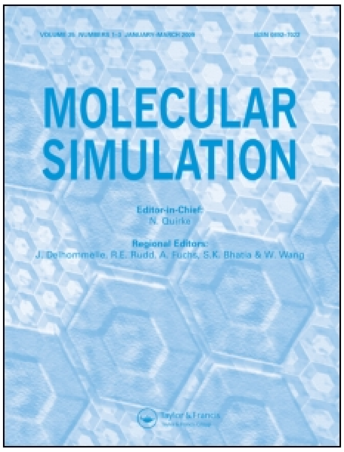

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Li, Yanxin , Brenner, Donald W. , Dong, Xialan and Sun, Chiachung(2000) 'First Principles Prediction of Gas-Phase Composition and Substrate Temperature for Diamond Film Growth', Molecular Simulation, 25: 1, 41 — 51
To link to this Article: DOI: 10.1080/08927020008044111
URL: http://dx.doi.org/10.1080/08927020008044111

Molecular Simulation, 2000, Vol. 25, pp. 41–51
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Printed in Malaysia.

FIRST PRINCIPLES PREDICTION OF GAS-PHASE COMPOSITION AND SUBSTRATE TEMPERATURE FOR DIAMOND FILM GROWTH

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(Received October 1999; accepted November 1999)

A model consisting of ten hydrocarbon species and eight reactions is proposed to describe the gas-phase chemistry of diamond film growth. Based on the model, the gas-phase compositions of the chemical species were computed assuming thermodynamic equilibrium using molecular and transition-state data predicted by *ab initio* molecular orbital theory, and thermodynamic quantities calculated by statistical mechanics. Although the absolute compositions predicted by the model are in fair agreement with experimental data available in the literature, the model qualitatively accounts for experimentally observed changes in the concentrations of various gas-phase species with increasing addition of methane to the feed gas. The calculations also predict the pattern of temperature variance in the gas-phase close to the substrate with changes in methane concentration in the feed gas, leading to first-principles predictions of favorable conditions for diamond growth.

Keywords: Chemical vapor deposition; diamond film; hydrogen; methyl; substrate temperature; methane; *ab initio*; molecular orbital; thermodynamics; calculation; vapor composition

INTRODUCTION

The rapid development of low-pressure diamond film growth technology by chemical vapor deposition (CVD) [1–8] has spurred extensive theoretical

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interest in its growth mechanism [9–22]. To obtain a detailed understanding of diamond deposition processes, it is necessary to understand the gaseous chemistry. Over the last ten years, much progress has been made in the diagnosis of gaseous environment [23–35].

Celii *et al.* [24] and Hsu [29] have experimentally characterized the effect of methane concentration in the feed gas on the concentration of H atoms and hydrocarbon species under diamond growth conditions. Using molecular beam mass spectrometry, they found that at a filament temperature of 2600 K the **H** atom concentration in the proximity of the growth surface decreases with increasing addition of methane to the feed gas, dropping by more than an order of magnitude when the methane percentage is increased from 0.4% to 7.2%. Concurrent with this decrease, large changes in the concentration of the hydrocarbon species were observed. They attributed the cause of this behavior to filament poisoning which apparently inhibits surface-catalyzed dissociation of $\mathbf{H_2}$ molecules. To date no theoretical analysis has been performed to predict or interpret these observations.

In this paper, results of a theoretical study are presented that was carried out to help explain the observed interdependence of species concentrations in diamond growth environments in terms of elementary reactions, and to characterize the underlying thermodynamics and kinetics in the gas-phase environment leading to vapor deposition of diamond films.

MODEL

To determine the gas-phase compositions of chemical species relevant to diamond growth, the following chemical model consisting of 10-species and 8-reactions was assumed:

$$H_2 = 2H \tag{1}$$

$$CH_4 + H = CH_3 + H_2 \tag{2}$$

$$CH_3 + CH_3 = C_2H_6 \tag{3}$$

$$C_2H_6 + H = C_2H_5 + H_2 \tag{4}$$

$$C_2H_5 = C_2H_4 + H \tag{5}$$

$$C_2H_4 + H = C_2H_3 + H_2 \tag{6}$$

$$C_2H_3 = C_2H_2 + H \tag{7}$$

$$C_2H_2 + H = C_2H + H_2 \tag{8}$$

This model is based on gas-phase kinetic reaction mechanisms proposed by Harris [34] and by Frenklach [32]. In our model, thermodynamic equilibrium (TE) for this carbon-hydrogen binary system is assumed.

The gas-phase chemistry associated with the vapor deposition of diamond films is largely nonequilibrium. However, TE has been accepted as a good approximation [5, 26]. The TE approximation [5, 26] is supported by the observation that a large fraction of CH_4 from the feed gas is converted to C_2H_2 [35]. It has been shown that using this approximation leads to reasonable predictions for both gaseous compositions [25, 26, 28] and elementary reaction directions [36, 37]. Even when the transport equation is solved [23, 27, 30, 32] to study the gas-phase chemical kinetics of CVD diamond film, equilibrium is generally assumed through the use of the ideal gas law at each fixed temperature.

The TE approximation for the purposes of our model means that within a hot filament reactor, the concentration distribution of gaseous species is a function of $\mathbf{z}$, the distance coordinate between the filament and the substrate. According to the continuity condition, the feed gas compensates for the consumption of gaseous species at the substrate. Therefore, each layer of $\delta\mathbf{z}$ for every fixed $\mathbf{z}$ can be assumed in TE. This consideration is in accordance with those of Frenklach [32] and Goodwin [27].

Based on TE approximation, two assumptions for the system can be made. First, for the continuous change of temperature from the filament to the substrate, there is a correspondence between the coordinate $\mathbf{z}$ and temperature T [32, 27]. Second, if we focus on the composition in the gas-phase only, the number of carbon atom is a constant for all values of $\mathbf{z}$ in the reactor (or correspondingly all temperatures in the gas-phase).

APPROACHES AND RESULTS

A problem in thermodynamic computation [25, 26, 28, 31] for diamond growth is that the available thermodynamic and kinetic data are not completely applicable to typical conditions of the CVD of diamond films [1, 25]. It is somewhat surprising that *ab initio* molecular orbital (MO) theory has not been used to overcome this problem given that it has been successfully employed to calculate kinetic and thermodynamic quantities for combustion [38, 39] and other [40–42] chemical processes. Properties of each of the species in our model have been previously calculated with *ab initio* MO methods. However, various levels of theory have been used, leading to inconsistent levels of error between calculations [38, 41]. For our purposes, a set of data is required that has a consistent error, and therefore a uniform level of theory. A thorough analysis of the work of Mebel *et al.*, [38, 39] conducted by the present authors showed that UHF/6-31G* calculation is an optimized level of MO *ab initio* theory that can account for both accuracy and efficiency.

In the light of the above high-level *ab initio* calculations were carried out using the Gaussian 94 programs [43] for the reactants, products, and transition-states involved in our model. Using UHF/6-31G* calculations [44], geometry was optimized, and vibrational frequencies, rotational parameters, and reaction barriers were determined. Using the calculated molecular and transition-state parameters, Gibbs free energies were calculated for each species using standard statistical mechanics. During this procedure, harmonic vibration, rigid rotor and ideal gas assumptions were used. This leads to eight simultaneous equations of Gibbs free energies with respect to gas-phase compositions in the form

$$\Delta G^0(T) = RT \ln K_{p,i} \quad i = 1, 2, \ldots, 8 \tag{9}$$

It should be noted that there are ten species and eight equations involved in Eq. (9). The two remaining unknown partial pressures were determined by considering the conservation of both the total pressure required by the experiment and the carbon atom number mentioned above. Using these constraints and Eq. (9), the temperature-dependent partial pressures of each species involved in our reaction model were numerically calculated. To compare to experiment, pressures of each species were systematically multiplied by 133.3. This value provides a reasonable fit to experimental data around the substrate temperature.

Plotted in Figures 1a and b is the log of the mole fraction of various gas-phase species calculated with our model *versus* gas temperature at feed gas methane concentrations of 0.3% and 30%, respectively. The gas species can be conveniently classified into four levels. The highest concentration level consists of $\mathbf{H_2}$ and **H**, with $\mathbf{H_2}$ dominating below about 2200 K. The second level consists of $\mathbf{CH_4}$, $\mathbf{C_2H_2}$ and $\mathbf{C_2H}$. The substrate temperature is limited to below 1100 K, suggesting that $\mathbf{C_2H}$ is likely not the main gas species governing the CVD diamond film growth. The species $\mathbf{CH_3}$ and $\mathbf{C_2H_4}$, which make up the third level, are predicted to have maximum concentrations at almost the same temperature, 1400 K. The remaining hydrocarbon species are at the lowest concentration level. Listed in Table I is the fraction of each primary gas species fraction at the temperature where $\mathbf{CH_3}$ has the maximum fraction. Given for comparison are experimental data from several research groups. The total pressure of this work was 20 tor.

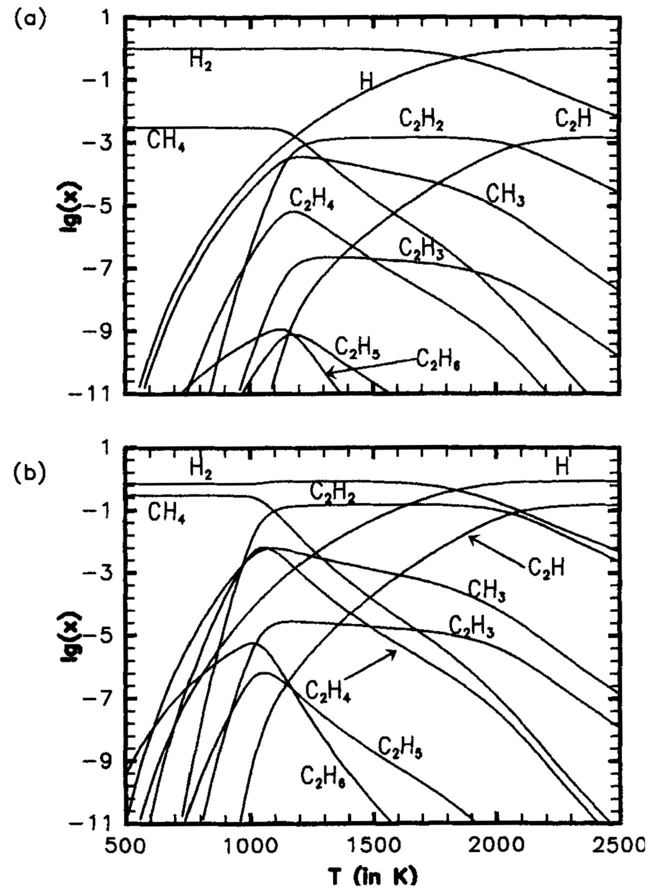

FIGURE 1 Temperature-dependent logarithm of mole fraction in gas-phase composition. CH_4 in feed gas is (a) 0.3%; (b) 30%.

TABLE I Gas-phase composition computed at the temperature of methyl mole fraction maximum and observed at the proximity of the substrate (Unit: 10^{-3})

	This work	*Harris* [34]	*Celii* [26]	*Hsu* [29]
H	1.5	10		2.3
CH_3	0.79	0.2	0.013	0.091
CH_4	3.8	1	5.0	0.39
C_2H_2	2.7	2	1.3	3.6
C_2H_4	0.05		0.0375	

To explore the thermodynamic cause of the observed changes in concentration of the gas-phase species with increasing addition of methane to the feed gas, we numerically investigated the effect of methane addition to the feed gas on the mole fraction of each species in Eqs. (1)–(8). Plotted in Figure 2 against the methane concentration in the feed gas is the log of the mole fraction of each species at the temperature for which the mole fraction of methyl is at its maximum. These compositions are assumed to be those near the growth surface of the diamond film. Also calculated was the effect of methane addition on the temperature corresponding to the methyl fraction maximum, *i.e.*, on the gas-phase temperature in the proximity of the substrate. The results of this calculation are plotted in Figure 3.

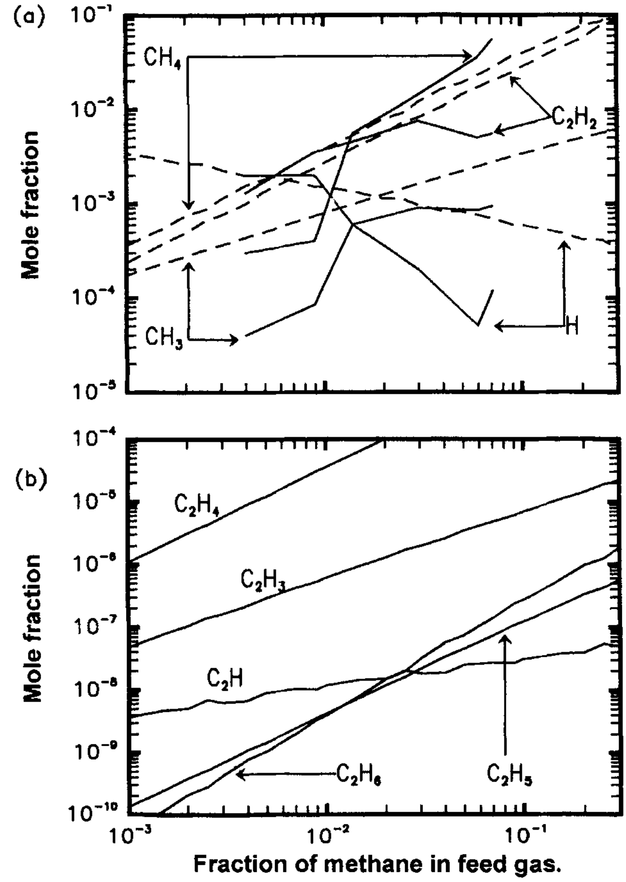

FIGURE 2 Feed-methane-dependent gas-phase composition in the proximity of surface. (a) Comparison with Ref. [29]. The solid curves are the observed, the dashed are the computational. (b) Theoretical prediction.

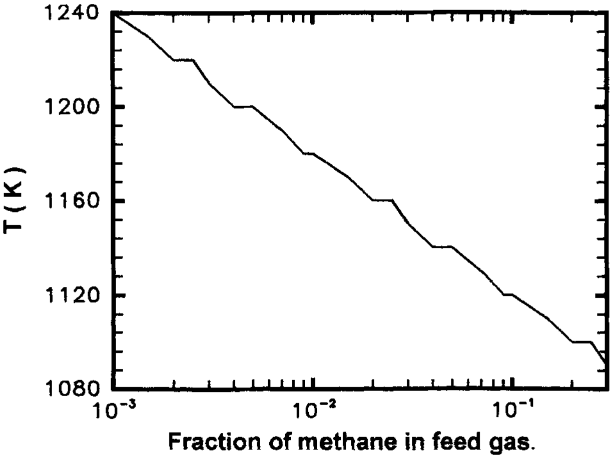

FIGURE 3 Theoretical prediction of gas-phase temperature in the proximity of surface as a function of feed methane fraction under condition favorable for diamond growth.

DISCUSSION

The validity of our model can be found from Figure 1. First, the figures show that the main gas species are H_2, H, CH_4, C_2H_2 and CH_3, in agreement with experimental observation [26, 29, 34]. Second, the CH_3 maximum mole fraction is consistent with other calculations using the TE approximation [25] as well as calculations considering transport and detailed chemical kinetics [23, 27, 30, 32]. This is not a surprising result because 100 sccm at 20 torr is sufficiently slow that TE should be a good approximation within every isothermal section parallel to the substrate.

From Figure 1, it is also clear that the present model reveals some important dynamic features of gas-phase chemistry within the temperature range suitable for diamond film growth. In the reactions (1)–(8), all carbon containing species except CH_4 and C_2H have both creation and elimination channels. Therefore, if these reactions indeed play roles in hot filament CVD system, the species concentration should have peaks within the temperature range for diamond growth. This is indeed the case in Figure 1.

From our model, the following insights for the role of the gas-phase environment in a hot filament CVD system can be drawn. Close to the substrate, the gas composition is almost the same as that of the isothermal section at the temperature where CH_3 has the maximum fraction. This is supported in two ways by our computation. First, our computational fraction for each species is within the range of the corresponding values observed by experiments (see Tab. I). Only $\mathbf{CH_3}$ is somewhat higher and **H** is slightly lower. This suggests that the experimental system may deviate slightly from TE. Second, we note from Figure 1 that with increasing temperature, the fraction of $\mathbf{CH_4}$ monotonically decreases, whereas the fractions of **H** and $\mathbf{C_2H_2}$ monotonically increase. Also, mole fractions of $\mathbf{CH_4}$ and $\mathbf{C_2H_2}$ always cross at a temperature that is almost the same as the temperature at which $\mathbf{CH_3}$ has the maximum fraction. This result implies that if TE is a good approximation, the following should be the case. If the observed $\mathbf{CH_3}$ fraction is smaller than the fraction predicted by our model, and the fraction of hydrogen is higher than predicted, the temperature of the gas-phase isothermal section near the surface should be higher than the temperature at which the $\mathbf{CH_3}$ fraction is at a maximum. Therefore the observed $\mathbf{CH_4}$ fraction should be lower than the observed $\mathbf{C_2H_2}$ fraction.

The above discussion indicates that this thermodynamic study can at least qualitatively interpret the observations for gas-phase compositions for CVD diamond deposition in terms of elementary reactions. The model was therefore used to understand the underlying thermodynamics embedded in the experimental fact that the concentration of the gaseous species changes greatly with increasing addition of methane to the feed gas. Figure 2 indicates that the **H** fraction monotonically decreases with addition of methane to the feed gas, while methane, acetylene and methyl monotonically increase. This is qualitatively in accordance with experimental observation [24, 29]. From Figure 3, the conclusion can be drawn that the temperature at which methyl fraction is at a maximum decreases with increasing methane fraction in the feed gas. This implies that if methyl is the main growth species, the substrate temperature should decrease with increasing feed methane to maintain favorable conditions for diamond growth.

CONCLUSION

A gaseous chemistry model consisting of 10-species and 8-reaction was developed. Chemical data, including structures, enthalpies and rates for these reactions, were obtained exclusively from *ab initio* methods. Thermodynamics properties were obtained from these data using statistical mechanics. While the absolute magnitude for the concentrations of gas-phased species was in fair agreement with experiment, the calculations qualitatively account for experimentally observed changes in the concentration of the gas-phase species with increasing addition of methane to the feed gas. The temperature changes in the gas-phase close to substrate needed to maintain favorable conditions for diamond deposition with increasing addition of methane to the feed gas were predicted.

Acknowledgements

Y. L. and D. W. B. are supported by the National Science Foundation. This work was supported by the National Key Laboratory of Theoretical and Computational Chemistry at Jilin University; the Chinese Major Key Project for Basic Researches, Large-scale Science and Engineering Computation; and the Chinese National Natural Science Foundation.

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