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Electron Irradiation and Heat Treatment of Polycrystalline CVD Diamond [and Discussion]

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Electron irradiation and heat treatment of polycrystalline CVD diamond

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Photoluminescence and Raman spectra have been used to characterize the properties of diamond films grown by microwave plasma assisted chemical vapour deposition. Measurements at 77 K and excitation wavelengths in the range 476.5 nm to 514.5 nm show the presence of two components, A and B, in the Raman spectrum in addition to the diamond Raman line. The A and B components are rather similar in appearance and show resonant Raman behaviour. Electron irradiation results in the removal of the A and B Raman components, but they return to their original strength after after heating at 600 °C. The Raman scattering species interact with other point defects in the CVD films during heat treatment, and may be related to the presence of silicon in the diamond film.

1. Introduction

Raman spectroscopy is often applied to the characterization of diamond films produced by chemical vapour deposition (CVD) because diamond has a strong sharp first order Raman line at 1332 cm^{-1} which is distinguished easily. A variety of other 'non-diamond' Raman features have been reported for CVD diamond, in addition to the 1332 cm^{-1} diamond Raman line. In principle the energies of the vibrational modes involved together with their associated Raman intensities can be used to assess the quality and purity of the diamond films being produced by different growth procedures. For this to be effective a good understanding of the nature of the Raman scattering species and their concentrations in the film are required.

The technique of photoluminescence in diamond is useful as a means of studying the behaviour of point defects in CVD diamond films because there is a substantial coverage of defect properties already in the scientific literature (see, for instance, the review article by Davies (1977) and the book edited by Field (1992)). In the present investigation measurements of Raman scattering and photoluminescence have been made simultaneously and an in-depth characterization study of three CVD diamond films has been carried out.

Figure 1 shows the emission spectra of three polycrystalline diamond films grown by microwave assisted CVD onto a silicon substrate. The spectra were recorded at 77 K under illumination with 514.5 nm light. The normalized emission spectra were obtained by dividing the recorded spectrum by the intensity of the first-order diamond Raman line at 1332 cm^{-1}. This procedure facilitates semiquantitative comparison of spectra recorded on the same fragment of sample after any electron irradiation or thermal annealing treatment. All the spectra presented in this paper

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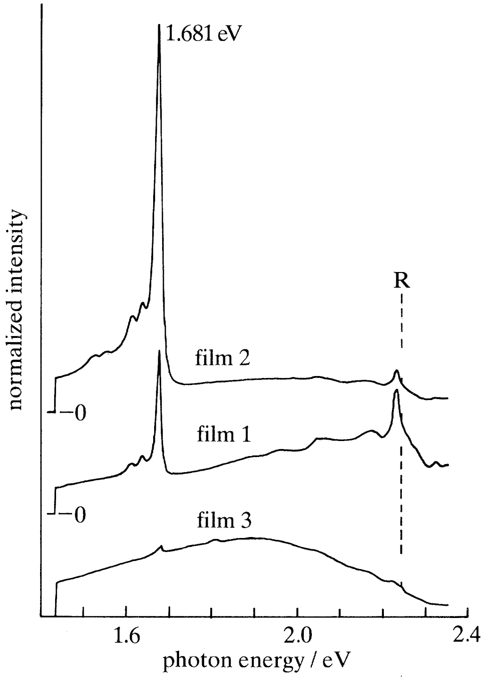

Figure 1. Emission spectra recorded at 77 K and excited with 514.5 nm light for CVD polycrystalline diamond films. The first order Raman line for diamond is indicated by R. The spectra have been displaced vertically for clarity of presentation. The zero levels of intensity are indicated.

have been corrected for the wavelength dependent response of the optical measuring system.

There are three major features of the spectra other than the first-order diamond Raman line at 1332 cm^{-1}, and they are present in different proportions in the three samples:

(i) a zero-phonon line at 1.681 eV with its weak vibronic sideband structure;

(ii) a Raman scattering spectrum between 2.0 and 2.4 eV, being strongest in film 1 and showing detailed structure which is much better resolved at 77 K than at room temperature;

(iii) a broad luminescence band at *ca.* 1.90 eV, being of greatest intensity in film 3.

The effects of heat treatment up to 2200 °C and of electron irradiation followed by heat treatment on the 1.681 eV centre for film 2 have been fully described in an earlier publication (Clark & Dickerson 1991). It has been established that the 1.681 eV centre is associated with silicon as an impurity in the diamond film.

A strong resonant Raman scattering behaviour also has been reported previously (Clark & Dickerson 1992) for the 'non-diamond' Raman spectrum. Two Raman components were identified and labelled A and B. The intensity of the B component was very sensitive to the wavelength of the exciting light in the range 476.5–514.5 nm. Only the A Raman component was present in the spectrum of film 3 and its normalized intensity increased as the excitation changed from 476.5–514.5 nm. In film 2 the B Raman component showed a substantial increase in intensity as the excitation wavelength increased, reaching about twice the intensity of the A

Figure 2

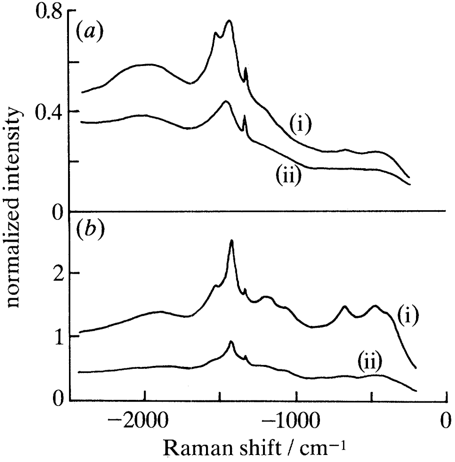

Figure 3

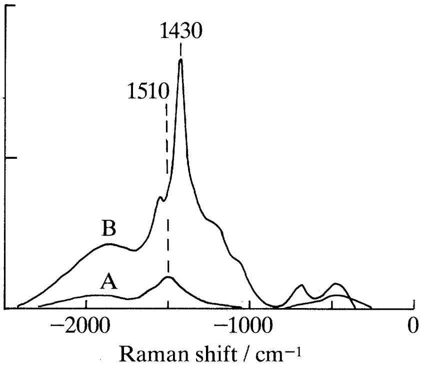

Figure 2. Raman shift spectra of film 2, recorded at 77 K and excited with (*a*) 488.0 or (*b*) 514.5 nm light, after heat treatments at (i) 1000 °C and (ii) 1300 °C.

Figure 3. Deconvoluted A and B Raman spectra for CVD film 2 at 77 K.

component under 514.5 nm excitation. Both Raman components seem to bear a strong resemblance to the Raman spectra of amorphous $Si_x\,C_{1-x}$ reported by Ramsteiner *et al.* (1988), and because of this have been associated at least in part with the presence of silicon in the diamond film.

Clark & Dickerson (1992) also have reported that the broad band luminescence at 1.90 eV and its variation in intensity in the temperature range 72–300 K has a strong resemblance to the photoluminescence behaviour of amorphous hydrogenated $Si_x\,C_{1-x}$ alloys as reported by Sussmann & Ogden (1981).

The purpose of this paper is to report the further behaviour of the same three diamond films reported in our earlier publications, as a result of electron irradiation and heat treatment.

2. Results

(*a*) *Heat treatment of as-grown* CVD *diamond film*

A small fragment of the as-grown film 2 has been subjected to a series of isochronal heat treatments for thirty minutes under high vacuum conditions in the temperature range 800–1350 °C. The Raman spectra excited by 488.0 and 514.5 nm light after the 1000 and 1300 °C anneals are shown in figure 2. The spectra have been normalized, but note that the 514.5 nm spectra are more intense than the 488 nm spectra. From 800–1200 °C some variations of normalized intensity were observed for both excitations but the general shapes of the two sets of spectra did not show much change. Up to 1200 °C each of the spectra could be deconvoluted quite well into the A and B Raman components shown in figure 3. These A and B components are refinements to the original A and B spectra resulting from the fitting of a wider range of spectra. Figure 2 shows that under 488.0 and 514.5 nm excitation there is a sharp increase in the measured Raman intensity after the 1300 °C heat treatment. With the exception of an obvious additional peak at *ca.* 1600 cm^{-1} the shape of the 488 nm spectrum was not appreciably altered. For the 514.5 nm excitation the relative intensities of the spectral features changed. Thus the features at 450, 670, 1070 and 1185 cm^{-1} in the 514.5 nm Raman shift spectrum showed a greater increase in

Figure 4

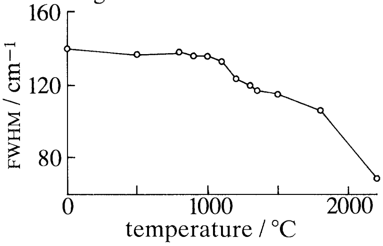

Figure 5

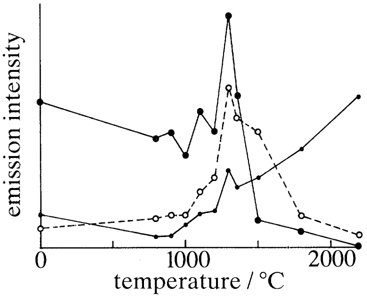

Figure 4. The change in the half-width (FWHM) of the 1.681 eV zero-phonon line in film 2 as a function of the annealing temperature. Measurements of half-width were recorded at 77 K.

Figure 5. The changes in emission intensity of the Raman signal at 1430 cm^{-1} (large spots), the 1.681 eV zero-phonon line (small spots) and the 1.967 eV zero-phonon line (open circles) for film 2 as a function of thermal annealing temperature. Spectra were recorded at 77 K using 514.5 nm exciting light.

strength than the peaks at higher energies. The 514.5 nm spectrum no longer could be described solely in terms of the A and B Raman components and an additional Raman spectrum appeared to have been produced.

The sharpening up of the peaks at 450, 670, 1070 and 1185 cm^{-1} suggests that the film may have been relieved of some of the strain which had been introduced during growth. Because of the large half widths and possible overlaps between these features it is difficult to obtain a quantitative measure of these linewidth changes. However, the 1.681 eV line is much sharper and shows a 13% reduction in linewidth between 1000 and 1350 °C as shown in figure 4.

The isochronal annealing has been extended to the temperature range 1500–2200 °C, but for these treatments the samples were subjected also to a hydrostatic pressure of 9 GPa to maintain diamond stability. At 1350 °C the Raman intensity of both A and B components showed a sharp reduction in strength and this was followed by a further reduction at 1500 °C. The overall annealing behaviour of the Raman scattering is shown in figure 5, where the background corrected Raman scattering signal at 1430 cm^{-1} (recorded under 514.5 nm excitation) is plotted as a function of the annealing temperature. The signal at 1430 cm^{-1} indicates the behaviour of the strongest feature in the Raman spectra, but all the other features exhibit a very similar behaviour. There are fluctuations in intensity up to 1200 °C which may be due to experimental uncertainties in the normalization procedures, but there is a clear peak in intensity at 1300 °C followed by a sharp reduction at 1500 °C.

During the isochronal heat treatment of as-grown films 1 and 2 a zero-phonon line was observed at 1.967 eV. A much weaker line at 1.923 eV is probably an associated, phonon-assisted transition, indicating a rather weak coupling to the lattice, rather similar to the 1.681 eV centre. The variations in the integrated intensities of the 1.967 eV and 1.681 eV zero-phonon lines with annealing temperature are compared with the Raman scattering behaviour in figure 5. All three features show an abrupt change in behaviour at 1300 °C indicating that the events are linked in some way. It is suggested that all three features may be influenced by the presence of silicon impurity in the films. As the heating sequence proceeds it appears that the silicon present in the film is converted into the form of the 1.681 eV centre.

Figure 6

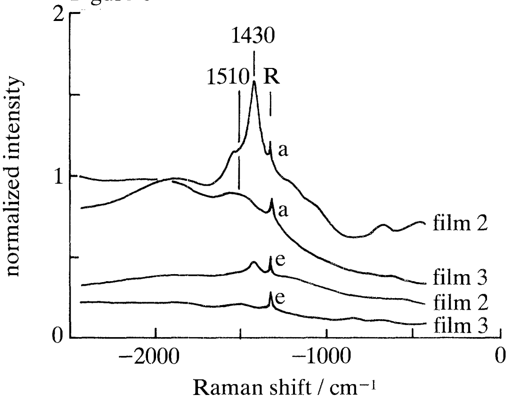

Figure 7

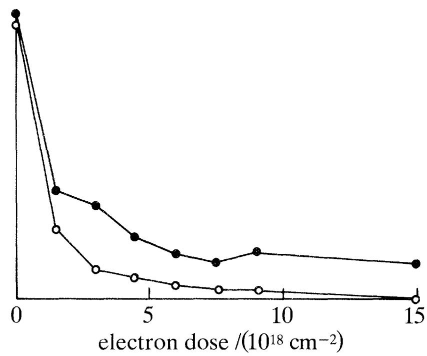

Figure 6. Raman shift spectra recorded at 77 K for films 2 and 3 in the as-grown condition (labelled a) and after electron irradiation (labelled e).

Figure 7. The Raman signal at 1500 cm^{-1} for CVD diamond film 2 as a function of 2.0 MeV electron dose (open circles). The emission was recorded at 77 K using 514.5 nm exciting light. The dots show the electron dose dependence of the signal at 1.90 eV for film 3 using 514.5 nm exciting light.

(*b*) *Electron irradiation of as-grown* CVD *diamond*

Small fragments of films 2 and 3 were irradiated at room temperature with 2.0 MeV electrons and the emission spectra excited with 514.5 nm light were measured as a function of the electron dose. The spectra in figure 6 were recorded before and after irradiation. That both the A and B Raman components were reduced in intensity can be seen because film 3 contains almost exclusively component A, whereas film 2 contains both the A and B components in roughly the same relative proportions.

Figure 7 shows the electron dose dependence of:

(*a*) the background corrected Raman signal at 1500 cm^{-1} for 514.5 nm excitation of film 2 (this parameter includes contributions from both the A and B Raman components);

(*b*) the photoluminescence signal at 1.90 eV for film 3.

It is apparent that both the A and B Raman scattering features and the broad band photoluminescence at 1.90 eV are substantially removed by an irradiation dose of 2×10^{18} electrons cm^{-2}.

(*c*) *Heat treatment of electron irradiated* CVD *film*

The changes in the Raman shift spectrum of an electron irradiated fragment of film 1 were recorded after a series of heat treatments and the results are summarized in figure 8. The spectra shown were recorded under 488 nm excitation. After the 300 °C anneal there appears to be a sharpening of the individual Raman components and, at the same time, there is an overall decrease in signal intensity. For heat treatments above 300 °C the Raman scattering signal increases in intensity and after heating at 600 °C the spectrum had recovered to be very similar to the intensity and form of the spectrum of the as-grown sample. A very similar set of results was obtained for film 2 under 514.5 nm excitation, so that it is concluded that both the A and B Raman components respond in the same way to electron irradiation and subsequent heat treatment.

It is not easy to investigate the thermal annealing behaviour of the 1.90 eV broad

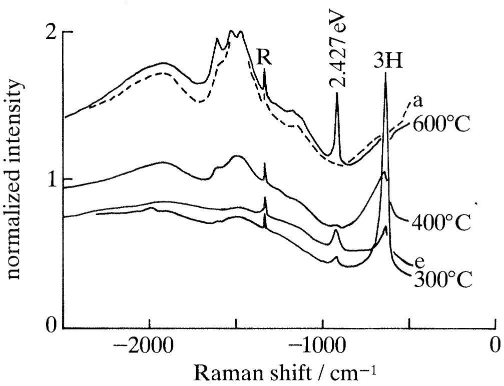

Figure 8. Raman shift spectra of film 1 in the as-grown condition (broken line), after electron irradiation (labelled e) and after thermal annealing at 300 °C, 400 °C and 600 °C. All the spectra were recorded at 77 K using 488.0 nm exciting light.

band luminescence because in film 3 the 2.156 eV centre (a centre thought to involve nitrogen impurity in association with a vacant lattice site) with strong vibronic sideband is generated as the vacancies become mobile, and this emission strongly overlaps with the 1.90 eV band. However, after heating at 1200 °C the 2.156 eV luminescence was no longer present in the emission spectrum and at this stage a broad band centred at 1.90 eV was observed at an intensity 1.4 times the intensity of the band observed in the as-grown condition. This behaviour is very similar to that of the Raman scattering.

3. Discussion

Irradiation of natural diamond with 2.0 MeV electrons usually produces a zero-phonon line at 1.673 eV with a strong vibronic sideband and it is generally accepted to be due to the neutral vacancy. It is often referred to in the literature as the GR1 centre. This line has been induced in the CVD diamond films studied in the present investigation but it is in close proximity to the 1.681 eV zero-phonon line when it too is present in the spectrum. These lines can be distinguished provided they are not seriously strain broadened and the absorption or luminescence measurements are carried out at low temperatures. The two lines also can be distinguished because they have very different vibronic sideband structures.

Since vacancies act as donor centres when introduced into the p-type semi-conducting diamonds measurements of the changing carrier concentration in semiconducting diamond can provide an estimate of the rate of production of intrinsic defects in diamond during electron irradiation. Clark *et al.* (1961) found that during 2.0 MeV electron irradiation the number of donor levels produced per incident electron was about 10. Since the depth of penetration of 2.0 MeV electrons in diamond is close to 2 mm, a dose of 2×10^{18} electrons cm^{-2} would be expected to produce a concentration of 10^{20} defects cm^{-3} in the surface layer. This corresponds to about 6 in 10^4 atoms being displaced. Similar proportions of displaced atoms would be expected for other non-ionically bonded bulk materials.

In view of the above discussion, since an electron dose of 2×10^{18} electrons cm^{-2} is sufficient almost to eliminate the A and B Raman components and the 1.90 eV band, it seems unlikely that they can be associated with bulk material. The complete recovery of the A and B Raman scattering by thermal annealing at 300 and 600 °C also is difficult to understand in terms of bulk material, but it could be explained more readily if the A and B Raman spectra are associated with defect-like species.

During the thermal annealing of the as-grown films, the A and B Raman components, the 1.681 eV centre and the 1.967 eV centre all show an abrupt annealing peak at 1300 °C. This seems to indicate that they are closely related to one another, and since the 1.681 eV centre is known to be a point defect in diamond, the other features are presumed also to be defects in diamond. In this respect it should be noted that silicon concentrations of between 15 and 50 ppm have been recorded in similar CVD diamond films by secondary ion mass spectroscopy (SIMS), and this is much lower than the estimated intrinsic defect concentration introduced by electron irradiation and described earlier.

The conclusion that the Raman scattering in the present work is associated with defects in CVD diamond implies that high Raman scattering cross sections are involved. It is not easy to propose models for the species which are responsible for the Raman scattering, but it is worth discussing their behaviour in relation to other more familiar point defects in diamond.

Vacancies in diamond are known to diffuse at temperatures in excess of 600 °C (Collins 1979) and they contribute to the formation of the 1.681 eV centre (Clark & Dickerson, 1991) in irradiated CVD diamond film. Since they are immobile below 600 °C vacancies would not seem to be involved in the Raman scattering behaviour below 600 °C.

There is no clear picture about the role of interstitial carbon atoms in diamond. Lomer & Marriott (1979) have suggested that interstitials might diffuse at temperatures as low as 50 K. It has further been speculated that mobile interstitials might become trapped at various sites from which they could be thermally released at different temperatures in the range up to 600 °C. Thus an involvement of interstitials with the Raman scattering centres might be a possibility.

Another mechanism which might affect the behaviour of the Raman scattering is charge redistribution amongst the defects present. In principle this can occur during electron irradiation or during optical illumination of the sample. In relation to this the defect known as 3H (with zero-phonon line at 2.462 eV, and illustrated in figure 8) has been reported to show charge exchange effects after irradiation and subsequent thermal annealing up to 600 °C (Palmer 1961). Figure 8 also shows the presence of a previously unreported defect with zero-phonon line at 2.427 eV which also exhibits reactivity during heat treatment up to 600 °C. A more detailed investigation of the removal and recovery of the Raman scattering spectrum is required.

Resonant Raman scattering behaviour in CVD diamond has been reported previously by Wagner *et al.* (1991) using a wide range of excitation photon energies (1.16–4.82 eV instead of 2.54–2.41 eV in the present study). The positions of peaks in their 290 K emission spectra depended upon the excitation photon energy, and the general shapes of the spectra were not the same as those reported here. It will be interesting to see how such features respond to the temperature at which they are measured, and to investigate their response to electron irradiation and heat treatment.

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Discussion

J. E. Butler (*Naval Research Laboratory, Washington, D.C., U.S.A.*): Raman features are observed with most of the characteristics of your A and B spectra in samples that do not show any evidence of the 1.681 eV photoluminescence feature attributed to a Si related defect. These were samples grown with an atmospheric oxygen–acetylene torch on molybdenum substrates. Your extensive analysis of these three Si containing CVD diamond films indicates interesting correlations of the non-1332 cm^{-1} Raman features (particularly in the 1340 to 1600 cm^{-1} region) with other point defect characteristics. Since the Raman spectra observed for various types and qualities of CVD diamond display similar features, please comment on the uniqueness of your deconvolution and the extention of your analysis to non-Si containing films.

C. D. Clark. In depth Raman scattering studies of the effects of heat treatment and electron irradiation need to be carried out on diamond films grown by other processes.