

In-situ mass spectrometric study of the gas-phase species involved in CVD of diamond as a function of filament temperature

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Abstract

We have used a molecular beam mass spectrometer to obtain quantitative measurements of the composition of the gas-phase species during the chemical vapour deposition (CVD) of diamond films as a function of filament temperature for a variety of different hydrocarbon precursor gases. For filament temperatures near to, and above, the optimum for diamond growth (ca. 2400 K), we find that the relative concentrations of the various stable hydrocarbon species (CH_4 , C_2H_2 and C_2H_4) present in the gas mixture, and the way that these concentrations vary with temperature, are remarkably insensitive to the particular choice of hydrocarbon feedstock gas.

Keywords: Heated filament CVD; Gas phase chemistry; In-situ diagnostics; Mass spectrometry

1. Introduction

High-quality diamond films can be deposited from a variety of source gas mixtures, subject to the C/H ratio being less than ca. 0.03. A survey of the different source gas mixtures used to produce diamond films is summarised in the well-known C/H/O phase diagram of Bachmann et al. [1]. However, the mechanisms by which different hydrocarbon precursors are able to produce high-quality CVD diamond are not fully understood. To date most models of diamond CVD have focused on hydrogen atoms, methyl (CH_3) radicals [2,3] and/or acetylene (C_2H_2) as key species in the growth process [4,5].

Identifying and understanding both the chemical reactions and the physical transport mechanisms that contribute to the CVD process requires an in-situ diagnostic technique that permits quantitative determination of the concentrations of both *free-radical* and *stable* species in the gas phase, with minimal perturbation of the process environment. Optical spectroscopy [6] is such a technique, but tends to be specific to a particular target species. Gas chromatographic [7,8] and mass spectrometric [9,10] studies have the advantage of generality and many stable species can be analysed simultaneously, though recombination in the probe used to sample the process gas in these studies precludes detection of reactive gas species. However, with careful design of the

gas sampling system, mass spectrometry can be used to detect free radicals. Molecular beam mass spectrometry (MBMS) of the diamond growth environment by Hsu and co-workers [11,12] has enabled quantitative measurement of the concentrations of H and CH_3 as well as stable species.

We have designed and constructed an MBMS system with which we have obtained quantitative measurements of the gas-phase composition under different process conditions in a hot-filament CVD reactor. Preliminary results probing the spatial distribution of both stable neutral and free-radical hydrocarbon species using an input gas mixture of 1% CH_4 in H_2 have been reported previously [13]. Here we present concentration measurements of the stable hydrocarbon species, CH_4 , C_2H_2 and C_2H_4 , as a function of filament temperature for a range of hydrocarbon precursors.

2. Molecular beam mass spectrometer design

The design of this MBMS has been optimised to sample from a hot-filament CVD process chamber operating at or near 20 Torr. Gas from the process chamber is extracted through a 100 μm diameter orifice in a stainless steel sampling cone. The sampled gas is collimated by a 1 mm diameter skimmer and has an unobstructed path to the electron ionisation chamber of a

HAL/3F PIC 100 quadrupole mass spectrometer (Hiden Analytical, Warrington, UK).

Since the typical process pressure is 20 Torr and the MS normally operates at pressures around 10^{-6} Torr, a two-stage pumping system using turbomolecular pumps is required, with the pressure in the first stage being typically ca. 10^{-3} Torr. The sensitivity of the system is aided by incorporating a *z*-translator to allow the distance from the extraction orifice to the skimmer to be varied, and an *x,y*-manipulator in order to align the MS skimmer with the molecular beam. During MS operation the distance from extraction orifice to skimmer is ca. 3 cm. Further details of the MBMS system will be given in a subsequent paper [14].

3. Experimental details

The deposition chamber was a standard hot-filament CVD reactor employing a coiled tantalum filament 0.25 mm thick to activate the gas mixture. The filament/substrate assembly was mounted on a translation stage allowing the filament-to-sampling orifice distance to be varied for spatial distribution studies [13]. Although we do not sample gas through the substrate, the sampling cone arrangement effectively samples the process gas mixture at the same radial distance from the filament as the substrate surface.

In the present study we replaced methane, the most widely used hydrocarbon precursor gas, with a range of different hydrocarbons, taking care always to maintain a carbon-to- H_2 ratio of 1:100 in the gas mixture. The gas flows were governed by calibrated mass flow controllers (Tylan General) and the total gas pressure was maintained at 20 Torr during all the measurements. The filament temperatures were measured using a two-colour optical pyrometer (Land Infrared).

3.1. MS calibration

The relationship between the signal intensity of a given species and its mole fraction X_i is given by

$$I_i = S_i X_i \quad (1)$$

where the sensitivity factor, S_i , depends on the ionisation cross-section, the MS parameters (e.g. electron ionising energy) and the local temperature of the gas sample. The concentrations of the stable species are determined by direct room-temperature calibration of mixtures of known composition (always at a total pressure of 20 Torr). However, we find that an additional temperature-dependent correction needs to be made (see Section 3.2).

When measuring the signal for species with a particular mass-to-charge (m/e) ratio it is important to eliminate or minimise interference from unwanted ions with the

same m/e or those arising from fragmentation of other species. This is possible by measuring the signal at an electron ionisation energy just below the ionisation potential of the interfering species. For example, we detected the signal for C_2H_4 ($m/e=28$) using an electron energy of 12.7 eV, so minimising signal interference from CO and N_2 . However, in cases where interference from fragmentation is unavoidable (e.g. detection of C_2H_4 in the presence of C_2H_6), corrections to the signals have to be made using measured fragmentation patterns. Detection of all hydrocarbon species other than C_2H_4 was made with an ionising electron energy of 14.7 eV.

3.2. Temperature dependence of MS sampling efficiency

Using pure H_2 at 20 Torr, the variation of I_{H_2} as a function of temperature, T , of the gas being sampled is shown in Fig. 1. Similar experiments using pure samples of He ($m/e=4$), Ne ($m/e=20$) and Ar ($m/e=40$) reveals that S_i shows the same temperature dependence for all these pure gases. In the following results we assume a similar temperature dependence to the mass spectrometer sampling efficiency for all the hydrocarbon species of interest, and correct accordingly (by reference to the attenuation of the H_2 signal). This assumption is justified on the grounds that for heavy species diluted in a large excess of hydrogen the transport of the process gas through the sampling orifice and subsequent formation of a supersonic molecular beam are dominated by the mass transport properties of the hydrogen.

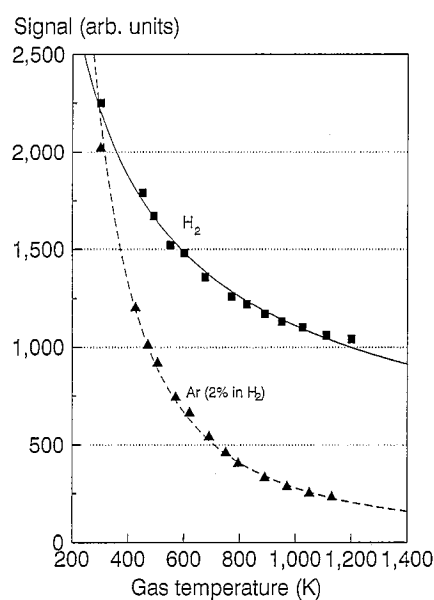


Fig. 1. Variation of detected signal as a function of the temperature of the gas sample (as measured using a K-type thermocouple placed next to the sampling orifice). For pure hydrogen the fit to the experimental data (solid line) shows a $T^{-0.6}$ dependence. For 2% Ar in H_2 the Ar signal shows a $T^{-1.6}$ dependence.

3.3. Thermal diffusion effects

For a two-component gas mixture, the temperature dependence of the detected ion signals is different from that measured for a pure gas. Fig. 1 shows that the Ar signal measured for a two-component gas mixture of 2% Ar in H₂ has a much greater temperature dependence than that for a pure gas. This indicates an additional thermal effect for a gas mixture whereby a temperature gradient induces the heavier component in the mixture to move away from the higher-temperature region.

This has a major effect on the total concentration of hydrocarbon species measured in the region of the hot filament (see Section 4).

4. Results

4.1. Gas composition as a function of filament temperature for input of 1% methane in hydrogen

Fig. 2 shows how the concentrations of the major hydrocarbon species [CH₄ (*m/e*=16), C₂H₄ (*m/e*=28) and C₂H₂ (*m/e*=26)] change as a function of filament temperature measured 6 mm from the filament for an initial CH₄/H₂ feedstock ratio of 1%, total flow rate

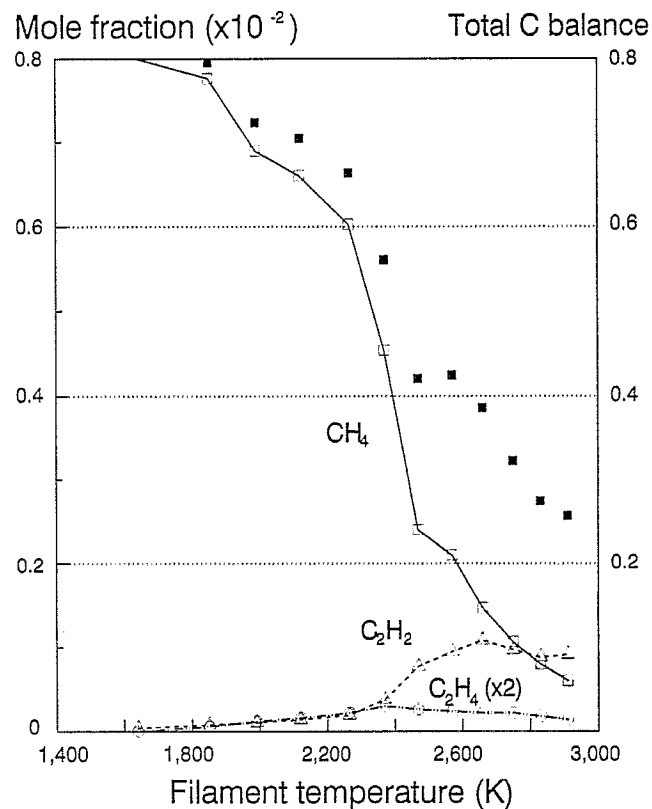
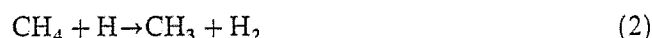


Fig. 2. Product distribution as a function of filament temperature measured 6 mm from the filament for an initial feedstock of 1% CH₄ in H₂, total flow rate of 100 sccm and process pressure of 20 Torr. The total carbon balance is indicated by ■.

of 100 sccm and pressure of 20 Torr. Note that the total carbon balance, defined as (total C fraction measured)/(C fraction in the feed gas), and shown as ■ in Fig. 2, decreases as the filament temperature increases, because of thermal diffusion effects as discussed above. We do acknowledge, however, that contributions to the total carbon balance from radical species, such as CH₃, are not included and these may be significant at the higher filament temperatures.

The main chemical conversion is that of methane to acetylene as the filament temperature is increased. This observation is consistent with chemical kinetics models in which the gas-phase chemistry is initiated by the dissociation of methane yielding methyl radicals:



Methyl recombination followed by successive H abstractions yields acetylene. Increasing the H atom concentration drives the equilibrium from CH₄, through C₂H₆ and C₂H₄ to C₂H₂, as the filament temperature increases. No C₂H₆ was detected, presumably because its instability in the presence of atomic hydrogen leads to very low steady-state concentrations.

4.2. Gas composition as a function of filament temperature for a variety of hydrocarbon precursor gases

Fig. 3 shows the temperature variation of the CH₄, C₂H₄ and C₂H₂ concentrations for similar conditions to those in Fig. 2 except that the input mixtures used were, respectively, 0.5% C₂H₂ (a), 0.5% C₂H₄ (b) and 0.5% C₂H₆ (c) in H₂.

We see that, regardless of the precursor gas used, methane is the dominant hydrocarbon species measured 6 mm from the filament when the filament temperature is ca. 2100 K. For higher filament temperatures the relative gas concentrations and the total carbon balance are remarkably similar to those found when using methane as the hydrocarbon precursor (Fig. 2).

The CH₄/C₂H₂/C₂H₄ product distributions obtained when pentane, n-butane and 1,3-butadiene were introduced (maintaining a C-to-H₂ ratio of 1:100) were also similar for filament temperatures above 2100 K.

5. Discussion

In-situ mass spectrometry has been used to obtain quantitative measurements of the stable hydrocarbon species under different diamond hot-filament CVD growth conditions.

We find that, regardless of the hydrocarbon precursor gas used, at filament temperatures between 2000 and 2100 K the hydrocarbons are reduced so that methane is the dominant hydrocarbon species. For filament temperatures near to, and above, the optimum for diamond

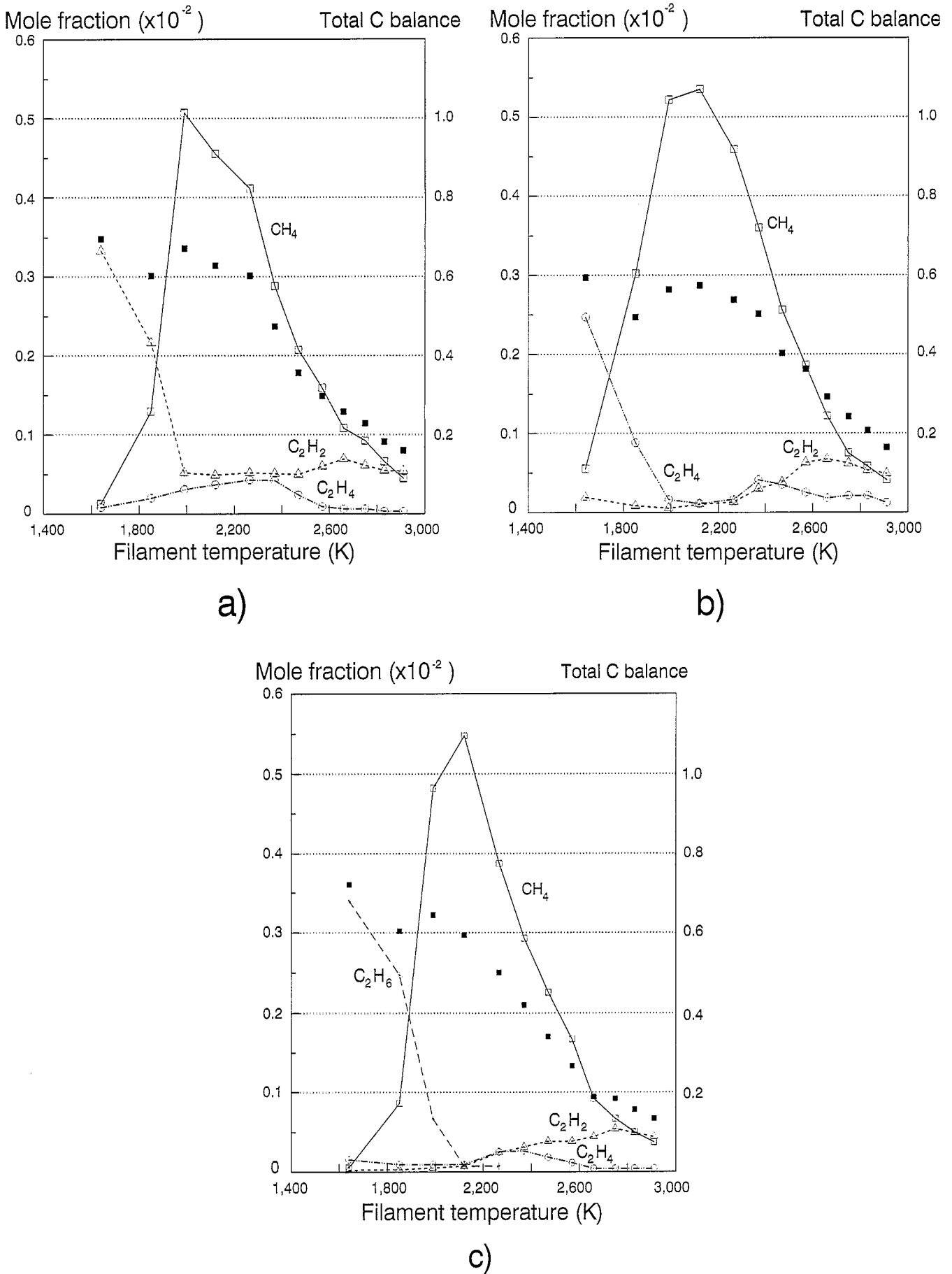


Fig. 3. Gas composition as a function of filament temperature measured 6 mm from the filament starting with (a) 0.5% C₂H₂ in H₂, (b) 0.5% C₂H₄ in H₂, and (c) 0.5% C₂H₆ in H₂. The total carbon balance is indicated by ■.

growth (ca. 2400 K), the relative concentrations of the various stable hydrocarbon species present in the gas mixture, and the way the concentrations vary with temperature, are both remarkably insensitive to the choice of hydrocarbon feedstock gas. We note that for filament temperatures of 2400 K we measured a CH_4 -to- C_2H_2 ratio of ca. 8:1 whichever hydrocarbon feedstock gas was used. Thus experiments which suggest that high-quality diamond films can be grown using acetylene as the hydrocarbon precursor do not necessarily lead to the conclusion that acetylene is the dominant diamond growth species. Broadly similar results were obtained in a gas chromatography study of the gas-phase environment in a hot-filament reactor using CH_4 and C_2H_2 as the hydrocarbon precursors [7]. In-situ Fourier transform infrared (FTIR) spectroscopy has also shown that the product distribution of stable hydrocarbon species in a microwave plasma as a function of C/H ratio is independent of the hydrocarbon in the source gas [15].

Most models of diamond growth by CVD state that high $[\text{CH}_3]$ is required for high growth rates and that large $[\text{H}]$ not only initiates the the gas-phase chemistry but is also essential to produce high-quality diamond. For our typical carbon-to-hydrogen feedstock ratio of 1:100, we find that the diamond growth rate on silicon substrates (whose temperature is independently controlled) does not simply increase as the filament temperature increases, but is maximised for a temperature of ca. 2400 K. This is consistent with the measured $[\text{CH}_4]$ vs. temperature profiles, convoluted by the fact that the concentration of atomic hydrogen increases with temperature. Thermal diffusion effects, inasmuch that they reduce the hydrocarbon concentration in the region of the substrate, also play a role in limiting growth rates at higher temperatures. We have also found [16] that, when lower-than-normal filament temperatures (ca. 1800 K) are used, the diamond deposition rate decreases with increasing hydrocarbon chain length, and is accompanied by an increase in the proportion of amorphous carbon in the resulting diamond film. This correlates with the incomplete dissociation of the hydrocarbon precursor at these lower-than-optimum temperatures for diamond growth (see Fig. 3).

We are currently augmenting these preliminary analy-

ses of the stable hydrocarbon species involved in diamond CVD with a detailed quantitative analysis of free-radical species (specifically H and CH_3). We are able to do this by modulating the molecular beam and using phase-sensitive detection; thus only gas from the molecular beam is detected.

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