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Influence of phosphine on the diamond growth mechanism: a molecular beam mass spectrometric investigation☆

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Abstract

We have used a molecular beam mass spectrometer to investigate the effects of addition of phosphine on the growth behaviour of diamond films in a hot filament chemical vapour deposition (CVD) reactor. Films were grown using gas mixtures of 1% CH_4 with increasing amounts of PH_3 (1000–5000 ppm). Gas phase species prevalent during the growth process (e.g. CH_4, CH_3, C_2H_2, PH_3 and HCP) have been monitored quantitatively and compared with the corresponding growth rates, quality and properties of the resulting films. We find that addition of up to 2000 ppm PH_3 increases the film growth rate by a factor of 2–3, and changes the crystal morphology in favour of (100). At higher PH_3 concentrations (3000–5000 ppm) the growth rate decreases again, with predominantly (111) faceted crystals. These observations are discussed in terms of a model of the gas phase chemistry during the growth process. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Diamond films; Gas phase chemistry; Molecular beam mass spectrometry; Phosphine

1. Introduction

The ability to obtain n-type diamond with reasonable conductivity remains a persistent obstacle towards the development of diamond based-electronic devices. It has already been demonstrated that nitrogen-doped CVD diamond and diamond-like carbon (DLC) films can exhibit semiconducting properties, which could have application in microelectronics and field emission display applications [1–4], though the amount of nitrogen incorporated into the diamond films was found to be very low [5–8]. Phosphorus-doping of CVD diamond [9–15] and diamond-like carbon films [16] has also been achieved to yield semiconductive n-type material using phosphine (PH_3) as a dopant source. Cao et al. [17] also studied the growth of phosphorus and nitrogen co-doped diamond films using a solid compound, ammonium–dihydrogen–phosphate ($NH_4H_2PO_4$), as a dopant. As yet, very little is known about the way in which phosphorus is incorporated into the diamond lattice. According to calculations performed by Kajihara et al. [18], phosphorus has a positive formation energy in diamond ($E_f = 10.4$ eV) which suggests that P incorporation is unlikely to occur under normal CVD process conditions. Nonetheless P incorporation was observed in all cases [9–15]. Furthermore, Spicka et al. [14] found that the experimental doping efficiency (in the range 1 to 1×10^{-3}) of P in the films grown using $CH_4/PH_3/H_2$ gas mixtures was greater than the theoretical value calculated by Jin et al. (1×10^{-4}) [6]. These papers have gained even more importance with the recent report by Koizumi et al. [19] of successful n-doping of diamond using PH_3 as a gas additive to their standard mixture of 0.15% CH_4 in H_2. Hall effect measurements indicated that the resulting films showed n-type conduction over a wide temperature range.

Despite this, detailed attempts to investigate the influence of phosphorus addition on diamond CVD have, to date, only been made by Bohr et al. [11], who discovered that introduction of small amounts of PH_3 to the standard 1% CH_4/H_2 gas mixture during the CVD process caused significant changes in the morphology, the quality and the growth rate of the resulting diamond films. The precise reaction mechanisms attributable to these observations, however, have not been studied in detail: this is the subject of the present work. Bohr et al. [11] suggested that P additions influenced the growth kinetics as a result of surface reactions, rather than changes occurring in the gas activation. Furthermore,

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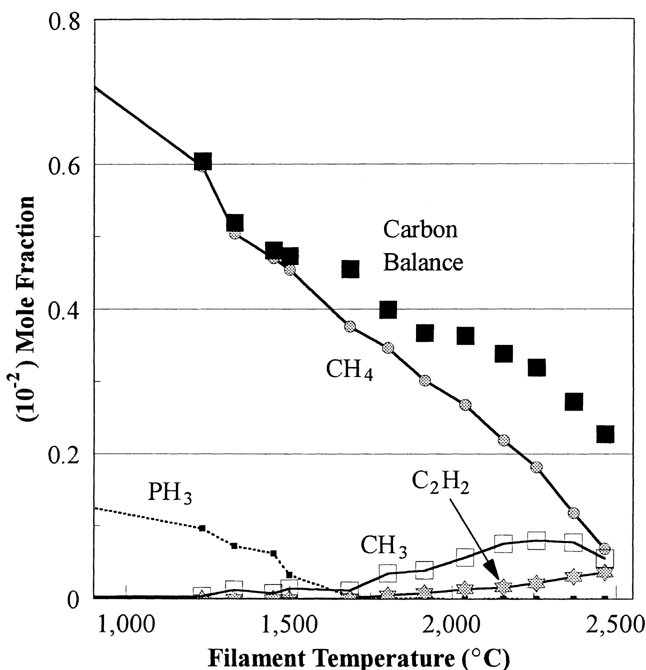


Fig. 1. Product distribution of major gas-phase species as a function of filament temperature measured 4 mm from the filament using 1% CH_4/0.2% PH_3 in H_2 as the input gas mixture (●, CH_4; ■, PH_3; ★, C_2H_2; and □, CH_3). The species concentrations are presented with no correction being made for the effects of thermal diffusion. The total carbon balance is indicated by ■.

they suggested on the basis of thermodynamic calculations that methinophosphide (HCP) was probably responsible for the deleterious P influences.

In this article we report on the behaviour of phosphine in hot filament assisted CVD of diamond in terms of the changes in the gas-phase chemistry when phosphine is present, using gas mixtures of 1% CH_4 with increasing amounts of PH_3 (1000–5000 ppm). In situ molecular beam mass spectrometry [20,21] was used to characterize the gas-phase environment, and to determine the mole fractions of the stable gas-phase species prevalent during the CVD process.

2. Experimental

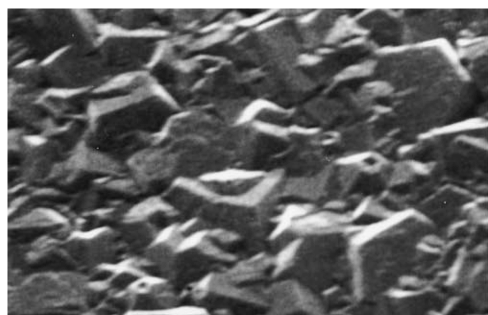
A standard hot filament CVD reactor was used to deposit diamond on silicon (100) substrates which were maintained at 900 °C. The substrates were manually abraded with 1–3 μm diamond powder prior to deposition. Films were grown using gas mixtures of 1% CH_4 with increasing amounts of PH_3 (1000–5000 ppm). The gas flows (total = 100 sccm) were governed using calibrated mass flow controllers, 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 films were investigated by scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and laser Raman spectroscopy (LRS). The LRS analysis was carried out using a Renishaw Raman System 2000 operating at an excitation wavelength of 514.5 nm. Quantitative measurements of the composition of the gas-phase species present during diamond deposition utilized 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 ionization source of a quadrupole mass spectrometer (Hiden Analytical). 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 [20]. An example of the data obtained in this way for the stable species CH_4, C_2H_2, PH_3 and for CH_3 radicals is shown in Fig. 1.

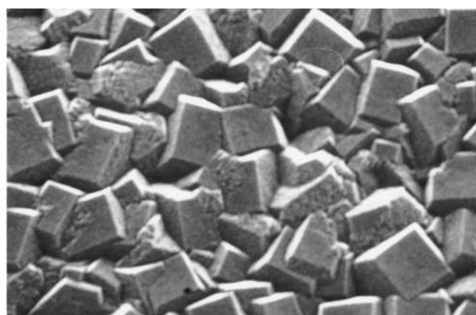
3. Results

3.1. Analysis of the films

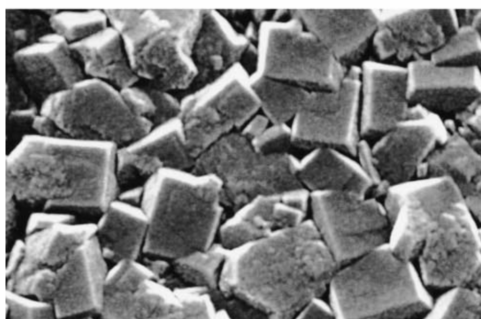
Scanning electron micrographs of films grown on Si (100) using 1% CH_4/H_2 with varying amounts of PH_3 as input gas mixtures are shown in Fig. 2. The film growth rates (Fig. 3) were calculated from the film thickness, determined from cross-sectional SEM images, divided by the time of growth (usually 6 h). The film growth rate increased with the addition of phosphorus, reaching a maximum value of 0.95 μm h^{-1} observed at a phosphine concentration of ~2000 ppm in the gas phase. The observed trend in the film growth rates as a function of [PH_3] in the input source gas mixture is consistent with Bohr et al. [11] who found similar characteristic maxima depending on the time of deposition. The crystal morphology changed from octahedral (111) facets (at 0 ppm PH_3) to predominantly square (100) facets at low [PH_3] (up to 2000 ppm). Higher phosphine concentrations caused a reversal in crystal morphology back to (111) facets. AES analysis showed presence of P in all the films grown with PH_3 amongst the source gases [22]. The "best quality" films, as evidenced by the wavenumber and full-width half-maximum (FWHM) of the diamond Raman line (Fig. 4) are obtained using a phosphine concentration of ~1500 ppm in the gas phase, comparable to but slightly lower than that giving the highest observed growth rates.



(a) 0.1% PH_3



(b) 0.15% PH_3



(c) 0.2% PH_3

(d) 0.3% PH_3

(e) 0.4% PH_3

(f) 0.5% PH_3

Fig. 2. Scanning electron micrographs of diamond films on silicon after 6 hours growth using precursor gas mixtures of 1% CH_4 in H_2 with additional PH_3: (a) 0.1%; (b) 0.15%; (c) 0.2%; (d) 0.3%; (e) 0.4% and (f) 0.5%. Notice that the crystal morphology changes from (111) to predominantly (100) facets at low [PH_3] (up to 0.2%); higher [PH_3] results in a reversal in crystal growth back to (111) facets.

3.2. Gas-phase composition measurements

Fig. 1 shows how the distribution of the most abundant stable gas-phase species other than H_2 [i.e. CH_4 ($m/e=16$), C_2H_2 ($m/e=26$), and PH_3 ($m/e=34$)] and methyl radicals ($m/e=15$) vary as a function of filament temperature for an initial feedstock of 1% CH_4+0.2% PH_3 in H_2 measured 4 mm from the filament. Inspection of Fig. 1 reveals that the CH_4 concentration steadily decreases with increasing filament temperature, whilst the PH_3 concentration decreases steadily, until by >1700 °C it was no longer observable. This is due to the relatively weak P–H bonds in phosphine (321 kJ mol^{-1}) [23]. The absolute mole fractions measured for both precursor gases in the vicinity of the filament decreases, not only as a result of chemical reactions but also because of thermal diffusion effects inherent in multi-component gas mixtures [20]. At

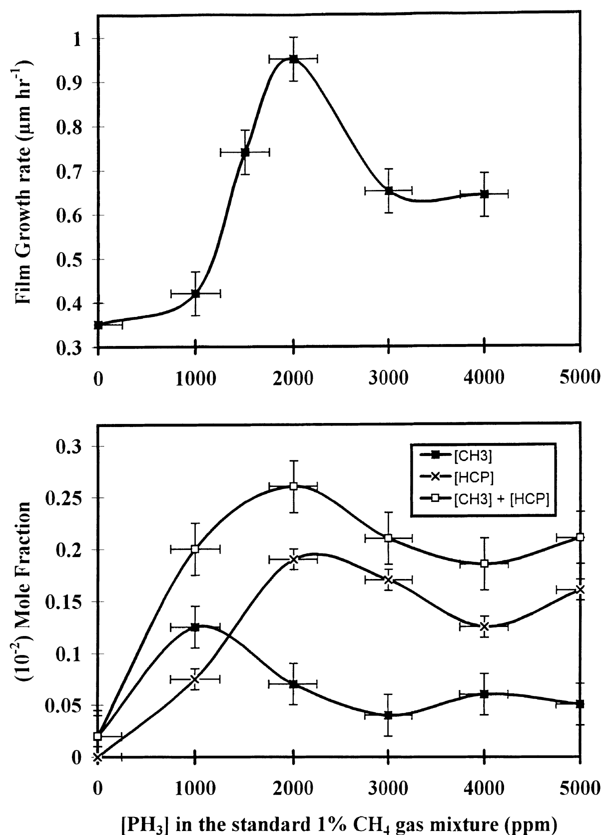


Fig. 3. Film growth rate (top) and relative mole fractions of methyl radicals (■), HCP species (×) and the sum (□) as a function of PH_3 addition to the standard 1% CH_4/H_2 source gas mixture at optimum growth conditions. Error bars have been included to give an estimate of the degree of reliability of the data, based upon measured values for the day-to-day reproducibility and the accuracy of the MBMS and gas flow meters. However, the HCP mole fraction should be interpreted with caution because the absolute mole fraction could not be determined using direct room temperature calibration, but via the indirect total carbon balance method outlined in the text.

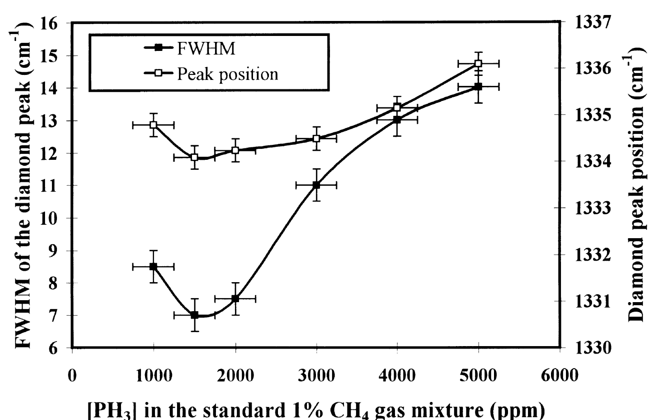


Fig. 4. The peak positions (□) and the FWHM (■) in cm^{-1} of the Raman diamond line as a function of $[PH_3]$ in the source gas mixture.

1700 °C almost all of the PH_3 is decomposed, much of it ending up as a coating of yellow/red coloured phosphorus on the walls of the CVD chamber.

The optimum growth conditions in terms of highest film growth rates and best quality were obtained using a gas mixture of ~0.15–0.2% PH_3 in 1% CH_4 at a filament temperature of 2300 °C. This may be due to the unusually high methyl radical concentrations measured. Since methyl radicals are considered to be the main growth precursors [24,25], the presence of higher $[CH_3]$ in the gas phase normally leads to higher deposition rates. Note that the carbon balance, defined as (total C fraction measured)/(C fraction in the feed gas) and shown as filled squares in Fig. 1, decreases as the filament temperature increases, partly because of the thermal diffusion effects mentioned above, and partly because of the omission of the C-containing HCP species (see below). Similar behaviour was observed with other PH_3/CH_4 input ratios. In all cases the presence of PH_3 resulted in greater $[CH_3]$ at growth temperatures, though (as Fig. 3 shows) the enhancement becomes less great with increasing $[PH_3]$.

Bohr et al. [11] suggest that the observed changes occurring in the CVD diamond growth process with phosphine addition are due to the creation and subsequent reactions of the HCP molecule — the phosphorus analogue of HCN identified in various nitrogen-doped diamond CVD experiments [5,26]. However, they were unable to detect such a species because it is long term stable only below −124 °C [27]. In contrast, MBMS permits detection of the transient HCP ($m/e=44$) species, though absolute concentration determinations are precluded by the impracticality of direct room temperature calibration. Checks were made to ensure that $m/e=44$ signal required the presence of PH_3, CH_4 and H_2 in the process gas mixture, and were not a result of gas phase impurities (e.g. CO_2). Qualitatively, both the HCP ($m/e=44$) and P ($m/e=31$) signal intensities were found to increase with increasing filament temperature, for all ratios of PH_3/CH_4 studied.

However, it is possible to estimate a value of the HCP mole fraction in the gas phase during the CVD process using an indirect method based upon the measured C-balance. This is possible by assuming HCP is the only significant additional C-containing species that results when trace amounts of PH_3 are added to a given CH_4/H_2 mixture, and that it is responsible for any "missing" component of the total C balance measured relative to that for the corresponding CH_4/H_2 mixture with no PH_3 added. The values obtained in this way are plotted as a function of $[PH_3]$ in the input gas mixture at growth temperatures (2400 °C) and are shown in Fig. 3. Inspection of Fig. 3 suggests that HCP is actually more abundant than CH_3 at this filament temperature, and that the maximum growth rate correlates (within experimental error) with both the HCP yield curve and the HCP+CH_3 yield curve (i.e. at $[PH_3]$ ~2000 ppm). Such conclusions accord with the results of thermodynamic calculations [11] which predict methane and

HCP to have the highest mole fractions in gas phase $H_2/CH_4/PH_3$ mixtures at growth temperatures.

The observed species composition may be explicable by considering the effects that PH_3 molecules have on the gas-phase chemistry during the CVD process. As Fig. 1 shows, because of the weakness of the P–H bond, almost all the PH_3 dissociates (ultimately to produce phosphorus and three hydrogen atoms) at temperatures below $\sim 1600\ ^\circ C$, that is, at temperatures where filament catalysed decomposition of H_2 is still rather inefficient:

$$PH_3 \rightarrow \rightarrow \rightarrow P + 3H \quad (1)$$

As a result, the dissociation of methane to yield methyl radicals, a reaction which is driven by H atoms, can occur more readily at lower temperature than in the conventional CH_4/H_2 gas mixtures. However, this cannot explain the five-fold increase in $[CH_3]$ observed at standard growth temperatures (Fig. 3) on addition of 1000 ppm PH_3. A possible explanation is that small amounts of P deposited onto the filament affects the heterogeneous processes responsible for H_2 decomposition, perhaps by lowering the activation energy for H atom formation.

However, there appears to be another, competing reaction, which serves to deplete $[CH_3]$ at higher PH_3 mole fractions. This, we suggest, could be either:

(1) a filament poisoning effect whereby too much P adsorbed on the filament now reduces its efficiency for H_2 decomposition; or

(2) a gas phase reaction such as:

$$CH_3 + P \rightarrow HCP + H_2, \quad (2)$$

the importance of which will depend critically on the gas-phase concentrations of the two reactants, namely P and CH_3. Inspection of the available thermodynamic data [28] indicates that this reaction is highly exothermic ($\Delta H = -312 \pm 15$ kJ mol^{-1}). Possible alternative routes to HCP involving, for example, reactions between CH_3 and PH_2 (or PH) radicals, or successive hydrogen abstractions from CH_3PH_2, seem less probable given that we do not detect any of these P-containing species in the MBMS.

In standard CH_4/H_2 gas mixtures, the main chemical conversion is that of methane to acetylene (C_2H_2), via methyl recombination and subsequent H abstraction reactions [21]. Since the formation of C_2H_2 depends on $[CH_3]^2$, the detection of large amounts of gas-phase acetylene in a hot filament CVD reactor is generally taken as an indicator of high steady state $[CH_3]$, and is correlated with increased film growth rate. Our MBMS results show that for a $CH_4/PH_3/H_2$ gas mixture, reactions leading to the formation of both HC≡CH (not shown in Fig. 3 for clarity) and HC≡P are possible, though, if our carbon-balance arguments are correct, acetylene was detected in much smaller quantities than HCP for any given $[PH_3]$ in the feed gas. This implies that CH_3 removal is predominantly via Reaction (2), leading to high [HCP], rather than by self-recombination. Unlike HCN which is thermodynamically very stable [5], the HCP species is both unstable and reactive in the presence of high [H]:

$$HCP \xrightarrow{2H} \rightarrow \rightarrow CH_3 + P \quad (3)$$

Thus, at the growth temperature, we anticipate rapid cycling between HCP and CH_3, with high steady-state concentrations of both. The presence of HCP in the gas phase is thus a result of equilibrium between reactions (2) and (3). We can therefore understand the process occurring in the gas phase if we consider reaction (2) at two different $[PH_3]$ regimes at high temperature. At low $[PH_3]$, (<2000 ppm) and hence low [P], reaction (2) will be suppressed, and the dominant processes will be those resulting from the additional [H] produced by improved catalytic efficiency of the partially P-covered filament.

At higher $[PH_3]$, however, there is now sufficient [P] in the gas phase for reaction (2) to become important and Fig. 3 shows that, at these higher $[PH_3]$ values, $[HCP] > [CH_3]$. As more $[CH_3]$ is removed from the gas phase, the growth rate plateaus and eventually begins to decrease. This behaviour is also reflected in the observed film quality (Fig. 4). Also at higher $[PH_3]$ there is the possibility of excess P deposition onto the filament reducing the efficiency for catalytic H_2 decomposition, causing a subsequent reduction in the reactions which rely on a high [H].

The role of HCP at the growing CVD diamond surface is still unclear, but may provide an alternative explanation for our observations. Bohr et al. [11] suggest that, under their experimental conditions, HCP has a deleterious influence on the gas–solid heterogeneous reactions occurring on the substrate surface. However, in the present work the correlation between the observed film growth rates and the measured [HCP], coupled to the fact that HCP is unstable and likely to decompose on the substrate surface, suggests that HCP could, under appropriate conditions, provide a beneficial low energy route to adding C_1 species to the diamond surface, resulting in faster growth rates, and the possibility of diamond growth at lower temperatures. Such a view is supported by the presence of phosphorus in all the films grown, as determined by AES.

4. Conclusions

The influence of phosphine on the diamond growth mechanism remains an area of research open for much discussion. In situ molecular beam mass spectrometry has enabled the detection of HCP, though an estimate

for its absolute concentration in the gas phase could only be obtained by an indirect method. Future work would include devising a suitable direct method to obtain absolute gas-phase concentrations of HCP, and acquiring a better understanding of its role in the CVD process in terms of changes in the surface chemistry, and the ability to incorporate P into CVD diamond films.

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