

# Influence of B- and N-doping levels on the quality and morphology of CVD diamond

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## Abstract

Diamond films have been grown by hot filament and microwave plasma assisted CVD using precursor gas mixtures of 1% methane in hydrogen with additional nitrogen and boron dopants. Structural and compositional characterisation of the as-grown films was carried out by scanning electron microscopy and secondary ion mass spectrometry. SIMS measurements show the B-doping efficiency is close to unity, whereas that of nitrogen is less than  $10^{-3}$ . In conjunction with modelling of the gas-phase CVD environment we show that variations in the film morphology and quality can be accounted for by changes in the concentrations of the gas-phase precursor species rather than incorporation of the dopant into the diamond lattice. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Chemical vapour deposition; Diamond; Secondary ion mass spectrometry

## 1. Introduction

Exploiting the good electrically insulating properties of diamond with the ability to selectively dope to produce films with specific p- and n-type semiconducting properties opens the door for diamond based high temperature, high power electronic devices which are resistant to radiation damage. During chemical vapour deposition (CVD) the control of the amount of gas-phase dopant which incorporates into the bulk diamond is crucial to the semiconducting characteristics of the film.

Boron is a dopant responsible for p-type behaviour in diamond. It can substitutionally dope diamond without significantly distorting the lattice, which results in a high doping efficiency. Boron has been incorporated into diamond films using a variety of precursors (e.g. diborane, triethylborane or boron trioxide) up to B/C levels of 0.01 in the diamond with a typical doping efficiency close to unity [1,2].

Theoretically, substitutional dopant atoms (nitrogen or phosphorous) can be used for n-type doping of diamond but in practice this has been harder to achieve. Analysis of films grown by microwave plasma CVD show the nitrogen

doping efficiency to be very low at around  $10^{-4}$  when the nitrogen to carbon ratio in the gas phase ( $N/C(\text{gas})$ ) is varied between 0.01 and 0.4 [3,4], although incorporation efficiencies up to  $6 \times 10^{-3}$  [5,6] have been reported. Analysis of films grown by hot filament CVD have indicated even lower doping efficiencies, with nitrogen incorporation levels below 100 ppm [2].

The addition of dopants to the gas-phase affects the crystallinity and growth rate of the diamond [6–8] which in turn influences the electrical properties of the films. Typically, with high concentrations of N or B in the gas-phase the diamond film quality deteriorates. In this work, we ask whether it is the incorporation of high levels of dopant within the bulk of the film which disrupts the diamond lattice and causes the quality of the films to deteriorate or whether the prevailing gas-phase chemistry is not suitable for successful diamond growth with high concentrations of dopant species in the gas-phase. Secondary ion mass spectrometry (SIMS) analysis of the films was used to quantify the levels of boron and nitrogen incorporated into the diamond films. We compare the doping efficiency when B and N are introduced into the gas-phase during hot filament CVD and also investigate the relative N-doping efficiencies by microwave plasma and hot filament CVD. Thermodynamic equilibrium calculations are also used to enable the concentration of the gas-phase species at typical CVD process parameters.

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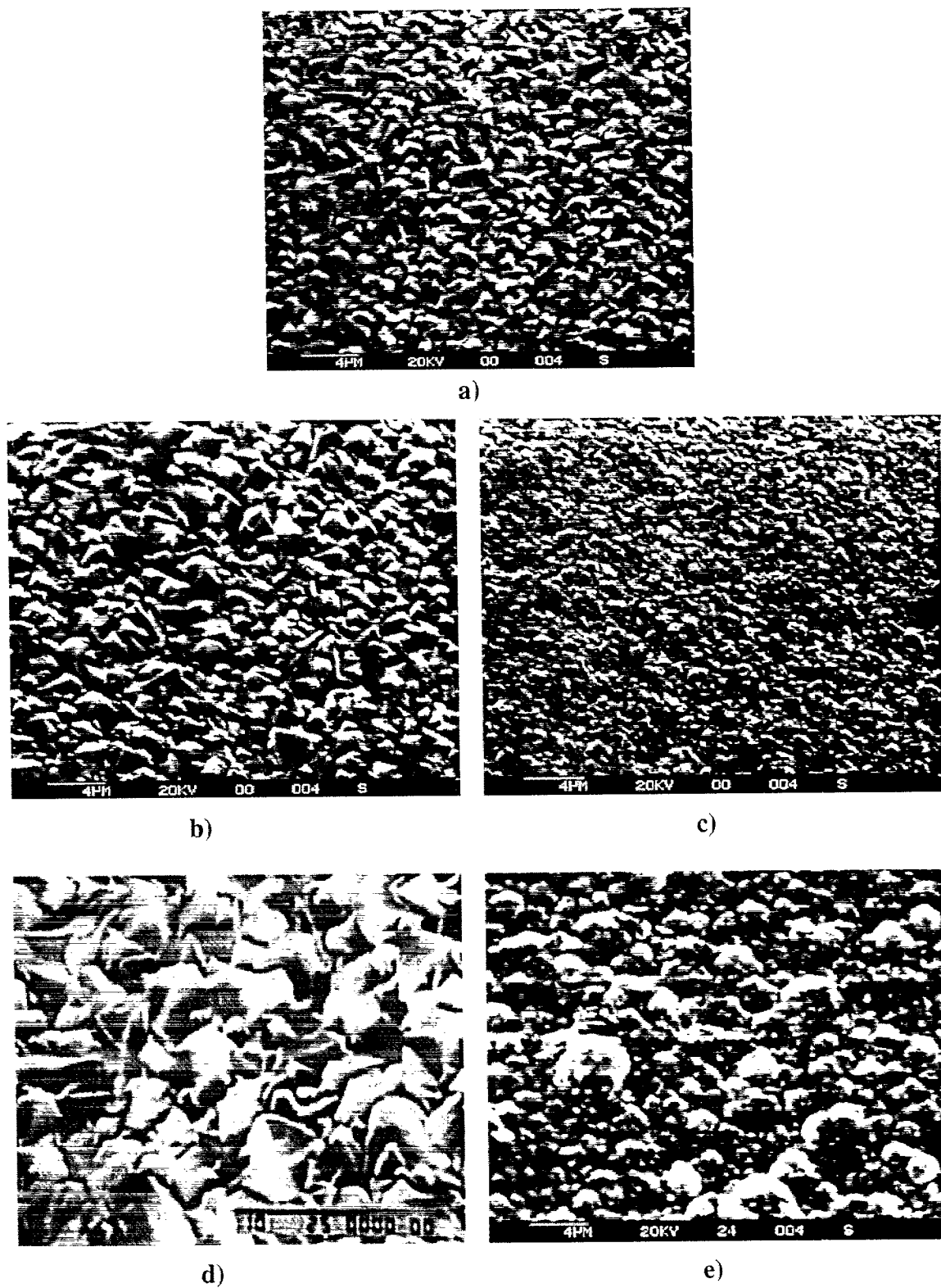


Fig. 1. Electron micrographs of diamond films grown on silicon using 1%  $CH_4$  in  $H_2$  with the following gas phase dopant levels: (a) undoped, (b)  $B/C = 10^{-4}$ , (c)  $B/C = 5 \times 10^{-3}$ , (d)  $N/C = 0.2$ , (e)  $N/C = 20$ .

Table 1  
Correlation of boron doping efficiency of the diamond with the surface resistance of the films

B/C(gas)	B/C(film)	Doping efficiency	Resistance ( $\Omega$ )
0	–	>2,500,000	–
Trace <sup>a</sup>	$5 \times 10^{-5}$	–	2000
$10^{-4}$	$7 \times 10^{-5}$	0.3	60
$5 \times 10^{-3}$	$7 \times 10^{-3}$	0.6	25

<sup>a</sup> Sample was deposited with no  $B_2H_6$  being added to the gas mixture, but the reactor chamber had previously been used with B-containing gas mixtures and so B has diffused from the chamber walls during growth.

## 2. Experimental

The diamond films were grown by hot filament and microwave plasma CVD. All films were grown on Si(100) which had been pre-abraded with 1–3  $\mu\text{m}$  diamond powder. During the deposition the substrate temperature was maintained at 900°C and the process pressure at 20 Torr.

In the hot filament doping experiments a coiled tantalum filament was maintained at a temperature of 2200°C and 0–26 ppm diborane ( $B/C(\text{gas}) = 0\text{--}5.2 \times 10^{-3}$ ) or 0–100 000 ppm nitrogen ( $N/C(\text{gas}) = 0\text{--}20$ ) was added to the standard 1%  $\text{CH}_4$  in  $\text{H}_2$  gas mixture. The plasma source consisted of an ASTeX 2.45 GHz microwave generator. The diamond films were grown using 1000 W power with additions of 0–47 000 ppm  $\text{N}_2$  to the 1%  $\text{CH}_4/\text{H}_2$  input gas.

The film morphology and growth rate were investigated by SEM. Positive and negative SIMS spectra of the diamond films were acquired using a benchtop chemical microscope (Millbrook Instruments), further details of which are given elsewhere [9]. A  $\text{Ga}^+$  primary beam (ion energy, 6.5 keV, ion current, 20 nA) was used to sputter the diamond films.

## 3. Results and discussion

Electron micrographs of selected diamond films with boron and nitrogen added to the standard  $\text{CH}_4/\text{H}_2$  gas mixture are shown in Fig. 1. Low levels of boron do not significantly change the growth rate (0.5  $\mu\text{m}/\text{hour}$ ) or morphology of the films compared to the undoped film. Two point probe measurements of the surface resistance of the as-grown films are shown in Table 1. The resistivity of the film decreases dramatically when trace levels of boron are introduced, whereas an increased dopant level leads to a much smaller decrease in the resistivity.

In contrast, the film morphology and growth rate depend critically on the nitrogen concentration in the source gas. The diamond phase purity is maximised with 200 ppm  $\text{N}_2$  in the gas mixture and when  $N/C(\text{gas}) > 0.2$  a steady deterioration of film quality, gauged by Raman spectroscopy, occurs [7].

The diamond films were also examined by SIMS, and a

typical negative spectrum (HF grown with  $N/C(\text{gas}) = 20$ ) is shown in Fig. 2. The spectrum is dominated by  $\text{C}_x^-$  clusters ( $x < 13$ ). The intensity of these  $\text{C}_x^-$  clusters was qualitatively very similar irrespective of the dopant (N or B), the dopant concentration in the gas-phase, or the growth method (hot filament or microwave plasma).

The peak of particular interest in the N-doped films is  $m/z = 26$  corresponding to  $\text{CN}^-$ . However, this mass is prone to interference from hydrocarbon and  $^{13}\text{C}$  containing species ( $^{12}\text{C}_2\text{H}_2^-$ ,  $^{13}\text{C}^{12}\text{CH}^-$ ,  $^{13}\text{C}_2^-$ ). The height of the  $m/z = 26$  peak relative to the peaks at  $m/z = 24$  ( $^{12}\text{C}_2$ ) and  $m/z = 25$  ( $^{12}\text{C}_2\text{H}^-$ ,  $^{12}\text{C}^{13}\text{C}^-$ ) appears relatively more intense in the surface monolayer of each sample. Between samples, the relative intensity of the  $m/z = 26$  peak does increase very slightly as  $N/C(\text{gas})$  is increased (Fig. 3a–c), suggesting a small contribution from  $\text{CN}^-$  superimposed on a large background due to the  $\text{C}_x\text{H}_y^-$  species. The change appears to be just significant at the higher  $N/C(\text{gas})$  values, implying that the nitrogen incorporated into the films is then just at the minimum detectable level. This level is estimated as 1000 ppm, giving an upper estimate of  $10^{-3}$  for the doping efficiency of nitrogen in both the hot filament and plasma grown diamond films.

In contrast, Fig. 3d–e show part of the positive SIMS spectrum for B-doped diamond films grown with  $B/C(\text{gas}) = 0\text{--}5 \times 10^{-3}$ . Both doped samples show peaks at  $m/z = 10$  and  $m/z = 11$  corresponding to the two natural isotopes of boron, whereas the undoped sample shows no peak at either  $m/z$  value. The peaks at  $m/z = 12\text{--}15$  are again due to hydrocarbon species, this time of the generic formula  $\text{CH}_x^+$  ( $x = 1\text{--}3$ ). A lower estimate of the boron concentration  $B/C(\text{film})$  was possible by calibration using a graphite sample for which  $B/C(\text{bulk})$  was measured as 50 ppm by colourimetric determination following solvent extraction. To do this, all peaks were normalised to the  $\text{C}^+$  peak at  $m/z = 12$  and the constant background noise subtracted from each spectrum. Finally the spectrum obtained from the undoped diamond was subtracted to resolve the  $\text{B}^+$  peak at  $m/z = 11$  from the rising edge of the  $\text{C}^+$  peak at  $m/z = 12$ . The results (see Table 1) show the boron doping

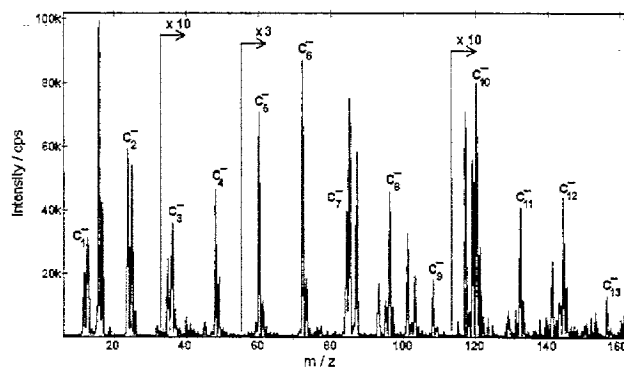


Fig. 2. Negative SIMS survey spectrum from film  $N/C(\text{gas}) = 20$  showing  $\text{C}_x^-$  clusters. Other peaks above  $m/z = 70$  can be assigned to  $\text{GaC}_n$  and  $\text{GaO}_n$  clusters, each present as twin peaks due to the natural isotopes of gallium.

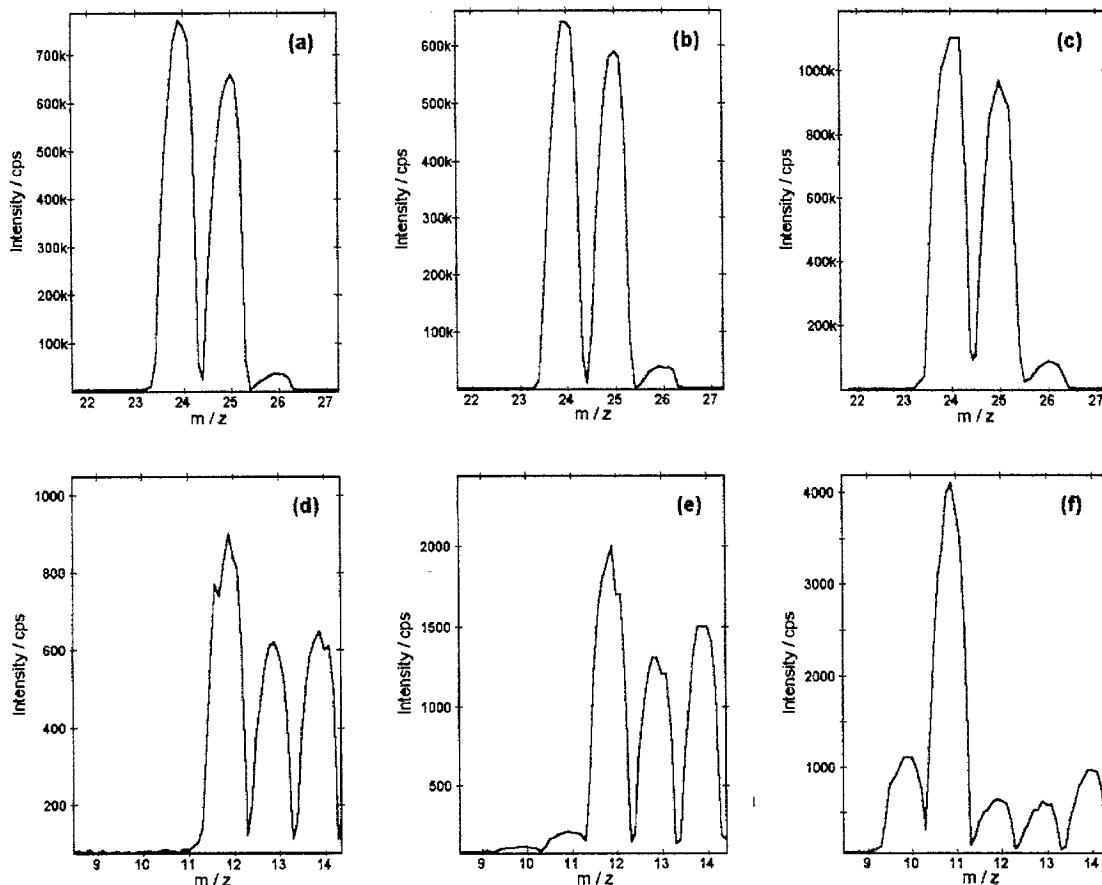


Fig. 3. Negative SIMS spectra of the nitrogen doped polycrystalline diamond films. The peak at  $m/z = 26$  increases slightly in intensity between (a)  $N/C(\text{gas}) = 0$  (microwave), (b)  $N/C(\text{gas}) = 0.5$  (microwave) and (c)  $N/C(\text{gas}) = 20$  (hot filament). For the positive SIMS spectra of the hot filament CVD boron doped diamond films, the peaks at  $m/z = 10$  and  $11$  increase strongly in intensity between (d) the undoped film, (e)  $B/C(\text{gas}) = 10^{-4}$  and (f)  $B/C(\text{gas}) = 5 \times 10^{-3}$ .

efficiency to be around unity in agreement with previous work and also theoretical predictions [2].

It is clear from the SIMS analysis that even though the level of nitrogen incorporated into the films is extremely

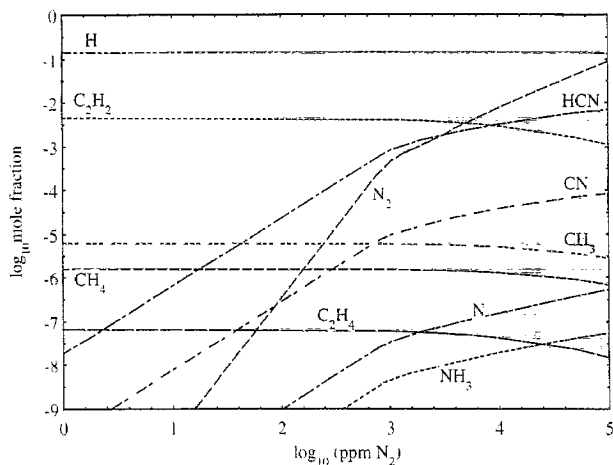


Fig. 4. Calculated equilibrium mole fractions of the C/N/H species as a function of nitrogen concentration in the feed gas. The  $\text{CH}_4$  concentration is constant at 1% with temperature held at  $2200^\circ\text{C}$  and a pressure of 20 Torr.

low, the diamond films deteriorate rapidly at high  $N/C(\text{gas})$ . In order to understand the changes in the gas-phase chemistry as a function of nitrogen concentration a thermodynamic equilibrium package (SENKIN [10]) was used to calculate the equilibrium gas concentrations as a function of nitrogen concentration for a gas mixture of 1%  $\text{CH}_4$  in hydrogen at 20 Torr and  $2200^\circ\text{C}$ , the filament temperature used in the deposition experiments (see Fig. 4). Further details of such calculations for  $N/C/H$  gas mixtures have been published elsewhere [7]. Such a simple thermodynamic model does not account for mass transport in the CVD chamber but does provide information about the gas-phase environment close to the filament.

At typical filament temperatures, the  $\text{CH}_4$  is primarily converted into  $\text{C}_2\text{H}_2$ ,  $\text{CH}_3$ , with the production of  $\text{HCN}$  and  $\text{CN}$  being highly favoured as  $\text{N}_2$  is added to the input gas. This is consistent with in-situ mass spectrometric analysis of the  $C/H/N$  CVD environment [11]. From equilibrium calculations of  $C/N/H$  gas mixtures as a function of temperature [7] we have shown that the gas-phase chemistry of the  $\text{CH}_3$  and  $\text{CN}$  radical species show a distinct similarity and that the relative concentration of  $\text{CH}_3$  and  $\text{CN}$  species is crucial for diamond growth. When  $N/C(\text{gas}) < 0.1$ , the

partial pressure of  $\text{CH}_3$  is greater than that of CN under typical deposition conditions and this corresponds to a growth regime of high quality diamond films. With greater amounts of nitrogen in the input gas mixture, the partial pressure of  $\text{CH}_3$  is reduced and the CN species dominates. The very low N-doping efficiency shows that the reactivities of  $\text{CH}_3$  and CN are remarkably different at the growing diamond surface. It is also clear that the deterioration in the quality of the diamond films at higher N/C(gas) must be due to an excess of the CN species which may competitively adsorb onto vacant diamond growth sites rather than leading to the incorporation of significant amounts of nitrogen into the bulk diamond which disrupts the lattice.

Modelling of the C/H/B gas-phase environment is not possible because of incomplete kinetic data required for the elementary reactions involved.

#### 4. Conclusions

Trace amounts of B- or N-containing species introduced into the gas phase during CVD diamond growth have a dramatic effect on the morphology and/or conductivity of the resulting films. SIMS measurements indicate that doping efficiency of B into the diamond films over a wide range of gas-phase B concentration of the diborane precursor is close to unity. In contrast, the doping efficiency of N into diamond

is below  $10^{-3}$ . Thermodynamic modelling of the gas-phase CVD environment confirms that the changes in the films grown with nitrogen introduced into the gas-phase can be accounted for by differences in concentrations of the precursor gas species rather than incorporation of the dopant into the diamond film.

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