

# Dependence of the gas composition in a microwave plasma-assisted diamond chemical vapor deposition reactor on the inlet carbon source: CH<sub>4</sub> versus C<sub>2</sub>H<sub>2</sub>

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## Abstract

Molecular beam mass spectrometry was used to measure the gas-phase composition near a growing diamond surface in a microwave plasma-assisted chemical vapor deposition reactor. The dependencies of the gas composition on changes in: (1) the carbon mole fraction in the reactor feed,  $X_C$ ; (2) the identity of the inlet carbon source (CH<sub>4</sub> versus C<sub>2</sub>H<sub>2</sub>); and (3) the surface temperature,  $T_s$ , were studied. Unlike the hot-filament case, the gas composition was independent of the identity of the inlet hydrocarbon source over the entire range of  $X_C$ . As expected from gas-composition measurements, films grown using either hydrocarbon exhibited similar growth rates, morphology and Raman spectra. The gas composition was also generally insensitive to changes in surface temperature suggesting that reported temperature sensitivities of film growth properties are primarily due to changes in the kinetics of surface processes rather than changes in the gas composition near the surface. For  $X_C \leq 0.01$ , the gas compositions measured in this study and in our previous studies conducted in a hot filament-assisted chemical vapor deposition reactor are quantitatively similar implying similar gas-phase chemistry in both reactors when sufficient atomic hydrogen is present. However, attempts to simulate the gas composition in the plasma environment using a numerical model based only on neutral-neutral gas-phase chemistry were generally unsuccessful over a wide range of  $X_C$ .

**Keywords:** Deposition mechanism; Gas phase chemistry; Gas phase diagnostics; Microwave plasma CVD

## 1. Introduction

For well over a decade, scientists have attempted to better define and optimize the reaction conditions that are capable of depositing diamond from the vapor phase. In general, the chemical vapor deposition (CVD) of diamond is accomplished by activating (energizing) a gaseous mixture in the reaction vessel such that it is capable of promoting diamond film growth. Typically, the reactor feed is composed of a small amount of a hydrocarbon (e.g. methane or acetylene) mixed with a large quantity of hydrogen; halogenated [1,2] and/or oxygenated species [3–6] have been shown to promote diamond film growth as well. Depending on the extent

of gas activation, the identity (and concentration) of the carbon source in the reactor feed can be a very important factor in determining the growth rate and quality of the deposited films. For example, when the decomposition of the inlet hydrocarbon is incomplete (e.g. in studies attempting to identify the precursor diamond growth [7–9]), the growth rate and film quality for films grown with a CH<sub>4</sub>/H<sub>2</sub> reactor feed are enhanced relative to the films grown with a feed containing C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>. On the other hand, when gas activation is more extensive (e.g. owing to either an increase in the H-atom concentration or plasma-induced dissociation and chemistry), film growth properties are insensitive to the identity of the carbon source and depend only on the relative concentrations of carbon and hydrogen in the reactor feed. For example, in a plasma-assisted deposition environment, Sato et al. [10] reported similar growth properties for diamond films grown from gaseous mixtures

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of various hydrocarbons when the C/H ratio in the reactor feed was fixed. Toyoda et al. [11] reported similar results for films grown from CH<sub>4</sub>/H<sub>2</sub> or C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> mixtures in a hot filament-assisted CVD (HFCVD) reactor under conditions where filament poisoning was negligible.

The relative independence of diamond growth on the nature of the inlet hydrocarbon species implies that similar concentrations of the growth precursor(s) are present above the growth surface when the gas is well activated. While the few attempts made to characterize the gas composition generated using different carbon sources confirm these expectations, the concentrations of only a limited number of gas-phase species have been quantified. In a microwave plasma-assisted CVD (MPCVD) environment, Mitomo et al. [12] reported that the product distributions of stable species (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>) generated from various hydrocarbon/hydrogen mixtures depend only on the C/H ratio in the inlet gas and not the identity of the carbon source. Consistent with their film growth measurements in a hot filament-assisted reactor, Toyoda et al. [11] reported the CH<sub>3</sub> concentration to depend only on the C/H ratio of the inlet gas and not on the chemical identity of the input hydrocarbon species. We have recently characterized the gas composition generated from CH<sub>4</sub>/H<sub>2</sub> or C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> mixtures in a HFCVD reactor using the molecular beam mass spectrometry (MBMS) technique [13]. This technique is advantageous relative to other diagnostic techniques because it provides direct, quantitative information for a large number of stable and radical gas species at, arguably, the most important region in a deposition environment; near the growth surface. At low carbon mole fractions in the feed,  $X_C$ , the concentrations of each of the detected stable and radical species are insensitive to changes in the identity of the carbon source. At higher values of  $X_C$ , where filament poisoning is significant, the gas compositions are dramatically different owing to reduced decomposition of the parent hydrocarbons.

Numerical models designed to simulate the environment in a diamond CVD reactor can complement gas-phase measurements by providing additional information regarding the processes that yield the measured species concentrations. By incorporating fluid and heat transport effects along with homogeneous and heterogeneous reaction kinetics, the temperature, velocity and concentration fields in a reactor can be calculated as a function of the inlet feed composition and various reactor parameters. Numerical simulations based on neutral-neutral chemistry have successfully accounted for the gas-phase composition measured during HFCVD [13–16]. However, these models might not be expected to predict the environment in a MPCVD reactor since plasma effects such as electron-neutral or ion-neutral reactions are not included. However, Hsu has recently

noted that the hydrocarbon chemistry in a microwave reactor may be dominated by neutral-neutral interactions [17]. To date, it has not been determined whether numerical models based on thermal chemistry can quantitatively predict the gaseous environment in a microwave plasma. Hence, additional measurements of the gas composition present in a microwave plasma-assisted diamond deposition reactor are required to assist in the future development of these models.

In this study, molecular beam mass spectrometry is used to determine how changes in the identity and concentration of the carbon source (CH<sub>4</sub> versus C<sub>2</sub>H<sub>2</sub>) fed to a MPCVD reactor affect the gas composition and the growth behavior of diamond films. The sensitivity of the gas composition to surface temperature is also measured. The results of these gas composition experiments are compared with data we have previously measured in a HFCVD reactor. Finally, we test the ability to simulate the microwave plasma reaction environment using a numerical model that is based solely on neutral-neutral reaction kinetics.

## 2. Experimental

The MBMS apparatus used in this study has been described in detail elsewhere [18]. Reactant gases are introduced into a deposition chamber where they are activated directly over the growth surface by a microwave plasma discharge. The discharge forms an approximately 8 cm diameter luminous plasma “ball” that rests on the growth surface. Gas very near the growth surface escapes the process chamber through a 300 μm collection hole located in the center of the substrate and is collimated to form a supersonic molecular beam. The beam subsequently enters the ionizing region of an electron-impact mass spectrometer located in the third stage of differential pumping (background pressure ≈ 10<sup>-7</sup> Torr). The gas composition in the beam can be related to the gas composition in the deposition chamber using a series of procedures that have been previously detailed [18]. Before entering the ionizing region of the mass spectrometer, the beam is modulated to distinguish species in the molecular beam from those in the background. Threshold ionization techniques are used to discriminate between stable and radical species. Formation of the supersonic molecular beam does not result in significant distortion of the gas composition near the surface. Calculations indicate that the spatial extent of gas sampling near the orifice is in the order of the collection hole diameter (300 μm) [19]. This distance is much less than the distance above the surface where gas activation is believed to occur.

Gas-phase composition and film-deposition experiments were conducted using slightly different substrate configurations. Film-deposition studies were performed

Table 1  
Reaction conditions used in these experiments

H <sub>2</sub> flowrate	98 sccm
Ar flowrate	12 sccm
CH <sub>4</sub> flowrate	0.52–8.7 sccm
C <sub>2</sub> H <sub>2</sub> flowrate	0.38–8.7 sccm
Reactor pressure	20 Torr
Substrate temperature	575–825 °C
Microwave power	850 W

on Si(111) wafers (resistivity = 150–250 Ωcm) pretreated by: (1) scratching the sample in an ultrasonic agitator for 30 min using a mixture of 2 and 40 μm diamond powder and ethanol; (2) etching the sample in a 50% HF bath for 1 min; and (3) rinsing in deionized water for 5 min. Film growth rates and morphology were determined from scanning electron microscopy (SEM) analysis, while film quality was assessed using Raman spectroscopy (laser beam diameter and power were 300 μm and 400 mW, respectively). For gas-phase measurements, no Si substrate was employed; the process gas in the near vicinity of the sampling orifice was in direct contact with the diamond-coated molybdenum substrate holder.

The reactor conditions used in these experiments are summarized in Table 1. The reactor pressure and microwave power were held constant at 20 Torr and 850 W, respectively, while the surface temperature was systematically varied from 575 °C <  $T_s$  < 825 °C. Either methane or acetylene was introduced into a feed mixture containing hydrogen and argon. The methane mole fraction in the feed was varied from 0.0035 to 0.075 while the acetylene mole fraction ranged from 0.0024 to 0.037. Argon was introduced at a mole fraction of  $0.08 \pm 0.01$  in the gas-composition measurements as a calibration reference and to eliminate mass discrimination effects that occur during the formation of the supersonic molecular beam [18]. The presence of Ar at this concentration level in a plasma environment has been previously reported to affect changes in the gas composition [20]; however, the magnitudes of these effects are in the order of our measurement errors for species concentrations ( $\pm 30\%$ ) and are considered negligible in these experiments.

### 3. Experimental results

The mole fractions of the major gas-phase species detected near the growth surface were monitored as a function of the carbon mole fraction in the inlet gas using either acetylene (Fig. 1(a)) or methane (Fig. 1(b)) as the carbon source. In order to directly compare the gas compositions measured in these systems at a fixed C/H ratio, the species mole fractions are shown as a function of the carbon mole fraction in the feed,  $X_C$  ( $X_C$

is equal to the mole fraction of the hydrocarbon in the feed multiplied by the number of carbon atoms in the carbon source). The mole fractions of the most abundant species (H<sub>2</sub> and Ar) were approximately equal to their mole fractions in the feed at all values of  $X_C$  and are not shown. In addition to H<sub>2</sub> and Ar, we also detected measurable concentrations of CH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. We were unable to detect the presence of C<sub>2</sub>H<sub>6</sub>, which sets the upper limit of its mole fraction to  $1 \times 10^{-6}$  under these experimental conditions. The species' mole fractions measured when the carbon source was methane (Fig. 1(b)) are nearly identical to those previously reported by Hsu [17] under similar reaction conditions. However, in this study we also measured the ethylene mole fraction as a function of  $X_C$ , which was not performed in the previous work. Using either carbon source, the measured mole fractions of the stable species (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>) are in good quantitative agreement with the previously reported results of Mitomo et al. [12] who only measured the concentrations of stable species in their reactor via in-situ Fourier transform infrared spectroscopy. Unlike their measurements, however, we were also able to quantify the concentrations of radical species such as H atoms and CH<sub>3</sub>. Quantification of the H atom and CH<sub>3</sub> mole fractions near the growth surface is important since these species are believed to play important roles in diamond film growth [21,22].

At most values of  $X_C$ , the gas composition in a microwave plasma-assisted reaction environment differs considerably from the gas composition generated when a hot filament activates the gas phase. In this study, the hydrocarbon mole fractions near the growth surface continuously increase as  $X_C$  increases. Regardless of the identity of the carbon source, methane is the most abundant hydrocarbon detected when  $X_C$  is small; however, for  $X_C > 0.01$  acetylene becomes the dominant hydrocarbon species. When a hot filament activates the gas mixture [13], the gas composition near the surface remains independent of the carbon source only when  $X_C < 0.02$ . At larger inlet carbon mole fractions, the inlet hydrocarbon becomes the most dominant hydrocarbon in the gas phase. We believe the differences between the gas compositions measured in the HFCVD and MPCVD reactors result, to a large extent, from differences in the H-atom profiles. When a filament is used to activate the reactant gas mixture, hydrocarbon decomposition on the hot filament surface poisons the catalytic production of H atoms from H<sub>2</sub> [16,23–28]. At larger values of  $X_C$ , filament poisoning becomes significant and the H-atom concentration drops precipitously. As a result, decomposition of the carbon source to form other hydrocarbon species decreases. In a plasma environment, H-atom production occurs homogeneously and the H-atom concentration remains essentially constant as  $X_C$  increases (Figs. 1(a) and 1(b)). As a result,

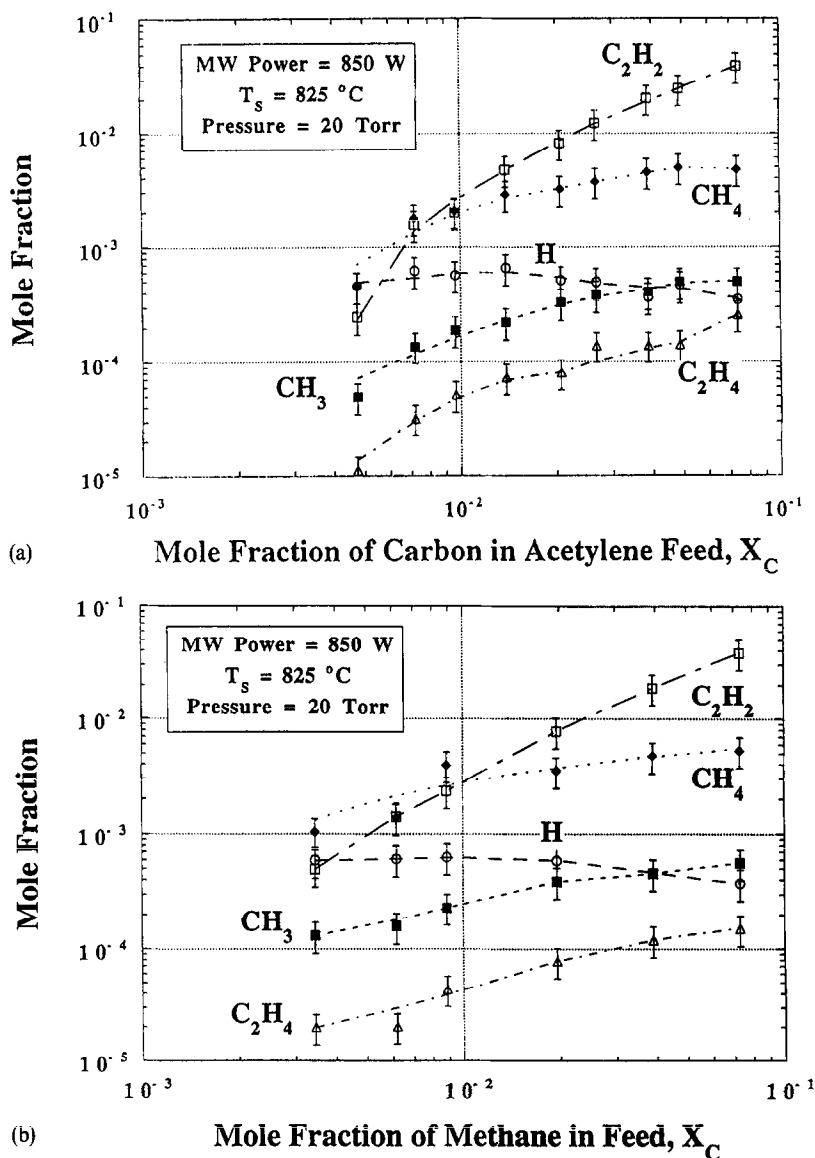


Fig. 1. Mole fractions of species measured in the MPCVD reactor as a function of the carbon mole fraction in the feed,  $X_C$ , for (a) acetylene and (b) methane. The microwave power, reactor pressure and surface temperature were held constant at 850 W, 20 Torr and 825 °C, respectively.

conversion of the carbon source to other hydrocarbon species remains significant as the inlet C/H ratio increases. In addition, other secondary effects giving rise to differences between the HFCVD and MPCVD systems include scrambling of the hydrocarbons on hot metal surfaces in the hot-filament system that actively participate in the overall chemistry, and electron-induced dissociation and ion-induced chemistry in the microwave system.

For all values of  $X_C$ , the gas composition in the microwave plasma-assisted environment is insensitive to the identity of the carbon source. At a fixed  $X_C$ , the mole fractions of all species measured near the surface for a  $C_2H_2/H_2$  feed are identical to those measured for a  $CH_4/H_2$  feed within the limits of experimental error. These results indicate that all history of the molecular

species fed to the MPCVD reactor is lost and the gas-phase composition depends only on the C/H ratio in the inlet gas stream. Mitomo et al. [12] previously reported that the concentrations of stable species in a MPCVD reactor depend only on the C/H ratio in the reactor feed and not on the identity of the carbon source. Our study shows this behavior extends to the radical species as well. Although their reactor pressure and microwave power were greater than in our study, Mitsuda et al. [29] used mass spectrometry sampling techniques and optical emission spectroscopy to report that the gas composition in atmospheric microwave plasma jets generated with different carbon sources in the reactor feed (acetylene versus methane) were dependent only on the C/H ratio in the inlet gas stream. In a hot filament-assisted reaction environment, the gas com-

position is also relatively independent of the carbon source under conditions where filament poisoning is negligible and the H-atom mole fraction is high ( $X_C < 0.02$ ) [11,13].

Our results suggest that films deposited in a microwave plasma-assisted environment under these experimental conditions will have nearly identical growth properties at a given value of  $X_C$ . In order to test how the identity of the carbon source affects film properties, films were grown with  $X_C = 0.0065$  and  $0.028$  using inlet mixtures of  $\text{CH}_4/\text{H}_2$  or  $\text{C}_2\text{H}_2/\text{H}_2$ . Reactor conditions ( $T_s = 825^\circ\text{C}$ ,  $P = 20$  Torr, microwave power =  $850$  W) and deposition times were held constant. Film properties were assessed using SEM (Figs. 2(a) and 2(b)) and Raman spectroscopy (Fig. 3) analysis. At either value of



(a)



(b)

Fig. 2. Scanning electron micrographs of films grown in the MPCVD reactor using mixtures of either (a) methane in hydrogen, or (b) acetylene in hydrogen. The inlet carbon mole fraction was fixed at  $X_C = 0.0065$ . The microwave power, reactor pressure and surface temperature were  $850$  W,  $20$  Torr and  $825^\circ\text{C}$ , respectively.

$X_C$ , the film growth rate, Raman spectra and surface morphology were nearly identical for the two source gases. These results provide further evidence that the gas composition above the growth surface was insensitive to the identity of the inlet carbon source under these experimental conditions provided the C/H ratio was fixed. Sato et al. [10] have previously grown diamond films from various hydrocarbon–hydrogen mixtures in a plasma environment and noted that the film growth features were similar when the C/H ratio was fixed. Films grown in a HFCVD reactor also depend only on the C/H ratio provided the reactor is operated under conditions where filament poisoning is negligible [11].

The hydrocarbon concentrations in either a HFCVD or MPCVD reactor are quantitatively similar when  $X_C < 0.01$ . Although the hydrocarbon mole fractions measured in these reactors do not exhibit exactly the same dependence on  $X_C$ , they differ in magnitude by less than a factor of 3. These results provide a better understanding why diamond films having comparable physical properties can be grown in these two types of reactors. These results suggest the reaction chemistry in both environments is similar under these reaction conditions. Hsu [17] has recently suggested that neutral–neutral reactions, which dominate the gas-phase chemistry in a HFCVD reactor, are more important than ion–neutral or electron–neutral interactions in the plasma system. This argument is primarily based on the fact that the charge densities are very low in the MPCVD reactor under these experimental conditions (ion or electron mole fractions are in the order of  $10^{-7}$ ). The low ionic concentrations offset the higher reaction rate constants for ion–neutral reactions relative to their neutral–neutral analogs [30,31]. Thus, the primary role of the plasma is to dissociate molecular hydrogen without having to raise the gas temperature significantly. As a result, plasma effects might not be expected to be as important as thermal chemistry in determining the hydrocarbon product distribution in a MPCVD reactor. However, as we investigate over a broader range of operating conditions and with other hydrocarbon inlet gases, we find that this conclusion no longer holds. To be discussed in the following section, the measured composition of the species cannot be predicted using purely a thermal treatment of the chemically reacting environment; plasma-induced chemistry must be taken into account.

Finally, we have also measured the sensitivity of the gas composition to changes in the surface temperature,  $T_s$ . Although surface temperature changes can dramatically affect film properties such as growth rate and morphology [32–37], they do not appear to significantly affect the gas-phase composition above the growth surface in this study. When the carbon mole fraction in the feed was held constant at  $0.0065$ , the concentrations of almost all of the gas species remained nearly independent

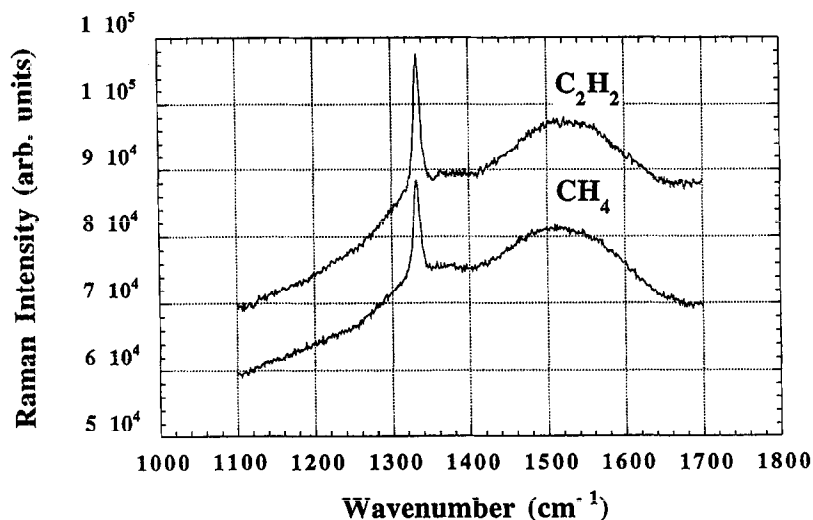


Fig. 3. Raman spectra of the films shown in Fig. 2.

of surface temperature as  $T_s$  increased from 575 to 825 °C; however, the ethylene mole fraction decreased by a factor of 5 (Fig. 4). Almost identical results were observed when acetylene replaced methane in the feed and  $X_C = 0.0065$ . An upper limit to the activation energy for homogeneous production of either methyl or acetylene under these experimental conditions is  $\leq 1$  kcal mol<sup>-1</sup>. These results are different from our previously reported measurements in a HFCVD reactor [13]. In that study, the temperature dependence of the gas composition was measured over a larger range of  $T_s$  (225 °C <  $T_s$  < 825 °C). The methyl and acetylene mole fractions exhibited larger increases with  $T_s$  and the methane concentration decreased as the surface temperature was raised. The temperature dependence of the  $\text{CH}_3$  and  $\text{C}_2\text{H}_2$  concentrations can each be described as

having an activation energy of  $3 \pm 1$  kcal mol<sup>-1</sup>. As in the hot-filament case, the H concentration remained constant with  $T_s$  [13]. It was explained in that paper that if the sticking probability of H on the diamond surface has an activation energy of 7.3 kcal mol<sup>-1</sup>, the H-atom mole fraction near the surface will not be expected to remain constant with  $T_s$ . Over the temperature range explored in this paper, the mole fraction is expected to change two-fold (increases with decreasing  $T_s$ ). The discrepancy can be explained if H loss by lateral transport to the reactor side-walls is included. This loss term is large and overshadows the smaller loss to the wafer surface, thus making the local H concentration nearly insensitive to  $T_s$ . We believe this to be the case in this study as well.

Over the same temperature range, the substrate-

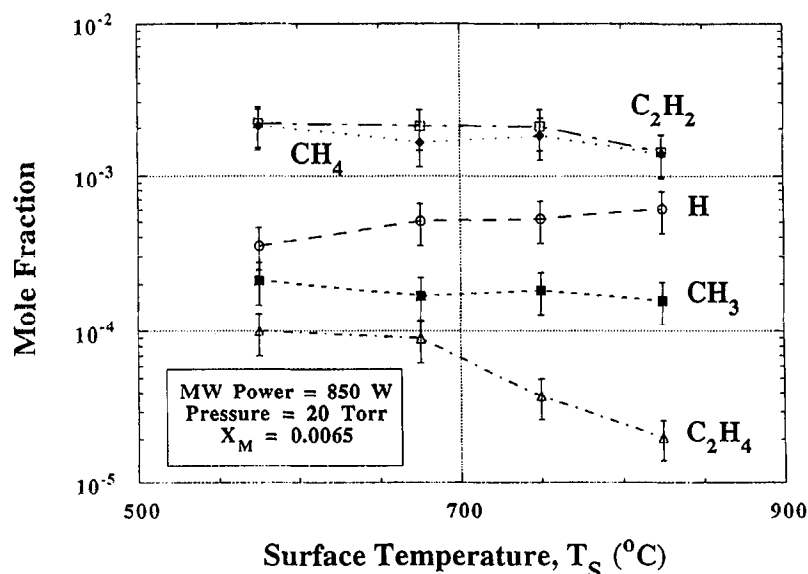


Fig. 4. Mole fractions of species measured in the MPCVD reactor as a function of the surface temperature,  $T_s$ . The methane mole fraction in the feed,  $X_M$ , the microwave power and the reactor pressure were fixed at 0.0065, 850 W and 20 Torr, respectively.

temperature sensitivity of the hydrocarbon product distribution in the plasma-assisted environment does not significantly differ from the distribution measured when the gas is activated by a hot filament. For  $575\text{ }^\circ\text{C} < T_s < 825\text{ }^\circ\text{C}$ , the  $\text{CH}_3$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$  mole fractions measured in the HFCVD reactor vary by less than a factor of two (the temperature dependence of the ethylene mole fraction was not measured in this study). In both studies, our estimates of the activation energies for net  $\text{CH}_3$  and  $\text{C}_2\text{H}_2$  production (often considered to be the primary precursors to diamond growth) are considerably less than the activation energies typically measured for diamond film formation ( $15\text{--}25\text{ kcal mol}^{-1}$ ) [36,37]. Thus, in both plasma and thermal reaction environments, changes in surface temperature affect growth properties primarily by affecting changes in the kinetics of surface processes rather than by changes in the gas composition present near the growth surface.

#### 4. Numerical model results

In an attempt to determine the relative importance of neutral–neutral reactions in a MPCVD reactor, we have used a numerical model based solely on thermal chemistry to simulate the reaction environment used in this study. The formalism for this model was developed by Coltrin and co-workers [38,39]. A detailed description of the model has been previously reported [38], so we present a brief summary here of its more salient features. The program models a one-dimensional stagnation flow through a “reaction zone” representative of the region from the source where the gas is activated (in these calculations, the gas is activated at the plasma “center”) to the growth surface; three dimensional effects are not included. Thermodynamic and chemical information is provided by the CHEMKIN [40] and SURFACE CHEMKIN packages [39]. The reaction mechanism [41] incorporates the kinetics of 34 homogeneous reactions; no plasma effects (such as ion–neutral or electron–neutral reactions) are included. The heterogeneous reaction kinetics include 24 heterogeneous reactions involving  $\text{C}_1$  and  $\text{C}_2$  species with the growth surface; reactions on the cold reactor walls are not included since the model assumes all surface reactions occur on the stagnation plane. Using this formalism, we have been able to quantitatively predict the near-surface gas composition in a HFCVD reactor under reaction conditions where diamond growth occurs ( $X_C \leq 0.02$ ) [13,16]. The ability of this model to predict the hydrocarbon product distribution when filament poisoning effects are negligible suggests that the neutral–neutral homogeneous hydrocarbon chemistry is well understood.

The model has several input parameters, including the reactor pressure, the surface temperature, the axial veloc-

ity at the inlet of the reaction zone, the inlet composition, the inlet gas temperature and the reaction distance. The reactor pressure and surface temperature were set equal to their experimental values. For these simulations, the axial velocity at the inlet of the reaction zone is set to  $1\text{ cm s}^{-1}$  as estimated from experimental conditions. Since diffusion dominates mass transport under these conditions, the exact magnitude of the axial velocity has no impact on the results. The composition of the gas entering the reaction zone was set equal to the composition of the gas stream fed to the reactor. Since direct dissociation of  $\text{H}_2$  to H atoms by electrons may be equally as important as thermally-induced dissociation in the microwave plasma system, the H-atom mole fraction at the inlet to the reaction zone is also an input parameter. Since we do not know the H-atom mole fraction in this region, we choose a value such that the simulations yield a H-atom mole fraction at the gas–surface interface that is close to the H-atom mole fraction measured experimentally. For these simulations, the H-atom mole fraction at the inlet was set to 0.03. The inlet gas temperature (1700 K) and reaction distance (13 mm) were set equal to the values used in the previous modeling of the HFCVD experiments [13]. The predictions of the model were not strongly dependent on these parameters. This value of the gas temperature is consistent with the gas temperatures measured in weakly ionized plasmas (1100–2000 K) [42,43].

Although the model is able to reproduce some features observed experimentally, it is generally unable to capture the near-surface gas composition measured in the plasma environment. As the acetylene concentration in the feed increases, the model predicts increases in the mole fractions of all the hydrocarbon species (Fig. 5). Although the  $\text{C}_2\text{H}_2$ ,  $\text{CH}_3$  and H-atom mole fractions are in quantitative agreement with experiment, the mole fractions of other hydrocarbons are not. For example, the predicted  $\text{CH}_4$  mole fraction is 2–3 times too low and the  $\text{C}_2\text{H}_4$  mole fraction is an order of magnitude too large. The large amount of  $\text{C}_2\text{H}_6$  predicted at larger values of  $X_C$  is particularly surprising since no ethane was detected in the experiment at any C/H ratio. When the calculations are repeated with methane in the feed, differences between the model and experiment are larger. Changing the values of the input parameters does not improve the agreement between the model predictions and the experimental results; a sensitivity analysis on the input parameters indicated that the values selected for these parameters were optimal. Not only does the model incorrectly calculate the near-surface gas composition generated using either carbon source, it also does not account for the insensitivity of the gas composition to the identity of the hydrocarbon source. This insensitivity to the starting reagent observed experimentally suggests the microwave plasma initially converts either source gas into a mixture of species that is determined

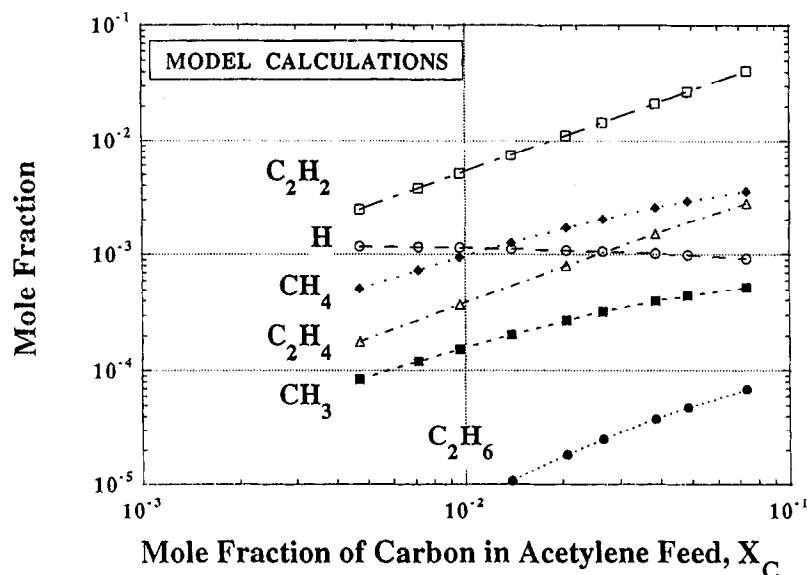


Fig. 5. Numerical model calculations of the species mole fractions versus the carbon mole fraction in a acetylene feed. Inputs for the surface temperature, gas temperature and pressure were at 825 °C, 1425 °C and 20 Torr, respectively.

only by the C/H ratio in the feed. Thus, with the same starting material in each system, subsequent reaction processes create a near-surface gas composition that is a function only of  $X_C$ . To include this possibility into the model, we performed a calculation assuming the inlet carbon source is immediately decomposed to atomic carbon and hydrogen. Then we allowed the numerical simulation to calculate the gas composition as before. This effort produces only minimal improvement in the calculated result; the ethylene and ethane mole fractions are much larger than those measured experimentally.

Although the plasma system is inherently three dimensional, at the region where the plasma makes contact with the wafer the geometry is relatively more planar than for the hot-filament case. In that situation, the model can simulate the chemically reacting environment of a methane/hydrogen mixture quite well, therefore, we do not believe the discrepancies between the model and experimental results originate from three-dimensional mass transport effects [13]. The simulations we have performed in this study demonstrate that neutral-neutral interactions are insufficient to characterize the microwave plasma-assisted reaction environment over a broad range of conditions. We believe future attempts to model the plasma-assisted reaction environment must include ion-neutral and electron-neutral chemistry.

## 5. Conclusions

At all hydrocarbon concentrations in the MPCVD reactor feed, the gas composition appeared to be nearly

independent of the identity of the inlet hydrocarbon and dependent only on the carbon mole fraction in the feed,  $X_C$ . Films grown at a fixed  $X_C$  using either hydrocarbon in the source gas exhibit similar properties providing further confirmation the gas composition immediately above the surface is not affected by the carbon source used. For  $X_C < 0.01$ , the species concentrations measured in this study are quantitatively similar to values measured in the hot filament-assisted reaction environment. The similarity breaks down as  $X_C$  is expanded to higher levels. A numerical model based solely on neutral-neutral reactions is generally unable to quantitatively predict the near-surface gas composition in this environment. The lack of success of this model suggests that effects of plasma-induced dissociation of the reactants must be included to simulate the MPCVD system.

The gas composition is relatively insensitive to surface temperature from 575 °C  $\leq T_s \leq$  825 °C suggesting that the temperature sensitivity of film growth properties is primarily due to changes in the kinetics of surface phenomena rather than changes in the gas composition near the surface. These results are consistent with our previous measurements in a HFCVD reactor.

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