MOLECULAR BEAM MASS SPECTROMETRIC STUDY OF THE SPATIAL DISTRIBUTION OF GAS-PHASE SPECIES INVOLVED IN THE GROWTH OF HFCVD DIAMOND FILMS

C.A. Rego, P.W. May, C.R. Henderson, M.N.R. Ashfold, K.N. Rosser, and N.M. Everitt*

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

* Department of Aerospace Engineering, University of Bristol, Bristol BS8 1TR, U.K.

Abstract

We have used a molecular beam mass spectrometer to obtain quantitative measurements of the composition of gas-phase species as a function of distance from the hot filament using 1% CH_4 in H_2 as the input gas mixture. We find that the concentration of both CH_3 radicals and C_2H_2 increase closer to the filament with a corresponding depletion of the methane precursor.

1. INTRODUCTION

Most models of diamond CVD have focused on hydrogen atoms, methyl (CH_3) radicals and/or acetylene (C_2H_2) as key species in the growth process.[1,2] Identifying and understanding both the chemical reactions and the physical transport mechanisms that contribute to the CVD process require a diagnostic technique that permits quantitative determination of the concentrations of both *free radical* and *stable species* in the gas phase.

We require an *in situ* analysis technique to allow direct measurement of the gaseous species, with minimal perturbation of the process environment. Optical spectroscopy[3] is such a technique but tends to be specific to a particular target species. Mass spectrometry[4] has the advantage of generality and many stable species can be analysed simultaneously. With careful design of the gas sampling system free radicals can also be detected. Molecular beam mass spectrometry (MBMS) of the diamond growth environment by Hsu and Tung[5] has enabled quantitative measurement of the concentrations of H and CH_3 as well as of stable species.

We have designed and constructed a MBMS system with which we have obtained quantitative measurements of the gas phase composition during diamond CVD in a hot filament reactor. Here we present these preliminary measurements for the hydrocarbon species CH_4, C_2H_2 and C_2H_4, and CH_3, radicals taken at different distances from the filament, as a function of filament temperature using 1% CH_4 in H_2 as the input gas mixture.

2. MOLECULAR BEAM MASS SPECTROMETER DESIGN AND CALIBRATION

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, England).

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 10^{-3} Torr. The sensitivity of the system is aided by incorporating a z-translator to allow the distance from the skimmer to the extraction orifice to be varied and a x,y-manipulator in order to align the MS skimmer with the molecular beam. Further details of the MBMS system will be given in a subsequent publication.

2.1 Mass spectrometer calibration

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

$$I_i = S_i X_i$$

where the sensitivity factor, S_i, depends on the ionisation cross section, the MS parameters (e.g. electron ionising energy - held at 14.7 eV for the detection of stable hydrocarbon species in this series of experiments) and the temperature of the gas sample. The concentrations of the stable species are determined by direct room temperature calibration of known gas mixtures but we find that an additional temperature dependent correction also needs to be made.

Using pure H_2 at 20 Torr, the variation of I_{H_2} as a function of temperature, T, of the gas being sampled (as measured using a K-type thermocouple placed next to the sampling orifice) shows a $T^{-0.6}$ dependence. Similar experiments using pure samples of He, Ne and Ar reveals that S_i shows the same temperature dependence of the sampling efficiency for all these pure gases. In the results following 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).

For a two component gas mixture the temperature dependence of the signals is different than that measured for a pure gas. For example, we have measured a $T^{-1.0}$ dependence of the argon signal for a 2% Ar in H_2 mixture. 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 at the substrate surface (see Results section).

3. RESULTS AND DISCUSSION

3.1 Spatial distribution of hydrocarbons

Figure 1 shows how the hydrocarbon concentrations change as a function of distance from the filament, with a filament temperature of 2400 K which is the optimum filament temperature for diamond growth in our CVD reactor. Initially 1% CH_4 in H_2 was input and maintained at a pressure of 20 Torr. Note that the measured total carbon balance, which is (total C fraction measured)/(C fraction in the feed gas), and shown as ■ in Fig.1, diminishes as we approach the hot filament. This is the inevitable result of the thermal diffusion effects discussed above. We do acknowledge, however, that contributions to the total carbon balance from radical species, e.g. CH_3 are not included and these may be significant near the filament.
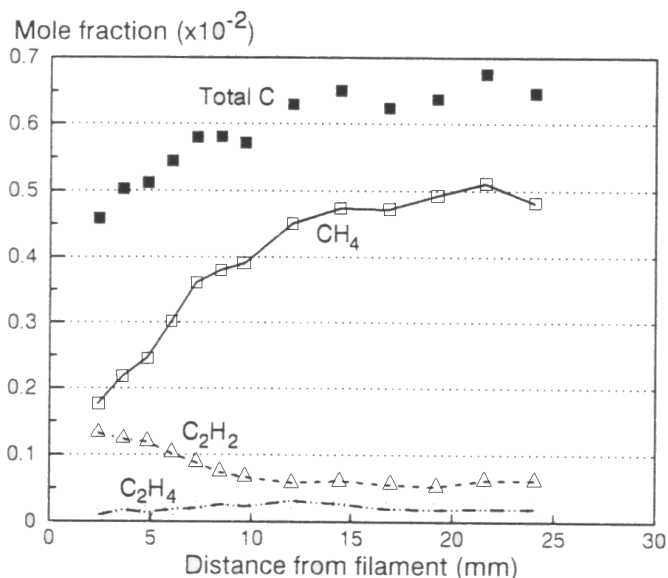
Fig. 1. Spatial distributions of the stable hydrocarbon species. A mixture of 1% CH_4 in H_2 was maintained at 20 Torr. The filament temperature was held at 2400 K.

The main chemical conversion is that of methane to acetylene as we approach the filament (Fig. 1) or as the filament temperature is increased. This observation is consistent with models in which the gas phase chemistry is initiated by the dissociation of methane into methyl radicals

$$CH_4 + H \rightarrow CH_3 + H_2$$
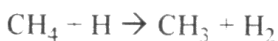
Methyl recombination followed by successive H abstractions yields acetylene. On approach to the filament, [H] increases, thereby shifting the equilibrium from CH_4, through C_2H_6 and C_2H_4 to C_2H_2 since high [H] favours stability of acetylene over methane. The C_2H_4 intermediate in this conversion has a maximum concentration at *ca.* 12 mm from the filament.

3.2 Spatial distribution of CH_3 radicals

A relative measure of the spatial distribution of methyl radicals was also made (absolute concentration measurements of radicals cannot be made without modulating the molecular beam). Detection of CH_3 in a large excess of CH_4 requires the use of the threshold ionisation technique which distinguishes ions generated by direct electron impact of the radicals from those generated by dissociative ionisation of the parent molecule. This is achieved by operating the ioniser close to the ionisation threshold of the radical (in this case 12.1 eV).

Figure 2 shows the relative methyl concentration as a function of distance from the filament measured at the same time as the data displayed in Fig. 1. It is noticeable that the concentrations of both CH_3 radicals and C_2H_2 increase closer to the filament. Additionally an increase in the filament temperature results in higher [CH_3] which is mirrored by increased [C_2H_2]. This is further evidence for the importance of CH_3 as an important intermediate in the methane/acetylene equilibrium.
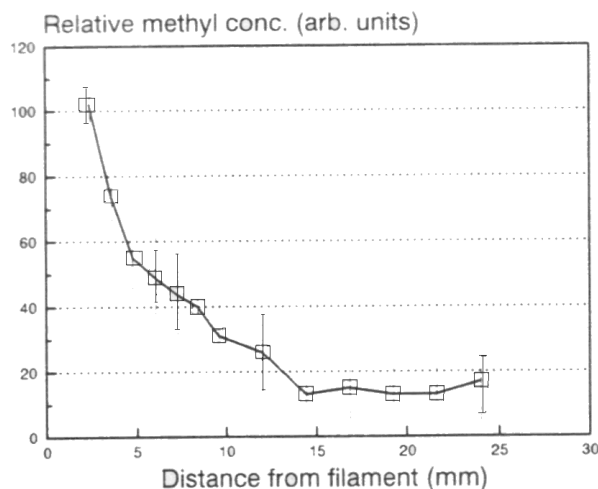
Fig. 2. Spatial distribution of CH_3 radicals. Filament temperature = 2400 K.

CONCLUSIONS

We have used a mass spectrometer to make quantitative measurements of the spatial distributions of stable hydrocarbon species under optimum diamond growth conditions in a hot filament CVD reactor.

For the carbon to H_2 feedstock ratio of 1:100 that we use, the concentrations of both CH_3 and C_2H_2 increase closer to the filament, which also indicates a concomitant increase in [H] on approach to the filament. Diamond growth models state that high $[CH_3]$ (and/or $[C_2H_2]$) is required for high growth rates, but complementary film growth studies have shown that the diamond growth rate does not simply increase when the substrate is placed closer to the filament but is maximised for a distance of *ca.* 5 mm. This is consistent with the measured CH_3 spatial distribution convoluted by the fact that the concentration of atomic hydrogen, which etches diamond, increases on approach to the filament. Thermal diffusion effects also surely play a role in limiting growth rates closer to the filament.

We are currently augmenting these preliminary analyses 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.

ACKNOWLEDGEMENTS

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