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Modelling of the gas phase chemistry during diamond CVD: the role of different hydrocarbon species

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Abstract

The CHEMKIN suite of computer programs has been used to model the concentration profiles of different hydrocarbon species present within a hot filament CVD reactor during diamond growth, and the calculated values are compared with those obtained by direct measurements using an in situ molecular beam mass spectrometer. Different hydrocarbon gases (CH_4, C_2H_2, C_2H_4 and C_2H_6) were used as the carbon source in the input gas mixture, ensuring that the ratio of C:H_2 remained constant at 1%. Calculations for when C_2H_6 is used as the precursor gas, after reaction and thermal equilibrium is realised, yield similar CH_4:C_2H_2 mole fraction ratios in the reactor under growth conditions to those obtained using CH_4, and to those measured experimentally. However, simulations using C_2H_4 or C_2H_2 as input gases do not reproduce the experimentally observed ratio of CH_4:C_2H_2 mole fractions. This suggests that the conversion of unsaturated C_2 species to C_1 species is not a straightforward gas phase process, and there must be one or more reactions occurring within the chamber that are not present in the standard models for hydrocarbon reactions. We suggest that these neglected reaction(s) probably involve surface-catalysed hydrogenation, which in this case, is most likely occurring on the surface of the filament.

Keywords: Catalytic processes; Computer simulation; Gas phase; Mass spectrometry

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1. Introduction

Chemical vapour deposition (CVD) of diamond thin films from hydrocarbon source gases is now a well-established technique [1], but there is still much uncertainty about some of the fundamental chemistry and physics that occur during growth. These problems arise from the sheer complexity of the chemical environment experienced by the growing diamond surface. In order to understand the growth mechanisms, it is first necessary to obtain accurate information about the nature and mole fractions of all the species present, both in the gas phase and on the substrate surface. To facilitate this, various in situ diagnostic techniques have been developed, such as optical emission spectroscopy [2], along with laser techniques such as cavity ring down spectroscopy [3], two-photon laser-induced fluorescence [4] and resonance-enhanced multiphoton ionisation [5]. Arguably the most universal of the current diagnostics techniques is molecular beam mass spectroscopy (MBMS), since this has the advantage of being able to measure simultaneously quantitative mole fractions of most of the major gas phase species, including stable and unstable species, atoms and molecules. MBMS measurements of diamond reactors were pioneered by Hsu and others [6–8], and then extended by our own group [9–13] to cover many important aspects of hot filament CVD growth using hydrocarbon–hydrogen mixtures, both with and without the presence of chlorine, nitrogen or phosphorus containing gases. These measurements have given a considerable insight into the roles played by many of the gas phase chemical reactions, and into the relative importance of the various species in the diamond growth process.

Complementary to these experimental studies are various theoretical models of the growth environment [14]. One of the most comprehensive models to be applied to diamond CVD is the CHEMKIN suite of computer programs from Sandia Labs [15]. These programs form a highly structured package which allows the calculation of the mole fractions of both stable and unstable species that are reacting together in the gas phase within a reaction chamber. The calculations evolve from an initial

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set of starting values using the various literature values for the temperature-dependent rate constants and activation energies for each of the reactions involved. For a process gas mixture starting with just 1% methane in H_2, there can be in excess of 20 separate species involved in over 30 different reactions, each of which needs to be calculated simultaneously. Other considerations included within the package are descriptions of the transport properties within the reactor, such as convection and diffusion, as well as simple heterogeneous gas–solid reactions occurring on the substrate. The latter can include important steps such as activation of the substrate by H atoms, recombination of H on the surface, chemisorption of CH_3 radicals onto activated sites and incorporation of these molecules into the diamond structure [14,16].

Various groups have used CHEMKIN to study the diamond growth environment [16–21]. Goodwin and Gavillet [17] showed that using typical CVD diamond growth conditions (1% CH_4 in H_2 at a process pressure of a few tens of Torr) homogeneous recombination of H may be neglected, suggesting that the H atoms are freely able to diffuse to the substrate. In similar calculations, Harris et al. [21] found that CH_3 and/or CH_4 have mole fractions at the substrate surface which are sufficient for them to be effective growth precursors. In a very comprehensive set of calculations, Dandy and Coltrin [18] performed the full simulation for a hot filament reactor, allowing the mole fractions of most of the major species to be calculated as a function of some of the important process parameters, such as methane percentage and filament–surface distance. In very recent work [13,22], the mole fractions of gas phase species within a hot filament reactor have been simulated using the full CHEMKIN package as a function of filament temperature, and these values gave excellent agreement with those measured using in situ MBMS. This work allowed the mole fractions of all of the chemically significant gas phase species to be derived, including the stable hydrocarbons, methyl radicals and hydrogen atoms.

However, one aspect of the gas phase chemistry which is still very poorly understood is the mechanism by which C_2 species, such as acetylene, can be reconverted to the C_1 species believed to be responsible for diamond growth. The forward reactions, $C_1 \rightarrow C_2$, have been studied in great detail [14], and there are well-developed reaction pathways that explain acetylene formation from methane precursors. The whole gas phase chemistry is based around hydrogen abstraction reactions from hydrocarbons, which drive the process forward to produce the most stable product, acetylene. The problem is that once C_2H_2 is formed, there are no known gas phase processes which can perform the reverse process, and readily create C_1 species from acetylene. This poses a problem since experiments in hot filament and in microwave CVD reactors [7,9] have shown that the mole fractions of the various hydrocarbon species are independent of the form in which gaseous carbon is introduced to the chamber. This means that, experimentally, there must be a route for acetylene-to-methane conversion that is not included within simple gas phase kinetic descriptions of the process. However, this problem has never been addressed using the sophisticated modelling available within the modern CHEMKIN package, which include improvements such as thermal diffusion and convection, as well as some simple models for gas–surface interactions. The aim of the present work, therefore, is to use CHEMKIN to investigate the $C_2 \rightarrow C_1$ process, and to see if a more thorough model such as this can provide a better insight into the conversion mechanism.

2. Experimental

In previous work [9] we have used a MBMS system to obtain direct values for the mole fractions of the hydrocarbon species during diamond growth. The geometry of the sampling method and the MBMS system has been described in detail elsewhere [11,13]. The MBMS experiments were performed in a standard hot filament reactor operating at 20 Torr with 1% CH_4 in H_2 at a total flow rate of 200 sccm. The filament was Ta wire 0.25 mm in diameter suspended approximately 4 mm above a Si (100) substrate. In order to determine the effect upon the gas phase chemistry of the presence of the substrate, some experiments were performed without the substrate and holder being present, such that there was just a filament and the MBMS sampling cone within the chamber. When a substrate was present, diamond growth occurred at a filament temperature of 2600 K, which was calibrated using a two-colour optical pyrometer. The substrate temperature was measured using a thermocouple as $\approx 900^\circ C$. The Si substrate was pre-abraded using 1–3 μm diamond grit, before being placed upon a heater unit. These conditions produced diamond films at a rate of $\approx 0.5\ \mu m\ h^{-1}$.

Calculations of the mole fractions of the gas phase species were performed using the CHEMKIN suite of computer programs [15], in particular the SPIN and SENKIN codes. The parameterisation of the necessary temperature-dependent gas phase reaction rate constants used in the present study were obtained from Refs. [23–25]. In order to run the main application code, SPIN, the user must enter values for the reaction conditions, such as process pressure, filament temperature, substrate temperature and filament–substrate distance, all of which can be obtained from the experimental values. Also required are trial values for the initial gas mole fractions at the inlet (the filament) and at the entrance to the MBMS sampling cone (equivalent to the substrate surface). Reasonable estimates for these can be obtained using the SENKIN code, which calculates equilibrium mole fractions for a fixed reaction mixture. A list of the initial values used can be found in Ref. [13].

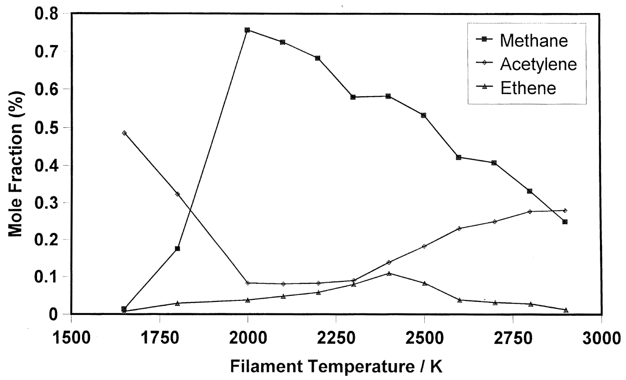

Fig. 1. An example of the experimental mole fraction measurements of selected species made by MBMS in a hot filament reactor [9]. These values have been corrected for thermal diffusion effects and data sampling calibration [11]. The plot is for 0.5% C_2H_2 in H_2 at a total pressure of 20 Torr as the source gas, and similar plots using CH_4, C_2H_4 and C_2H_6 as source gases can be found in Ref. [9]. The ratios of the mole fractions of CH_4:C_2H_2 and CH_4:C_2H_4 at the growth temperature of 2600 K have been tabulated in Table 1.

3. Results and discussion

Fig. 1 shows the species mole fractions in this reactor as a function of filament temperature, as measured by the MBMS, using C_2H_2 as the initial source gas. At low temperatures the C_2H_2 signal decreases, whilst the signals for C_2H_4 and CH_4 increase, showing that in this system, acetylene is, indeed, being converted to methane. With further increases in temperature, the resulting higher H atom concentration initiates hydrogen abstraction reactions which begin to reconvert the methane into acetylene. At the growth temperature of 2600 K we can see that there is roughly twice as much methane as acetylene, and about 20 times as much methane as ethene. From plots given in Ref. [9], the ratios for these three species obtained from MBMS data using different hydrocarbon gases as input sources are shown in Table 1. We can see that irrespective of the choice of hydrocarbon, at the growth temperature the ratios of CH_4:C_2H_2 and CH_4:C_2H_4 are very consistent, and always ≈2 and ≈20, respectively. We also find that for each of these source gases the growth rate, quality and morphology of the resulting diamond films are indistinguishable, suggesting that the growth chemistry is identical in each case.

Table 1
The ratio of CH_4:C_2H_2 and CH_4:C_2H_4 measured using an MBMS system [9] and simulated using CHEMKIN, for a variety of different source gases in H_2. The ratio of C:H_2 in the source gas mixture was maintained at 1%

Source gas	MBMS		CHEMKIN	
	CH_4:C_2H_2	CH_4:C_2H_4	CH_4:C_2H_2	CH_4:C_2H_4
1% CH_4/H_2	2.1	21	1.4	27
0.5% C_2H_2/H_2	1.8	22	9.6×10^{-5}	0.22
0.5% C_2H_4/H_2	2.8	16	0.02	0.25
0.5% C_2H_6/H_2	3.6	22	0.5	12

By way of comparison, the SPIN code was used to calculate the gas phase mole fractions of three species (CH_4, C_2H_4 and C_2H_2) when using the four different hydrocarbon/H_2 input gas mixtures listed in Table 1. In each case the ratio of C:H_2 was maintained at 1%. Fig. 2 shows the results of these simulations as a function of distance from the filament. In our case, we need to compare these results with the data obtained from the MBMS system situated 4 mm from the filament. Table 1 presents the ratios of CH_4:C_2H_2 and CH_4:C_2H_2 obtained

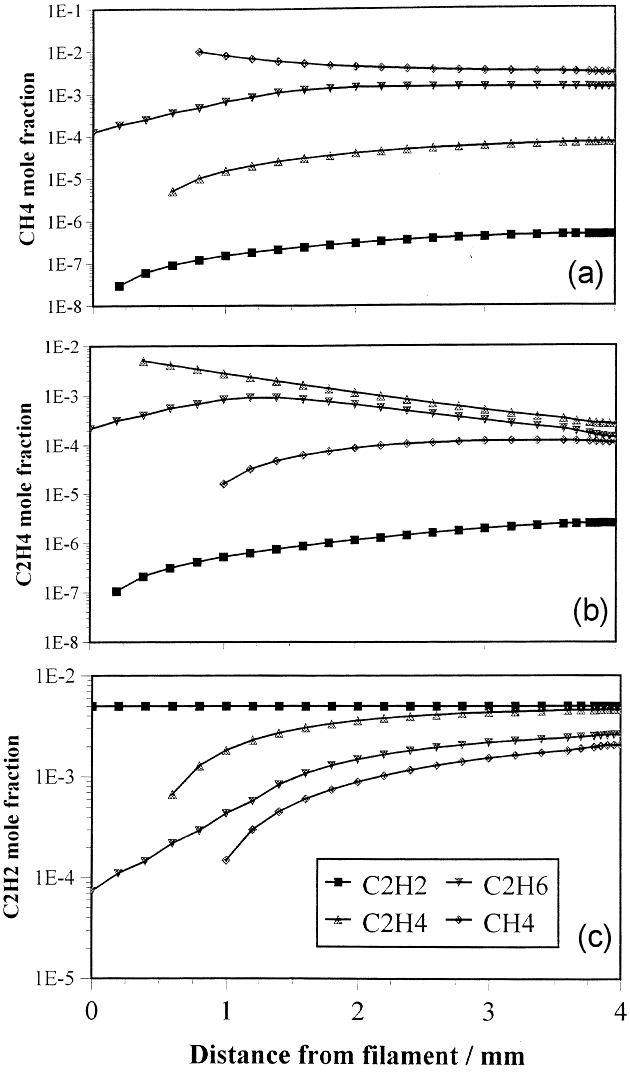

Fig. 2. CHEMKIN simulations of the mole fractions of (a) CH_4, (b) C_2H_4 and (c) C_2H_2 within a hot filament reactor as a function of distance from the filament. The four plots relate to the four different input hydrocarbon source gases in H_2 (with C:H_2 ratio maintained at 1% and a nominal filament temperature of 2600 K). The calculated CH_4:C_2H_2 and CH_4:C_2H_2 mole fraction ratios at 4 mm from the filament (corresponding to the position of the Si substrate and also the gas sampling orifice of the MBMS) are given in Table 1.

from these plots at 4 mm. This allows direct comparison between the experimentally determined ratios and those predicted by CHEMKIN. Clearly, for CH_4 as input gas, the calculated CH_4:C_2H_2 and CH_4:C_2H_4 ratios match experimental values to within 30%. For C_2H_6 also the agreement is generally satisfactory — the simulated ratios are within factors of 7 and 2 of the two experimental values, respectively. This suggests that for methane, as well as for saturated hydrocarbons that easily dissociate/react to form methane (e.g. C_2H_6) the CHEMKIN simulation can provide an accurate description of the important gas phase processes.

However, such is clearly not the case for C_2H_4 and C_2H_2 as input gases. In both these cases the simulated ratios are very different from the experimental values. In the case of C_2H_2 this discrepancy is 4 orders of magnitude! This shows that for doubly- and triply-bonded hydrocarbons such as C_2H_4 and C_2H_2, even the highly sophisticated descriptions of the gas phase processes within CHEMKIN are not sufficient to reproduce the observed mole fractions.

What vital reaction mechanism for the conversion of unsaturated C_2 species (especially C_2H_2) to C_1 might the model be missing? Since data for the reactions of hydrocarbons in flames have been studied extensively over a number of decades, it is unlikely that the missing step will be a gas phase reaction. The most likely possibility, therefore, is a heterogeneous process [14], such as catalytic dissociation on the reactor walls, the filament surface, or on the diamond surface itself. Evidence from our MBMS measurements, which are often performed in the absence of a substrate (i.e. in a reactor containing just a filament and the sampling probe), suggests that the presence of a diamond surface is *not* essential for C_2 dissociation. Also, in many reactors the geometry is such that the chamber walls are a long way from the filament and reactive gases, and are often water cooled. It therefore seems unlikely that these will provide appropriate sites for the relevant $C_2 \rightarrow C_1$ conversion. The remaining option is, therefore, a reaction on the surface of the filament itself. This could involve chemisorption of the relevant C_2 species and subsequent hydrogenation, either before or after pyrolysis and conversion to carbon on the filament surface [26]. Circumstantial evidence for this mechanism may come from the "filament poisoning" effects which have been observed when using high concentrations of methane [27]. Filament poisoning is the effect whereby the efficiency of H atom production rapidly decreases with increasing hydrocarbon concentration, and has been explained by the filament becoming covered in a thin layer of carbon, thereby reducing its ability to dissociate H_2.

The issue of $C_2 \rightarrow C_1$ conversion remains a problem for any complete understanding of the chemistry of CVD diamond growth. Here, we have concentrated upon hot filament systems. Future work will focus on microwave systems, with the aim of determining the similarities and differences in the chemical mechanisms [28].

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References

[1] M.N.R. Ashfold, P.W. May, C.A. Rego, N.M. Everitt, Chem. Soc. Rev. 23 (1994) 21.
[2] L.R. Martin, M.W. Hill, Appl. Phys. Lett. 55 (1989) 2248.
[3] E.H. Wahl, T.G. Owano, C.H. Kruger, P. Zalicki, Y. Ma, R.N. Zare, Diamond Relat. Mater. 5 (1996) 373.
[4] L. Schäfer, C.-P. Klages, U. Meier, K. Kohse-Hoinghaus, Appl. Phys. Lett. 58 (1991) 571.
[5] F.G. Celii, J.E. Butler, Appl. Phys. Lett. 54 (1989) 1031.
[6] W.L. Hsu, J. Appl. Phys. 72 (1992) 3102.
[7] M.C. McMaster, W.L. Hsu, M.E. Coltrin, D.S. Dandy, C. Fox, Diamond Relat. Mater. 4 (1995) 1000.
[8] W.L. Hsu, M.C. McMaster, M.E. Coltrin, D.S. Dandy, Jpn. J. Appl. Phys. 33 (1994) 2231.
[9] C.A. Rego, P.W. May, C.R. Henderson, M.N.R. Ashfold, K.N. Rosser, N.M. Everitt, Diamond Relat. Mater. 4 (1995) 770.
[10] R.S. Tsang, C.A. Rego, P.W. May, J. Thumim, M.N.R. Ashfold, K.N. Rosser, C.M. Younes, M.J. Holt, Diamond Rel. Mater. 5 (1996) 359.
[11] C.A. Rego, R.S. Tsang, P.W. May, M.N.R. Ashfold, K.N. Rosser, J. Appl. Phys. 79 (1996) 7264.
[12] R.S. Tsang, C.A. Rego, P.W. May, M.N.R. Ashfold, K.N. Rosser, Diamond Relat. Mater. 6 (1997) 247.
[13] R.S. Tsang, Ph.D. Thesis, School of Chemistry, University of Bristol, UK, 1997.
[14] D.G. Goodwin, J.E. Butler, in: M.A. Prelas, G. Popovici, L.K. Bigelow (Eds.), Handbook of Industrial Diamonds and Diamond Films, Dekker, New York, 1998, pp. 527–581.
[15] R.J. Kee, F.M. Rupley, J.A. Miller, Sandia National Laboratories Rep. SAND89-8009B, 1989.
[16] M.E. Coltrin, D.S. Dandy, J. Appl. Phys. 74 (1993) 5803.
[17] D.G. Goodwin, G.G. Gavillet, J. Appl. Phys. 68 (1990) 6393.
[18] D.S. Dandy, M.E. Coltrin, J. Appl. Phys. 76 (1994) 3102.
[19] D.G. Goodwin, Appl. Phys. Lett. 59 (1991) 277.
[20] T. Lang, J. Laimer, H. Störi, Diamond Relat. Mater. 3 (1994) 470.
[21] S.J. Harris, A.M. Weiner, T.A. Perry, Appl. Phys. Lett. 53 (1988) 1605.
[22] R.S. Tsang, P.W. May, J. Cole, M.N.R. Ashfold, to appear in Diamond Relat. Mater. as part of ICNDST-6, South Africa, 1998.
[23] S.J. Harris, J. Appl. Phys. 65 (1989) 3045.
[24] E. Meeks, R.J. Kee, D.S. Dandy, M.E. Coltrin, Combustion Flame 92 (1993) 144.
[25] K.Y. Lee, M.H. Yang, I.K. Puri, Combustion Flame 92 (1993) 419.
[26] R.R. Rye, Surf. Sci. 69 (1977) 653.
[27] W.L. Hsu, Appl. Phys. Lett. 59 (1991) 1427.
[28] S.M. Leeds, P.W. May, E. Bartlett, M.N.R. Ashfold, K.N. Rosser, to appear in Diamond and Relat. Mater. as part of ICNDST-6, South Africa, 1998.