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**MOLECULAR BEAM MASS SPECTROMETRY STUDIES OF THE CHEMICAL
VAPOR DEPOSITION OF DIAMOND**

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Abstract

We have developed a novel molecular beam mass spectrometry technique that can quantitatively analyze the gas-phase composition in a CVD reactor. The technique simultaneously monitors a wide variety of radical and stable species, and their concentrations can be determined with sensitivities approaching 1 ppm. Measurements performed in a diamond deposition system have given us keen insights into the important phenomena that affect the growth environment. This paper first discusses the primary gas sampling design issues. In the second part, the details of the experimental results and their implications will be described.

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I. Introduction:

The growth rate and film quality of materials synthesized by chemical vapor deposition (CVD) processes depend critically on the composition of the species generated. Mass spectrometry has proven useful for characterizing the gas-phase environment in CVD reactors; however, the identities of many reactive species are lost using conventional sampling techniques [1]. We have developed a molecular beam mass spectrometry (MBMS) technique capable of detecting both radical and stable species in a diamond CVD reactor [2]. Furthermore, we have defined a procedure to quantitatively determine the mole fraction of each species with a sensitivity approaching 1 ppm (parts per million). Since temperature and pressure at the sampling orifice are monitored, the concentrations at the point of detection can be derived.

Many other techniques exist for detecting radical species, such as optical emission spectroscopy, laser excitation techniques, and absorption spectroscopy; each with its own strengths and shortcomings. A major advantage of MBMS over other techniques is its ability to monitor a wide spectrum of species simultaneously. It truly shines when the experimenter does not know *a priori* what species to expect. This broader perspective provides a more robust test of computational models that attempt to simulate the reacting environment. A second advantage is its adaptability to a wide variety of process environments. We have applied this technique in thermal and plasma systems [3], it is also used extensively in combustion flame systems [4]. To minimize intrusion into the reacting environment, our sampling orifice is fixed at the center of the growth substrate. The lack of spatial information is its primary shortcoming.

In this paper we summarize the basic design concept of the MBMS technique. We will focus the discussion on two potential areas of concern and show that they have a limited effect on the accuracy of the measurements. More detailed description of the sampling technique has been

previously reported in reference [1]. The rest of this paper will present results from the investigation of diamond deposition in a hot-filament system.

II. Experimental Setup

The sampling orifice is a 300- μm aperture located at the center of the substrate. This location is the least intrusive and allows one to determine the gas composition in the immediate vicinity of the growth surface. The diagnostic system was designed to sample from a reactor that can be pressurized to a maximum of 60 Torr with the substrate heated to 900°C. These conditions are considered optimal for diamond growth [5]. The orifice should have a low aspect ratio to limit recombination of reactive species on the side-walls. In our system, the orifice is machined to a channel length less than 1/5 of the orifice diameter.

Gas exiting the sampling orifice traverses through three stages of differential pumping before entering the ionizing region of the mass spectrometer. The sampled gas is collimated into a beam as it travels through a skimmer from the first stage into the second stage. The beam gets further collimated as it enters the third stage that houses the ionizer. During operation, the pressures in stages #1, #2, and #3 are typically 10^{-3} , 10^{-6} , and 10^{-7} Torr, respectively. The sampled beam travels directly from the orifice to the ionizer without striking any surfaces, thus preserving the identities of the reactive species. It is possible that chemical reactions can occur over the duration of the passage from the orifice to the ionizer, but with proper design reactions can be made negligible to "freeze" the composition. This is discussed in more detail below.

As seen in the schematic diagram of Fig. 1, the beam passes through a mechanical chopper before entering the last stage. The chopper is made out of a tuning fork that vibrates at a fixed

frequency of 210 Hz — away from multiples of the power line frequency of 60 Hz. Two components give rise to the ionizer signal: a modulated component originating directly from particles in the beam and a background component originating from particles in the ambient of stage #3. The former is the component needed for quantitative analysis and is obtained by taking the difference in intensity between the un-chopped and the chopped portion of the signal. This is accomplished by using a lock-in amplifier. All signals used for analyses are obtained in this fashion.

The schematic also shows an effusive source. This section is inserted into the beam path only during calibration to determine the mass discrimination factor. Even if no chemical reactions were to occur in the beam the relative concentration of the species at the ionizer will be different from that at the orifice. This difference is caused by the supersonic expansion of the sampled gas as it enters the first stage. Lighter species will naturally free stream radially out of the beam faster than the heavier species. Steep pressure gradients formed during the early stages of expansion can also cause lighter species to diffuse radially outward faster. Both effects predict the mass discrimination factor to scale as $\sqrt{m}$, where m is the species mass (i.e. the higher the mass the higher the relative concentration in the central portion of the beam downstream).[6,7] This phenomenon has been verified in our system and is accounted for in our analyses.

III. Estimate of Probe Distortions

a. Gas Expansion Characteristics

Aside from the mass discrimination effect discussed earlier, there are two other effects that can distort the measurements. Let us consider the flow dynamics in the near-vicinity of the orifice.

With a pressure of 20 Torr and a local temperature of 1100 K the mean free path for particle collision is $\sim 20 \mu\text{m}$, which is much smaller than the orifice diameter. The situation is that of a continuum free jet expanding from a high pressure source P_0 (in the reactor) to a low pressure regime P_1 (in the first stage). It can be shown that when the pressure ratio P_0/P_1 is greater than a critical value, which is less than 2.1 for all gases, the flow first reaches the sonic speed at the orifice and becomes supersonic as it expands into the first stage.[8] This expansion continues until it over-expands. Eventually it must be recompressed to adjust to the ambient pressure. This recompression is accomplished by forming shock waves. The thickness of the shock wave, or Mach disk, is on the order of the local mean free path. Askenas and Sherman [9] developed an empirical relation for the location x_m of the Mach disk:

$$x_m/d = 0.67 (P_0/P_1)^{1/2} \quad (1)$$

where d is orifice diameter. For our system, $P_0/P_1 \sim 20,000$, thus $x_m/d \sim 100$. As we will show later, the continuum pressure just upstream of the Mach disk is predicted to be $\sim 10^{-7}$ Torr with a mean free path of $> 100 \text{ cm}$. Since the shock wave thickness becomes comparable to the scale of the system, to define a shock structure in this scale becomes meaningless — or to say it in another way, no shocks are formed. The flow will transition smoothly from continuum to free-molecular flow.

b. Transition to Free-Molecular Flow

One issue that can be raised is whether the particles in the beam will chemically react and change their composition as they traverse from the orifice to the ionizer. Clearly, once the flow has expanded to free-molecular flow the particles can no longer react and the chemistry will be frozen.

We need to consider how quickly the beam reaches this condition and whether this time is short compared to the reaction time scale.

For an ideal gas undergoing isentropic free expansion, conservation of energy requires that the sum of the specific enthalpy h and kinetic energy is a constant along the streamline,

$$h_0 = h + V^2/2 \quad (2)$$

where V is the convective flow velocity. Upstream of the orifice where V is zero, this constant is equal to the specific enthalpy in the source region h_0 . Assuming the specific heat capacities under constant pressure and constant volume, c_p and c_v , respectively are constant, the downstream temperature T , velocity V , pressure P , and density n , can be expressed solely as a function of the Mach number M [8]:

$$T/T_0 = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-1} \quad (3a)$$

$$V/V_\infty = M \left(\frac{\gamma - 1}{2}\right)^{1/2} \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-1/2} \quad (3b)$$

$$P/P_0 = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-\gamma/(\gamma - 1)} \quad (3c)$$

$$n/n_0 = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{-1/(\gamma - 1)} \quad (3d)$$

V_∞ is the terminal velocity (when $M \rightarrow \infty$), $\gamma = c_p/c_v$, the local sound speed $V_s = \sqrt{\gamma RT/W}$, $M = V/V_s$, and W is the molar molecular weight. Using the method of characteristics, an analytical expression for the variation of M as a function of downstream distance x/d can be derived [10]:

For $0 < (x/d) < 0.5$

$$M = 1 + A (x/d)^2 + B (x/d)^3 \quad (4a)$$

where $A = 3.19$ and $B = -1.61$ for $\gamma=1.4$

$$\text{For } 0.5 < (x/d) < 6$$

$$M = (x/d)^{\gamma-1} \left(C_1 + \frac{C_2}{(x/d)} + \frac{C_3}{(x/d)^2} + \frac{C_4}{(x/d)^3} \right) \quad (4b)$$

where $C_1=3.606$, $C_2=-1.742$, $C_3=0.9226$, $C_4=-0.207$ for $\gamma=1.4$

$$\text{For } (x/d) > 6$$

$$M = D \left(\frac{x - x_0}{d} \right)^{(\gamma-1)} - \frac{\frac{1}{2} \left(\frac{\gamma + 1}{\gamma - 1} \right)}{D \left(\frac{x - x_0}{d} \right)^{(\gamma-1)}} \quad (4c)$$

where $D = 3.65$ for $\gamma=1.4$.

In eqn. (4c), x_0 is the distance between the orifice and an imaginary point source from which all streamlines radiate. This has the value of 0.4 for $\gamma=1.4$. The parameters A , B , C 's, and D depend only on γ . The other flow properties can now be expressed as a function of x/d , these results are shown in Fig. 2a and 2b. The gas temperature drops by an order of magnitude within 10 orifice diameters downstream, the density drops even faster. The cooling due to gas expansion results in a rapid rise of the convective flow velocity. The mean free path for collision λ_{mfp} depends only on the density n : $\lambda_{mfp} = 1/\sigma n\sqrt{2}$. For H_2 , the cross section $\sigma \sim 2.1 \times 10^{-15} \text{ cm}^2$. We can use $\lambda_{mfp} = 1 \text{ cm}$ as an approximate demarcation for the transition to free-molecular flow; this occurs at $x/d \sim 7$. Since the convective flow velocity is always larger than the sonic velocity (it is sonic at the orifice),

the time it takes to traverse this distance at sound speed will be an upper bound of this duration. At 1100 K, $V_s = 2.5 \times 10^5$ cm/s, the transit time has a maximum value of $\tau_s < 0.8$ μ s.

One of the fastest reactions that will be encountered in the diamond deposition system is the following:

As we will see, the mole fraction of methyl is $\sim 10^{-3}$, and that of H_2 is ~ 1 . The rate coefficient in the forward direction has been reported as $k = 1.5 \times 10^{13} \exp(-E/RT)$ $\text{cm}^3/\text{mol-s}$, with an activation energy $E = 64.9$ kJ/mol.[11] At 1100 K, $k = 1.24 \times 10^{10}$ $\text{cm}^3/\text{mol-s}$; the time scale for the destruction of methyl, $\tau_r = k/n_{\text{H}_2} \sim 286$ μ s, is significantly longer than τ_s . Thus, the beam will very quickly transition to free-molecular flow and preserve its composition.

c. Spatial Extent of Sampling

Another question is the spatial extent of the sampling. Because free expansion accelerates gas particles towards the orifice, the region of sampling extends far beyond just a mean free path from the surface of the substrate. A large sampling extent can cause the sampled flux to deviate from the flux that would have impinged onto the surface if the orifice were not present. This problem was investigated by Yi and Knuth [12]. In their analysis they first generated a non-distorted one-dimensional concentration profile in a binary one-dimensional stream that includes mass-diffusion and chemical-relaxation effects. When a conical sampling probe is present, the changes in the flow and concentration fields are numerically calculated by taking into account compressibility, and the non-zero sampling orifice diameter. The boundary condition requires that

at the probe surface the concentration gradient normal to the probe surface be zero, and at the orifice exit the flow velocity be at the sonic speed. The concentration at the centerline of the orifice was found to be higher than the non-distorted value — as expected. This higher sampled concentration is equal to the non-distorted value at a position axially shifted by δ upstream from the orifice. A best fit to the calculations is given by:

$$\delta/d = 0.19(V_s d/D)^{1/2} \quad (6)$$

where D is the mass diffusion coefficient. For our case with H_2 at 20 Torr and 1100 K, $D \sim 500 \text{ cm}^2/\text{s}$, and $V_s \sim 2.5 \times 10^5 \text{ cm/s}$, the axial shift δ/d is estimated to be 1. Since the separation between the filament and the substrate in our CVD reactor is on the order of $\sim 1 \text{ cm}$, this distortion is considered minimal.

IV. Results and Discussions

a. Diamond Deposition Setup

In the diamond reactor used for these studies, reactive species were generated by flowing a methane-argon-hydrogen mixture past an un-coiled filament heated to $\sim 2600 \text{ K}$. The flow ratios of the gases were typically 1:10:100, respectively, with a total flow rate $\sim 200 \text{ sccm}$ (standard cubic centimeter per minute). The filament was made out of either tungsten or rhenium. The filament can be single, or multi-stranded with each strand having a diameter of $250 \text{ }\mu\text{m}$ (10-mil). The separation between the filament and the substrate was $\sim 1.5 \text{ cm}$. The substrate was heated to $\sim 1100 \text{ K}$, and the operating pressure $\sim 20 \text{ Torr}$. The experiments discussed in this paper were

mostly conducted with the inlet methane flow rate as the only variable. The filament temperature, substrate temperature, and gas pressure were maintained constant by feedback control.

b. Chemically Reacting Flow Dynamics

A list of the key reactions occurring in the system are given in Table I.[13,14] The first seven are reactions in the gas-phase, reaction #8 for hydrogen dissociation can occur both in the gas-phase and on surfaces, and the last two occur on the growing diamond surface. Undoubtedly, there are other reactions involved but not listed, however, they play a lesser role in dictating the gas-phase composition.

The picture we want to describe for this chemically reacting flow environment is the following: As the feed gas flows past the heated filament, H atoms are formed by dissociation on the hot-filament surface (reaction #8). Although H_2 can homogeneously dissociate in the hot region surrounding the heated filament, it is much more likely to occur via the catalyzed dissociation pathway. Once H atoms are formed, they quickly undergo reactions with methane to form methyl (reaction #1). The methyl radicals react with each other to form ethane through reaction #2, and by a sequence of reactions with H atoms it is reduced to form acetylene. H atoms are primarily lost by recombination on the diamond surface. The loss of H atoms by homogeneous three-body recombination is negligible at this low pressure condition. Reaction #9 describes the reaction of an incoming H atom with a H-terminated diamond surface to form an empty site. Reaction #10 describes the attachment of a H atom to a radical site.

The chemically reacting flow environment is numerically modeled using the SPIN code.[15] SPIN solves the stagnation flow problem, subject to the assumptions that the flow is uniform at some distance from the substrate, and that edge effects can be neglected. The full three-

dimensional governing conservation equations are reduced to a set of coupled, one-dimensional ordinary differential equations. For our calculations, the set of homogeneous reactions includes the C₁ and C₂ chemistry of which the list given in Table I is a subset. There is a similarly long list for reactions on the diamond surface, however, virtually identical results are obtained if only the two H recombination reactions in Table I are used. Several investigators have used this approach to model diamond deposition systems.[14,16,17]

c. Hydrogen-only Case

Table I clearly shows that H atoms plays an important role in affecting the CVD gas-phase environment. It also controls the concentration of free radical surface sites where hydrocarbon species can be attached and result in film growth. It has also been speculated that H etching prevents the buildup of graphite in the deposited film.

To simplify the problem, we first look at the case in which hydrogen is the only feed gas. We have previously reported that in the hydrogen-only case, the H-atom mole fraction at $T_f = 2600$ K was measured to be $\sim 2 \times 10^{-3}$ [18]. The equilibrium mole fraction at 2600 K, however, is 0.21. There are several indications that the H-H₂ mixture in the immediate vicinity of the filament is in fact close to equilibrium. Chen et al. [19] indirectly determined the H-atom concentration near the filament and found it to be close to the equilibrium level. Our study on the effect of the filament surface area, to be discussed below, also confirms this view. This reduction in concentration from the filament to the growth substrate is caused by the loss from surface recombination.

Using a relatively simple one-dimensional diffusional flow calculation, one can determine the H-atom concentration at the substrate. The loss rate from surface reactions is expressed as

$\dot{R}_H = \gamma_s [H] \frac{\bar{c}_H}{4}$, where γ_s is the sticking probability, $[H]$ the local concentration at the surface of the substrate, and $\bar{c}_H$ the mean thermal speed. Using the same analysis as done by Goodwin [20], the ratio of the H mole fraction at the surface, $X_{H,s}$, to that at the filament, $X_{H,f}$, is approximately given by $\frac{X_{H,s}}{X_{H,f}} \approx \frac{1}{\gamma_s} \frac{\lambda_H}{l}$. With a rigid sphere model for gas collisions [21], λ_H is related to the mean free path of collision by $\lambda_H = \frac{4}{3} \lambda_{mp}$; in our calculations the H₂ collision diameter is assumed to be 2.75 Å [22]. The separation l between the filament and the substrate is taken to be 1.5 cm. A comparison of the calculated and measured results are shown in Fig. 3. The closed data points are the equilibrium values at the filament temperature. The H-atom mole fraction at the substrate would have exactly the same values if loss at the surface is zero ($\gamma_s = 0$). Good agreement with measured values can be obtained if $\gamma_s = 0.2$. The apparent sticking probability used is x2 higher than that measured by Harris and Weiner [23], however, it is consistent with the value expected based on gas-phase reaction rates.[20]. A more complete modeling using the full transport description of the reacting gas gives essentially the same result.[17] One should not expect an agreement better than a factor of two since the filament-substrate geometry is intrinsically two-dimensional.

d. Hydrogen + Methane Feed

Sommer and Smith [24] reported that tungsten and rhenium filaments exhibited sharp increases in power consumption as they are heated to high temperatures. They associated this increase to an increase in filament activity, presumably to the production of H atoms. They also proposed that the presence of a nonreactive carbon layer on the filament surface can strongly decrease the catalytic activity. They analyzed this "filament poisoning" phenomenon using a quasi-equilibrium model. It assumes that thermochemical equilibrium exists between the solid carbon

surface and the vapor species desorbed from it. Using the equilibrium constants of the reactions of solid carbon with H or H₂, and by imposing conservation of H atoms they derived a phase-diagram of the C-H system. The analysis showed that graphite can be deposited only for carbon mole fractions above 1×10^{-4} . The threshold rises with increasing H-atom concentrations due to the etching of graphite. One way of increasing the H-atom concentration is by increasing the filament temperature. As the temperature is increased from 2270 to 2600 K, their predicted threshold for graphite deposition increased from a carbon mole fraction of 5×10^{-3} to 2×10^{-2} . Celii and Butler [25] reported that the H-atom concentration was suppressed when the inlet methane fraction was increased.

Fig. 4 shows the measured composition for a single tungsten filament heated to a temperature $T_f = 2600$ K.[26] The mole fractions of the detected species are plotted against the inlet methane fraction. The hydrogen and argon flow rates were held fixed at 1.28 and 0.1 Torr-l/s, respectively, while methane was varied from 5.43×10^{-3} to 0.11 Torr-l/s. This mixture translates to an inlet methane fraction ranging from 3.9×10^{-3} to 7.5×10^{-2} . The dominant gaseous species measured are H₂ and Ar. Their mole fractions are essentially constant with values of 0.9 and 0.07, respectively and are not shown in the plot. The next four major species detected are methane, acetylene, methyl, and atomic H.

The H mole fraction is observed to decrease by an order-of-magnitude as the inlet methane fraction increased to 7.5%. At low inlet methane feed, a significant portion of the methane has been converted to acetylene making it the most abundant hydrocarbon species. The conversion efficiency is significantly reduced at higher methane feeds when the H-atom mole fraction is low. The decrease in conversion can be seen more quantitatively. From the reactions shown in Table I., the conversion to acetylene must follow several sequential H abstraction steps. How fast this conversion can happen depends on the H-atom concentration. If the conversion is rapid, the

concentrations of acetylene and methyl will scale as $[C_2H_2] = A [CH_3]^2$ (see reaction #2 in Table I), with A as a measure of the conversion efficiency remaining approximately constant over the full range of methane feed. Using the measured mole fractions shown in Fig. 4, the factor A was found to decrease by an order of magnitude at the high methane feed regime (Fig. 5).

A similar phenomenon is observed at lower filament temperatures (Fig. 6). When $T_f = 2600$ K, the onset of the H-atom decrease occurs when the inlet mole methane fraction was increased above 0.01 (Fig. 4), however, at $T_f = 2270$ K the decrease occurs at a lower inlet methane fraction. This agrees qualitatively with the predictions of Sommer and Smith [24]. With the overall H-atom mole fraction lower in the 2270 K case, the acetylene and methyl mole fractions are also reduced.

The order-of-magnitude drop in the H-atom mole fraction seen in Fig. 4 cannot be explained solely by homogeneous gas-phase reactions. To illustrate this, the SPIN code is used to calculate the expected composition with the assumption that the H-atom mole fraction at the filament position is given by the equilibrium level in the limit of zero methane feed. Figure 7 plots the calculated results, the filled data points are the predicted values; the curves are smoothed fit to these values to help guide the eyes. Predicted values do not quantitatively and qualitatively match the measured values. The calculated H mole fraction remains relatively flat with increasing methane feed. Acetylene is predicted to be the dominant hydrocarbon species over the entire range of the inlet methane mole fraction while the concentrations of methyl and methane are an order-of-magnitude lower than their measured values. Additionally, methyl is predicted to scale linearly with methane, which disagrees with the experimental observation.

These discrepancies bring to question the validity of assuming an initial H-atom mole fraction equal to the equilibrium level. In past modeling studies, the starting H-atom mole fraction

was either assumed to be at the equilibrium level in the limit of zero methane feed [17] (as done in our calculations represented by Fig. 7), or modified by allowing the gas mixture to react toward equilibrium for a specified duration [2,16,27]. This "incubation" period was needed to give a good match with experimental results, but its justification was not explained. Using the SPIN code we have investigated this issue more carefully. Two types of calculations were performed. In the first scenario, called the "incubating" mode, the code SEMKIN [28] was used to determine the resulting composition when a hydrocarbon-hydrogen mixture was first allowed to react homogeneously at 2600 K for 200 ms. The resulting composition was then used as the starting mixture for the SPIN calculations. This procedure was used by Goodwin and Gavillet [16]. It should be noted that SPIN does not model heterogeneous reactions on the surface of the *heated filament*. Table IIa compares the measured and the predicted composition at the surface of the substrate using the incubating mode. Two methane feed cases were studied, 0.4% and 7.2%. For the 0.4% case, the predicted mole fractions are mostly within 50% of the measured values, except for methyl which is off by a factor of three. At 7.2%, the two sets of values differ by at least a factor of seven. Although the 200-ms incubation period does a good job predicting the measured results at 0.4%, it fared poorly at 7.2%. In particular, it overestimates the amount of H atoms generated when the catalytic activity of the filament is very much reduced. A better agreement can be obtained if a much shorter incubation period of 10 ms is used instead (not shown in Table IIa). As the filament reactivity becomes reduced, the incubation period also needs to be reduced. The incubation mode is therefore a crude way of circumventing the limitation of not modeling filament reactivity in SPIN.

If SPIN is used to self-consistently determine the inlet mixture, rather than rely on SEMKIN, one would expect predictions and measurements to better match at 7.2% where surface reactivity is suppressed. For this second scenario, called the "non-incubating" mode, an unreacted mixture was allowed to flow from inlet to surface past a region that was first heated from room

temperature to 2600 K and then back down to 1100 K. The heating region was chosen to be 3 cm in length, the ramp down region 1.5 cm, and the inlet flow velocity was 1 cm/s. Consistent with our expectations, the agreement is poor at 0.4%, but relatively good at 7.2% (see Table IIb). At 7.2%, the predicted and measured values for atomic H are within 50% of each other.

Rhenium filaments were also found to be poisoned at high methane feeds (Fig. 8). Since rhenium does not form a carbide the observation is consistent with the explanation of Sommer and Smith [24] that the reduced reactivity is caused by the deposition of a carbon layer. With rhenium it is observed that the transition to a poisoned state occurs much more suddenly and fluctuations in the mole fractions are larger than in the case of tungsten.

We do not know the details of filament poisoning, however, we can account for its effects by using the measured dependence of H-atom mole fraction on inlet methane fraction as an input and calculate the behavior of the hydrocarbon species. This result is shown in Fig. 9; the filled data points are the predicted values, they are connected by smoothed curves to guide the eyes. The measured values of Fig. 4 are reproduced as open data points for comparison. The experimental results are now reproduced quite well.[17] At low methane feed when the hydrogen concentration is high most of the methane molecules are converted to acetylene. As the H-atom concentration drops (due to filament poisoning), the conversion to acetylene becomes less effective.

e. Effect of Filament Surface Area

Since H_2 dissociation is induced primarily on the filament surface, increasing the filament surface area should increase the H atom concentration. However, as thermodynamic equilibrium is approached the fractional increase would become less. Eventually, no increase is expected once

the system reaches thermodynamic equilibrium. Figure 10 shows the increase in H-atom mole fraction as the surface area is increased. The filament surface area was increased by bundling multiple strands of 10-mil tungsten wires. Also shown is a solid linear line which would be the expected rate of increase if the system is far from equilibrium. The observed rate of increase is lower than linear scaling, and at the highest surface areas the curve begins to flatten out as would be expected when the system approaches equilibrium.

Figure 11 shows that with the highest filament area the H-atom mole fraction does not exhibit the sharp decrease as the methane feed percentage is increased up to 5%. Over the full range of the methane feed, acetylene is now the dominant hydrocarbon species as methane is effectively converted. The methyl mole fraction scales linearly with the methane mole fraction over the entire range of inlet methane mole fraction, which differs from the results observed using a single filament (Fig. 4). At the lowest methane feed, the amount of carbon detected is $\sim x5$ less than the amount fed into the system. This imbalance is believed to be caused by diffusion driven by thermal gradients.[2] The Soret effect is mass sensitive and tends to drive heavier species toward colder regions. Since our filament-substrate geometry is intrinsically a two-dimensional problem, we believe that the heavier species are displaced away from the region directly between the filament and the substrate when the filament surface area is high.

f. Effect of Filament Geometry

Finally, we wish to point out that the filament geometry strongly affects the local composition. In all previous discussions, the experiments were conducted with either a single strand or multi-stranded filaments bundled together. A very different composition would be obtained if the filaments were a sheet of heated fine mesh. In this case one would expect the H-

atom concentration to be slightly higher (approaching the concentration dictated by thermodynamic equilibrium) than in the single strand. Since most of the inlet methane had already converted to acetylene, a further increase in the H atom concentration would not significantly increase the acetylene concentration. However, methane and methyl cannot reach the substrate by diffusing around the hot mesh as they can in a single strand/bundle case. Instead they are forced to pass through the heated region between the mesh and suffer significant conversion to acetylene. We experimentally simulated a sheet of fine-mesh by spacing three 10-mil filaments 0.5 cm apart maintained at 1.5 cm from the substrate. The measured composition at an inlet methane percentage of 0.9% is shown in Table III.[18,26] The results under the same operating condition, but taken with a single filament, are also shown for comparison. The mole fraction of acetylene is virtually unchanged, that of H-atom is slightly higher in the three-filament case, while those of methane and methyl are reduced by ~ 3.5 . These results confirm our general expectations. Other investigators have reported that when using multiple filaments spaced apart the diamond growth rate directly underneath the filaments is much lower than on the outer edges.[29] The implication of our measurements is that methane/methyl are the primary species that lead to diamond growth.

V. Summary

Molecular beam mass spectrometry is a versatile technique for determining the gas-phase composition in chemical vapor deposition systems. In this paper we presented results from a thermal CVD system, but the technique can be equally applied to plasma systems. The principal attractiveness of this technique is its ability to monitor several species simultaneously. With careful design, reactive species can be detected with a sensitivity approaching 1 ppm. We have also developed a procedure to convert the measured signals to actual concentrations.

The diagnostic tool was instrumented onto a diamond deposition reactor operating at conditions typically required for film growth. Analyses showed that filament poisoning causes the H-atom concentration to decrease sharply when the inlet methane fraction exceeds 0.01. This behavior strongly affects the composition of the hydrocarbon species. By taking into account the poisoning effect, the hydrocarbon compositions can be accurately modeled. The composition is also strongly affected by filament size (surface area) and its geometry. Based on our investigations we believe that methane/methyl is more likely to lead to diamond growth than acetylene.

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Table I. List of key reactions in the C-H system for diamond chemical vapor deposition.

	Reaction
1.	$\text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2$
2.	$\text{CH}_3 + \text{CH}_3 + \text{M} \rightleftharpoons \text{C}_2\text{H}_6 + \text{M}$
3.	$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}$
4.	$\text{C}_2\text{H}_6 + \text{H} \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}_2$
5.	$\text{C}_2\text{H}_5 + \text{M} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H} + \text{M}$
6.	$\text{C}_2\text{H}_4 + \text{H} \rightleftharpoons \text{C}_2\text{H}_3 + \text{H}_2$
7.	$\text{C}_2\text{H}_3 + \text{H} \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}_2$
8.	$\text{H}_2 + \text{M} \rightleftharpoons \text{H} + \text{H} + \text{M}$
9.	$\text{H} + \text{CH(s)} \rightleftharpoons \text{C(s,r)} + \text{H}_2$
10.	$\text{H} + \text{C(s,r)} \rightleftharpoons \text{CH(s)}$

Table II. Calculated and measured compositions at two methane feed percentages.

(a) Calculations using the incubating mode with an incubation period of 200 ms.

Species	Incubating Mode		Measured	
	0.4% CH ₄	7.2% CH ₄	0.4% CH ₄	7.2% CH ₄
	200-ms	200-ms		
CH ₄	1.1x10 ⁻³	8.3x10 ⁻⁴	9.9x10 ⁻⁴	6.0x10 ⁻²
CH ₃	7.34x10 ⁻⁵	7.1x10 ⁻⁵	2.0x10 ⁻⁴	1.3x10 ⁻³
C ₂ H ₂	2.2x10 ⁻³	4.6x10 ⁻²	2.0x10 ⁻³	6.4x10 ⁻³
H	8.4x10 ⁻⁴	9.4x10 ⁻⁴	1.2x10 ⁻³	1.2x10 ⁻⁴

(b) Calculations using the non-incubating mode assuming a heating region of 3 cm and an inlet flow velocity of 1 cm/s..

species	non-incubating		measured	
	0.4% CH ₄	7.2% CH ₄	0.4% CH ₄	7.2% CH ₄
CH ₄	2.33E-03	3.80E-02	9.9x10 ⁻⁴	6.0x10 ⁻²
CH ₃	5.18E-06	6.02E-04	2.0x10 ⁻⁴	1.3x10 ⁻³
C ₂ H ₂	1.53E-07	3.19E-03	2.0x10 ⁻³	6.4x10 ⁻³
H	4.71E-05	1.76E-04	1.2x10 ⁻³	1.2x10 ⁻⁴

Table III. Measured mole fractions with an inlet methane fraction of 0.009.

SPECIES	three filaments	single filament
H	2.3×10^{-3}	1.3×10^{-3}
CH ₃	9.1×10^{-5}	3.11×10^{-4}
CH ₄	3.9×10^{-4}	1.6×10^{-3}
C ₂ H ₂	3.6×10^{-3}	3.7×10^{-3}

Figure 1. Schematic diagram of the diamond deposition reactor instrumented with the molecular beam mass spectrometry diagnostic system.

Figure 2a. Thermodynamic properties along the centerline of an expanding free jet. The temperature T , density n , and pressure P , normalized to the source stagnation values, are plotted versus downstream stream distance from the orifice. Distance is given in terms of the orifice diameter d ; $\gamma = 1.4$.

Figure 2b. The Mach number M , mean free path λ , and convective flow velocity V along the center line of the expanding free jet.

Figure 3. H-atom mole fractions versus filament temperature. Gas feed is pure hydrogen, pressure and substrate temperature are kept fixed. Solid curve is calculated assuming a H atom surface sticking probability of $\gamma_s = 0.2$ and the inlet at the equilibrium level corresponding to the filament temperature.

Figure 4. Mole fractions of species in the vicinity of a diamond coated substrate measured as a function of the inlet methane fraction. The mole fractions of H_2 and Ar remained relatively constant at 0.9 and 0.07, respectively, and are not shown. The single strand of hot-filament is located 1.5 cm away from the substrate.

Figure 5. Ratio of the acetylene mole fraction to the square of the methyl mole fraction using the data shown in Fig. 3.

data shown in Fig. 3.

Figure 6. Mole fractions of the species measured with a tungsten filament at a temperature of 2273 K.

Figure 7. Calculated species mole fractions when neglecting the filament poisoning effect.

Figure 8. The species composition when using a rhenium filament. The mole fractions are plotted against increasing methane feed fraction.

Figure 9. Comparison of calculated and measured mole fractions. The solid data points are calculated assuming the H-atom mole fraction follows the behavior of the measured values (reproduced from reference [17]) The data points are connected by smoothed curves to help guide the eyes. The open data points are the measured results reproduced from Fig. 4

Figure 10. Changes in H-atom mole fraction with changing filament surface area. The solid line is for linear increase, the dashed curve is a cubic spline fit to the data.

Figure 11. Mole fractions of species using a hot-filament bundle consisting of four strands of 0.25 mm tungsten wires.

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