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Raman and photoluminescence spectra of as-grown CVD diamond films

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Abstract. Emission spectra of diamond films grown by microwave-plasma-assisted CVD have been carried out at 77 K. The Raman spectra are not the same for different wavelengths of excitation. Deconvolution of these spectra shows two major components (A and B) in addition to the first-order diamond Raman line. The scattering cross sections of these components are large by comparison with the scattering cross section of diamond. The B component decreases in intensity with respect to the diamond Raman line as the wavelength of excitation is decreased. Component A is very similar to the spectrum from amorphous $Si_{0.3}C_{0.7}$:H by Ramsteiner and co-workers. It is suggested that the B component may be associated with a silicon-rich form of amorphous silicon carbide. There is a broad-band luminescence at 1.95 eV whose excitation behaviour and temperature dependence is similar to that associated with donor–acceptor recombination radiation in amorphous $Si_{0.3}C_{0.7}$:H as reported by Sussmann and co-workers.

1. Introduction

Raman spectroscopy has been applied to the characterization of diamond films produced from the vapour phase by many investigators, because diamond has a distinctive sharp first-order Raman line at 1332 cm^{-1} when measured at 300 K. A non-diamond Raman feature at about 1500 cm^{-1} is frequently reported, and is generally associated with C–C sp^2 bonding. The band has been variously attributed to glassy or amorphous carbon, disordered graphite or polycrystalline graphitic structures. From the point of view of the production of diamond films it is important to ascertain the true nature of the non-diamond Raman features and to know what proportion of the film is associated with them.

Knight and White (1989) have compared the Raman spectra of diamond and diamond-like films with a wide range of carbon materials. Shroder *et al* (1990) have studied powder composites of boron nitride/diamond and graphite/diamond to try and simulate the features of diamond films. They demonstrated that different component concentrations and crystallite sizes influenced the ratios of Raman intensities for mixtures. They also found that the Raman scattering at about 1500 cm^{-1} in the films is much stronger than that from single-crystal or microcrystalline graphitic structures.

Yoshikawa *et al* (1988) and Wagner *et al* (1989) have reported two overlapping Raman features close to 1500 cm^{-1}, the relative intensities of which are altered by changing the wavelength of excitation for the Raman spectrum. Wagner *et al* (1989)

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have suggested that an amorphous silicon/carbon network may be associated with the Raman behaviour of diamond films close to 1500 cm^{-1}.

Vavilov *et al* (1980) were the first investigators to recognize that ion implantation of natural diamonds with silicon produced a point defect with an associated zero-phonon line at 1.681 eV. Collins *et al* (1990) have observed this zero-phonon line in the optical absorption and cathodoluminescence spectra of a small diamond single crystal produced by chemical vapour deposition. Clark and Dickerson (1991) have reported that the strength of the 1.681 eV line in the photoluminescence spectrum of a CVD diamond film may be enhanced by electron irradiation and thermal annealing. This last result indicates that the silicon in the diamond film is not all in the same environment immediately after growth of the film.

The present paper reports on a further study, (using photoluminescence and Raman scattering) of CVD diamond films which are known to contain a small proportion of silicon.

2. Experimental details

Photoluminescence and Raman scattering measurements were recorded using a SPEX 1401 double-grating monochromator, an RCA C31034 low-noise photomultiplier cooled to -30 °C, and a Thorn EMI mark II photon-counting system. A Spectra Physics 2000 series argon-ion laser was used for excitation of the spectra, and the samples under test were mounted in an Oxford Instruments continuous-flow cryostat at temperatures between 77 K and 300 K.

All the spectra presented here have been corrected for the wavelength-dependent response of the photomultiplier and the optical system by making measurements on a calibrated standard tungsten halogen lamp.

The diamond film samples were grown by microwave-assisted CVD from a $CH_4(1\%)-H_2$ gas mixture on to silicon substrates, at 50 Torr and a temperature of about 800 °C, using apparatus similar to that described by Saito *et al* (1986). The silicon substrate was removed from the back of the film by chemical dissolution prior to spectroscopic investigation.

The relative intensities of the various features in the emission spectrum of each CVD film were found to be different from one place to another on a film. In order to overcome this inhomogeneity problem, a small fragment about 0.3 mm long was used for spectroscopic study. Emission was excited throughout the whole of the fragment, and the 'normalized' spectrum was obtained by dividing the recorded emission spectrum by the integrated intensity of the first-order diamond Raman line at 1332 cm^{-1}. Repeated measurements of the emission spectra gave normalized emission spectra for which the intensities were reproducible to within 2%. The normalizing procedure also facilitated the semi-quantitative comparison of spectra recorded on the same fragment after growth and after subsequent electron irradiation and thermal annealing treatments.

3. Results and discussion

The emission spectra of three different CVD diamond films have been studied. Films 1, 2 and 3 had thicknesses of ~10 μm, 140 μm and 17 μm, respectively. Typical

emission spectra excited by 514.5 nm light at 77 K are shown in figure 1. The spectra are plotted on the same scale of normalized intensity, but are displaced vertically for clarity of presentation. The marks on the right-hand ordinate axis indicate the levels of zero intensity for each of the spectra taken in turn. Spectra are illustrated for two different fragments of film 1 to give some idea of the variations in homogeneity that have been observed. Films 2 and 3 showed better homogeneity.
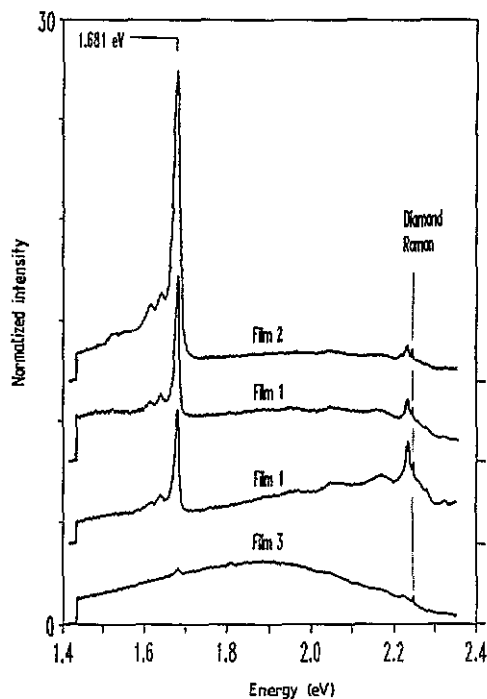

Figure 1. Comparison of the emission spectra of the three diamond films used in the present investigation. The spectra were excited by 488.0 nm light and were recorded at 77 K. The spectra labelled film 1 were recorded on two different fragments of the film.

At least three easily recognisable spectral characteristics seem to be present in different relative proportions in the spectra shown in figure 1:

(i) the 1.681 eV sharp line with its phonon side band is strongest in films 1 and 2;

(ii) the broad-band luminescence centred at about 1.90 eV shows very strongly in the spectrum of film 3, but is present at much weaker intensity in films 1 and 2;

(iii) the Raman-scattering features in the range 2.1 to 2.4 eV include the first-order diamond Raman line as indicated in the figure. Careful spectral scans of very high resolution give the integrated intensity of this line used for normalizing the spectra.

The 1.681 eV centre is already known to be associated with the presence of silicon in diamond, as indicated in the introduction, and we now discuss the characteristics of the spectral features (ii) and (iii).

3.1. The 1.90 eV broad band

The temperature dependence of the broad-band luminescence under excitation with 488.0 nm light is shown in figure 2. The peak position is close to 1.94 eV at 72 K,

but moves closer to 1.90 eV at 200 K. The Raman spectrum in figure 2 shows some evidence for a weaker broad-band component centred somewhere between 2.1 and 2.2 eV. The shape of the band is not quite the same as that observed under 514.5 nm excitation.
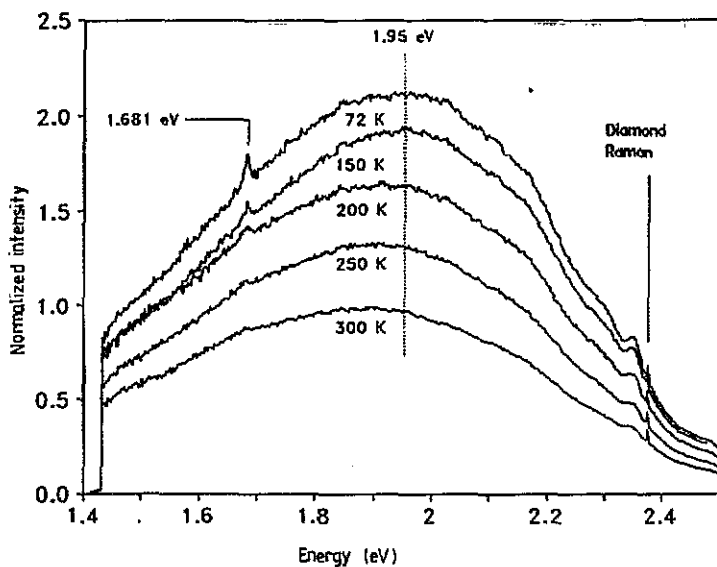

Figure 2. Temperature dependence of the 1.95 eV broad-band luminescence observed in film 3. The spectra were excited by 488.0 nm light.

As the low-energy tails of the 1.90 eV broad band are beyond the scan range of the spectra, a true baseline for the band is not well established. If it is assumed that the baseline corresponds to zero normalized intensity for the band, then the full width at half maximum is 0.71 eV at 72 K, increasing to 0.74 eV at 300 K. The intensity of the band is quenched by about 50% as the temperature is raised from 72 to 300 K.

Several broad emission bands have been reported in cathodoluminescence spectra of bulk diamonds. Davies (1977) has tabulated several bands which have been observed in a variety of natural and synthetic diamonds, and Gippius *et al* (1982) have given evidence of further broad cathodoluminescence bands observed in diamonds after ion implantation. There appear to be no references to a band at 1.90 eV for diamond. However, a luminescence band is often reported to underlie the Raman spectra measured from CVD diamonds and it is possible that this luminescence may be associated with the 1.90 eV band.

Sussmann and Ogden (1981) have produced Si_xC_{1-x} hydrogenated alloys by plasma decomposition of various gas mixtures of silane (SiH_4) and ethylene (C_2H_4). Under 442 nm excitation these alloys showed a luminescence band which became broader and shifted to higher energies as the carbon content increased (i.e. as x decreased). For $x = 0.32$ a band of half-width ~0.7 eV was observed at ~1.95 eV. Moreover, the intensity of this band increased by a factor of about two when the temperature was lowered from 300 K to 77 K. Transmission electron diffraction studies of the alloys showed diffuse rings characteristic of amorphous materials.

3.2. *Raman scattering*

High-resolution Raman shift spectra of the as-grown diamond film 2, excited with 514.5 nm light, are shown in figure 3 where the variation with temperature of the sample is illustrated. Once again the spectra are plotted on the same ordinate scale and are displaced vertically, the marks on the right-hand ordinate axis corresponding in turn to each of the zero-intensity signals. There is an overall increase in intensity of the spectrum as the temperature is lowered. This is due partly to the temperature dependence of the 1.90 eV broad band which extends into this region of the spectrum. Due to line-overlap and line-broadening effects it is not easy to determine how the intensities of some of the Raman features respond to a change in temperature. The Raman features are distinguished much more easily in the 77 K spectrum. Measurements at 77 K have been adopted throughout the present study, and it is for this reason that the 514.5 nm spectra reported here have a rather different appearance to those reported in previous Raman characterization studies in the literature, which have all been carried out at room temperture, and show features similar to the 300 K spectrum of figure 3.
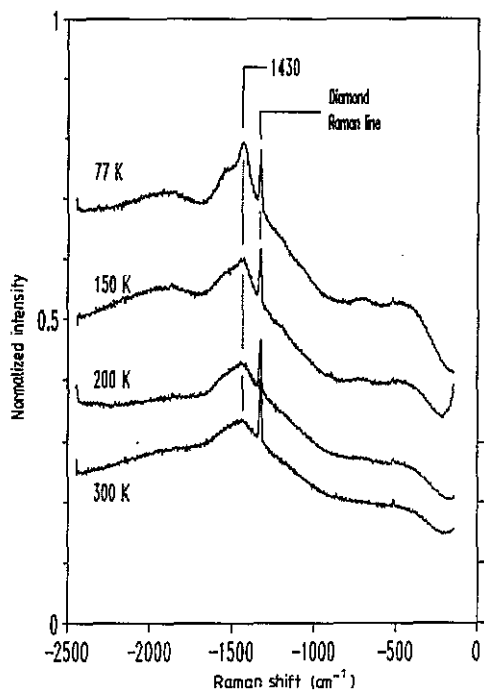

Figure 3. Variation with temperature of the Raman spectrum for diamond film 2. The spectra were excited by 514.5 nm light.
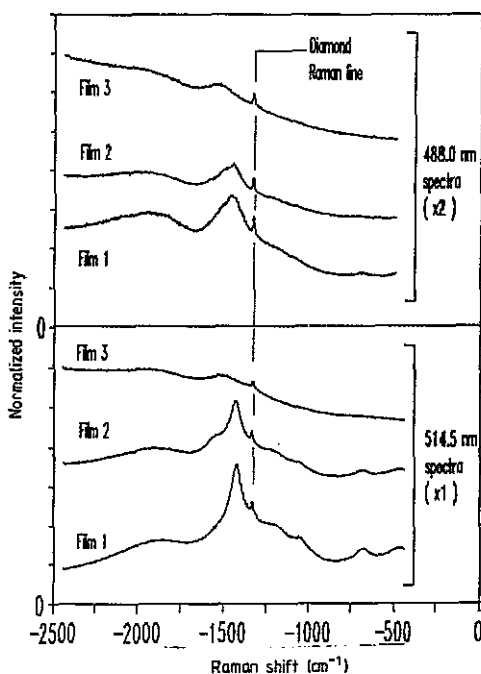
Figure 4. Raman shift spectra for diamond films 1, 2 and 3 using 514.5 nm and 488.0 nm exciting light. All spectra were recorded at 77 K.

The 77 K Raman shift spectra excited by 488.0 and 514.5 nm light for films 1, 2 and 3 are shown in figure 4. All spectra were recorded using unfocused laser beams of power 0.4 W. The 488.0 nm spectra all show the same features but in different relative proportions to the diamond Raman line intensity. The shapes of the 488.0 nm

and 514.5 nm spectra for film 3 are very similar to one another. However, for films 1 and 2 the 514.5 nm spectra exhibit much more structure than the corresponding 488.0 nm spectra. This data suggest that there are two components to the Raman spectrum, the intensity of one (which will be referred to as component A) showing little variation with the wavelength of the exciting light, whilst the other (component B) is strong under 514.5 nm but very weak under 488.0 nm excitation. Only films 1 and 2 exhibit component B.

There are two possible explanations for a change in the normalized intensity of the Raman component B. Firstly, resonant enhancement of the 1332 cm^{-1} diamond Raman line as the exciting photon energy is increased could account for an apparent decrease in the normalized intensity of the B component. However, Calleja *et al* (1978) report that there is no significant change in the intensity of the first-order diamond Raman line in natural diamond with excitation wavelengths between 620 and 250 nm. Secondly, a rapidly increasing optical absorption with decreasing wavelength in the solid phase (corresponding to the Raman component B) can account for the changes in intensity of the B Raman spectrum.

Four normalized Raman shift spectra for the same fragment of film 2, and for four different wavelengths of excitation are shown in figure 5. All the spectra were recorded for a laser beam power of 0.4 W. Several very sharp lines in the range of 0–700 cm^{-1} are due to laser plasma emission that was not completely eliminated by the narrow-band filters used in the laser beam to select the wavelength of the exciting light. Progressively less Raman structure was observed as the excitation wavelength decreased.
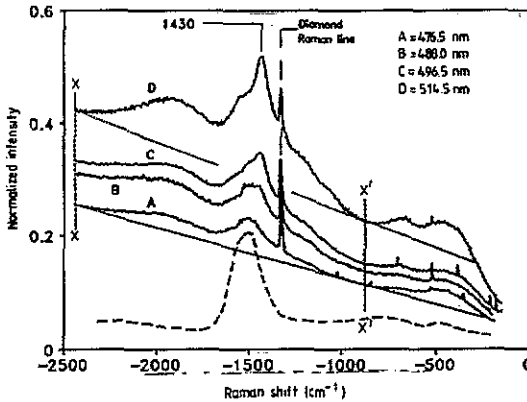

Figure 5. Raman shift spectra for the same fragment of diamond film 2 for four different wavelengths of excitation. All spectra were recorded at 77 K. The broken line curve is a tracing of the room temperature emission spectrum for $Si_{0.3}Co_{0.7}$ alloy reported by Ramsteiner *et al* (1988).

An attempt has been made to separate and identify the B Raman component. The first requirement is to try and eliminate the effects of the underlying 1.90 eV broad-band luminescence. Since the 1.90 eV band is always accompanied by Raman scattering in these experiments, we have adopted the procedure detailed below. The shape of the 1.90 eV band is not the same for each of the spectra of figure 5 because each of the Raman spectra occur in a different region of the visible spectrum due to the various excitation wavelengths. It has been assumed that the background

luminescence spectrum is determined in each case by a straight line which is the common tangent to the spectrum at the points X and X′ at 2440 and 800 cm^{-1}, as indicated by the dotted lines for the 476.5 and 514.5 nm spectra in figure 5.
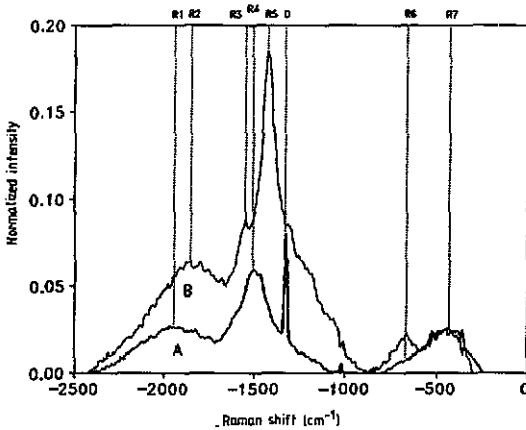

Figure 6. The Raman components A and B derived from the 476.5 nm and 514.5 nm spectra of figure 5.

It was next assumed that the background-corrected Raman spectra for film 2 contained only the two components A and B. It was assumed that the 476.5 nm Raman spectrum corresponded to component A alone, and that it was present at the same intensity for all the other wavelengths of excitation. The 488.0, 496.5 and 514.5 nm spectra were considered to be due to both A and B components in different proportions. The shape of the B Raman component was obtained by subtracting the 476.5 nm spectrum from the 514.5 nm spectrum. The two components are illustrated in figure 6.
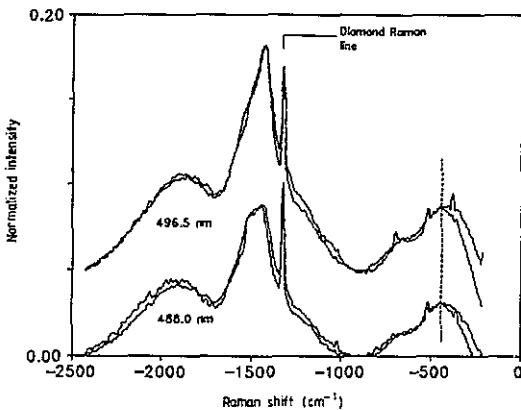

Figure 7. Comparison of the measured and synthesized spectra for the 488.0 nm and 496.5 nm excited Raman spectra.

Raman component A also includes the first-order Raman line for diamond, and this is virtually absent in the B spectrum since this is the difference between two

normalized spectra. The A and B components of figure 6 have been used as a basis for synthesizing the 488.0 and 496.5 nm Raman spectra, and comparison of these synthesized and measured profiles is presented in figure 7. In view of the experimental complications of obtaining normalized spectra and the simplicity of the assumptions made in the above analysis, it is remarkable that such good agreement is achieved. The fit is not so good for Raman shifts below $\sim$500 cm^{-1}, but the linear baseline assumption is not entirely satisfactory judging from the 514.5 nm spectrum of figure 5. The ratio of intensities of the B components for the 514.5, 496.5 and 488.0 nm excited spectra were 1:0.5:0.3.

Table 1. Positions of the Stokes-shifted Raman lines of figure 6. The line labelled D is the first-order Raman line for diamond.

Line	R1	R2	R3	R4	R5	D	R6	R7
Component	A	B	B	A	B		A,B	A,B
Shift (cm^{-1})	1940	1845	1548	1510	1430	1333	670	450 '
Bond	Si–H			C–C	C–C		Si–C	Si–Si

The Raman shifts for the peak positions of the spectral components (labelled R1–R7 and D in figure 6) are set out in table 1. The above behaviour of the Raman spectra strongly suggests that in film 2 there are three different phases, i.e. diamond, together with the A and B phases. The A and B phases have spectra which are similar to one another, the strongest peaks in the Raman-shift spectra being at 1510 cm^{-1} (A) and 1430 cm^{-1} (B) at 77 K.

Now a broad room-temperature Raman shift line at $\sim$1500 cm^{-1} has been reported for CVD diamond films by several authors, including Etz *et al* (1988), Wagner *et al* (1989), Zhu *et al* (1989) and Shroder *et al* (1990). Matsumoto *et al* (1982) attributed the line to disordered graphite, while Wada *et al* (1980) associated it with amorphous carbon. Nemanich *et al* (1988) suggested that the 1500 cm^{-1} line may be due to an amorphous network of sp^{2}- and sp^{3}- bonded carbon atoms, or a carbon-rich silicon carbide alloy.

Ramsteiner *et al* (1988) have measured the room-temperature Raman spectra from amorphous hydrogenated Si_xC_{1-x} films produced by CVD, with the composition parameter x in the range 0 to 0.5. A tracing of their spectrum for $Si_{0.3}C_{0.7}$, excited with 431.1 nm light, is shown as the broken line in figure 5. The spectrum has a striking similarity to the 476.5 nm excited Raman spectrum of film 2 shown in the same diagram. A peak at $\sim$1500 cm^{-1} is the dominant feature in the $Si_{0.3}C_{0.7}$ spectrum of Ramsteiner *et al* , with two weaker bands having Raman shifts similar to those for R6 and R7 (table 1). Ramsteiner *et al* (1988) found that the dominant peak moved to a Raman shift of $\sim$1470 cm$^{0.1}$ for $x = 0.5$, and that similar movements of $\sim$30 cm^{-1} to lower wavenumber also occurred for the bands corresponding to R6 and R7. Raman studies on hydrogenated amorphous Si_xC_{1-x} by Inoue *et al* (1983) for $0.8 > x > 0.47$ also show a peak at $\sim$1450 cm^{-1} which decreases in intensity as x increases. Thus it is suggested that phase B is also associated with Si_xC_{1-x} for $x \geqslant 0.5$.

4. Discussion

It seems that most of the features observed in the photoluminescence and Raman-scattering spectra of diamond-like films presented here may be associated with the presence of silicon in one form or another. The films described here had been grown onto silicon substrates, but investigations have also been carried out on polycrystalline CVD diamond films deposited on a diamond substrate. These films have also shown the 1.681 eV centre and the A and B Raman spectra. This latter result suggests that the silicon enters the films during CVD growth via the vapour phase. In this respect it is interesting to note that films 1 and 2 were grown in a reactor where the microwave plasma extended to the silica walls of the reaction chamber, whereas film 3 was grown in a reactor where the plasma did not reach the silica walls. The Raman features and the 1.681 eV lines are much weaker for film 3 than for films 1 and 2 (see figure 3). The silicon may have been leached from the silica walls, but it is also possible that the walls had become slightly contaminated with Si during earlier diamond depositions onto silicon substrates.

The decrease in the relative intensity of the Raman spectrum of phase B with decreasing excitation wavelength may be explained if there is an increase in optical absorption with increasing photon energy for this phase. Sussmann *et al* (1981) have shown how the optical gap for $Si_x C_{1-x}$ depends upon the composition. For $x = 0.3$ they found that $E_g \approx 2.6$ eV, whereas for $x > 0.55$, E_g was less than 2.4 eV. The photon energies of excitation for the spectra in figure 5 are 2.602 eV (476.5 nm), 2.541 eV (488.0 nm), 2.497 eV (496.5 nm) and 2.410 eV (514.5 nm). Thus for phase A all the excitation energies are below the energy gap, whereas this is not the case for phase B. This is consistent with there being no change in strength of the A spectrum and a reduction in the strength of the B spectrum with increasing excitation energy.

Some idea of the overall composition of the films has been achieved using the technique of secondary ion mass spectroscopy (SIMS) in which a mass analysis is carried out on the ions sputtered from the surface of the film. Overall silicon concentrations lying between 15 and 50 ppm were recorded for films similar to those used in the present study. This result implies that any amorphous $Si_x C_{1-x}$ phases (with $0.3 < x < 0.7$) must be present in very small proportions. Since the associated Raman features are so strong with respect to the diamond Raman line, it is concluded that the Raman efficiencies for the $Si_x C_{1-x}$ resonances are very high.

The bottom row of table 1 shows the bonds with which the various Raman resonances may be associated. The Raman frequencies are in close proximity to sharper Raman resonances observed for amorphous silicon, ion-implanted crystalline silicon carbide, SiH_4 etc. This allocation was first discussed for the $Si_x C_{1-x}$ alloys by Inoue *et al* (1983).

The values given in the literature for the frequencies of the non-diamond Raman features in CVD diamond show considerable scatter. A number of factors may contribute to this situation. It has been shown that the frequency of the C–C bond at about 1500 cm^{-1} depends upon the composition parameter, and upon the temperature at which the Raman spectra were recorded. A further source of variation can arise from inhomogeneous mixtures of $Si_x C_{1-x}$ alloys with different compositions—it is perhaps optimistic to suppose that the alloys are restricted to the two discrete phases A and B discussed earlier. The degree of hydrogenation of the amorphous Si/C alloys and the possible existence of hydrogen bonding may have a significant effect on the relative intensities and positions of the Raman features. It is also inter-

esting to note that changes in substrate temperature during growth can also give rise to spectroscopic inhomogeneity: the spectra presented by Robins *et al* (1989) suggest that the 1.681 eV centre is induced at 850 °C but is not present in films grown at 800 °C.

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