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Gas-phase concentration measurements and diamond film composition from chlorine assisted CVD

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Abstract

Molecular beam mass spectrometry has been used to obtain quantitative measurements of the composition of the gas-phase species prevailing during diamond chemical vapour deposition (CVD) using a variety of chlorine containing source gases. Gas mixtures used were 1% of a chlorinated methane ($CH_{4-n}Cl_n$, $n=1$–4) in H_2 and 1% CH_4 in H_2 with added chlorine varying from 1%–4%. At filament temperatures optimum for diamond growth (≈2300 °C) the relative concentrations of the various hydrocarbon species (CH_4, C_2H_2, C_2H_4) in the gas mixture are remarkably similar to those measured when the carbon precursor species is CH_4. At these filament temperatures almost all the chlorine is reduced to HCl, its concentration being proportional to the chlorine fraction in the source gas, regardless of the form of the chlorine in the input mixture. Auger electron spectroscopy analysis of the as-grown diamond films indicated that no chlorine was present in the bulk of the films, though trace amounts of chlorine were detected on the film surface. These observations are consistent with the supposition that chlorine atoms are involved in the gas-surface reactions which produce active growth sites on the diamond surface.

Keywords: Diamond CVD; Chlorine; Gas phase chemistry; Mass spectrometry

1. Introduction

One persisting limitation of the growth of high quality diamond films by chemical vapour deposition (CVD) using carbon/hydrogen gas mixtures is the requirement to maintain substrate temperatures at or near to 900 °C. At significantly lower temperatures growth rates and quality are compromised. Modification of the standard CVD process to deposit quality films at lower substrate temperatures would enable coating of a larger range of substrate materials, including lower melting point substances such as aluminium, thereby increasing the number of potential applications for diamond films.

Recently there has been considerable interest in reduced temperature diamond deposition using either chlorine containing source gases, e.g. $CH_{4-n}Cl_n$ ($n=1$–4) in excess hydrogen [1–5] or by the addition of small amounts of Cl_2 [6] or HCl [7] to the standard methane/hydrogen source gas mixture. These studies indicate that the presence of Cl, in concentrations of the order of a few percent in the C/H_2 input mixture, can cause some increase in diamond growth rates at normal substrate temperatures (900 °C). Furthermore, the enhancement in growth rates relative to the standard C/H mixtures is significantly enhanced at lower substrate temperatures. For example, the addition of 1.75% HCl to 0.5% CH_4 in H_2 has been reported to double the growth rate at 670 °C [7].

The precise reaction mechanisms leading to the apparent catalytic activity of chlorine in the deposition process have yet to be studied in detail: this is the subject of the present work. Two basic mechanisms have been proposed: one relies on changes in the gas-phase chemistry, whereby the presence of chlorine in the reaction mixture enhances the production of methyl (CH_3) radicals and enables formation of chloromethyl radicals. The latter species has been suggested as a more effective growth precursor than CH_3 because of the ease of dehydrochlorination reactions on the diamond surface [1,2]. The other, invokes a change in the gas-surface chemistry whereby abstraction of surface terminating C–H by atomic Cl, or removal of surface adsorbed Cl by H atoms, has a significantly lower activation energy than

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H abstraction of surface hydrogen [7]. Active surface growth sites are thereby created at lower substrate temperatures.

In order to understand and identify the changes in the reaction mechanisms when chlorine is present in the CVD process we wish to correlate the concentrations of the gas-phase species prevalent during deposition when using $CH_{4-n}Cl_n$ ($n=1-4$) in H_2 or alternatively various concentrations of Cl_2 in CH_4/H_2 as the input gas mixture, with the quality of the resulting diamond films.

2. Experimental details

A standard hot filament CVD reactor was used to deposit diamond on silicon (100) substrates which were maintained at 900 °C. The substrates were manually abraded with 1–3 μm diamond powder prior to deposition. In the present study, methane, the most commonly used hydrocarbon precursor was replaced by: (1) a range of different chloromethanes, $CH_{4-n}Cl_n$ ($n=1$–4), always maintaining a ratio of 1% carbon in H_2; and (2) a mixture containing 1% CH_4 in Cl_2/H_2, the amount of chlorine varying from 1%–4%. The gas flows (total = 100 sccm) were governed using calibrated mass flow controllers (Tylan General) and a chamber pressure of 20 Torr was maintained during the deposition. The precursor gas mixture was activated by a 0.25 mm-thick coiled tantalum filament heated electrically to 2300 °C and placed 4 mm from the Si substrate.

The as-grown diamond films were investigated by scanning electron microscopy (SEM) and Auger electron spectroscopy (AES). The AES analysis was carried out using a Perkin-Elmer PHI 595 scanning Auger microprobe equipped with a double-pass cylindrical analyser. The electron gun was maintained at 3 keV with a beam current of 70 nA and a beam diameter of ≈ 0.3 μm. A base pressure less than 10^{-9} Torr was maintained in the Auger spectrometer chamber during imaging and analysis.

Quantitative measurements of the composition of the gas-phase species present during diamond deposition utilised a differentially pumped molecular beam mass spectrometer (MBMS). Gas from the CVD chamber is sampled through a 100 μm diameter orifice in a stainless steel sampling cone located at the same radial distance from the filament as is the substrate surface. The extracted gas is collimated by a 1 mm diameter skimmer on route to the ionisation source of a quadrupole mass spectrometer (Hiden Analytical). The absolute concentrations of the stable species are determined by direct room temperature calibration of mixtures of known composition. A more detailed description of the MBMS design and the data collection and reduction procedures enabling quantitative analysis of the gas-phase species is available elsewhere [8].

3. Results

3.1. Analysis of the diamond films

Scanning electron micrographs of diamond films grown on silicon when using 1% each of $CH_{4-n}Cl_n$ ($n=1$–4) in H_2 as the process gas mixture are shown in Fig. 1. The SEM images in Fig. 2 show that polycrystalline diamond films were also grown successfully using $CH_4/Cl_2/H_2$ gas mixtures with input ratios of 1:1:98 and 1:2:97. Further increasing the Cl_2 input proportion, to 4%, results in a significant change in the film morphology (see Fig. 2(c)) with a concomitant reduction in the film quality and growth rates.

Fig. 3(a) shows a typical AES spectrum of the diamond film surface grown using a $CH_4/Cl_2/H_2$ gas mixture in the ratio 1:2:97. The fine structure of the *KLL* carbon peak (Fig. 3(b)) is typical of that obtained for natural diamond [9,10]. We note that this peak is slightly shifted to lower energies (by ca. 4 eV) compared with the peak obtained from the very poor quality diamond when 4% Cl_2 was used for growth. This energy shift arises mainly from charging effects on the diamond relative to the more conducting amorphous or graphitic carbon.

Also evident at an electron energy of 178 eV is a small peak indicative of the presence of chlorine on the diamond surface. After argon ion sputtering for 30 s, resulting in etching of the diamond film to a depth of ≈ 120 Å, the chlorine was no longer detectable indicating that this chlorine is present only on the film surface and not in the bulk diamond. The relative intensity of the surface Cl peak suggests a chlorine concentration of $\approx 0.53\%$ which is limited to the top four diamond monolayers, as calculated from the inelastic mean free paths of the detected Auger electrons [11]. Given that the chlorine is present only on the diamond surface then about 2% of the surface carbon atoms are terminated by chlorine rather than hydrogen.

Similar AES results indicating high quality diamond with only a trace of chlorine on the film surface were obtained for all the as-grown films where the Cl atom input fraction was 0.06 or below (i.e. $\leqslant 3\%$ Cl_2 in the process gas mixture). However, for growth conditions where the Cl fraction was greater than 0.06 the fine structure of the *KLL* carbon peak showed that the resulting films were of poor quality with significant deposition of non-diamond carbon phases. We also detect significant amounts of tantalum and chlorine incorporated into the films, indicating degradation of the filament at higher chlorine concentrations.

3.2. Gas-phase composition measurements

Fig. 4(a) shows the way in which the mole fractions of the major carbon and chlorine containing species [CH_4 ($m/e=16$), C_2H_2 ($m/e=26$) and HCl ($m/e=36$)] depend upon the input precursor gas, $CH_{4-n}Cl_n$

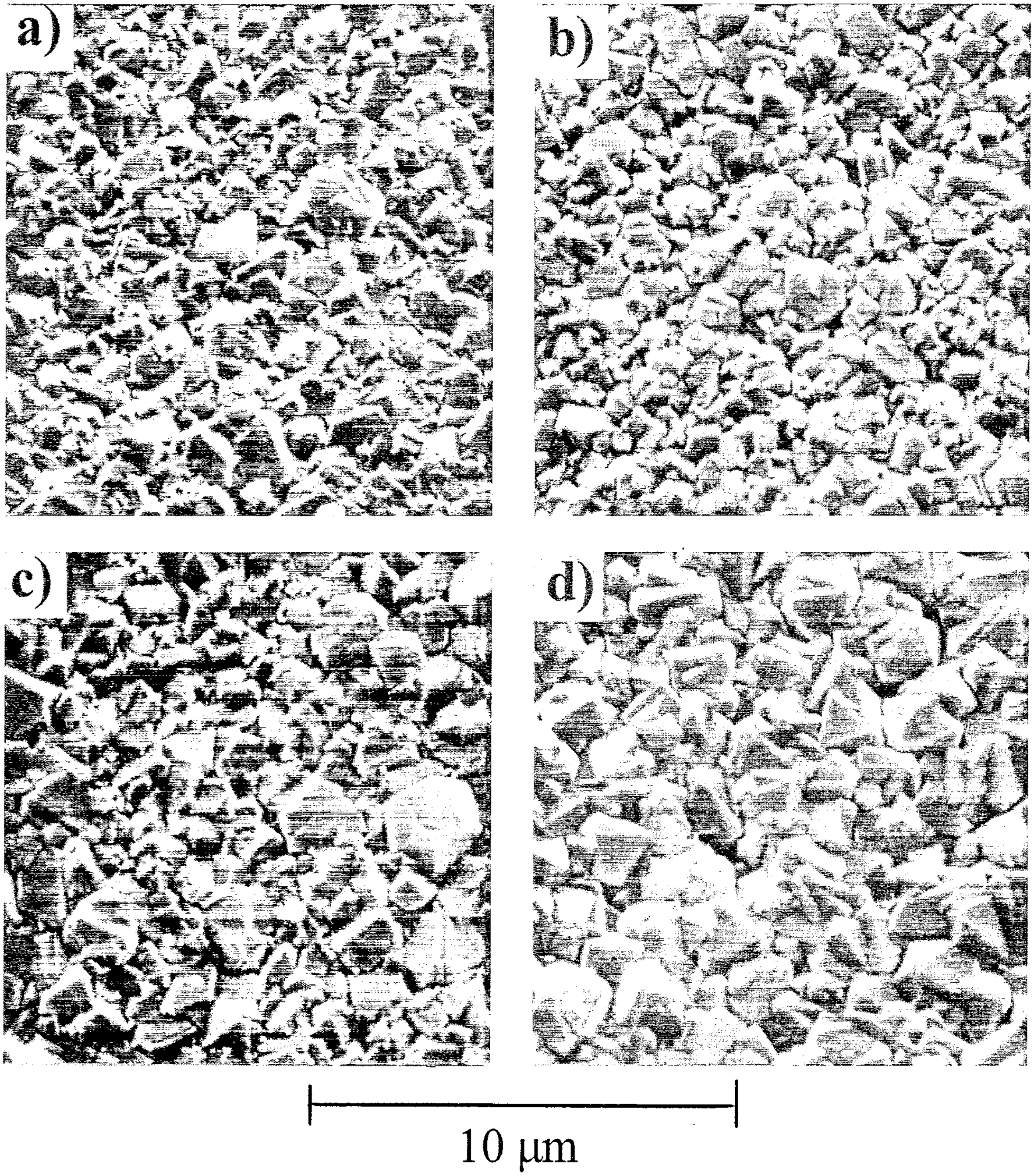


Fig. 1. Electron micrographs of diamond films grown on silicon using input gas mixtures of 1% each of: (a) CH_3Cl; (b) CH_2Cl_2; (c) $CHCl_3$; and (d) CCl_4, in hydrogen.

($n=0$–4). Similarly Fig. 4(b) shows the concentrations of CH_4, C_2H_2 and HCl measured under the same process conditions when the input gas mixture consists of 1% CH_4 seeded in Cl_2/H_2, the molecular chlorine concentration varying from 1%–4% (i.e. 2–8 at.%). It is clear from Figs. 4(a) and 4(b) that both the carbon and chlorine fractions measured are significantly reduced compared with their input concentrations. This is a consequence of thermal diffusion effects in multicomponent gas mixtures whereby any temperature gradient induces the heavier species in the mixture to move away from the higher temperature region [8].

Comparison of Figs. 4(a) and 4(b) indicates that at these filament temperatures (2300 °C) both the chlorocarbon and Cl_2 input precursors are completely dissociated producing HCl in near stoichiometric proportions. Thermal diffusion effects again account for the reduction in the concentration of HCl measured 4 mm from the filament. At such filament temperatures the H atom concentration is of the order of 1%–2% [12] and abstraction of Cl from the relatively weak Cl–Cl and C–Cl bonds (see Table 1) by H atoms to form HCl is predicted on thermodynamic grounds. In fact, reduction of the chloromethanes to produce HCl is observed to

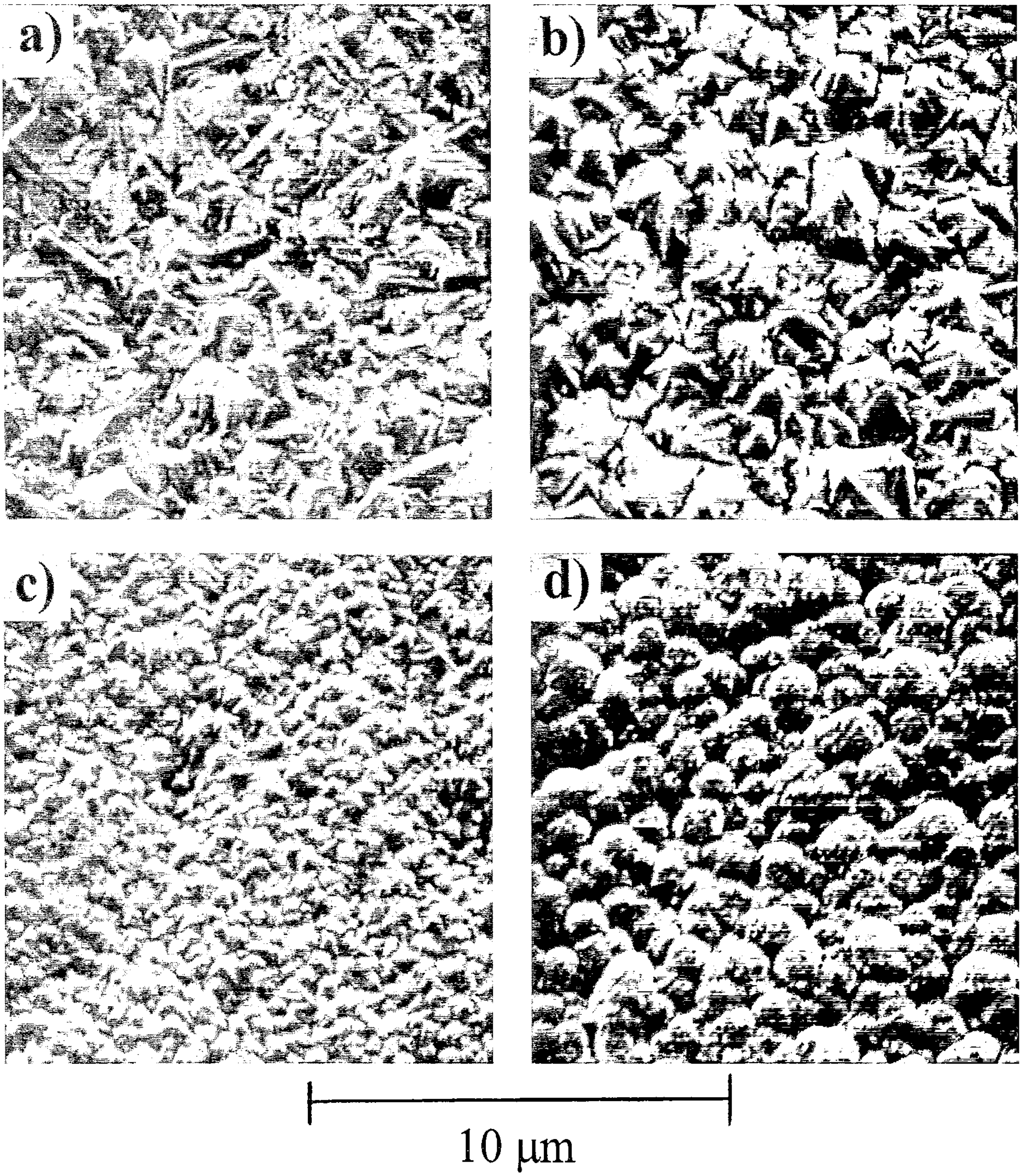


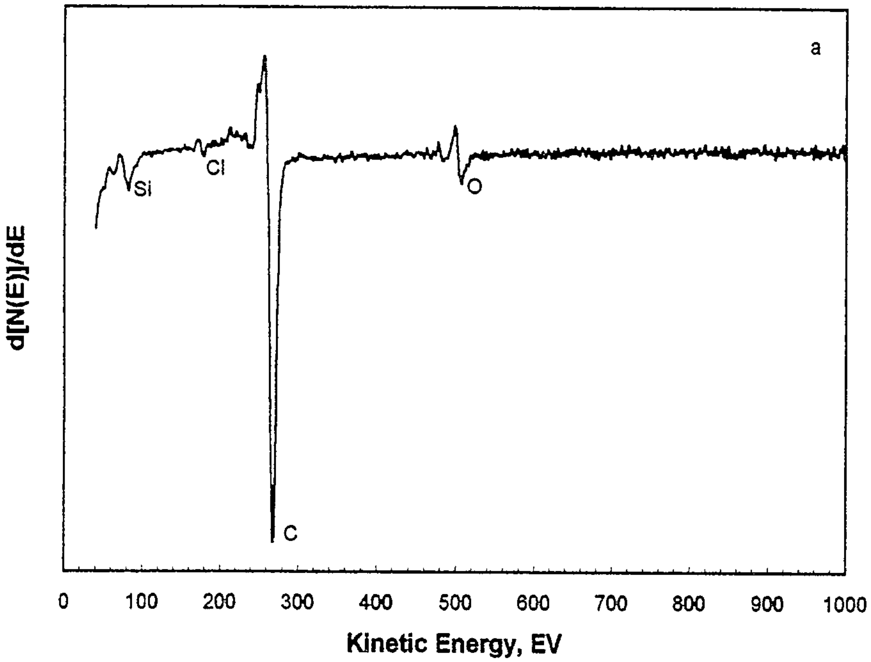
Fig. 2. Diamond films grown on silicon using precursor gas mixtures of 1% CH_4 in H_2 with additional Cl_2: (a) 1%; (b) 2%; (c) 3%; and (d) 4%.

be largely complete at filament temperatures of ≈1800 °C and that of Cl_2 at temperatures less than 900 °C [8].

The breakdown of the chlorocarbon precursors to form HCl produces a concomitant increase in the concentration of methane such that at 2300 °C it is the dominant carbon-containing species. The H atom concentration at these temperatures may also initiate H abstraction from methane yielding significant amounts of methyl (CH_3) radicals. Methyl recombination to form C_2H_6 followed by successive H abstractions produces significant amounts of acetylene (C_2H_2), the other main carbon containing species observed (see Fig. 4). No C_2H_6 and only small concentrations of C_2H_4 were detected, presumably because their thermodynamic instability in the presence of atomic hydrogen leads to low steady-state concentrations. Previous gas-phase composition studies on CH_4/H_2 mixtures [14] indicate that C_2H_2 is the most stable two-carbon species as the H atom concentration increases, and at standard growth temperatures a CH_4 to C_2H_2 ratio of ≈8:1 is observed.

4. Discussion

Diamond films were successfully deposited using standard growth conditions and a number of different



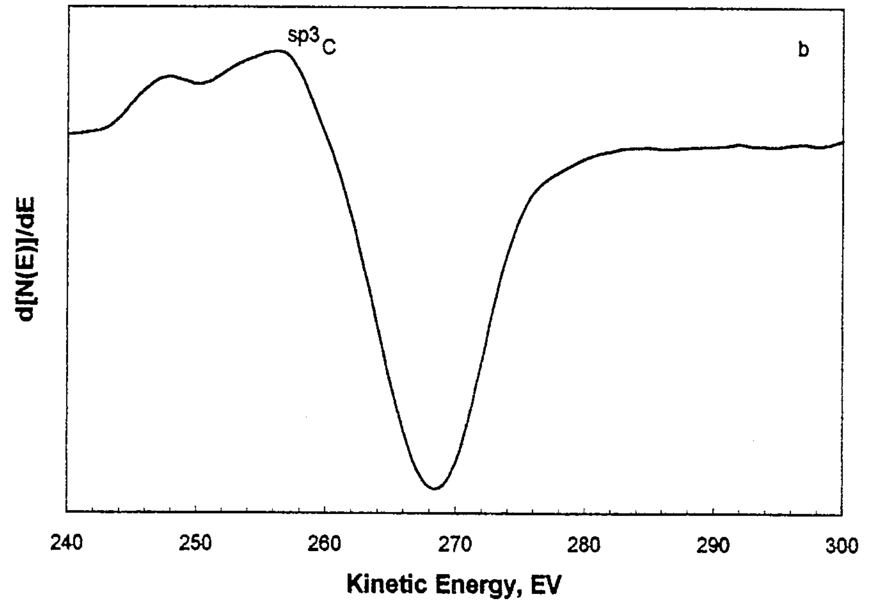


Fig. 3. AES spectra of the diamond film surface shown in Fig. 2(b). The input gas mixture was 1% CH_4 in H_2 with 2% Cl_2 added: (a) wide scan spectrum, the Si and O peaks are from debris on the film surface after the substrate was cleaved in preparation for Auger analysis; (b) expanded spectrum of the sp^3 C region. The film was 2 μm thick.

chlorine containing gas mixtures subject to the relative Cl atom fraction in the input gas being less than ≈0.06. For higher chlorine concentrations only poor quality diamond films were deposited which incorporated significant tantalum and chlorine impurities. These chlorine assisted growth results broadly agree with the diamond growth domain outlined in the C/H/Cl ternary gas-phase composition diagram of Bachmann et al. [15].

As with the higher hydrocarbon input gases in excess H_2 [14] chlorocarbon precursor gases are effectively reduced to methane at standard filament temperatures of ≈2300 °C due to the rapid abstraction of chlorine by thermally produced H atoms. The other major product from this reaction is HCl whose concentration is seen to be directly related to the Cl mole fraction in the source gas. However, the addition of chlorine to the precursor gas mixture, either as a chloromethane or Cl_2, does lead to a slight reduction in the measured [CH_4] which is mirrored by a small increase in C_2H_2 concentrations. This might indicate the existence of transient

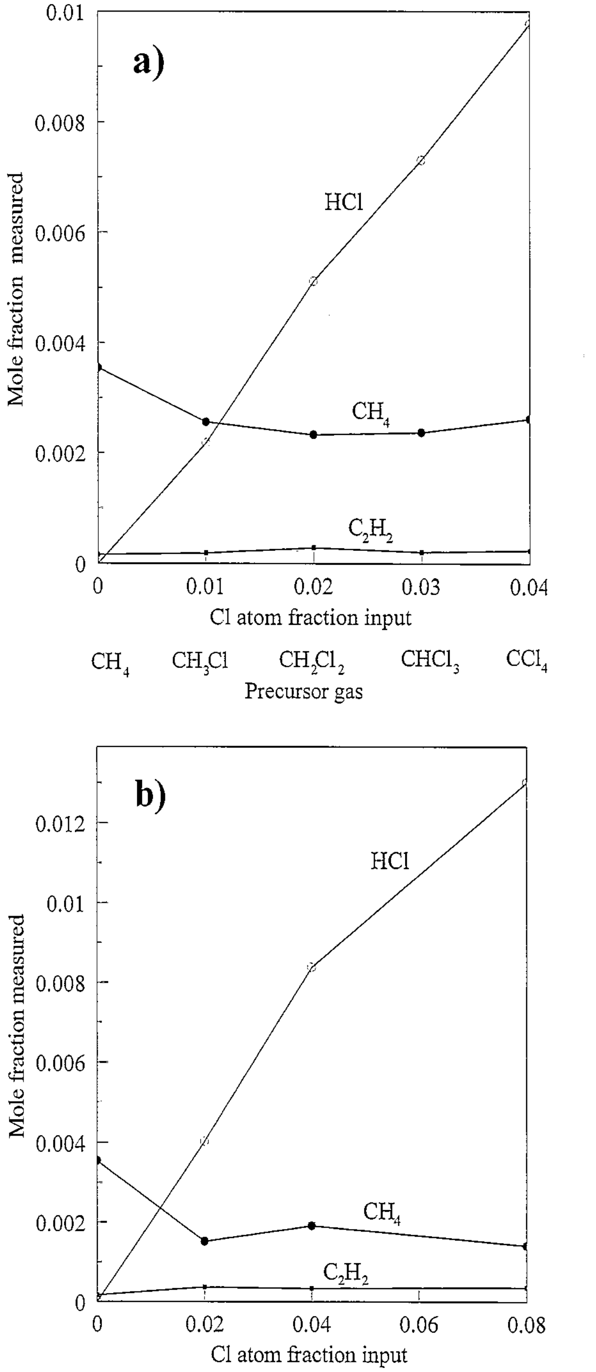


Fig. 4. Gas composition versus Cl atom fraction in the input gas, measured 4 mm from the filament with a filament temperature of 2300 °C. The input gas mixtures consisted of: (a) 1% each of $CH_{4-n}Cl_n$ ($n=0$–4) in hydrogen; and (b) 1% CH_4 in H_2 with additional Cl_2 varying from 0%–4%.

Table 1
Bond strengths (taken from ref. 13)

Bond	Bond strength/kJ mole^{-1}
H–H	432
Cl–Cl	239
H–Cl	428
H–CH_3	435
Cl–CCl_3	305
Cl–$CHCl_2$	331
Cl–CH_3	351

chlorine-containing radical species supplementing the CH_3 radicals as precursors to acetylene formation. However, the instability of such chlorocarbon species relative to HCl in a largely hydrogen atmosphere at 2300 °C lead to their having low steady state concentrations which we are not able to detect with the MBMS. Alternatively, such small concentration changes may simply be the result of changes in the relative rates of thermal diffusion or deviations in the MBMS sampling characteristics when chlorine is introduced into the system.

With the $CH_4/Cl_2/H_2$ gas mixtures at filament temperatures near to the optimum for diamond growth the Cl_2 is found to be entirely reduced to HCl. However, in this case, the MBMS measurements as a function of filament temperature [8] show that it is atomic chlorine produced by thermal dissociation of Cl_2 which reacts rapidly with H_2 to form HCl. Comparison of Figs. 4(a) and 4(b) indicates that the HCl concentration measured 4 mm from the filament is proportional to the Cl fraction in the source gas mixture regardless of the form of chlorine in the input mixture. Furthermore the relative Cl/H atom concentrations in such a HCl/H_2 atmosphere are proportional to the Cl fraction input since atomic Cl and H rapidly equilibrate [1] via

$$H + HCl \rightleftharpoons Cl + H_2$$

At typical substrate temperatures the equilibrium constant for this reaction is close to unity.

The possible changes in reaction mechanisms that might account for the reports of diamond growth at lower temperatures by chlorine activated CVD can be summarised as either: (a) modifications of the gas-phase chemistry enhancing the production of diamond precursor species; or (b) changes in the gas-solid heterogeneous reactions which open up active surface growth sites at reduced substrate temperatures.

Our gas-phase composition measurements show that the concentrations of the major carbon-containing species at typical filament-substrate distances are rather insensitive to variation in the chlorine input fraction. Furthermore, the H atom concentration prevailing at standard deposition temperatures results in the effective reduction of chlorocarbon species to HCl, as expected on thermodynamic grounds. Thus, we consider that neither an enhanced production rate of the CH_3 precursor species nor formation of significant concentrations of chloromethyl radical species are likely explanations for diamond growth at lower substrate temperatures in chlorine assisted CVD.

However, the AES and MBMS results are both consistent with the premise that Cl atoms play some part in gas-surface reactions involved in the production of active surface growth sites at reduced substrate temperatures. Gas-phase kinetic calculations have shown [7] that the rate of hydrogen abstraction by Cl atoms from a (110) diamond surface at 670 °C is some 60 times faster than abstraction by gas-phase H atoms. As indicated above, the Cl atom concentration at standard filament temperatures is directly related to the Cl fraction in the input gas, regardless of the form of the chlorine precursor. We find that if the Cl input fraction is too high (>0.06) the quality of the diamond grown at normal substrate temperatures (≈900 °C) is reduced probably because a large fraction of surface sites are activated, leading to the graphitisation of the diamond surface. However, at lower substrate temperatures the presence of chlorine in the process gas mixture would result in an increased deposition rate due to the greater efficiency of surface hydrogen abstraction by Cl atoms.

5. Conclusions

This report accomplished an understanding in the behaviour and applicability of chlorine-assisted CVD in a hot filament reactor. We found that at filament temperatures at and above the optimum for diamond growth (≈2300 °C), the relative concentrations of the various hydrocarbon species (CH_4, C_2H_2, C_2H_4) in the gas phase are insensitive to the choice of various Cl containing hydrocarbon precursors used. Cl_2 is effectively reduced to HCl at standard growth temperatures, whose concentration is proportional to the chlorine fraction input in the feed gas.

The as-grown diamond films were analysed using AES and SEM techniques. No chlorine was detected in bulk structure of the films but ≈1%–2% was found on the diamond surface. The apparent catalytic activity of Cl atoms in the CVD process is therefore likely to be due to its role in abstracting surface terminating hydrogen or H abstraction of surface C–Cl, at lower substrate temperatures, rather than a gas-phase mechanism.

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References

[1] B.J. Bai, C.J. Chu, D.E. Patterson, R.H. Hague and J.L. Margrave, *J. Mater.Res.*, *8* (1993) 233.

[2] F.C.-N. Hong, G.-T. Liang, J.-J. Wu, D. Chang and J.-C. Hsieh, *Appl. Phys.Lett.*, *63* (1993) 3149.

[3] C.H. Chu and M.H. Hon, *Diamond Relat. Mater.*, *2* (1993) 311.

[4] T. Nagano and N. Shibata, *Jpn. J. Appl. Phys.*, *32*, (1993) 5067.

[5] F.C.-N. Hong, J.-J. Wu, C.-T. Su and S.-H. Yeh, in *Advances in New Diamond Science and Technology*, MYU, Tokyo, 1994, p.85.

[6] C. Pan, C.J. Chu, J.L. Margrave and R.H. Hague, *J. Electrochem. Soc.*, *141* (1994) 3246.

[7] N.J. Komplin, B.J. Bai, C.J. Chu, J.L. Margrave and R.H. Hague, in J.P. Dismukes and K.V. Ravi, (eds.), *Diamond Materials,* Vol.93–17, The Electrochemical Society Proceedings Series, Pennington, NJ, 1993, p. 385.

[8] C.A. Rego, R.S. Tsang, P.W. May, M.N.R. Ashfold and K.N. Rosser, to be published in *J. Appl. Phys.*

[9] P.G. Lurie and J.M. Wilson, *Surface Sci.*, *65* (1977) 476.

[10] Q.S. Chia, C.M. Younes, P.G. Partridge, G.C. Allen, P.W. May and C.A. Rego, *J. Mater. Sci.*, *29* (1994) 6397.

[11] M.P. Seah and W.A. Dench, *Surf. Interface Anal.*, *1* (1979) 2.

[12] D.S. Dandy and M.E. Coltrin, *J. Appl. Phys.*, *76* (1994) 3102.

[13] G.W.C. Kaye and T.H. Laby (eds.), *Tables of Physical and Chemical Constants*, 15th edn., Longman, 1989.

[14] C.A. Rego, P.W. May, C.R. Henderson, M.N.R. Ashfold, K.N. Rosser and N.M. Everitt, *Diamond Relat. Mater.*, *4* (1995) 770.

[15] P.K. Bachmann, H.J. Hagemann, H. Lade, D. Leers, F. Picht, D.U. Wiechert and H.Wilson, *Mat. Res. Soc. Symp. Proc.*, *339* (1994) 267.