



ELSEVIER

Diamond and Related Materials 8 (1999) 226–230

**DIAMOND
AND
RELATED
MATERIALS**

Molecular beam mass spectrometry studies of nitrogen additions to the gas phase during microwave-plasma-assisted chemical vapour deposition of diamond

S.M. Leeds *, P.W. May, M.N.R. Ashfold, K.N. Rosser

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

Received 27 July 1998; accepted 5 October 1998

Abstract

In-situ molecular beam mass spectrometry has been used to study the effects of nitrogen-containing gases on the gas-phase composition during microwave plasma chemical vapour deposition (CVD) of diamond. The molecular beam mass spectrometer used in this work extracts gas directly from the plasma bulk via a small sampling orifice inserted into the side of the plasma. The plasma composition was examined for a variety of nitrogen-containing gases added to a standard 1% C:H₂ feedstock. Nitrogen was added to this mixture at a carbon-to-nitrogen ratio, C:N=1:1, in one of the following forms: N₂, NH₃, CH₃NH₂, or HCN. For N₂ and NH₃, the carbon source was CH₄, whereas CH₃NH₂ and HCN required no added carbon. Mass spectrometer signals from hydrocarbons, nitrogen-containing species, and the methyl radical were recorded. These were calibrated to give absolute mole fractions of the main carbon- and nitrogen-containing species present at detectable levels. The content of N₂ and NH₃ in the feed was also varied while holding the CH₄ content at 1%. Results are compared with those found during hot-filament CVD. The relevance of the measured abundance of various nitrogen-containing species in the plasma to attempts to create p-type diamond is discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: CVD diamond; Microwave plasma; Molecular beam mass spectrometry; Nitrogen

1. Introduction

The presence of nitrogen in the reactant gases used when producing diamond films by microwave plasma chemical vapour deposition (MWCVD) is known to affect the film morphology, quality, and growth rate [1–3]. Many previous studies of nitrogen additions have focused on the (inefficient) incorporation of nitrogen into the growing film [4,5]. There is, to date, no firm consensus as to whether gas-surface or gas-phase chemical reactions, or both, are necessary to account for these observations. In order to supplement the data concerning properties of films deposited in the presence of nitrogen, we have undertaken a study of the plasma composition during MWCVD. The technique of in-situ molecular beam mass spectrometry (MBMS) [6,7] has been used to determine concentrations of stable and

radical species in the plasma. This study parallels previous work carried out in our laboratories for hot-filament (HF) CVD [8].

2. Experimental

Unlike previous MBMS studies carried out during MWCVD [9,10], the present experiments use a molybdenum probe to sample gas from the side of the plasma region, 15 mm from the reactor's vertical axis. The probe has a 100- μ m orifice laser drilled into its tip to extract plasma gas as a supersonic expansion. According to the calculation of Hsu [6], the time spent in the gas expansion by a typical molecule is <1 μ s, compared with the characteristic time scale for the destruction of CH₃ by reaction with H₂ (~286 μ s), a particularly fast reaction encountered during diamond CVD. Thus, collisions rapidly cease in the expansion, even for reactive species

* Corresponding author. Fax: +44 117 925 1295;
e-mail: stuart.leeds@bris.ac.uk

such as radicals, preserving the composition of the sampled gas, which is then analysed using mass spectrometry [11,12]. This system has many similarities with that used in Bristol to study HF CVD [13–15], including studies of the effect of added nitrogen-containing gases [8]. The system and experimental method used in this work are identical to those used to study hydrocarbon/H₂ plasmas [11]. The present work employed a pressure of 20 Torr and C:H₂ ratios of 1%, except where otherwise stated. Quantities of N₂, NH₃, HCN, or CH₃NH₂ were added to this mixture. As the last two of these gases also contain carbon, the amount of input CH₄ was altered to maintain C:H₂ at 1%. All gases were obtained as high-quality commercial products, except HCN, which was synthesized by the reaction of NaCN and H₃PO₄ in vacuo.

The mass spectrometer data presented here were corrected and calibrated according to the methods previously used when studying the hot-filament reactor [8,13–15]. This procedure consists of corrections for background signals, and the temperature dependence of the sampling orifice gas throughput. Calibration of the stable species was carried out using a known quantity of each gas in H₂ (usually 1%, at the process pressure and room temperature) to convert the mass spectrometer signals into species mole fractions. This worked well for most species, but it was difficult to obtain mole fractions of N₂ in some experiments for several reasons. An extra N₂ signal arises as a consequence of the ultimate vacuum produced by pumps and small air leaks. Consequently, the measured background for N₂ is higher than expected, having a constant component (N₂ in mass spectrometer), and a variable component depending on the gas flow from the CVD chamber (gas-temperature-dependent). N₂ has the same mass as C₂H₄, requiring the mass-to-charge ratio (m/e)=28 signal to be taken at two electron ionizer energies (11.9 and 30 eV for C₂H₄ and N₂, respectively). Signals from one species can then be deconvoluted from the other, provided the background signals are reliably known. These effects make it difficult to measure N₂ accurately, and therefore, N₂ was not measured in every experiment. Instead, since equal amounts of C and N were added to the gas phase, the total measured N atom mole fraction is required to equal the total measured C atom mole fraction. We then subtract from this quantity the total N atom mole fraction of the other nitrogen-containing species and divide by two to obtain a value for the N₂ mole fraction. This procedure was used instead of direct calibration only for Fig. 1a. We examined the mass spectra for the plasma under different conditions but did not observe any stable nitrogen-containing species other than those displayed in the data. This does not rule out some radical species, e.g. NH₂, the signal for which would occur at m/e =16 and thus interfere with that of CH₄. No attempt was made to measure NH₂.

3. Results and discussion

3.1. Variation of applied microwave power

Plasmas were generated in gas mixtures containing C:N:H₂=2:2:200 sccm for N₂, NH₃, and CH₃NH₂ source gases in H₂ at 20 Torr. HCN was used at C:N:H₂=1:1:200, since only a small quantity was synthesized when necessary. As N₂ and NH₃ do not contain carbon, CH₄ was introduced to the feed such that C:N=1:1. The effect of applied power used to sustain the plasma was investigated, and the results are presented in Fig. 1. A similar study was performed for hydrocarbon-in-H₂ feed gases only [11], and it was found that above a certain power level (~700 W), the plasma composition became independent of the nature of the hydrocarbon source. Also noted in that study was the dramatic effect of thermal diffusion on the results. The measured carbon total was found to fall far short of that which was input. It was concluded that heavy species are driven from the centre of the plasma via temperature gradients to the cooler zone surrounding the plasma. It can be seen that the data in Fig. 1 also show this effect. When interpreting the data in these figures, it must also be noted that the size of the plasma ball changes with the applied microwave power. At low powers (~300 W), the sampling probe tip is close to, and only just inside, the visible plasma edge. At high powers (~1000 W), the plasma completely encompasses the probe tip, and thus the sampling location relative to the plasma changes with microwave power (see Ref. [11]).

3.2. 0.5% N₂/1% CH₄ in H₂

The results for this feed gas mixture are shown in Fig. 1a. The important point to notice is that only a small proportion of the input N₂ has been dissociated by the plasma. The decomposed nitrogen has formed HCN and a small amount of NH₃. The hydrocarbon species are thus free to react with the excess of hydrogenic species, reproducing the trends observed during MWCVD in the absence of nitrogen [11]. These data are similar to results found during HFCVD at low filament temperatures (~1600 °C), where very little N₂ dissociation occurred [8]. At high filament temperatures, more N₂ was found to dissociate, which is not seen under the conditions of this study. This indicates that the hot filament dissociates N₂ more readily than the plasma environment under the conditions used in this study. In the hot-filament system, gas activation is believed to occur on the filament surface (~2600 K), whereas in our plasma, activation occurs throughout the plasma whose temperature is typically 1400 K [11]. Thus, the results for HFCVD and MWCVD can be compared meaningfully when the temperature of the

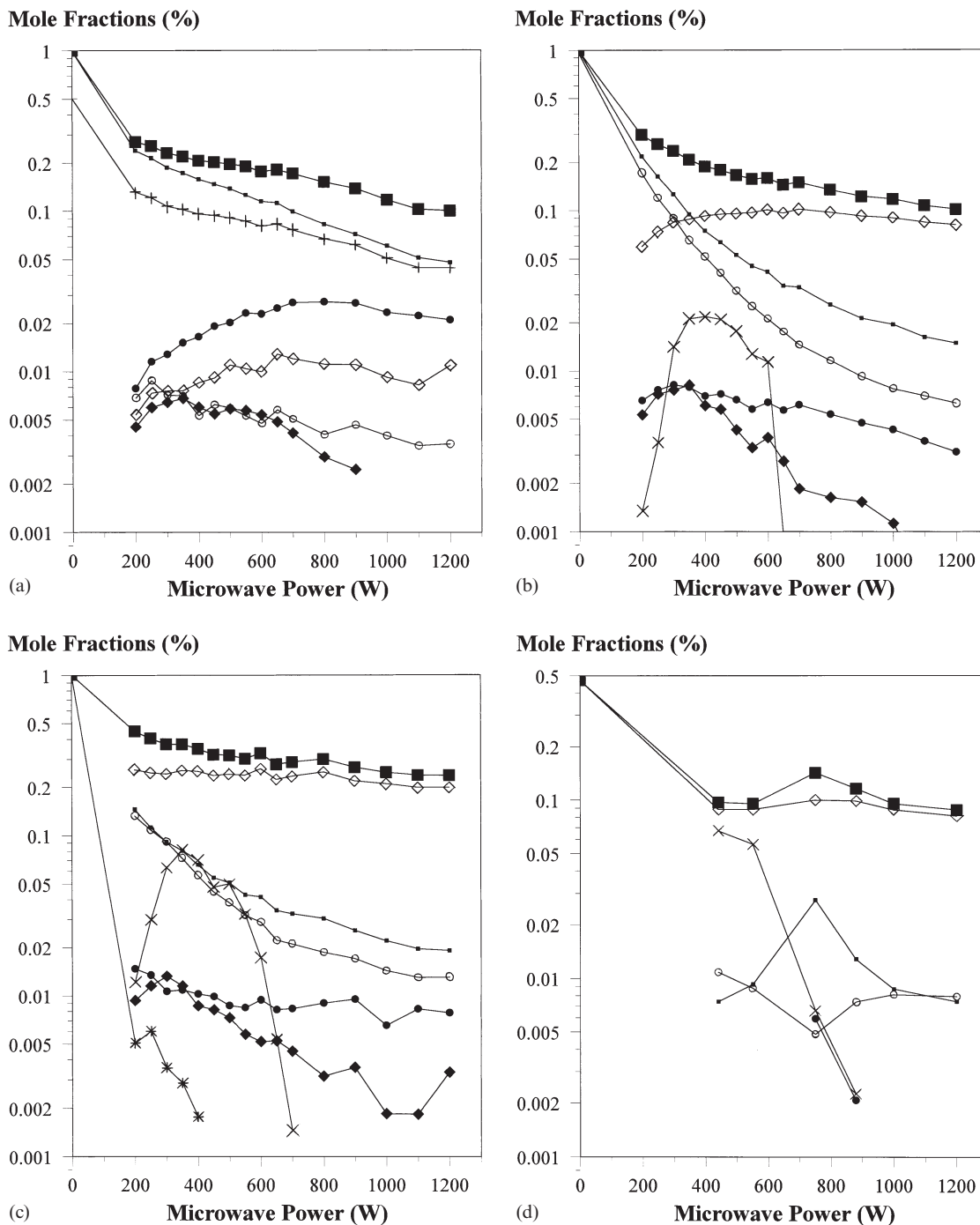


Fig. 1. Measured species mole fractions as a function of microwave power for a variety of gas mixtures: (a) 1% $\text{CH}_4/0.5\% \text{N}_2/\text{H}_2$ feed gas. N_2 determined from nitrogen balance. (b) 1% $\text{CH}_4/1\% \text{NH}_3/\text{H}_2$ feed gas. (c) 1% $\text{CH}_3\text{NH}_2/\text{H}_2$ feed gas. (d) 0.5% HCN/H_2 feed gas. Key: CH_4 —■; CH_3 —◆; C_2H_2 —●; measured carbon total—□; N_2 —+; HCN —◇; NH_3 —○; CH_3NH_2 —*; and measured nitrogen total—□. The points marked × indicate species with $m/e=28$, which we associate with the radical CH_2NH_2 (see Section 3.2). Mole fraction calibration of this species is not possible; hence the vertical scale for this species is in arbitrary units and has not been included in the displayed carbon and nitrogen totals.

activation zone (filament/plasma) is similar for both. It may be possible to decompose a larger fraction of N_2 at higher pressures, or powers, due to the increased gas temperature, but this was not attempted in this work.

3.3. 1% $\text{CH}_4/1\% \text{NH}_3$ in H_2

Fig. 1b shows the effect of using a CH_4/NH_3 mixture in H_2 . As the power is increased, NH_3 and CH_4 are

consumed in the plasma to form the highly stable moiety HCN. Between 200 and 600 W, a sizable signal at $m/e = 28$ was detected in this experiment (and in those reported in Sections 3.3 and 3.5). Common ions with $m/e = 28$ are CO, N₂, and C₂H₄. Only C₂H₄ could ionize at the electron kinetic energy used here, but a high C₂H₄ concentration would be very surprising, given our previous work on hydrocarbon–H₂ mixtures, which showed C₂H₄ to be present at a concentration close to the ultimate resolution of our instrument under all conditions studied [11]. Hence, we do not believe that the $m/e = 28$ signal is due to C₂H₄. However, we note that by increasing the applied power, we are effecting the conversion of CH₄ and NH₃ to HCN. This requires an intermediate species containing a C–N bond, which will undergo H abstraction reactions to form HCN. Species such as CH₂NH₂ (or CH₃NH) are possible intermediates. Both are radicals and will have low ionization potentials. Electron bombardment of the former should produce CH₂NH₂⁺ and, conceivably, HC≡NH⁺ by dissociative ionization. HC≡NH⁺ will have $m/e = 28$, and a stable electronic structure analogous to C₂H₂. Consistent with this view, the $m/e = 28$ signal is found at power levels where the NH₃ and CH₄ signals are falling, yet where the HCN mole fraction is rising, as would be expected for an intermediate in the conversion of CH₄ and NH₃ to HCN. We thus assign the $m/e = 28$ signal to a radical, which we cannot calibrate. Therefore, measured carbon totals on all graphs in this work are those determined excluding the $m/e = 28$ signal.

3.4. 1% CH₃NH₂ in H₂

The plasma composition determined using CH₃NH₂ as the source of C and N is shown in Fig. 1c. Even at the lowest powers used, the CH₃NH₂ concentration falls close to the minimum detectable. CH₄, NH₃ and HCN are observed instead. Two reaction pathways arise for the CH₃NH₂ molecule in the plasma environment. Firstly, H abstraction reactions can occur, producing a strong C≡N bond (as in the observed product HCN). Secondly, fission of the weak C–N bond in the CH₃NH₂ molecule is possible, followed by reaction with H or H₂ to produce the observed products CH₄ and NH₃. The measured CH₄ and NH₃ concentrations track each other closely, as would be expected if they were produced by fission of the C–N bond in CH₃NH₂. The amounts of CH₄ and NH₃ are reduced with increasing microwave power, with a concomitant rise in the HCN mole fraction. Again, a sizeable quantity of species with $m/e = 28$ was measured in the low-power region (200–600 W).

3.5. 0.5% HCN in H₂

As mentioned earlier, only a small quantity of HCN was synthesized for each experiment, and therefore, less

data were taken for this gas. The plasma composition for a 0.5% HCN/H₂ plasma is shown in Fig. 1d. Most of the gas remains as HCN, but at low powers, a small quantity of CH₄ is seen. The fact that little HCN is decomposed emphasizes the stability of the HCN molecule under conditions found in our plasma.

3.6. Variation of N₂ concentration in the feed gas

A 1% CH₄/H₂ plasma was examined as a function of N₂ added to the feed. The results are shown in Fig. 2. The measured carbon total remains constant at a lower value than the input amount due to thermal diffusion effects. As the concentration of N₂ is increased, the concentrations of the hydrocarbon species are reduced slightly, due to the formation of HCN. This indicates that under these conditions, N₂ only participates in the gas-phase chemistry to a limited extent, even when several per cent of N₂ is added. This has implications for growth studies using gas-phase N₂ additions to form p-type diamond, since almost all added nitrogen remains as gas-phase N₂. Diamond films grown using this gas mixture with N₂ concentrations of 0–4.7% were examined for incorporated nitrogen by the technique of secondary ion mass spectrometry (SIMS) [16]. In common with previous authors, we find a very low nitrogen incorporation efficiency ($< 10^{-3}$) [4,5].

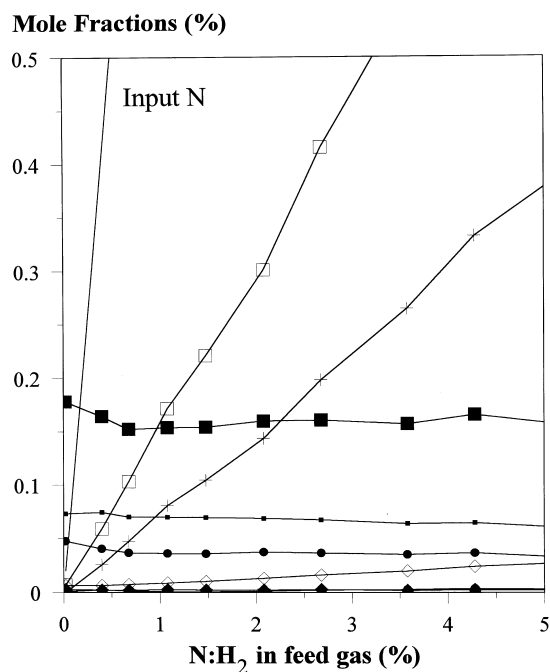


Fig. 2. CH₄/H₂ (1%), with variation of N₂ concentration, measured using a microwave power of 1000 W. The symbols used are the same as those defined in Fig. 1. The N₂ signal was directly measured by MBMS in these experiments.

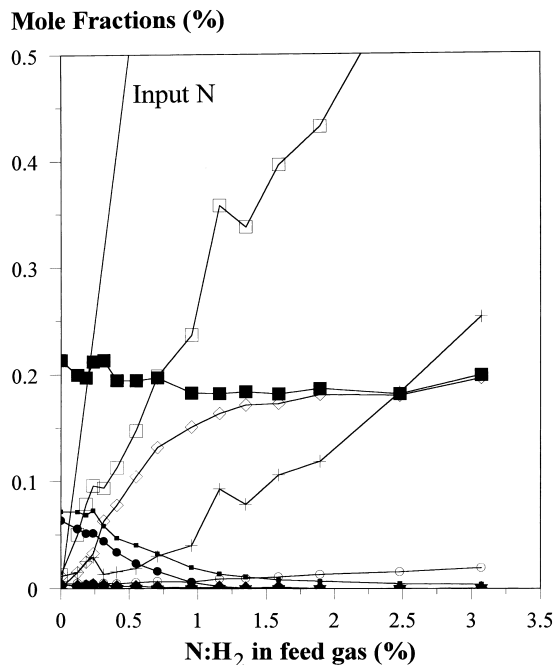


Fig. 3. As Fig. 2, except with variation of NH_3 concentration.

3.7. Variation of NH_3 concentration in the feed gas

The previous experiment was repeated with the addition of NH_3 to the feed gas instead of N_2 . The data are shown in Fig. 3, and it is apparent that the NH_3 reacts more readily than N_2 with the hydrocarbon species to produce HCN. Most of the measured carbon has been “locked up” as HCN by the time the NH_3 concentration becomes stoichiometric with the input CH_4 (1%). Once the NH_3 concentration increases beyond the 1% input carbon limit, additional HCN can no longer be formed, and excess NH_3 is largely converted to N_2 . Presumably, this occurs in an analogous fashion to the case of CH_3 recombination followed by H abstraction reactions forming C_2H_2 , which occurs in the absence of nitrogen. These results suggest a method of selectively tailoring the gas-phase composition between species containing one nitrogen atom and N_2 by varying the concentration of ammonia relative to CH_4 .

4. Conclusions

In-situ MBMS has been used to study the gas-phase composition during MWCVD, with the addition of

nitrogen to the gas phase. The gas-phase composition was found to be sensitive to the form of the nitrogen-containing precursor, in contrast to corresponding studies of hydrocarbon/ H_2 mixtures where the gas-phase composition appears insensitive to the identity of the hydrocarbon source [11]. For all feed-gas molecules used in this study, except N_2 , carbon is locked up in HCN. This was not the case for N_2 , which did not undergo significant dissociation in the plasma environment studied here. The nitrogen that did dissociate, however, primarily formed HCN. The comparative unreactivity of N_2 in the plasma is of relevance to studies of nitrogen doping of diamond using N_2 in the feed gas. It may be possible to achieve a higher degree of N_2 dissociation using higher pressures or powers.

Acknowledgement

We would like to thank the EPSRC for project funding, the Royal Society for the award of a University Research Fellowship (PWM).

References

- [1] R. Locher, C. Wild, N. Herres, D. Behr, P. Koidl, *Appl. Phys. Lett.* 65 (1994) 34.
- [2] S. Jin, T.D. Moustakas, *Appl. Phys. Lett.* 65 (1994) 403.
- [3] P. Hartmann, R. Haubner, B. Lux, *Diamond Relat. Mater.* 6 (1997) 456.
- [4] S. Jin, T.D. Moustakas, *Appl. Phys. Lett.* 63 (1993) 2354.
- [5] R. Samlenski, C. Hauge, R. Brenn, C. Wild, R. Locher, P. Koidl, *Appl. Phys. Lett.* 67 (1995) 2798.
- [6] W.L. Hsu, M.C. McMaster, M.E. Coltrin, D.S. Dandy, *Jpn. J. Appl. Phys.* 33 (1994) 2231.
- [7] W.L. Hsu, D.M. Tung, *Rev. Sci. Instrum.* 63 (1992) 4138.
- [8] R.S. Tsang, C.A. Rego, P.W. May, M.N.R. Ashfold, K.N. Rosser, *Diamond Relat. Mater.* 6 (1997) 247.
- [9] W.L. Hsu, *J. Appl. Phys.* 72 (1992) 3102.
- [10] M.C. McMaster, W.L. Hsu, M.E. Coltrin, D.S. Dandy, C. Fox, *Diamond Relat. Mater.* 4 (1995) 1000.
- [11] S.M. Leeds, P.W. May, E. Bartlett, M.N.R. Ashfold, K.N. Rosser, Presented at ICNDST-6, Pretoria, South Africa, September 1998. *Diamond Relat. Mater.* in press.
- [12] S.M. Leeds, Ph.D. Thesis, University of Bristol, 1999.
- [13] 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.
- [14] C.A. Rego, R.S. Tsang, P.W. May, M.N.R. Ashfold, K.N. Rosser, *J. Appl. Phys.* 79 (1996) 7264.
- [15] R.S. Tsang, Ph.D. thesis, University of Bristol, 1997.
- [16] A.J. Eccles, T.A. Steele, A. Afzal, C.A. Rego, W. Ahmed, P.W. May, S.M. Leeds, *Thin Solid Films*, in press.