Simulations of the hot-filament diamond CVD gas-phase environment: direct comparison with experimental measurements

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Abstract

The CHEMKIN suite of computer programs (Sandia Labs) has been used to simulate the mole fractions of the important gas phase species within a hot filament CVD diamond reactor. These simulations have been compared to data measured using an in-situ molecular beam mass spectrometer. Excellent agreement between simulation and experiment was obtained by using just two fitting parameters. The first of these, the local gas temperature, was found to be a relatively insensitive parameter, and values could be varied by several hundred degrees centigrade with no appreciable effect on the results of the calculation. However, the second parameter, the mole fraction of hydrogen atoms, was found to be very important since it controlled the whole gas-phase chemistry. Comparison of experimental data with simulations, therefore, has allowed us to derive absolute mole fractions of not only the stable hydrocarbon species, but also the methyl radicals and the hydrogen atoms, simultaneously, during a typical CVD process. These results are presented as a function of filament temperature. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Although chemical vapour deposition (CVD) of diamond thin films from hydrocarbon source gases is now a well established technique [1], there is still much uncertainty about some of the fundamental mechanisms that occur during growth. These problems arise due to 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 this end, various in-situ diagnostic techniques have been developed, such as optical emission spectroscopy [2] and specialist laser techniques such as cavity ring spectroscopy [3] two photon-laser-induced fluorescence [4] and resonance enhance multiphoton ionization [5]. Arguably the most universal of the diagnostics techniques in use today is molecular beam mass spectroscopy (MBMS), since this has the advantage of being able to measure quantitative mole fractions of most of the major gas-phase species,

both stable molecules and unstable radicals and atoms, simultaneously. MBMS measurements on diamond reactors were pioneered by Hsu and others [6–8], and then extended by our own group [9–12] to cover many important aspects of hot-filament CVD growth using hydrocarbons, both with and without the presence of chlorine, nitrogen or phosphorus-containing gases. These measurements have given considerable insights 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 [13]. One of the most comprehensive models to be applied to diamond CVD is the CHEMKIN suite of computer programs from Sandia Labs [14]. These programs form a highly structured package that 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 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

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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 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 on to activated sites and incorporation of these molecules into the diamond structure [13,15].

Various groups have used CHEMKIN to study the diamond growth environment [15–20]. For example, Goodwin and Gavillet [16] showed that under typical CVD diamond growth conditions (1% CH_4 in H_2), 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. [20] found that CH_3 and/or CH_4 have mole fractions at the substrate surface that are sufficient for them to be effective growth precursors. In a very comprehensive set of calculations performed by Dandy and Coltrin [17], the full simulation for a hot-filament reactor was performed, 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. However, in all the above simulations, the gas-phase temperature was not varied, and therefore its effect upon the chemistry was not determined. Also, it has been very difficult to compare the results of these simulations with direct experimental measurements, since accurate mole fractions of the gas-phase species, particularly the reactive radicals, have been hard to obtain.

In the present work, therefore, we aim to present a numerical simulation of the gas-phase composition using the standard 1% CH_4 in H_2 mixture as a function of filament temperature, and directly compare these calculations with measurements that we have made in a hot-filament reactor using MBMS. By adjusting selected fitting parameters within the CHEMKIN program so as to make the simulated species mole fractions match those measured, it is possible to derive mole fractions of various other species, in particular atomic H, which cannot easily be measured by direct experiment. In this way, we can estimate absolute mole fractions of all important species involved in a typical diamond CVD process simultaneously.

2. Experimental

The MBMS experiments were performed in a standard hot filament reactor operating at 20 Torr with 1% CH_4 in H_2. The filament was a 0.25-mm-diameter Ta wire suspended approximately 4 mm above a Si (100) substrate. The filament was heated to $\sim 2300°C$ and calibrated using a two-colour optical pyrometer. The substrate was pre-abraded using 1–3-μm diamond grit, before being placed upon a heater unit. The substrate temperature was measured using a thermocouple to be $\sim 900°C$.

The geometry of the sampling method and the MBMS system has been described in detail elsewhere [10,12]. In brief, gases are extracted from the reactor using a 100-μm-diameter orifice in a sampling cone that is positioned a few millimetres away from the filament. The orifice-to-filament distance can be varied smoothly using a z-translator and bellows arrangement. Gases pass through the orifice into a differentially pumped region at a pressure of ~ 1 mTorr, forming a molecular beam. This beam is then collimated by a second orifice (1 mm in diameter) which is at the entrance to the mass spectrometer maintained at 10^{-8} Torr. Thus, once the gas-phase species have passed through the initial orifice, collisions are minimized, allowing even highly reactive species such as CH_3 to survive the flight time to the detector. Note that the gas sampling is performed not through the substrate (as in Ref. [6]), but at the same radial distance from the filament as the substrate. Although any intrusive sampling method will undoubtedly affect the gas chemistry to some degree, every effort has been made to ensure that any perturbations are minimal or negligible. The cone-shape of the extraction orifice is critical since it reduces the possibility of gas–surface interactions affecting the gas passing through the orifice. Furthermore, the cone does not have any additional heating above that which it receives from radiation from the filament and the ambient gas temperature. Being metal, it will be quite a large heat sink and so remain relatively cold compared to the surrounding gas. This will significantly reduce the rate of any H-atom recombination reactions on the surface, allowing us to sample the gas with, we believe, very little disturbance.

The MBMS data allow accurate mole fraction determination for most of the important hydrocarbon species, including CH_4, C_2H_2, CH_3, as well as H_2, but lack sufficient sensitivity to measure the mole fractions of H atoms. Thus, the mole fraction of H is an important unknown in the system, and is treated as one of the fitting parameters in the modelling.

Calculations of the mole fractions of the gas phase species were performed using the CHEMKIN suite of computer programs [14], in particular the SPIN and SENKIN codes. It might be argued that a 1-D uniform flow model such as PREMIX could have been used instead of SPIN in order to take account of the stagnation region above a surface. However, since we are modelling the chemistry that is being sampled through the tip of a cone, there is no 'substrate surface', as such, to produce a significant stagnation region. There may be a slight effect at the rim of the orifice or in the walls of the

orifice itself, but this will probably be minimal due to the low pressure (~ 1 mTorr) and the presence of the molecular beam. Evidence for this is the fact that by using this system, we can detect highly reactive CH_3 radicals directly—if there was a significant stagnation region around our sampling orifice, all the CH_3 would have been reacted away before being detected.

The parameterization of the necessary temperature-dependent gas-phase reaction rate constants used in CHEMKIN in the present study were obtained from Refs. [21–23]. 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. [12].

3. Results

In previous work [9,12], we have shown how the mole fractions of selected species within the reactor vary with filament temperature, as measured by the MBMS system. Given sensible initial values, we find that the mole fractions predicted by SPIN for the various hydrocarbon species (CH_4, C_2H_2, CH_3, etc.) agree well with these experimental values. The values that are the least well known are the filament and substrate temperatures, and the initial atomic H mole fraction. We shall discuss these in turn.

3.1. Filament/substrate temperature

It is known from thermocouple measurements [20,24] that within only a few mean free paths from the filament surface, the gas temperature drops sharply, and this initial sharp drop can be as large as $500°C$. From then on, the temperature decrease is much less rapid and roughly proportional to distance from the filament until a similar sharp drop occurs at the substrate surface. The size and extent of the initial sharp drop depend upon many factors, including the filament material, filament 'poisoning' [25] (variation in H_2 dissociation efficiency due to the filament being coated in a layer of carbon) and the gas pressure, and is difficult to measure accurately without performing a specialized experiment, such as REMPI [5,26]. Therefore, it is worth exploring how sensitive our relative mole fraction calculations are to the gas temperature.

Fig. 1a shows the CH_4 mole fractions measured as a
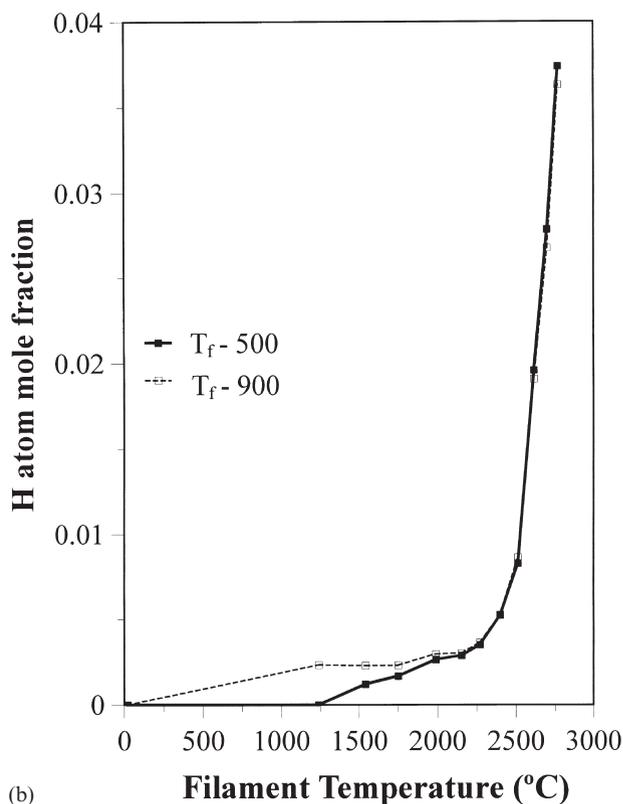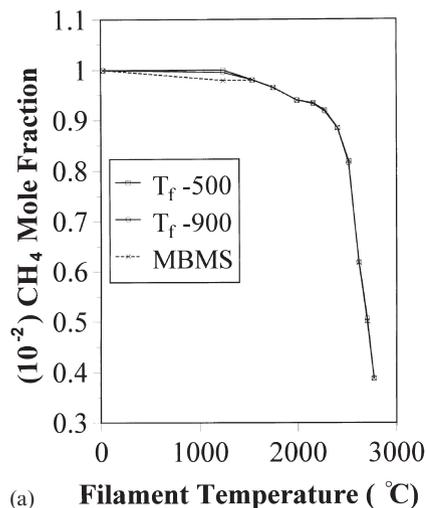
Fig. 1. (a) CH_4 mole fractions measured as a function of filament temperature (T_f) using the MBMS, together with the results of two model calculations using the SPIN code. Two separate sets of input gas temperatures were used: $T_g = (T_f - 500°C)$ and $(T_f - 900°C)$. The calculations require only one remaining fitting parameter, the atomic hydrogen mole fraction, and if a sensible choice is made for this, the curves from experimental data and the simulations overlay one another almost exactly. (b) Plot showing the way in which the best-fit H atom mole fraction required to match the experimental data in (a) varies with T_f, for the two different assumed temperature drops. It can be seen that above about $1700°C$, the required value of H atom mole fraction is identical for both temperatures, showing that the model is not sensitive to gas temperature.

function of filament temperature, using the MBMS, together with the results of two model calculations using the SPIN code. The calculations assume two different gas temperatures, namely $T_g = T_f - 500°C$ and $T_f - 900°C$, where T_f is the explicitly measured filament temperature and require, as the only remaining variable, a value for the H atom mole fraction at each T_f. Fig. 1b shows a plot of the way in which the best-fit H atom mole fraction required to reproduce the experimentally measured CH_4 mole fractions (Fig. 1a) varies with T_f, for the two different assumed $T_f - T_g$ temperature drops. Clearly, both calculations fit the experimentally measured data well, despite the (deliberately) large difference in temperatures used as input values. This shows that the mole fractions predicted by SPIN are rather insensitive to the poorly known value of the gas temperature.

3.2. Atomic H mole fraction

This is an important quantity, since it is the abundance of highly reactive atomic H that drives most of the chemical reactions within the reactor, and is therefore ultimately responsible for diamond growth. Since H is the one important species that we cannot measure directly with the MBMS, we must determine its value by treating it as the fitting parameter in our CHEMKIN simulations. However, depending upon which species we decide to fit, the best-fit value of the H mole fraction may show some variation. We can test the reliability and the self-consistency of this approach by fitting to experimentally measured mole fractions of two different species in turn, e.g. CH_4 and C_2H_2, and comparing the values required for the H atom mole fraction measured for each.

Fig. 2 shows the H atom mole fraction required by SPIN to simulate the variation of the mole fraction of CH_4 and C_2H_2 as a function of filament temperature, assuming $T_f - T_g = 500°C$. When fitting the CH_4 data, the values predicted for C_2H_2 (and the other hydrocarbon species) were only consistent to within a factor of ~ 2 at relevant process temperatures ($> 2200°C$), and showed even larger discrepancies at lower temperature. Similar results were found when fitting the observed mole fraction of C_2H_2. It can be seen that an average value of these two curves predicts that H atom mole fractions vary from around 0.5% at typical growth temperatures, but above about 2500°C increase rapidly to $> 4\%$.

We note that the value for the H atom mole fraction we require to fit our experimental data (0.01–0.02) is reassuringly very close to the values measured by recent non-intrusive techniques [25,27], which (after re-scaling to our process conditions) both obtain measured values for the H atom mole fraction 4 mm from the filament of around $\sim 2 \times 10^{15}$ cm^{-3} (equivalent to 0.01–0.02). This is compelling evidence that our sampling system is,
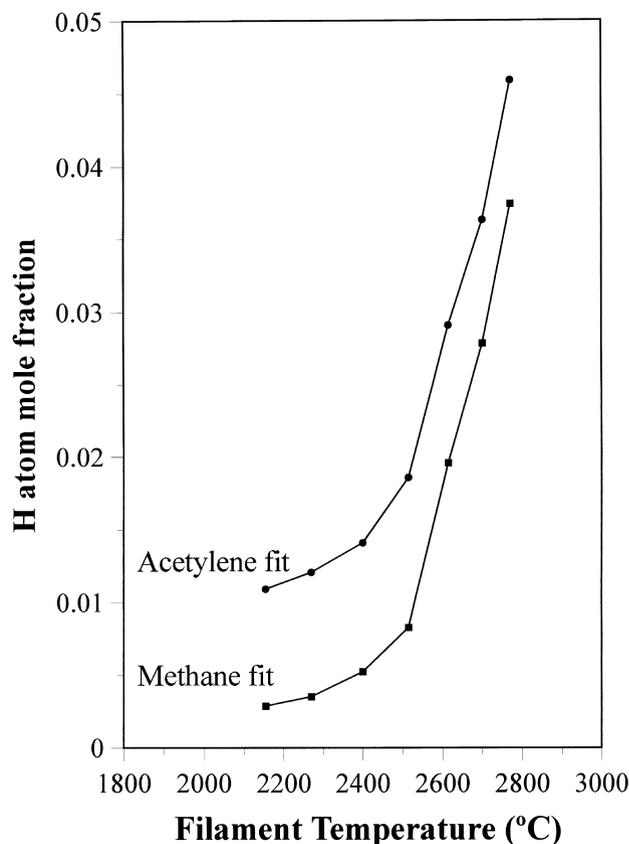
Fig. 2. H atom mole fraction required by SPIN to simulate the variation of CH_4 (squares) and C_2H_2 (circles) mole fractions at a position ~ 4 mm away from the filament, as a function of filament temperature. At higher temperatures, both curves are very close, but at lower temperatures, the reliability of the C_2H_2 fit decreases due to the inaccuracy of the smaller measured signal levels.

therefore, not significantly disturbing the H atom concentration close to the orifice and that we can place a reasonable level of confidence upon our measured mole fractions.

By combining these results, we can derive mole fractions for all the important hydrocarbon species within the hot-filament reactor as a function of filament temperature. Fig. 3a shows measured data for the hydrocarbons present in mole fractions less than 0.2%, and Fig. 3b shows experimental mole fraction data for CH_4, C_2H_2 (again), along with the simulated values for atomic H.

4. Conclusions

We have shown that by comparing simulations made using the CHEMKIN suite of computer programs with data measured using an in-situ molecular beam mass spectrometer, excellent agreement can be obtained by using only two fitting parameters. The local gas temperature was found to be a relatively insensitive parameter,

(a)

(b) **Filament Temperature (°C)**
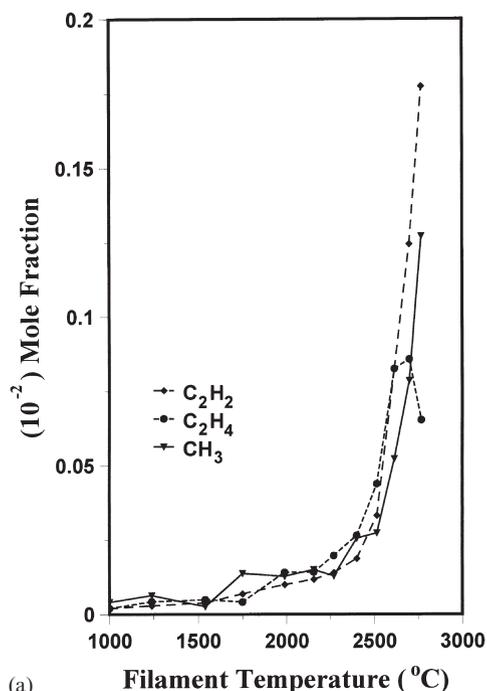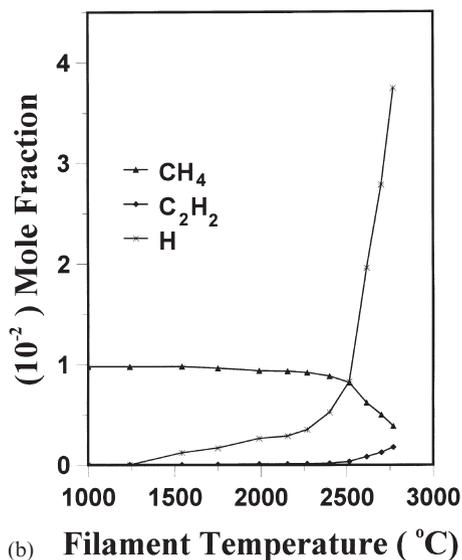
Fig. 3. Distributions of the important gas phase species within a hot filament reactor using 1% CH_4 in H_2, as a function of filament temperature. All values have been corrected for the effects of thermal diffusion by requiring that the total carbon balance remain constant at all temperatures. (a) Distributions for CH_3, C_2H_4 and C_2H_2 measured using MBMS. (b) Distributions for CH_4 and C_2H_2 measured using MBMS, together with atomic H simulated using CHEMKIN. For the purpose of these simulations, the H mole fraction obtained from fitting CH_4 at an assumed gas temperature of $T_f - 500°C$ was used.

whereas the mole fraction of hydrogen atoms was found to be much more important. We have been able to derive absolute mole fractions of not only the stable hydrocarbon species, but also the methyl radicals and, by modelling, the hydrogen atoms simultaneously during a typical CVD process, as a function of filament temper-

ature. Such studies have recently been extended [12] to include simulations of the effects of the addition of dopant gases, such as N_2 or NH_3, and will soon be applied to MBMS measurements taken from a microwave plasma [28].

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