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Examination of the effects of nitrogen on the CVD diamond growth mechanism using in situ molecular beam mass spectrometry

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Abstract

Molecular beam mass spectrometry (MBMS) has been used to obtain quantitative measurements of the composition of the gas-phase species prevalent during diamond hot filament CVD using a variety of nitrogen-containing source gas mixtures. The ratio of C:N in the feedstock was maintained at 1:1, and the gas mixtures used were 0.5% each of CH_3NH_2 and HCN in H_2, and 0.5% CH_4 in H_2 with added NH_3 and N_2 at 0.5 and 0.25% respectively. The deposition rate and resulting film quality at optimum growth temperatures depend critically on the origin of carbon-containing species. At the relevant process temperatures, most of the gas-phase carbon exists in the form of unreactive HCN (~70–90%) for all precursor gas mixtures (except CH_4/N_2), with very little C_2H_2 detected. As a result, poor quality diamond films were deposited at rates of less than 0.1 μm h^{-1}. For CH_4/N_2 mixtures, however, equal amounts of HCN and C_2H_2 were detected, and well-faceted diamond films were produced at higher deposition rates (~0.45 μm h^{-1}). These observations are explained in terms of the effects that nitrogen, and its resulting reaction products (NH_3, HCN, CH_3NH_2, etc.), have on the gas-phase chemistry occurring during the CVD process. In particular, we suggest that N_2 can act as a catalyst for the destruction of H atoms, which in turn leads to significant changes in the gas-phase chemistry.

Keywords: Nitrogen; CVD diamond growth; In situ molecular beam mass spectrometry; Gas-phase species

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1. Introduction

Owing to its outstanding mechanical, optical and electronic properties [1], diamond has enormous potential for many industrial applications. Since low-pressure chemical vapour deposition (CVD) of diamond was discovered in the 1970s [2–4], continual efforts have been made to search for new ways to grow better quality, more uniform diamond films at higher rates and lower process temperatures. Over the last 15 years, optimum conditions for diamond growth have been arrived at empirically for various deposition techniques [5]. However, the incorporation of unwanted impurities invariably present in reactant gases remains one of the main drawbacks in CVD diamond growth. The most commonly occurring impurity in both natural and synthetic diamond is nitrogen. Inclusion of small amounts of this element has a noticeable effect on the growth of CVD diamond films and on many of the physical properties of the material [6–8], namely its optical transparency and thermal and electrical conductivity. The presence of nitrogen in the reactant gases can also seriously alter the morphology of deposited diamond films which restricts their usefulness for some applications, especially those that require high-quality electronic-grade diamond [9]. Alternatively, however, nitrogen-doped CVD diamond and diamond-like carbon (DLC) films may have very useful semiconducting properties, which are particularly important for microelectronics and field emission display applications [10–13]. These discoveries have attracted widespread research interest, and prompted many groups to investigate the effects of nitrogen on the growth of CVD diamond films using CH_4/H_2 gas mixtures [6–8,14–16]. Hong et al. [17] also studied the influence of adding nitrogen gas to a more unconventional CH_4/CO_2 gas mixture.

Recent studies have shown that addition of nitrogen to the input gas mixtures causes significant changes in the morphology, the quality and the growth rate of diamond films. Jin and Moustakas [6] found that the growth habit and deposition rate using $CH_4/N_2/H_2$ mixtures in a microwave CVD system depended strongly

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on the ratio of carbon-to-nitrogen in the feed gas; in the region of the N_2 mole fraction relevant to the present work they observe the overall growth rate to be little affected by N_2 addition (up to 1%), but some compromise in film quality as revealed by laser Raman spectroscopy. However, at high N_2 concentrations they observe improved film quality, larger growth rates and a change in the surface morphology from (111) to predominantly (100) facets. In a somewhat related study, Badzian et al. [16] grew diamond using a CH_4/N_2 mixture both in the absence of H_2, and with added H_2. They observed a considerable amount of distortion in the crystal structure of the grown diamond films with N doping, and a reduction in the growth rate with nitrogen addition in the input gas mixture. To date, the precise reaction mechanisms attributable to these observations have not been studied in detail. Although various mechanisms have been proposed involving gas-phase and/or gas–solid reactions [16,17], it is difficult to draw any parallels between them since very different source gas mixtures were being used. In many cases however, the amount of nitrogen incorporated into the diamond films was found to be very low [6,16,17], regardless of the choice of precursors used, which suggests that the growth mechanism is likely to be dominated by gas-phase chemistry rather than gas–solid heterogeneous reactions. In this article we report on the behaviour of nitrogen in hot filament-assisted CVD of diamond in terms of the changes in the gas-phase chemistry when nitrogen is present, using various C/N-containing source gases. In situ molecular beam mass spectrometry [18,19] was used to characterise the gas-phase environment, and to determine the mole fractions of the stable gas-phase species prevalent during the CVD process. Such information provides valuable understanding of the reaction mechanisms involved when nitrogen is added to the gas mixtures.

2. Experimental details

Diamond deposition was carried out on silicon (100) substrates (previously abraded with 1–3-μm diamond powder) in a standard hot filament CVD reactor, employing a heated 0.25-mm thick coiled tantalum wire to activate the gas mixtures. The gas flows (total = 200 sccm) were regulated by calibrated mass flow controllers (Tylan General), and the total gas pressure was held at 20 Torr during all deposition experiments. The filament was electrically heated to 2400°C, and positioned 4 mm above the substrate surface. The Si substrates were heated independently to 900°C by a resistive wire heater. For these conditions, and using a gas mixture of 0.5% CH_4 in H_2, typical growth rates of microcrystalline CVD diamond were $\sim 0.35\ \mu m\ h^{-1}$.

In the present study, methane was replaced with a variety of C- and/or N-containing precursor gases, always ensuring a constant C:N ratio of 1:1. The C/N source gases were introduced into the reaction chamber in three different forms: (1) the C and N present in separate small molecules, such as CH_4+NH_3 (or N_2); (2) the C and N bonded together in the same molecule, as in methylamine (CH_3NH_2); and (3) the C and N present as $C{\equiv}N$ in hydrogen cyanide gas (HCN). All the precursors were obtained as commercial products except for HCN, which was synthesised by the reaction of NaCN with phosphoric acid (dried by addition of P_2O_5) in vacuo.

The as-grown films were investigated by scanning electron microscope (SEM) and Auger electron spectroscopy (AES). Secondary ion mass spectroscopy (SIMS) was also carried out on the films produced by $CH_4/N_2/H_2$ gas mixtures. The composition of films produced by the other C/N precursor gases has been determined using other spectroscopic techniques, such as transmission electron microscopy (TEM), X-ray diffraction (XRD) and laser Raman Spectroscopy (LRS), and is reported elsewhere [20]. Quantitative measurements of the composition of the gas-phase species prevalent during diamond deposition were obtained using a quadrupole mass spectrometer (Hiden Analytical HAL/3F PIC 1000), which has been optimised to sample from a hot filament CVD reactor operating at 20 Torr [18]. The absolute concentrations of the stable species are determined by direct room temperature calibration of mixtures of known composition. A detailed description of the MBMS design and the data collection and reduction procedures enabling quantitative analysis of the gas-phase species is available from our earlier report [18].

3. Results and discussion

Electron micrographs of diamond films grown on silicon (100) using various C/N source gases are shown in Fig. 1, and the growth rates (Table 1) were calculated from the film thickness, determined from cross-sectional SEM images, divided by the time of growth (usually 6 h). The deposition rate and resulting film quality at optimum growth temperature (2400°C) depended on the choice of C/N precursor used. For a 1:1 C/N ratio in the feed gas, continuous films were produced only by CH_4/N_2 mixtures, showing predominantly (100) diamond facets (Fig. 1(d)). AES analysis of these films indicated that reasonable quality diamond was deposited; however, no nitrogen was detected in the bulk of the films, suggesting very low nitrogen doping efficiency. This is consistent with the model of film growth predicted by Jin and Moustakas which involves simultaneous deposition and etching [6]. SIMS analysis, which is much more sensitive to nitrogen than AES, detected

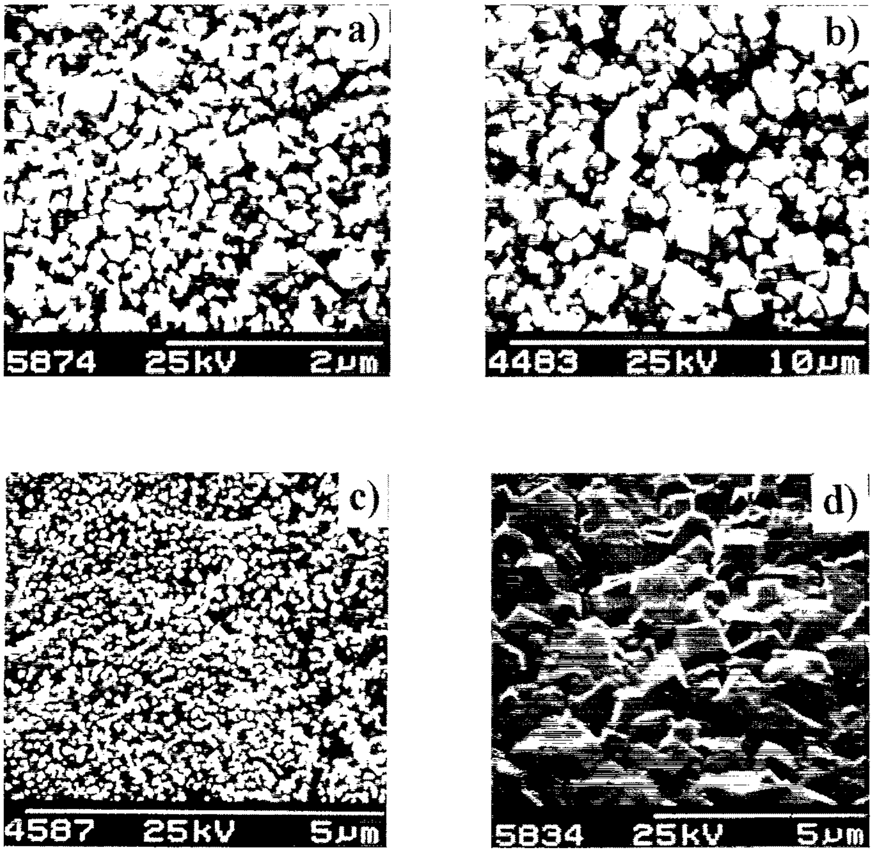

Fig. 1. Scanning electron micrograph of diamond film grown on silicon after 6 h growth using input gas mixtures of: (a) 0.5% CH_4/0.5% NH_3 in H_2, showing isolated diamond crystals; (b) 0.5% CH_3NH_2 in H_2, showing similar surface morphology as in (a); (c) 0.5% HCN in H_2, showing isolated diamond nanocrystals; and (d) 0.5% CH_4/0.25% N_2 in H_2, showing a continuous diamond film with predominantly [100] crystal facets. Note that the C:N ratio for all precursors is 1:1.

Table 1
Diamond growth rates and relative concentrations of major stable species measured at filament temperatures (2400°C) for different C/N source gases

C/N precursor gas	Growth rate (µm h^{-1})	CH_4	NH_3	C_2H_2	HCN	CH_3NH_2
0.5% CH_4/0.5% NH_3	<0.07	25	18	2	77	0
0.5% CH_3NH_2	~0.05	16	28	1	73	4
0.5% HCN	<0.10	13	5	2	90	0
0.5% CH_4/0.25% N_2	~0.45	27	60	21	20	26
0.5% CH_4	~0.35	30	–	24	–	–

only very small amounts of nitrogen in the films, consistent with results obtained from Hong et al. [17]. A more detailed account of the film analysis produced by $CH_4/H_2/N_2$ precursor gases is in preparation [21].

3.1. *Gas-phase composition versus filament temperature for methane + ammonia mixtures*

Fig. 2(a) shows how the mole fractions of the major carbon and nitrogen containing species gases (CH_4 ($m/e=16$), NH_3 ($m/e=17$), C_2H_2 ($m/e=26$) and HCN ($m/e=27$)) vary as a function of filament temperature for an initial feedstock of 0.5% CH_4+0.5% NH_3 in H_2 measured 4 mm from the filament. The deposition rate under optimum growth conditions is very low (<0.07 µm h^{-1}), because the dominant gas-phase reactions occurring between the C-containing and N-containing species have the effect of "locking up" the carbon in the form of the stable cyanide product, HCN. The CH_4 concentration steadily decreases with increasing filament temperature, whilst the NH_3 concentration drops sharply at ~1600°C. The absolute concentrations of the two precursor gases in the vicinity of the filament decrease, not only as a result of chemical reactions but also because of thermal diffusion effects inherent in multicomponent gas mixtures [18], whereby any temperature gradient induces the heavier species in the mixture to move away from the higher temperature regions. At

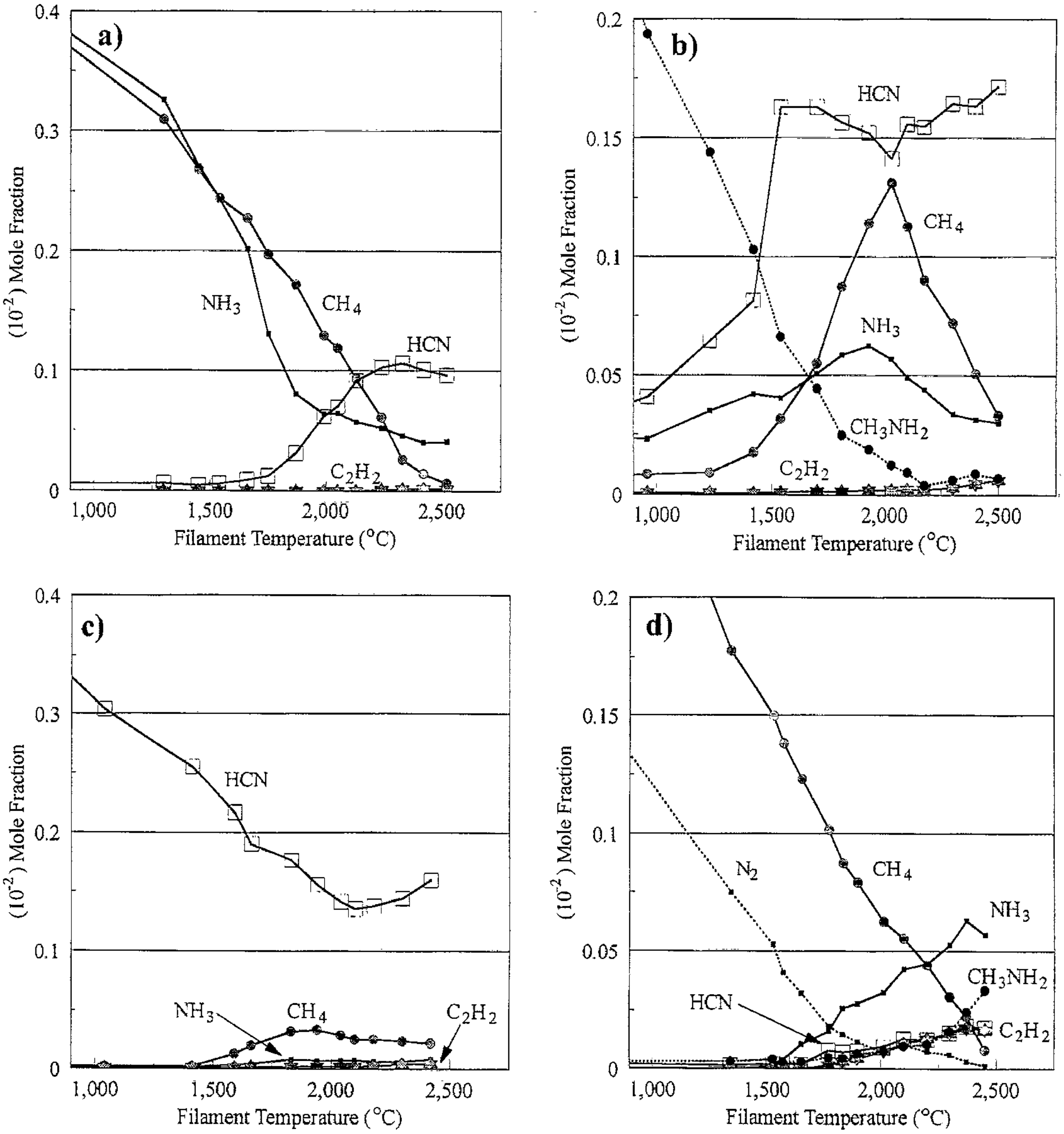

Fig. 2. Product distribution of major stable gas-phase species as a function of filament temperature measured 4 mm from the filament using: (a) 0.5% CH_4/0.5% NH_3, (b) 0.5% CH_3NH_2, (c) 0.5% HCN and (d) 0.5% CH_4/0.5% N_2 in H_2 as input gas mixture (CH_4 (——●——), NH_3 (——■——), C_2H_2 (——★——), HCN (——□——), N_2 (- - -■- - -) and CH_3NH_2 (- - -●- - -)). The species concentrations are presented with no correction being made for the effects of thermal diffusion. N.B., the *y*-axis scale for (b) and (d) is exactly half that of (a) and (c).

~1900°C filament temperature, the HCN concentration increases rapidly, reaching a maximum value at the growth temperature (2400°C), significantly higher than that of either of the two precursor gases. It is interesting to note that very little N_2 was detected; most of the N is locked up either as unreacted NH_3 or HCN (see Table 1).

A prerequisite for the formation of HCN is the reaction between the C- and N-containing precursor gases to create an initial C–N bond. This requires the presence of $CH_3^{\cdot}$ and/or $NH_2^{\cdot}$ radicals. These species could result from pyrolysis of the parent hydride or by H abstraction from methane and ammonia by H atoms created at the filament as a result of the thermal dissociation of H_2. Inspection of the available kinetic data [22] suggests that, at all filament temperatures, pyrolysis of NH_3 is the dominant source of $NH_2^{\cdot}$, and that both of the two reactions mentioned above contribute comparable amounts to the $CH_3^{\cdot}$ yield. Furthermore, the data show that at all relevant temperatures the steady-state NH_2 concentration exceeds $[CH_3^{\cdot}]$ by one or two orders of magnitude. These radicals can then undergo the following reactions:

$$CH_4 + NH_2^{\cdot} \rightleftharpoons CH_3NH_2 + H^{\cdot} \qquad (1)$$

$$CH_3^{\cdot} + NH_3 \rightleftharpoons CH_3NH_2 + H^{\cdot} \qquad (2)$$

both producing methylamine, and hence the vital C–N bond. The sharper decrease observed for the NH_3 concentration at lower temperatures is consistent with our findings that $[NH_2^{\cdot}] \gg [CH_3^{\cdot}]$ and therefore that reaction (1) is the preferred route to methylamine formation. Once formed, the methylamine can either redissociate or, more probably, undergo successive H abstractions to produce HCN:

$$CH_3NH_2 \overset{-H}{\dashrightarrow} \overset{-H}{\dashrightarrow} CH_2{=}NH \overset{-H}{\dashrightarrow} \overset{-H}{\dashrightarrow} HC{\equiv}N \qquad (3)$$

This reaction is thermodynamically favourable due to the stability of the $C{\equiv}N$ bond. No gas-phase methylamine or $CH_2{=}NH$ were detected in these particular experiments, owing to their thermodynamic instability (and thus very low steady-state concentration) in the presence of high H atom concentrations, [H]. Qualitatively, the chemistry leading to HCN production is analogous to that for acetylene, which is the most stable hydrocarbon product when using standard hydrocarbon/H_2 mixtures and growth temperatures, regardless of the choice of hydrocarbon precursor used [19]. For a CH_4/H_2 gas mixture, the reaction is initiated by the "cracking" of methane (by hydrogen abstraction) to produce CH_3 radicals. In such a case, where no $NH_2^{\cdot}$ radicals are present, there is a greater steady-state $[CH_3^{\cdot}]$ and the increased likelihood of methyl recombination, followed by consecutive H abstractions yields larger $[C_2H_2]$. Since the formation of $[C_2H_2]$ depends on $k[CH_3]^2$, the detection of large amounts of gas-phase acetylene in a hot filament CVD reactor is generally taken as an indicator of steady state $[CH_3^{\cdot}]$, and thus of fast diamond film growth. Inspection of Fig. 2(a) shows that for a CH_4/NH_3 gas mixture, reactions leading to the formation of both $HC{\equiv}CH$ and $HC{\equiv}N$ are possible, though acetylene was detected in only very small quantities. This implies that the above reaction scheme ((1) and/or (2), followed by (3)) is the preferred route, leading to HCN formation. Furthermore, the presence of surplus $NH_2^{\cdot}$ radicals at lower temperatures reduces the effective concentration of CH_x species, thus suppressing diamond deposition.

Quantitative measurements of the same gas-phase species were performed with different CH_4/NH_3 ratios, but still maintaining the total at 1% in H_2. In a methane-rich mixture (e.g., 3:1 C/N ratio) the product distribution versus filament temperature shows similar trends to that observed for a 1:1 stoichiometric mixture, except for a considerable increase in the absolute acetylene concentration at growth temperatures, consistent with higher diamond deposition rates [19,20]. However, the HCN concentration, and its variation with filament temperature, did not change with increasing $[CH_4]$ in the source gas mixture, because the formation of HCN is limited by the amount of NH_3 in the feed gas. Almost all the NH_3 is converted to HCN, thus enabling any excess methane in the gas-phase to take part in reactions leading to acetylene formation, and hence diamond deposition. In an ammonia-rich mixture (e.g., 1:3 C/N ratio), $NH_2^{\cdot}$ radicals are present in much larger quantities and, as a result, reaction with CH_4 will occur more readily forming CH_3NH_2 and ultimately HCN. The prevalence of reaction (1) is therefore likely to account for the fact that no acetylene was detected at any given filament temperature and, consequently, no diamond deposition occurred. To a lesser extent, ammonia gas itself also has a negative effect on the deposition rate because it is capable of etching diamond from a growing surface during CVD [20].

3.2. *Gas-phase composition versus filament temperature for methylamine mixtures*

The product distribution of the major stable species (CH_4, NH_3, C_2H_2, HCN and CH_3NH_2 ($m/e=31$)) versus filament temperature for a 0.5% CH_3NH_2 initial feedstock in H_2 is shown in Fig. 2(b). Here, the methylamine concentration diminishes rapidly at 1300°C, and above 1800°C almost all the CH_3NH_2 has disappeared, either via reaction with H atoms (the reverse of reactions (1) and (2)) producing CH_4 and NH_3, or via H atom abstraction producing HCN. At filament temperatures of ~2000°C the methane and ammonia concentrations reach peak values. Above 2000°C their absolute concentrations decrease because of thermal diffusion effects as well as chemical reactions (1) to (3) to form HCN. It is interesting to note the sharp rise in the HCN concentration at lower filament temperatures. This may be due to the inherent C–N bond in the methylamine molecule which can convert readily to HCN in the presence of H atoms, since the requirement of C–N bond formation via reactions (1) and (2) is by-passed. These reactions rely not only on the production of CH_3 and NH_2 radicals, which takes place at relatively high filament temperatures (~1700°C), but also on the relatively low probability step of the two precursor species meeting and reacting together. Competing reactions, such as acetylene formation, are also significantly reduced, due to the ease by which HCN is formed, thus accounting for the low deposition rate observed ($\sim 0.05\ \mu m\ h^{-1}$). In addition, at filament temperatures at and above 2000°C, there is a secondary increase in [HCN] when reactions (1) and (2) take place, between the C- and N-containing species.

3.3. *Gas-phase composition versus filament temperature for hydrogen cyanide mixtures*

Fig. 2(c) shows how the gas composition for an initial feedstock of 0.5% HCN changes versus filament temperature. Compared to ammonia and methylamine, a much more gradual decrease in the HCN concentration is observed as a function of filament temperature, owing to its thermodynamic stability. Thermal diffusion effects account for most of the reduction in the absolute concentration measured as a function of filament temperature. However, the fact that diamond could be deposited using hydrogen cyanide gas shows that some cycling of the carbon must be occurring, and evidence for this is shown in the detection of trace amounts of CH_4, NH_3 and C_2H_2. The deposition rate is again very low ($<0.1\ \mu m\ h^{-1}$) due to the preferential regeneration of HCN by reactions between the C- and N-containing species at higher temperatures.

3.4. Gas-phase composition versus filament temperature for methane + nitrogen mixtures

Fig. 2(d) shows the characterisation of the gas-phase environment and its variation with filament temperature for an initial feedstock of 0.5% CH_4/0.25% N_2 in H_2, such that the C:N ratio is again maintained at 1:1 during analysis. The methane and nitrogen concentrations decrease steadily with filament temperature, accompanied by a rise in HCN, C_2H_2, CH_3NH_2 and NH_3 concentrations at ~1700°C. The attenuation of the absolute mole fractions measured for both precursors with increasing filament temperature is again largely a result of thermal diffusion effects. Comparison of the relative concentrations of these major stable species measured at optimum filament temperatures (see Table 1) indicates that for a CH_4/N_2 gas mixture, the acetylene concentration is around an order of magnitude greater than that of the other C/N precursor gases, whilst the HCN concentration is reduced by a factor of ~4. The prevalent N-containing species in the gas-phase is NH_3, not HCN. The differences in the species composition can be explained in terms of the effects N_2 molecules have on the gas-phase chemistry and the way in which the C is locked up in the CVD process at different temperatures.

At lower temperatures (~1600°C), unlike CH_4/NH_3 gas mixtures, very few NH_2 radicals will form because the dissociation of the strong N≡N bonds requires much more energy. However, CH_3 radicals will arise from the H + CH_4 abstraction reaction as in the normal hydrocarbon/H_2 CVD process, and be free to undergo recombination and H abstraction reactions to form acetylene. The result is that not only the formation of HCN is reduced (because reactions (1) to (3) are now terminated), but competing C_1 reactions to produce C_2 species are far less restrained. Thus, at lower temperatures, N_2 is seen as being virtually a spectator to the CVD process.

At higher temperatures (>1600°C), addition of N_2 results in a slightly higher deposition rate (Table 2) but of poorer quality diamond (as determined by LRS). This is consistent with the results obtained by Jin and Moustakas [6], when using similar amounts of N_2 in the feed gas. We suggest that this can be explained if N_2 is acting as a catalyst, effectively scavenging H atoms and returning them to the gas system as H_2. This will be a multi-step process, such as:

$$N_2 + H^{\cdot} + M \rightleftharpoons N_2H^{\cdot} + M \quad (4)$$

$$N_2H^{\cdot} + H^{\cdot} \rightleftharpoons N_2 + H_2 \quad (5)$$

$$N_2H^{\cdot} + H^{\cdot} \overset{M}{\rightleftharpoons} N_2H_2 \quad (M = N_2/H_2) \quad (6)$$

Similar subsequent hydrogenation reactions will occur to produce N_2H_4. All of these reaction steps are reversible, but would require H abstraction, initiated by yet another H atom to occur. For example:

$$N_2H_4 + H^{\cdot} \rightarrow N_2H_3^{\cdot} + H_2 \quad (7)$$

The net effect is that the introduction of only a small amount of N_2 in the system (<0.5%) removes a significant amount of H atoms, thereby slowing all the subsequent gas-phase chemistry. Thus all the reactions which depend upon high H atom concentrations will be reduced (e.g., reactions (1) to (3)), resulting in the observed depletion in HCN compared to the amounts seen with the other gas additions. The unusually high methylamine concentration observed at high filament temperatures can also be explained by the fact that the attenuation of H atom concentration reduces the effective H abstraction reactions of existing methylamine species, thus allowing higher steady-state concentrations. Additional MBMS measurements [21] show that increasing the N_2 concentration (for a given C/H_2 mixture) further suppresses HCN, while allowing the presence of increasing concentrations of both NH_3 and CH_3NH_2. This theory is in good agreement with observations of Hong et al. [17] who found that the amount of atomic hydrogen decreased relative to the increase of nitrogen.

The rates for reactions (4) and (5) at standard growth

Table 2
Bond dissociation energies

Bond	Bond strength (kJ mol^{-1})
H–H	435.9
N≡N	945.4
C≡C	838.0
H–NH_2	442.0
H–CH_3	435.0
C–N	286.0
C=N	615.0
C≡N	887.0
C–C	347.0

Taken from Ref. [23], except for H–NH_2, which is taken from Ref. [22].

temperatures are 10^{12} to 10^{13} $cm^3 mol^{-1} s^{-1}$ [24], which are similar in magnitude to that for most of the other nitrogen gas-phase reactions in this system [25]. This means that reactions (4) and (5) can take place readily under the process conditions. Indeed, Bozzelli and Dean [24] state that when the H atom mole fraction is high, i.e., under high temperature reaction conditions, N_2H formation from $H+N_2$ is very rapid. The result is equilibrium, or near equilibrium, concentrations of N_2H which are high enough to undergo bimolecular reactions with other important radical species, in our case hydrogen atoms, $H^{\cdot}$. The driving force in this rapid cycling of $N_2 \rightarrow N_2H \rightarrow N_2$ is the very strong and stable $N \equiv N$ bond. However, inspection of Fig. 2(d) shows that less thermodynamically favourable side reactions do occur to produce NH_3, CH_3NH_2 and ultimately HCN.

Further supporting evidence for the H atom depletion mechanism is provided by the fact that, with increasing N_2 concentrations, our resulting diamond films were of poorer quality than those without N_2 addition, as evidenced by LRS. This is consistent with there being a reduction in the H atoms required to etch away the non-diamond phases on the film surface. Hong et al. [17] also found that increasing the N_2 concentration reduces the growth rate, partly as a result of the additional etching caused by NH_3, but probably also because of a decrease in available atomic H.

4. Conclusions

The effects of nitrogen on the CVD diamond growth mechanism have been investigated using in situ molecular beam mass spectrometry. The deposition rate at optimum growth conditions depends critically on the choice of C/N precursor used, and the origin of the carbon-containing species. The reactions occurring in the gas-phase seem to lead predominantly to the formation of HCN (except for CH_4/N_2 gas mixtures). The stability of this species precludes most of the cycling of carbon during the CVD process, resulting in low rates of diamond deposition. Thermodynamic equilibrium calculations [9] confirm that HCN production is highly favoured in H/C/N gas mixtures at high gas processing temperatures.

For a 1:1 C:N ratio in the feed gas, continuous films were produced after 6 h deposition only by $CH_4/H_2/N_2$ gas mixtures. Incorporation of nitrogen in the grown diamond films was very low, consistent with the conclusions of Jin and Moustakas [6], who calculated a theoretical value for the doping efficiency of nitrogen in diamond of around 10^{-4}. At lower temperatures N_2 simply acts as a spectator to the CVD process, as evidenced by the significant increase in the C_2H_2 concentration and reduction in the HCN concentration in the gas-phase compared to other N source gas additions. At optimum filament temperatures ($\sim 2400°C$), addition of N_2 to a CH_4/H_2 gas mixture leads to higher deposition rates of poor quality diamond films (determined by LRS). We believe that this can be explained if N_2 is acting as a catalyst for the destruction of H atoms, thereby reducing the etching rate of non-diamond phases on the film surface. Thus addition of a tiny amount of N_2 to the hot filament CVD process will affect not only the gas-phase chemistry, but the growth rate, the morphology and the quality of the resulting diamond films. One consequence of this is that diamond CVD process may be more dependent on gas purity and ultimate vacuum than has often been appreciated.

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