused by the hot filament act to cool the substrate. For the heavier gases, e.g. Ar and N₂, at pressures greater then 50 torr, the substrate temperature increase drops. This is due to the effect of convection and is consistent with independent estimates of the Grashof number and computer modelling [32].

The monotonic and slow rise in the temperature increase in helium is consistent with the slow increase in thermal conductivity with pressure in the viscous regime [42] and the absence of convection.

At 25 torr, the temperature increase in hydrogen is approximately 250 degrees higher than in helium whereas the thermal conductivity of hydrogen is only about 15% higher [32,43]. From the above discussion it is clear that radiation and convection and conduction cannot account for the anomalous heating in a hydrogen ambient. It is proposed that atomic hydrogen recombination on the substrate surface causes the high heating in hydrogen. In hydrogen, the temperature increase diminishes slowly for pressures between 30 and 250 torr. This is consistent with the increase in homogenous gas phase recombination of atomic hydrogen, see section 3.4.5.
3.4.2 Power Measurements

The difference in electrical power to the substrate, required to maintain a constant temperature when the hot filament is on and when the hot filament is off, is, to a good approximation, equal to the net power transported from the hot filament to the substrate. A detailed energy balance about the substrate is given in section 3.4.3. This heat transport can occur via radiation, thermal conduction, mechanisms of mass flow, i.e., free convection (flow driven by gravity and density differences) and forced convection (flow driven by pressure gradients), or chemical reactions.

Experiment 1 in table 3.1 shows that there is little heat transport between the hot filament and the substrate at low pressure. This indicates that most of the heat is transported by gas phase mechanisms and not by radiation. Similar experiments performed at 0.1 torr in nitrogen, argon and hydrogen also showed little radiation heating of the substrate. The present reactor has a very small view factor for radiation between the hot filament and the substrate. Radiation can be an important mechanism of heat transport in reactors of conventional geometry (see section 3.5.2).

Experiments number 2 and 3 give similar power differences for the substrate when the hot filament is on and off, although the pressure in experiment 2 is 20 torr and in experiment 3 is 200 torr. Since the same gas is used for both experiments, the rate of heat transport by free convection scales with \( \rho^2 \), where \( \rho \) is the density [30]. Hence experiments 2 and 3 indicate that negligible heat is transported by free convection in helium. Examination of the viscosity data for helium and hydrogen reveals that, for the relevant pressure and temperature range, the heat transfer by free convection in helium is greater than in hydrogen [13]. Hence, experiments 2 and 3 show that there is negligible free convective heat transport in hydrogen. This result is consistent with an estimate of the Grashof number and associated heat transfer coefficient and with
the results of detailed modelling studies [32,33].

Under typical diamond HFCVD conditions, heat transfer by forced convection is small compared to conduction [32]. Also, there is no significant forced convection from the hot filament to the substrate because of the flow pattern in the reactor [32].

Figure 3.4 shows the power supplied to the substrate in order to maintain the substrate temperature at 1485°C plotted vs. hot filament temperature for both helium and hydrogen ambients. In inert gases, or in conditions where hydrogen atom concentrations are negligible, the energy balance (see section 3.4.3) shows that the temperature of the substrate filament is primarily determined by the balance of electrical power supplied to the substrate, \( Q_{\text{elec}} \), and the net power conducted away from the substrate through the gas to the walls of the reactor, \( Q_{\text{c.w}} \), through the electrodes, \( Q_{\text{c.e}} \), and the radiated power \( Q_{\text{rad}} \).

\[
Q_{\text{elec}} = Q_{\text{c.w}} + Q_{\text{c.e}} + Q_{\text{rad}}
\]  

(3.1)

Figure 3.4 shows that at hot filament temperatures below approximately 1800°C, more power is required to heat the substrate filament in hydrogen than in helium. At the same substrate temperature, \( Q_{\text{c.e}} \), and \( Q_{\text{rad}} \), will be the same in hydrogen and in helium. Therefore, at low temperatures, \( Q_{\text{c.w}} \) in hydrogen is greater than in helium, which is consistent with the higher thermal conductivity of hydrogen gas. \(^1\)

Figure 3.4 also shows that the power requirement in helium decreases approximately linearly with increasing hot filament temperature. This arises from the increase in heat conducted to the substrate from the hot filament as the hot filament

\(^1\)The thermal conductivities of helium and hydrogen at room temperature are 0.14 and 0.18 W/m K, respectively [32].
temperature increases. The behaviour in hydrogen is quite different. At high hot filament temperatures, the substrate power requirement drops far below that for helium. Clearly, the modest difference in thermal conductivity of the gases cannot account for this dramatic change.

Since radiation, convection, and conduction cannot account for the results described above, there must be another mechanism of heat transport to the substrate in hydrogen. Atomic hydrogen is created at the hot filament and diffuses to the substrate where it recombines to form molecular hydrogen. The energy released by atomic hydrogen recombination accounts for the low power requirement in hydrogen at hot filament temperatures above 1900°C. A quantitative estimation of this effect is given in the following section.

3.4.3 Calculation of Atomic Hydrogen Recombination Rate.

The energy transported to the substrate by recombination can be determined by an energy balance about the substrate. We assume steady state and equate the power added to the substrate to the power leaving the substrate. When the hot filament is turned off, the steady state energy balance about the substrate is:

$$Q'_{elec} = Q'_{c.e} + Q'_{c.w} + Q'_{gen} + Q'_{rad}$$  \hspace{1cm} (3.2)

When the hot filament is turned on, the energy balance becomes:

$$Q_{elec} + Q_{c.HF} + Q_{rad.HF} + Q_{rec} = Q_{c.e} + Q_{c.w} + Q_{gen} + Q_{rad}$$  \hspace{1cm} (3.3)

In equation 3.2, the primes indicate that the hot filament is off. $Q_{elec}$ is the electric power supplied to the substrate. $Q_{c.HF}$ is the power conducted from the hot filament to the substrate. $Q_{rad.HF}$ is the power radiated from the hot filament to the substrate.
$Q_{\text{rec}}$ is the power delivered to the substrate by hydrogen atom recombination. $Q_{\text{c,e}}$ is the power conducted from the substrate to the substrate electrodes. $Q_{\text{c,w}}$ is the power conducted from the substrate through the gas to the reactor walls. $Q_{\text{gen}}$ is heat loss from the substrate due to the generation of atomic hydrogen. $Q_{\text{rad}}$ is the power radiated from the substrate.

Measurements of $Q_{\text{elec}}$ and $Q'_{\text{elec}}$ are made with the hot filament on and off, respectively, with the substrate temperature and other parameters held constant. The difference $Q'_{\text{elec}} - Q_{\text{elec}}$ is obtained from equations 3.2 and 3.3.

$$Q'_{\text{elec}} - Q_{\text{elec}} = (Q_{\text{rad}}' - Q_{\text{rad}}) + (Q_{\text{c,e}}' - Q_{\text{c,e}}) + (Q_{\text{c,w}}' - Q_{\text{c,w}}) + (Q_{\text{gen}}' - Q_{\text{gen}}) + Q_{\text{c,hf}} + Q_{\text{rad,hf}} + Q_{\text{rec}}$$

(3.4)

The first four (bracketed) terms on the right hand side of equation 3.4 are each individually small because the average substrate temperature is the same during the measurement of $Q'_{\text{elec}}$ and $Q_{\text{elec}}$. Small differences from zero of these terms could arise from differences in the temperature distribution along the substrate filament. The term $(Q_{\text{c,w}}' - Q_{\text{c,w}})$ could also be non-zero if the change in the temperature field arising from turning on the hot filament influences conduction from the substrate to the walls of the reactor. Since the substrate temperatures used are under 1500°C, the hydrogen generation terms $Q_{\text{gen}}'$ and $Q_{\text{gen}}$ are each individually extremely small ensuring that $(Q_{\text{gen}}' - Q_{\text{gen}})$ is small. An experimental confirmation that the first three terms are negligible is given in Appendix A. Using these results, equation 3.4 becomes:

$$Q'_{\text{elec}} - Q_{\text{elec}} = Q_{\text{c,hf}} + Q_{\text{rad,hf}} + Q_{\text{rec}}$$

(3.5)

$Q'_{\text{elec}} - Q_{\text{elec}}$ is a measured quantity. $Q_{\text{c,hf}}$ can be found by measurements at low pressure in helium, see Table 5.1, experiment 1. $Q_{\text{rad,hf}}$ cannot be measured independently of $Q_{\text{rec}}$, but it is shown in Appendix A that $Q_{\text{c,hf}}$ is small in helium, and in Appendix B, that this term can be estimated for hydrogen from a measurement in helium. Hence,
$Q_{\text{rec}}$ can be found

Experiment 4 in table 3.1 shows that in hydrogen, measurements of the substrate power with the hot filament off and on gave $Q'_{\text{elec}} = 32.67 \text{ W}$, and $Q_{\text{elec}} = 1.64 \text{ W}$. From Appendix B, $Q_{e,hf} = 1.77 \text{ W}$. From experiment no. 1 in table 3.1, $Q_{\text{rad, hf}} = 0.85 \text{ W}$. Hence from eq. 3.5, $Q_{\text{rec}} = 28.41 \text{ W}$. In this reactor, atomic hydrogen recombination heating accounts for 90% of the heat reaching the substrate.

Another approach to determine the contribution of atomic hydrogen recombination to substrate heating is presented below. The power requirement to maintain the substrate at a temperature of 1316°C was measured in 4 different ambient gases: Ar, N$_2$, He and H$_2$. The results are shown in figure 3.8. The data for Ar, N$_2$ and He fall on approximately a straight line indicating that thermal conduction can account for the power requirement. However, the measured power in H$_2$ is about 10W less than the value given by extrapolating the line to the H$_2$ thermal conductivity data point. Thus, the contribution of atomic hydrogen recombination to substrate heating is about 10W. In this experiment, the distance between substrate and hot filament was approximately 1 cm. This is higher than in the experiments which were used for the energy balance considerations. This led to a lower power contribution of atomic hydrogen recombination to substrate heating in this case. This effect is examined in detail in section 3.4.4.

The number of recombination events per sec, $f$, is given by:

$$f = \frac{Q_{\text{rec}}}{\alpha \Delta H} \quad (3.6)$$

where $\alpha$ is the thermal accommodation coefficient which is defined as the ratio of energy transferred to the substrate per recombination to the total energy released by recombination. $\Delta H$ is the enthalpy of formation of molecular hydrogen from atomic hydrogen and equals 4.69eV ($7.51 \times 10^{-19} \text{ J}$) at 1658K. The thermal accommodation coefficient, $\alpha$, -
was taken as unity [28,29]. Hence,

\[ f = \frac{28.41 \, J \, s^{-1}}{7.51 \times 10^{-19} \, J} = 3.78 \times 10^{19} \, s^{-1}. \]  \hspace{1cm} (3.7)

### 3.4.4 Effect of Filament to Substrate Distance and Filament Length

In order to determine whether atomic hydrogen is recombining over the entire substrate area or over some fraction of it, the substrate area was varied by changing the distance, \( l \), between the electrodes. Fig. 3.7 shows the dependence of \( Q'_{\text{elec}} - Q_{\text{elec}} \) on substrate length and substrate to filament distance. For the case where the substrate is close to the hot filament, \( Q'_{\text{elec}} - Q_{\text{elec}} \) increases with substrate area. This indicates that the recombination occurs over the entire substrate area. For the case where the substrate is further from the hot filament, \( Q'_{\text{elec}} - Q_{\text{elec}} \) remains approximately unchanged with increasing substrate length. This indicates that at larger distances from the hot filament, the recombination occurs primarily in the center region of the substrate, i.e., in the region closest to the hot filament. The results for the case where the substrate is closer to the hot filament were used in the calculation for the atomic hydrogen concentration given in section 3.4.7.

### 3.4.5 Homogenous Recombination of Atomic Hydrogen

Where gas phase recombination occurs, the concentration gradient no longer determines the flux. In order to find the concentration gradient of atomic hydrogen from the measured flux, it is necessary to first consider the effect of homogenous recombination of atomic hydrogen on this gradient. It is shown below that the atomic hydrogen concentration gradient due to homogenous recombination is negligible with respect to the concentration gradient due to surface recombination.
Considering only homogenous recombination in the reactor volume and atomic hydrogen generation at the hot filament there will be steady state when the homogenous recombination rate equals the generation rate. The reaction $H + H \rightarrow H_2$ requires a third body to dissipate the energy release. Hence for recombination,

$$-\frac{dc}{dt} = 2kc^2c_m$$  \hspace{1cm} (3.8)

where $c_m$ is the total concentration of species in the reactor, and the factor of 2 comes from the fact that 2 atomic hydrogens are annihilated per recombination event (stoichiometric factor). Since diffusion dominates the transport of atomic hydrogen, we have:

$$t = \frac{x^2}{D}$$  \hspace{1cm} (3.9)

where $D$ is the diffusion coefficient, $t$ is the time until recombination and $x$ is the distance travelled from the hot filament before recombination. Hence,

$$dt = \frac{2xz}{D}$$  \hspace{1cm} (3.10)

and from 3.8 and 3.10:

$$\frac{dc}{dt} = \frac{D}{2x} \frac{dc}{dx} = 2kc^2c_m$$  \hspace{1cm} (3.11)

and

$$\frac{dc}{dx} = \frac{4zkc^2c_m}{D}$$  \hspace{1cm} (3.12)

where $dc/dx$ is the gradient due to recombination.

It is shown in section 3.5.1 that the atomic hydrogen concentration gradient caused by surface recombination can be approximated by the diffusion equation (Fick's Law). Hence,

$$\frac{dc}{dx} = \frac{J}{D}$$  \hspace{1cm} (3.13)

where $c$ is the concentration, $D$ is the diffusion coefficient, $J$ is the flux of atomic hydrogen, and $dc/dx$ is the gradient due to surface recombination. The ratio, $R$, of
gradients is:
\[ R = \frac{J}{4kc^2c_mx} = \frac{J}{4kc^2c_mx} \]  \hspace{1cm} (3.14)

Note that \( R \) is independent of \( D \) since \( D \) effects both gradients equally. Now, \( J = \frac{2J'}{A} = 4 \times 10^{24} \), and \( k = 10^{-44} m^{-6} s^{-1} \) \cite{28}. Using 1\% dissociation of atomic hydrogen and a total pressure of 20 torr, one has \( c \sim 10^{21} \) and \( c_m = 10^{23} \), giving \( R = 4000 \).

Hence diffusion is the dominant factor in determining the concentration gradient, and neglecting homogenous atomic hydrogen recombination in the analysis of atomic hydrogen diffusion is justified at 20 torr. Note, however, that at 200 torr, \( R \sim 4 \) and homogenous recombination is significant.

### 3.4.6 Atomic Hydrogen Mean Free Paths

The recombination rate per atomic hydrogen can be expressed from eq. 3.8,

\[ -\frac{1}{c} \frac{dc}{dt} = 2kc_{c_m} = 2 \times 10^{-44} \times 10^{21} \times 10^{23} = 2 s^{-1} \]  \hspace{1cm} (3.15)

Hence the average time, \( r \), for a recombination of atomic hydrogen in the gas is \( \frac{1}{2}s \).

The average diffusion length for atomic hydrogen before a recombination event is given by

\[ \sqrt{Dr} = \sqrt{0.175 \times 0.5} = 0.3 m \]  \hspace{1cm} (3.16)

The distance between the hot filament and the substrate is about 0.01m hence most of the atomic hydrogen will not recombine over that distance.

At 200 torr we have

\[ -\frac{1}{c} \frac{dc}{dt} = 2 \times 10^{21} \]  \hspace{1cm} (3.17)

Taking \( D = 0.0175 m^2 s^{-1} \) we have \( r = 5 \times 10^{-3} \) and \( x = \sqrt{0.0175 \cdot 5 \times 10^{-3}} = 10^{-2} m \).

In this case the diffusion length before recombination is of the order of the distance
between the hot filament and the substrate and gas phase recombination is significant. This result is consistent with figure 3.3 which shows a reduction in substrate heating in hydrogen at higher pressures.

It is instructive to compare the collisional mean free path, $\lambda$, to the average diffusion length before recombination. The collisional mean free path of atomic hydrogen is given by

$$\lambda = \frac{3D}{v}$$

where $v$ is the average kinetic velocity. This gives $\lambda = 90\mu$ at 20 torr and $\lambda = 9\mu$ at 200 torr. The collisional mean free path, $\lambda$, is much less than the distance travelled until a recombination event occurs. This reflects the fact that two body collisions involving atomic hydrogen and molecular hydrogen do not result in recombination.

3.4.7 Estimate of Atomic Hydrogen Concentration.

The collision rate of atomic hydrogen with the surface can be related to the gas phase concentration of atomic hydrogen by kinetic gas theory:

$$J = \sqrt{\frac{kT}{2\pi m}} C_H$$

(3.19)

where $J$ is the collision flux, $C_H$ is the concentration, $m$ is the mass, $k$ is the Boltzmann constant, and $T$ is the temperature. The recombination coefficient, $\beta$, is defined as the ratio of the recombination rate, $f$, to the collision rate, $JA$, i.e.

$$\beta \equiv \frac{f}{JA}$$

(3.20)

where $A$ is a surface area. Thus from 3.19 and 3.20.

$$C_H \frac{f}{JA} \sqrt{\frac{2\pi m}{kT}}$$

(3.21)

The sticking coefficient for atomic hydrogen, $S$, is defined as the ratio of the net adsorption rate to the collision rate. At typical substrate temperatures, atomic hydrogen
desorption from the substrate is very slow [26]. Steady state coverage is achieved when the molecular hydrogen desorption rate equal to half the atomic hydrogen adsorption rate. Therefore, it follows from the definition of $\beta$ and $S$ that $\beta = \frac{1}{2}S$. Both $\beta$ and $S$ decrease with coverage, i.e., with increasing pressure and decreasing substrate temperature. The sticking coefficient of hydrogen on tungsten has been extensively studied under UHV conditions. It was found that for low coverages $S = 0.5$ [37,38,39,40]. However, our pressure regime is 9 orders of magnitude higher than the pressures at which surface coverage of hydrogen on tungsten is reported. A value of $\beta = 0.06$ was found at a pressure between 0.01 to 0.1 torr and it was also found that for tungsten $\beta$ is independent of substrate temperature in the range 353-1083K [27]. The effective adsorption surface area of tungsten can be as high as 40 times the geometrical area due to surface roughness [42]. Substituting $\beta = 0.06$ and using the geometrical area, as a lower bound and 40 times the geometrical area as an upper bound for the surface area, eq. 3.21 gives the bounds for the atomic hydrogen concentration as

$$6.1 \times 10^{10} \text{ m}^{-3} < C_H < 2.4 \times 10^{22} \text{ m}^{-3} \quad (3.22)$$

This range corresponds to a mole fraction range of 0.0052 to 0.21 at 20 torr. The estimated values of $C_H$ are in agreement with direct gas phase measurements of others.

For example, Schaffer et al. [34] used two photon laser induced fluorescence measurements to measure the atomic hydrogen concentration. Their results for the concentration at a separation of 0.6 cm between the hot filament and the substrate, vary between $1 \times 10^{21}$ m$^{-3}$ and $4 \times 10^{22}$ m$^{-3}$ depending the hot filament temperature, diameter, material and methane concentration.

Hsu [35] measured the atomic hydrogen concentration using molecular beam mass spectrometry. Hsu used a total pressure of 20 torr, and a tungsten hot
filament of diameter 0.25 mm at a distance of 13 mm from the detector. At a temperature of 2300K, with pure hydrogen ambient, the atomic hydrogen mole fraction was 0.0007 or a concentration of $8.24 \times 10^{19} \text{ m}^{-3}$.

Harris and Weiner [36] found the atomic hydrogen mole fraction near the substrate as a function of methane concentration using a mass spectroscopic technique. Their results can be extrapolated to zero methane concentration to give an atomic hydrogen mole fraction of 0.014, or a concentration of $1.63 \times 10^{21} \text{ m}^{-3}$. They used a higher hot filament temperature (2600K) as well as a smaller hot filament to substrate distance (3-5mm) and a different experimental geometry.

3.4.8 Effect of Methane on Hydrogen Recombination Rate

Fig. 3.5 is a plot of $Q'_{dec} - Q_{dec}$ vs. methane flow rate. The hydrogen flow rate is 100 sccm. The value of $Q'_{dec} - Q_{dec}$ decreases with increasing methane flow rate. This indicates a reduction in the hydrogen recombination rate on the substrate. A reduction in atomic hydrogen concentration in the gas phase with methane was reported recently [34]. It can be seen from equations 3.21, 3.6, and 3.5 that $Q'_{dec} - Q_{dec} \propto C_H$ where $C_H$ is the concentration of atomic hydrogen. Hence, if the entire decrease in energy flow to the substrate is due to a decrease in atomic hydrogen concentration, then the approximate 3-fold decrease in $Q'_{dec} - Q_{dec}$ in fig 3.5 implies a 3-fold decrease in $C_H$ when the methane flow rate is increased from zero to 7 sccm. The decrease in atomic hydrogen concentration can be explained by gas phase destruction of atomic hydrogen according to the reaction $CH_4 + H \rightarrow CH_3 + H_2$. However, due to the complex geometry, detailed three dimensional modelling is necessary to quantify this effect. Alternative explanations of the reduction in energy flow to the substrate are changes in the atomic hydrogen generation rate on the hot filament or recombination
rate on the substrate caused by carburization of the filaments.

3.4.9 Effects of Substrate Temperature

Fig 3.6 shows that for tungsten the power difference, \( Q'_{dec} - Q_{dec} \), at substrate temperatures between 975 and 1450°C is approximately constant. Applying equation 3.5 to figure 3.6 shows that \( Q_{dec} \) must be constant over this range of substrate temperatures. From equations 3.6 and 3.21, \( \beta \) must also be independent of substrate temperature. For a platinum substrate, the power difference increases with substrate temperature indicating an increase in \( \beta \). Both dependencies of \( \beta \) on substrate temperature are in agreement with the results reported by Wood and Wise [27]. There is, currently, very little understanding of the dependence of the recombination coefficient on material properties [27].

3.5 Energy and Atomic Hydrogen Transport in Conventional HFCVD Reactors.

3.5.1 Atomic Hydrogen Transport

We consider a simple one dimensional transport model and equate the arrival rate of atomic hydrogen at the substrate by diffusion to the substrate recombination rate.\(^2\)

\[
\bar{D} \frac{C_{H,at}}{l} = 2\beta J A
\]

(3.23)

where \( \beta \) is the recombination coefficient defined by eq. 3.20 and \( J \) is the collision flux of atomic hydrogen. Using eq. 3.23 and 3.19 one finds,

\[
\frac{C_{H,at}}{C_{H,\text{eq}}} = \frac{1}{1 - \left( \frac{T}{T_m} \right) \left( \frac{\mu}{\mu_0} \right)}
\]

(3.21)

\(^2\)Thermal diffusion (Soret effect) has been shown to be negligible for hydrogen [20,32].
For $T = 1300\text{K}$, $l = 0.01\text{m}$, $\overline{D} = 0.175\text{m}^2\text{s}^{-1}$ and $\beta = 0.06$,

$$\frac{C_{H_i}}{C_{H_{A_i}}} = 0.1$$  \hspace{1cm} (3.25)

This result implies that, under normal operating conditions, significant concentration gradients exist between the substrate and hot filament. The transport of atomic hydrogen is under mixed diffusion and surface reaction rate control. For any material where $\beta > 0.06$, the recombination rate can be considered to be dominated by the diffusion rate of atomic hydrogen to the substrate. The result that the atomic hydrogen flux to the surface can be diffusion limited is quite surprising because of the large diffusion coefficient of atomic hydrogen. In fact, at least one recent analysis of a hot filament reactor has explicitly stated the opposite [36]. The results here imply that careful attention to reactor geometry, pressure and temperature are required for hot filament reactor analysis and design.

3.5.2 Energy Transport

In the reactor described above about 90% of the energy is transported to the substrate by atomic hydrogen recombination, i.e., $Q_{rec} = 32.67\text{W}$, $Q_{c, H_f} = 1.77\text{W}$, and $Q_{rad, H_f} = 0.85\text{W}$. In more conventional reactors, the relative values of the various energy fluxes will differ significantly from these because of the different geometries, temperatures, and concentrations. Accurate calculation of the fluxes can only be achieved by detailed three dimensional modelling of the particular reactor [32]. However, an estimate of the ratio $\frac{Q_{rec}}{Q_{c, H_f}}$ can be made for simple one dimensional transport. The rate of energy transport by conduction and by recombination can be written,

$$Q \rightarrow k \frac{dT}{dx}$$  \hspace{1cm} (3.26)

$$Q_{rec} = -\frac{\Delta H}{2}DA \left( \frac{dC_H}{dx} \right)$$  \hspace{1cm} (3.27)
where $k$ is the thermal conductivity and $dz$ is a differential distance normal to $A$. Dividing eq. 3.27 by eq. 3.26 one obtains,

$$\frac{Q_{rec}}{Q_{c,hf}} = \left( \frac{D\Delta H}{2k} \right) \left( \frac{dC_H}{dT} \right)$$  (3.28)

Integrating eq. 3.28,

$$\frac{Q_{rec}}{Q_{c,hf}} = \left( \frac{D\Delta H}{2k} \right) \left( \frac{\Delta C_H}{\Delta T} \right)$$  (3.29)

where $\overline{D}$ and $\overline{k}$ are averaged values for $D$ and $k$ over the appropriate interval of $C_H$, and $T$. Eq. 3.29 may be used to estimate $\frac{Q_{rec}}{Q_{c,hf}}$ for a simple geometry such as a flat substrate facing an array of parallel hot filaments. Typical values during HFCVD of diamond are $\Delta T = 1000$K, $\overline{D} = 0.175$ m$^2$s$^{-1}$ and $\overline{k} = 0.85$ W/m. Using the results of the analysis in section 3.5.1 we can set $\Delta C_H \sim C_{hf} = 10^{22}$ m$^{-3}$. Taking $\Delta H = 7.51 \times 10^{-19}$J we obtain,

$$\frac{Q_{rec}}{Q_{c,hf}} = 0.8$$  (3.30)

Therefore, the total energy carried to the substrate by recombination can be about the same as that carried by conduction through the gas. In most conventional HFCVD reactors the energy transfer by radiation will be higher than that observed in the present reactor because of a larger geometric view factor.

Heat flux measurements are very difficult to perform in conventional reactors. However, substrate temperatures can be measured and used to qualitatively confirm the importance of atomic hydrogen recombination as a means of energy transport. Table 3.2 shows the substrate temperatures in hydrogen and helium in a conventional HFCVD diamond reactor. In this reactor a thermocouple was pressed against the back side of a silicon wafer that was positioned 1 cm from 3 parallel hot filaments held at 2000°C. The discussion in section 3.4.2 shows that convection can be neglected in the analysis of the heat transport. At 1 torr, the gas is in mixed molecular and viscous flow and the thermal conductivity is much lower than at 20 torr [42]. Hence the contribution
of conduction to substrate heating can be assessed by subtracting the substrate temperature at 1 torr from the substrate temperature at 20 torr. For helium, table 3.2 shows that this difference is 130°C. At 20 torr, the temperature of the substrate in hydrogen is 140°C higher than in helium. Clearly then, the extra heating in hydrogen cannot be due to the 20% increase in thermal conductivity of hydrogen relative to helium because the extra heating is of the same approximate magnitude as the total temperature change due to conduction. These results show that atomic hydrogen recombination is an important heat transport mechanism in conventional HFCVD reactors for diamond deposition.

A qualitative estimate for the relative contribution of radiation to substrate temperature can also be made from table 3.2. At low pressures in helium, radiation and conduction contribute to substrate heating, although the conduction heating is reduced from its value at 20 torr. Under these conditions, the substrate temperature rise from room temperature (25°C) is an upper limit to the effect of radiation, i.e., a temperature rise of 245°C. In hydrogen at 20 torr, the substrate temperature change from room temperature is 515°C, more than twice 245°C. Radiation heat loss from the substrate increases as $T^4$ where $T$ is substrate temperature. Hence, radiation heating is less than the combined heating by conduction and atomic hydrogen recombination.

### 3.6 Summary of Transport Analysis

The exact contribution of the various energy transport mechanisms in a typical diamond deposition reactor depend on the specific experimental conditions, and reactor geometry. It was shown that in a reactor where the substrate is a filament at right angles to the hot filament, 90% of the heating is due to atomic hydrogen recombination. Measurement of the energy liberated by hydrogen atom recombination can be used to
estimate the recombination rates and gas phase atomic hydrogen concentrations. The
atomic hydrogen concentrations at the substrate and hot filament were determined
and found to be in reasonable agreement with published values. Addition of up to 7%
methane to the gas caused a 3-fold decrease in atomic hydrogen recombination rate on
the substrate. This decrease may be caused by 1) gas phase annihilation of atomic hy-
drogen by methane, 2) a reduction in atomic hydrogen production by the hot filament
due to surface carburization or 3) a reduction in atomic hydrogen recombination on
the substrate surface due to surface carburization. For a reactor with the more con-
ventional geometry of three parallel hot filaments positioned above a silicon substrate,
it was found that gas phase conduction and atomic hydrogen recombination contribute
approximately equally to the energy transport to the substrate.

3.7 Appendix A

Estimation of Conduction and Radiation Terms in the Energy Balance for
the Substrate.

The terms \((Q'_{rad} - Q_{rad})\), \((Q'_{c,e} - Q_{c,e})\) and \((Q'_{c,w} - Q_{c,w})\) were neglected
in the derivation of equation 3.5, which is used to calculate the recombination term
\(Q_{rec}\). The relative magnitude of these terms can be assessed by measurements of
\(Q'_{elec} - Q_{elec}\) performed using an inert ambient gas. For an inert gas \(Q_{rec} = 0\) and
equation 3.4 becomes:

\[
Q'_{elec} - Q_{elec} = (Q'_{rad} - Q_{rad}) + (Q'_{c,e} - Q_{c,e}) + (Q'_{c,w} - Q_{c,w}) - Q_{c,Hf} + Q_{rad,Hf} \quad (3.31)
\]

Consider the special case where the substrate temperature, \(T_s\), and the hot filament
temperature, \(T_{ef}\), are equal. At this point, \(Q_{c,e} \approx 0\), and \(Q_{c,w} \approx 0\). Equation 3.31
becomes

\[
Q'_{elec} - Q_{elec} = (Q'_{rad} - Q_{rad}) + (Q'_{c,e} - Q_{c,e}) + (Q'_{c,w} - Q_{c,w}) \quad (3.32)
\]
Measurements of $Q_{elec}' - Q_{dec}$ in helium at 20 torr at a substrate and hot filament temperature of 1966°C gave $Q_{elec}' - Q_{dec} = 0.48$ W. In hydrogen, at the same temperature $Q_{elec}' - Q_{dec} = 31.03$ W. Therefore, to a good approximation, the terms on the right hand side of equation 3.32 can be neglected.

The value of $Q_{c, hf}$ can also be estimated using measurements performed in helium. In the absence of recombination, $Q_{rec} = 0$. Therefore equation 3.5 becomes

$$Q_{elec}' - Q_{dec} = Q_{c, hf} + Q_{rad, hf} \quad (3.33)$$

Substituting the values for $Q_{elec}'$ and $Q_{dec}$ from experiment 2 and for $Q_{rad, hf}$ from experiment 1 in table 3.1 we have $Q_{c, hf} = 15.16 - 13.13 - 0.85 = 1.18$ W. The heat conducted from the hot filament to the substrate, $Q_{c, hf}$, is therefore small compared to the recombination term, $Q_{rec}$.

### 3.8 Appendix B

Estimate of the Power Conducted from the Hot Filament to the Substrate in Hydrogen.

Fourier's law of heat conduction is:

$$\frac{dQ}{ds} = k \frac{dT}{dx} \quad (3.34)$$

where $dQ$ is the rate of heat flow across area $ds$, $k$ is the thermal conductivity, $T$ is temperature and $dx$ is a differential distance perpendicular to $s$. We assume that the variables can be separated and equation 3.34 rewritten.

$$Q \int_{s}^{x} dx \cdot \int v \cdot \tau \rightarrow$$

or,

$$Q = \gamma \int kdT \quad (3.36)$$
where \( \gamma \) is a purely geometrical factor and is independent of the gas used. Applying equation 3.36 to both helium and hydrogen ambient gases and cancelling \( \gamma \),

\[
Q^{H_2}_{c,Al} = Q^{He}_{c,Al} \frac{\int_{T_s}^{T_f} k_{H_2}dT}{\int_{T_s}^{T_f} k_{He}dT} \tag{3.37}
\]

which is the required expression for the corrected conduction term in hydrogen.

Equation 3.37 was evaluated using a four term polynomial fit to experimental data [31] for \( k_{H_2} \) and \( k_{He} \) in the integration range \( T=1316-2000^\circ C \) giving

\[
\frac{\int_{T_s}^{T_f} k_{H_2}dT}{\int_{T_s}^{T_f} k_{He}dT} = 1.5 \tag{3.38}
\]

Therefore, under the conditions used in these experiments, the heat conducted from the hot filament to the substrate by hydrogen is only 1.5 times as large as that conducted by helium. From appendix A: \( Q^{He}_{c,Al} = 1.18 \text{ W} \), hence \( Q^{H_2}_{c,Al} = 1.77 \text{ W} \).
<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>T_s (°C)</th>
<th>Gas</th>
<th>Pressure (torr)</th>
<th>$Q'_{elec}$ (W)</th>
<th>$Q_{elec}$ (W)</th>
<th>$Q'<em>{elec} - Q</em>{elec}$ (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1371</td>
<td>He</td>
<td>0.3</td>
<td>6.87</td>
<td>6.02</td>
<td>0.85</td>
</tr>
<tr>
<td>2</td>
<td>1168</td>
<td>He</td>
<td>20</td>
<td>15.16</td>
<td>13.13</td>
<td>2.03</td>
</tr>
<tr>
<td>3</td>
<td>1171</td>
<td>He</td>
<td>200</td>
<td>22.78</td>
<td>19.62</td>
<td>3.16</td>
</tr>
<tr>
<td>4</td>
<td>1371</td>
<td>H_2</td>
<td>20</td>
<td>32.67</td>
<td>1.64</td>
<td>31.03</td>
</tr>
<tr>
<td>5</td>
<td>1966</td>
<td>He</td>
<td>20</td>
<td>26.91</td>
<td>26.43</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Table 3.1: Substrate power measurements in hydrogen and helium. $T_s$ is the substrate temperature, $Q'_{elec}$ is the power to the substrate when the hot filament was off, and $Q_{elec}$ is the power to the substrate when the hot filament was on.
Figure 3.1: Substrate filament resistance vs. temperature. The temperature was measured by a two-color pyrometer.
Figure 3.2: Electrical diagram for the temperature measurement and control for the substrate.
Figure 3.3: The increase in substrate temperature when the hot filament is turned on vs. reactor pressure for 4 ambient gases: argon, nitrogen, helium and hydrogen.
Figure 3.4: The power supplied to the substrate in order to maintain the substrate temperature at 1485°C vs. hot filament temperature for both helium and hydrogen ambients.
Figure 3.5: Effect of methane flow rate on the power transported to the substrate.

$Q'_{\text{m,eff}} = Q_{\text{m,eff}}$ at 1265°C. The hot filament temperature is 2000°C.
Figure 3.6: $Q'_{elc} - Q_{elc}$ vs. substrate temperature for tungsten and platinum substrates.
Figure 3.7: Measured power difference, $Q'_{elec} - Q_{elec}$, vs. substrate length for substrate to hot filament distance of 0.5 cm and 2.5 cm.
<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Gas</th>
<th>Pressure (torr)</th>
<th>Substrate Temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>He</td>
<td>0.7</td>
<td>270</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>20</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>H₂</td>
<td>1.06</td>
<td>350</td>
</tr>
<tr>
<td>4</td>
<td>H₂</td>
<td>20</td>
<td>540</td>
</tr>
</tbody>
</table>

Table 3.2: Substrate temperature measurements in hydrogen and helium for conventional reactor geometry.
Figure 3.8: Substrate power requirement vs. thermal conductivity in pure argon, nitrogen, helium and hydrogen.
Chapter 4

Catalytic Deposition of Fibers

4.1 Introduction

Carbon fiber embedded in resin is now the material with the highest available strength-to-weight ratio. This achievement is based on the strength of the carbon-carbon \( \text{sp}^2 \) bond, the low mass of carbon and the intensive research into carbon fibers and composites. For a review see reference [44].

Carbon fibers can be made by extruding organic precursors, e.g., pitch, into fibers and then subjecting the fibers to heat treatments up to 3000°C. Rayon and more recently Polyacrylonitile (PAN) fibers are widely used as the precursor fiber. Another method is the deposition of carbon fibers on a heated substrate from hydrocarbon gases in the presence of catalyts. The latter method is called Catalytic Chemical Vapor Deposition (CCVD).

The fibers are composed of sheets of 6-membered unsaturated carbon rings in varying degrees of disorder. In general, the higher the temperature of the heat treatment, the more ordered the layers and the more the structure resembles that of
graphite. For heat treatments at $T > 1300^\circ$C, flat carbon layers appear which are called graphene layers. In-layer rotational disorder of the rings persists in each layer, and the layers are rotationally disordered with respect to each other. This material is referred to as turbostratic graphite.

Diamond fibers or whiskers, if they could be made, would possess remarkable mechanical properties, in some ways surpassing those of graphite. In addition, diamond fibers would have a much greater resistance to oxidation and other forms of chemical attack than graphite. One of the earliest reports of low pressure diamond growth was the use of a vapor-liquid-solid (VLS) method to grow diamond whiskers ("filamentary diamond") using molten iron as the catalyst [46]. These results have never been duplicated. One of the purposes of this part of the research was to look for any evidence of diamond whisker growth.

We have used the CCVD process to deposit carbon fibers in a hot filament assisted CVD reactor under conditions that are close to the growth conditions of diamond films. The catalysts were transported to the substrate surface by gas phase diffusion. The structure of the fibers was determined by Secondary and Transmission Electron Microscopy (SEM and TEM), and their composition by Auger Electron Spectroscopy (AES).

4.2 Experimental Procedure

The reactor is described in detail in section 2.1. The carbon is supplied via an ethanol bubbler where hydrogen gas is bubbled through ethanol and the flow of ethanol is determined by the partial pressure of ethanol (see section 2.3). The substrate used was
Table 4.1: Experimental conditions for the two steps of fiber growth. $T_s$ is the substrate temperature (°C), $P$ is reactor pressure (torr), $F_{eth}$ is the flow rate of hydrogen through the ethanol bubbler (sccm), and $F_{H_2}$ is the hydrogen flow rate (sccm).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Diamond Growth</th>
<th>Fiber Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>20-30</td>
<td>20-30</td>
</tr>
<tr>
<td>$T_s$</td>
<td>900-1100</td>
<td>1200-1500</td>
</tr>
<tr>
<td>$F_{eth}$</td>
<td>10-20</td>
<td>10-20</td>
</tr>
<tr>
<td>$F_{H_2}$</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

tungsten wire 0.75 mm in diameter. During the deposition process, both the substrate and hot filament are carburized to some extent.

A two step process was used for fiber deposition. First, a diamond film was deposited under normal diamond growth conditions, then the substrate temperature was raised to between 1200 and 1500°C. In this range (approximately) fibers are deposited. The substrate temperature is measured by a calibrated double wavelength pyrometer or a disappearing filament pyrometer. The pyrometer can only be used when the hot filament is off. The values for the substrate temperature are therefore, minimum values. Actual surface temperature at the substrate during fiber deposition may be up to 300°C higher. The growth conditions are shown in table 4.1.
4.3 Results and Analysis.

4.3.1 Secondary Electron Microscopy (SEM).

The morphology of the fibers can be seen in fig. 4.1 and fig. 4.2. The morphology varies from blunted to pointed and the surface roughness of the fibers varies from 0.1 – 0.3μ. The growth rate varies between 1 and 10μ/hr and the number density of fibers was up to 10^6 cm^-2.

4.3.2 Auger Electron Spectroscopy.

Figures 4.3 and 4.4 show typical Auger Electron Spectroscopy (AES) results from CCVD fibers. Fe impurities were only found if steel screws were used to attach the substrate to the electrodes. The amount of iron was estimated by the Auger quantitative analysis program to be 4%. When steel screws were not used, 4% Si was found on the fibers. In both cases, the oxygen content was also about 4%. The impurities were found to be approximately evenly distributed over the fibers and the substrate. These impurities did not appear when the substrate temperature was kept under 1200°C.

CCVD fibers are thought to grow by the Vapor Liquid Solid (VLS) or Vapor Solid Solid (VSS) mechanism [47,48]. In this mechanism, small catalyst particles act as a fast attachment site for gas phase carbon species. The deposited carbon diffuses through or around the catalyst and accumulates at the interface between the catalyst and the substrate. As the process continues, the catalyst is raised from the substrate surface by the accumulation of carbon underneath, thus building a fiber under each catalyst particle. If the temperature is high enough, the evaporation rate of the liquid is high and the liquid droplet shrinks in size during the growth process. This leads to the pointed morphology shown in fig. 4.2. In a deposition experiment, small glass particles
Figure 4.1: An SEM image of fibers grown using the diamond deposition reactor showing typical morphology of VLS growth.
Figure 4.2: An SEM image of fibers showing the pointed morphology.
Figure 4.3: Auger spectrum of a fiber grown with an iron based catalyst.
Figure 4.4: Auger spectrum of a fiber grown with a silicon based catalyst.
were placed on a Si substrate prior to deposition. Fibers were found clustered around the glass particles indicating that the glass particles acted as preferred nucleation sites for the fibers, see figure 4.5. This result is consistent with the assertion that SiO₂ acts as a catalyst for the growth of the fibers.

The transport of the impurities to the substrate is different for the two different catalysts. For the case of Si and O, no SiH₄ was detected by repeated Residual Gas Analysis (RGA) at different substrate temperatures and gas pressures. It seems likely, therefore, that the Si is transported by evaporation of SiO. The SiO may be formed by atomic hydrogen reduction of the quartz tube. The product of such an attack is H₂O and HO, both always detected by the RGA. Since the RGA probe is located far from the hot zone, SiO is not expected to be detected and indeed was not detected.

Fe may be either transported by evaporation and condensation or by chemical reaction with carbonyls (e.g., Fe(CO)₅). Repeated attempts to find a significant partial pressure of these molecular masses, by using a mass spectrometer equipped with an electron multiplier, failed. The source of Fe appears to be a small stainless steel screw used to attach the cold filament to its electrode. When that screw was replaced by a molybdenum screw no iron was found on the substrate or the fibers.

A high energy resolution view of the region near the 285eV carbon Auger peak is shown in fig. 4.6. The carbon peak has the characteristic graphite shape [49] (compare with fig. 4.13).
Figure 4.5: An SEM image of fibers grown using small glass particles as seeds. The fibers are clustered around the seed particles.
Figure 4.6: A high energy resolution view of the region near the 285eV carbon Auger peak shows the typical graphite 'shoulder' at 260eV.
Figure 4.6: A high energy resolution view of the region near the 285eV carbon Auger peak shows the typical graphite 'shoulder' at 260eV.
4.3.3 Transmission Electron Microscopy.

Image Analysis

Fig. 4.7 shows a transmission electron microscope (TEM) image of a fiber. The fibers were grown on tungsten TEM specimen grids, so that no specimen preparation was necessary prior to TEM observation. TEM images reveal that each fiber consists of two distinct layers.

1. A narrow (70-100A) core region.

2. A 300-1500A region of material with layers parallel to the fiber axis and with faults perpendicular to the fiber axis.

No contrast was ever seen in the core region and it may be hollow [50,51]. Graphite fibers are thought to be made up of graphene planes rolled up into a scroll. Recently, it was also proposed that they may be concentric closed shells or Bucky-tubes [45]. An analysis of the structure of region 2 is given below.

Analysis of Diffraction Patterns.

In order to analyse the electron diffraction results, the diffraction effects from diamond and turbostratic graphite are considered first. Turbostratic graphite is polycrystalline graphite with disordered stacking of the basal planes. In general, all translational and rotational degrees of freedom of any basal plane relative to another may contribute to the disorder. This leads to a large set of possible diffraction patterns. In this section, the analysis is restricted to aspects of the diffraction from turbostratic graphite which may lead to the mis-identification of turbostratic graphite as diamond.

In a single graphite basal plane, the atoms are arranged in a hexagonal array and the nearest neighbour distance is 0.1415 nm (slightly less then diamond
Figure 4.7: Bright field TEM image of a graphite fiber.
which is 0.1545 nm). The interplanar spacing in graphite, \( d_{hkl} \), is given by:

\[
d_{hkl} = \frac{a c \sqrt{3}}{\sqrt{4(h^2 + k^2 + h k) c^2 + 3l^2 a^2}}
\]

(4.1)

where \( a \) and \( c \) are the lattice constants (\( a = 0.245 \) nm, and \( c = 0.669 \) nm). For a single basal plane, set \( l = 0 \):

\[
d_{hk} = \frac{a \sqrt{3}}{\sqrt{4(h^2 + k^2 + h k)}}
\]

(4.2)

where \( d \) is now the inter-line spacing in the two dimensional lattice of a basal plane.

Rotation of the reciprocal lattice about a lattice point will generate rings of radii \( r_{hk} \) where \( r_{hk} = 1/d_{hk} \). These rings correspond to the diffraction rings expected from rotationally disordered graphite basal planes and where the axis of rotation is parallel to the basal plane normal. Table 4.3.3 compares these diffraction rings to diamond diffraction rings. The last column in the table is the percent change in the radii of the rings between diamond and graphite. It can be seen that the reciprocal lattice ring diameters of diamond and rotationally disordered graphite basal planes are very close to each other and hence it is very difficult to distinguish between graphite and diamond using diffraction. Especially confusing is the case where the normal to the turbostratic stacks is parallel to the electron beam. In this case no diffraction spots or rings typical of graphite will appear and only rings which "match" diamond will be observed. This point may have been overlooked in the early reports on diamond whiskers as well as recently by one or two researchers in the diamond community with very unhappy consequences.

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1 The radius \( R \) of the rings in a diffraction pattern is given by \( R = \frac{a}{\lambda L} \), where \( \lambda = \) wavelength, \( L = \) camera length.
Table 4.2: Comparison of $hk$ graphite reciprocal lattice rings with polycrystalline diamond reciprocal lattice rings.

<table>
<thead>
<tr>
<th>Graphite Basal Plane</th>
<th>Diamond</th>
<th>$\delta \equiv \frac{r_{hkl} - r_{hkl}}{r_{hkl}} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>$hk$</td>
<td>$r_{hkl}$ [nm]</td>
</tr>
<tr>
<td>1</td>
<td>01</td>
<td>4.71</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>8.16</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>9.42</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>12.46</td>
</tr>
</tbody>
</table>

The diffraction from carbon fibers has been studied extensively [44,52,53]. Fig. 4.8 shows a typical diffraction pattern of a single fiber. Fig. 4.9 shows a sketch of the atomic structure and associated diffraction pattern from Oberlin [52]. It can be seen that the diffraction pattern is identical to the sketch. Hence, the structure of the fiber grown by HFCVD is found to be similar to other previously reported graphite fibers. The main features of the diffraction pattern are described and explained in terms of Oberlin's proposed crystallographic structure for the fibers. For a more detailed analysis of the diffraction effects from turbostratic graphite, the reader is referred to several references in the bibliography [44,52,53].

In fig. 4.8, the $(0,0.2n)$ spots arise from order in the c-direction of the hexagonal lattice. The presence of only one row implies that the reciprocal planes bend away from the Ewald sphere. Since only one row is present, even at the maximum sample rotation about the fiber axis, this bending must be continuous around the fiber axis. Graphite basal planes must be wrapped around the fiber axis. The graphite inter-basal plane distances measured from the fiber diffraction patterns are 3.82 Å. This value is 14% larger than graphite inter-basal plane spacing (3.35 Å). A somewhat larger
Figure 4.8: An electron diffraction pattern of a typical fiber.
Figure 4.9: A sketch of the atomic structure and associated diffraction pattern of distorted turbostratic graphite. (from A. Oberlin).
inter-basal plane spacing is typical of turbostratic graphite [52].

The low intensity polycrystalline graphite rings indicate the presence of small amounts of polycrystalline graphite. A dominant feature of the diffraction pattern are the rings of streaked spots where the rings match diamond but also coincide with diffraction from graphite basal planes or \((h,k)\) planes (see table 4.3.3). The rings are explained by azimuthal disorder of the graphite basal planes about the electron beam direction. The real space region which gives rise to this diffraction feature is the part of the fiber where the surface normal is parallel to the beam.

The streaks emanating out from the \(hk\) rings are parallel to the \((0,0,2n)\) direction. The streaks that are not at the poles of the rings are asymmetrical and extend only from the ring outward, never into the rings. Hence they can not arise from a Fourier transform. The asymmetrical streaks are caused by the bending of the graphite basal planes around the fiber axis. The bending of these planes will extend their reciprocal lattice lines into sectors of circles that yield streaks when intersected by the Ewald sphere. The symmetric streaks at the poles of the \(hk\) rings are simply due to the Fourier transform of the thin fiber wall. The basal planes that contribute to this feature are those whose normal lies perpendicular to the electron beam.

### 4.4 Deposition of Diamond on Carbon Fibers

#### 4.4.1 Deposition of Diamond on Turbostratic Graphite Fibers

Diamond was grown on CCVD turbostratic graphite by adding a diamond deposition step after the graphite fiber growth steps.

Isolated diamonds were deposited that nucleated on the graphite fibers.
The structure was often beautiful, where relatively large diamond crystals were supported by very thin graphite fibers (see fig. 4.10). When using ethanol as the carbon source, and a substrate temperature under 1000°C, the graphite fibers were completely etched away in a short time and diamonds were deposited on the underlying WC substrate. At higher growth temperatures (1000-1200°C) the graphite fibers were sufficiently stable to allow diamond nucleation.

### 4.4.2 Diamond Deposition on Commercial Carbon Fibers.

Commercial carbon fibers\(^2\) woven into carbon cloth were used as substrate. The cloth was heated electrically to 850°C and the usual diamond deposition conditions were applied. Diamond nucleated on the fibers at an approximate coverage of 40% after 7 hrs of deposition (see fig. 4.11).

An identical experiment was then performed except that the graphite cloth was subjected to a 15 sec ultrasonic bath in ethanol and 1/2 - 1/4\(\mu\) diamond powder before deposition. The result was 100% coverage of the fibers by diamond as confirmed by SEM (see fig. 4.12) and AES (see fig. 4.13). Bending the cloth did not cause the diamond to delaminate from the carbon fibers (see fig. 4.14).

This new composite, namely, diamond coated carbon fibers, will have superior oxidation resistance, and thermal conductivity, compared to the widely used carbon fibers. The strength the modulus may also be higher but this has not been confirmed.

### 4.5 Summary of Catalytic Fiber Deposition.

For the first time, a HFCVD reactor for diamond was used to deposit graphite fibers. Silicon and iron were transported to the substrate via the gas phase and catalysed the

\(^2\)From Johnson and Matthey Electronics.
Figure 4.10: Diamonds nucleated on turbostratic graphite fibers that were grown by CCVD.
Figure 4.11: Diamonds nucleated on commercial carbon fibers without pre-treatment.
Figure 4.12: Diamonds nucleated on commercial carbon cloth that was subjected to ultrasonic immersion in ethanol and diamond powder. The diamond entirely covers the graphite fibers. Shown are low and high magnifications of the same sample.
Figure 4.13: AES of diamond coated graphite fibers. The fine structure of the spectrum is typical of diamond.
Figure 4.14: Diamonds nucleated on carbon cloth were not delaminated by bending the cloth.
deposition. Electron images and diffractions provide ample evidence that the fibers are composed of turbostratic graphite and are not diamond whiskers (filamentary diamond). The graphite basal planes are wrapped around the fiber axis. A large degree of rotational disorder exists between the layers but interlayer separations remain approximately equal to graphite.

No evidence was found for the growth of diamond whiskers in the low pressure diamond growth regime in the presence of iron and silicon catalysts. Turbostratic graphite fibers were grown by a modest variation in the diamond growth conditions. It was also shown that diffraction rings from turbostratic carbon can easily be mistaken for diffraction rings from diamond polycrystals.

The presence of Si and Fe catalysts does not interfere with further diamond deposition and diamond was deposited on top of the fibers. A diamond coating was deposited on commercial carbon fibers. This new composite material may have superior oxidation resistance, thermal conductivity and strength compared to the widely used carbon fibers. Thus, it is possible to produce both the graphite fiber and the diamond coating in the same reactor.
Chapter 5

Summary and Future Work

A new kind of HFCVD reactor for diamond thin films was designed and built. This enabled, for the first time, a measurement of the recombination of atomic hydrogen on the substrate under diamond growth conditions. The novel geometry enables the decoupling of the hot filament and substrate temperature. This permits detailed analysis of the energy transport to the substrate. The analysis showed that atomic hydrogen recombination is a significant form of heat transport to the substrate and a direct measurement of the atomic hydrogen recombination rate was made. Atomic hydrogen concentration was estimated from the recombination rate and the conditions under which atomic hydrogen transport to the substrate is diffusion controlled were found.

The ability of the new reactor to reach high substrate temperatures enabled the deposition of graphite fibers by a catalytic VLS process. The fibers were coated with diamond film. This new composite material may be technologically useful.

Several interesting experiments are suggested based on the above results.

- It was shown in section 3.1.0 that the temperature dependence of the recombination coefficient, $\beta$, is different for tungsten and for platinum. Of particular interest to the diamond community is the temperature dependence of $\beta$ for dia-
mon. This can be found by first depositing diamond on the substrate and then measuring $Q'_{dec} - Q_{elec}$ at different substrate temperatures. This result may indicate the role of atomic hydrogen recombination in determining the temperature dependence of the growth rate of diamond.

- In section 3.4.7, the inaccuracy of the effective area of adsorption led to an approximate result for the atomic hydrogen concentration. The accuracy can be improved by an independent measurement of the effective area for adsorption. It may be possible to measure the surface area by BET techniques [42]. Alternatively, smoother wires can be used.

- It was found in section 3.5.1 that atomic hydrogen transport is diffusion limited. Increasing the atomic hydrogen flux to the substrate may be the key to faster growth of diamond. This could be done effectively in this reactor by using nozzles for the hydrogen feed or reactor exhaust. For a constant gas flow rate, the smaller diameter of the nozzles creates high velocity flows in the vicinity of the nozzle. By placing the substrate near the nozzle, a convective component can be superposed to the diffusive transport that already exists in the reactor. This reactor is particularly suited for exploratory work of this kind because the substrate wire can be extended and thus act as a probe for the growth conditions over a large region of the reactor.

- The unique ability of this reactor to measure substrate temperature accurately suggests the study of nucleation and growth as a function of temperature. The nucleation density, growth rate and diamond morphology can be measured along the wire and compared with modelling. Such experiments may lead to an understanding of the effects of the local gas composition and substrate temperature on diamond nucleation, growth and morphology.
• It is also interesting to expand the temperature stepping idea that was used to deposit diamond, fibers and diamond on the fibers. For example, a low temperature nucleation step could be followed by a high temperature growth step to better control the final morphology of the films. Due to the low heat capacity of the wire substrate, high frequency temperature variations of large magnitude are possible. Such variations influence the surface chemistry by transient adsorption and desorption effects and have hitherto never been explored for diamond deposition.
Bibliography


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