phys. stat. sol. (a) **154**, 255 (1996)

Subject classification: 78.30; 68.55; S5

H. H. Wills Physics Laboratory[1] *(a), School of Chemistry*[2] *(b), and*
Interface Analysis Centre[3] *(c), University of Bristol, and*
Renishaw plc, Transducer Systems Division, Wotton-under-Edge[4] *(d)*

Laser Raman Studies of Polycrystalline and Amorphic Diamond Films

By

W. N. WANG (a), N. A. FOX (a), P. W. MAY (b), M. P. KNAPPER (b),
G. MEADEN (c), P. G. PARTRIDGE (c), M. N. R. ASHFOLD (b), J. W. STEEDS (a),
I. P. HAYWARD (d), and G. D. PITT (d)

(Received August 22, 1995; in revised form November 20, 1995)

This report describes the results of a number of different, but related, laser Raman studies on various CVD diamond samples. It attempts to show the versatility of Raman spectroscopy as a diagnostic tool for the quality of diamond films, by demonstrating its use in a few novel applications. The studies of the laser Raman spectra of amorphic diamond and CVD diamond films are performed using lasers of different excitation wavelength (632.8, 514.5, and 780 nm). For CVD diamond films, a significant reduction in unwanted laser induced fluorescence is observed when using the near-IR diode laser (780 nm) compared to excitation using the shorter (visible) wavelengths. The luminescence peak at a Raman shift of 2260 cm^{-1} coinciding with the graphite G band, can be used as a reliable indicator of poor quality diamond. Additional information about the stress of the diamond films on hard substrates can be obtained from the intensity of the luminescence peak at a Raman shift of 2600 cm^{-1}. Laser Raman spectra of CVD diamond films that have previously been used in electron emission tests show that graphitisation had occurred around emission sites. Direct Raman imaging was used to investigate the cut, exposed surface of a diamond fibre reinforced metal matrix composite. Amorphic diamond films prepared by laser ablation are examined by both Raman and transmission electron diffraction, and the presence of nanocrystalline diamond clusters embedded within the amorphic diamond matrix is verified.

1. Introduction

Recently there has been a surge of interest in diamond films prepared on non-diamond substrates using various forms of assisted chemical vapour deposition (CVD) from hydrocarbon–hydrogen mixtures [1]. Developments of such films for application as cold cathode emitters, structural composites, grinding tools, IR-transmitting films, thermal management materials, and other purposes, require a rather precise characterisation of the material. As such, a number of specialised diagnostic techniques are used to study diamond films, arguably the most important of which is laser Raman spectroscopy.

This report presents the results of a number of different, but related, laser Raman studies on various CVD diamond samples. It attempts to show the versatility of Raman

---

[1] Tyndall Avenue, Bristol BS8 1TL, UK.

[2] Cantock's Close, Bristol BS8 1TS, UK.

[3] Oldbury House, St. Michael's Hill, Bristol BS2 8BS, UK.

[4] Old Town, Wotton-under-Edge, Gloucestershire GL12 7DH, UK.

spectroscopy as a diagnostic tool for diamond films, by demonstrating its use in a few novel applications. Laser Raman spectroscopy is an ideal choice for characterising diamond and other forms of carbon. It can provide detailed information about the chemical composition, the film morphology [2, 3], the crystallite orientation [4] and size [5], the stress [6, 7], and defects [8, 9]. Additional information about the films, such as the amount of stress and defects, can also be obtained from the associated photoluminescence spectra [10]. Furthermore, by correlating the field emission properties and luminescence spectra of CVD diamond films it might be possible to facilitate the optimisation of materials preparation for cold cathode emission applications. The interaction of the diamond film and substrate is also important, especially for electronic applications. Laser Raman spectroscopy is sensitive enough to distinguish between diamond films grown on substrates of only slightly different material. For example, we will show later, that diamond films grown on n-type and p-type Si substrates show marked differences in their Raman characteristics.

In most laser Raman studies of diamond films, the spectra are only taken at one excitation wavelength, usually 632.8 nm. This is unfortunate, since the observed Raman spectra can depend critically upon the excitation wavelength, as this determines the penetration depth (due to significant absorption by included graphitic impurities within the film), the background fluorescence level, and in principle, the whole mechanism of phonon excitation within the crystalline material. Sensitivity is also affected, since the scattering efficiency scales as ν^4 (where ν is the frequency). Use of shorter-wavelength lasers, therefore, should lead to a lower detection limit and an increase both in the spectral resolution and the wavelength accuracy. A great deal more information about the film properties can therefore be determined if spectra of the same samples are taken at a number of different laser excitation wavelengths.

Laser Raman spectroscopy is also useful in determining the presence of sp^3-bonded clusters in the presence of an amorphous carbon background. This is particularly important for so-called ‘amorphic diamond’ films. These are hard carbon films which contain a high proportion of sp^3-bonded carbon [11], and may be said to exhibit short-range order but no long-range order. Compared to diamond-like carbon (DLC) films, which can contain up to 30% hydrogen, amorphic diamond films contain very little, or no, hydrogen. Amorphic diamond films can be made by a number of methods, one of which is laser ablation of a graphite rod in a high vacuum. Such films are receiving a lot of attention at the moment due to their possible use as coatings for cold cathode emission devices. The quality of the film, in other words its sp^3:sp^2 character, is essential in determining the electron emission properties of the film. Raman spectra of laser ablated amorphic diamond films generally show a broad band centred around $1500\,\mathrm{cm}^{-1}$ with a large tail towards lower wavenumber. This should be contrasted with the Raman spectrum from DLC, which typically displays a band peaking at around $1555\,\mathrm{cm}^{-1}$. What is of more interest in the characterisation of amorphic diamond films is the determination of the presence of small sp^3-bonded carbon clusters within the bulk of the film; these may be important as electron emission sites. These can be observed and are generally designated as the D-line ($1350\,\mathrm{cm}^{-1}$) [12, 13]. In itself, the presence of the D-line does not prove the presence of sp^3 sites, and so an additional characterisation method, such as electron diffraction by TEM is required.

CVD diamond films have also been proposed for use as field emission devices. The lifetime for electron emission from such films depends critically upon the current drawn from the device. Drawing too much current causes the diamond film surface to degrade rapidly, and the emission to reduce and finally cease. Drawing moderate currents allows extension of device lifetimes, but eventually the device degrades and fails. The mechanism by which the surface degrades is obviously of interest if we are to produce high brightness, long lifetime devices and displays. Laser Raman spectroscopy is a quick and simple method of studying the degraded diamond surface after device burn-out and should provide clues to the understanding of device failure.

The Raman technique can also be used in 'imaging mode', whereby a two-dimensional representation of a surface can be made by observing only one wavelength component of the Raman signal scattered from a sample – all other wavelengths being filtered out. If the wavelength chosen is that for diamond ($\approx 1332\,\mathrm{cm}^{-1}$), it is easy to identify and differentiate the regions of diamond and non-diamond on an otherwise featureless surface. Apart from characterising the homogeneity of amorphic diamond films, one area where this might be of use is in studying the cross-section of diamond laminates or composites. These materials are currently the subject of a great deal of research, since they may lead to strong, stiff, but very light materials for use in say, aerospace applications [1]. They consist of diamond-coated wires or fibres, embedded into a matrix material, such as titanium. Of interest is the integrity of the composite. Does the metal fill all the voids? Do the fibres pull out? Is there a clean metal/diamond interface? Cross-sectioning such a composite is difficult, but can be done using a high power, highly focused laser. Imaging Raman can then be used to study the exposed surface, looking for voids, cracks in the diamond coating, and, in this particular case, intermixing of diamond and Ti.

2. Experimental

Raman measurements were made with various Raman microscopes manufactured by Renishaw plc, using HeNe (632.8 nm), argon (514.5 nm), and near-infrared semiconductor (780 nm) laser excitation sources. A ×50 microscope objective was used to focus the laser onto a spot approximately 1 μm in diameter, and to collect the scattered light, which then passed through the spectrometer onto a CCD detector. For photoluminescence studies, the laser power was reduced to 1% of its maximum output (10 mW) in order to prevent saturation of the CCD. In imaging mode, the laser spot was defocused so that the spectrometer illuminated a large region of the sample (≈ 500 μm across), and the scattered light was passed through a $10\,\mathrm{cm}^{-1}$ (half-width at half-maximum) band-pass filter and directly imaged onto the CCD detector. The filter was angle-tuned to select the $1332\,\mathrm{cm}^{-1}$ diamond band in which the image was recorded.

CVD diamond films studied in this report were prepared using microwave plasma CVD (MWCVD), utilising both 1 kW and 5 kW ASTEX microwave sources, and hot filament CVD (HFCVD) [1]. Growth conditions were typically 1% methane in hydrogen, and the films were usually about 5 μm thick. Amorphic diamond films on Si and quartz substrates were prepared by laser ablation using the third harmonic of a pulsed (10 Hz) Nd:YAG laser (355 nm) in a high vacuum system (1.3×10^{-4} Torr). Pulse energies in the range 30 to 100 mJ were used and focused to an area of $\approx 0.02\,\mathrm{cm}^2$. The target was a high density graphite rod (99.99% pure), mounted vertically and rotated so that each laser shot encountered a fresh area of surface. The substrate–target distance in the horizontal plane was typically 0.6 cm, and rear of the substrate was attached to a manipulator by high vacuum grease.

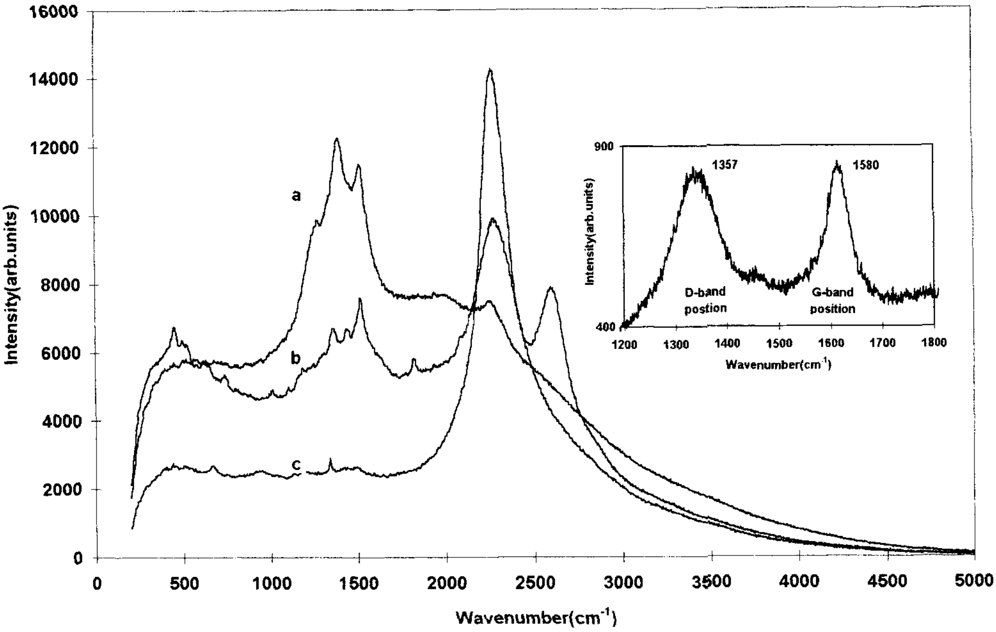

Fig. 1. Raman spectra (HeNe laser, 632.8 nm, 0.1 mW) of CVD diamond films deposited on (a) p-Si, (b) n-Si, and (c) molybdenum substrates. (a) and (b) were prepared by bias enhanced MWCVD without diamond pre-abrasion, (c) by HFCVD with diamond pre-abrasion. Inset is the Raman spectrum of a highly graphitised grain boundary of MWCVD diamond film with strong D and G bands

Diamond-coated wires were made by hot filament CVD onto W wire [14]. Both the core diameter and the diamond coating thickness were varied to give diamond volume fractions of up to about 97%. An aligned sample of these continuous diamond-coated wires were sputtered with Ti and embedded in Ti–6Al–4V alloy at 900 °C either by hot vacuum pressing under superplastic conditions, or by hot isostatic pressing, to produce a diamond fibre reinforced metal matrix composite. The inter-fibre spacing was about 0.25 to 1.0 times the fibre diameter, leading to a high volume fraction of fibre.

A pulsed (10 Hz) Nd:YAG laser, equipped with unstable resonator optics, operating at a wavelength of 355 nm and focused to a line using a 15 cm focal length cylindrical lens, was used to cut the composite since this produced a nice smooth surface finish without apparently damaging the matrix or diamond fibres [15].

3. Results and Discussions

3.1 Raman and photoluminescence spectra of CVD diamond films

Raman spectra (632.8 nm excitation wavelength, 0.1 mW laser power) of diamond films (all at ≈5 μm thickness) deposited onto (a) p-type Si, (b) n-type Si, and (c) molybdenum substrates are shown in Fig. 1. The most obvious features are the strong peaks in the 1300 to 1600 cm^{-1} region, the strong broad luminescent background, and the sharper luminescent peaks visible at 2260 and 2600 cm^{-1}. The 1332 cm^{-1} diamond first-order phonon band is less obvious due to the reduced laser power.

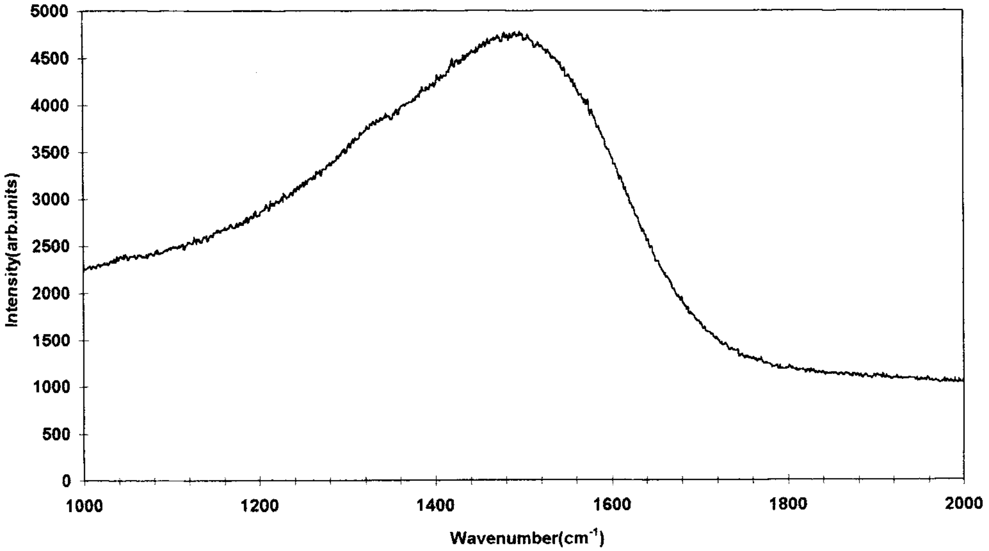

Fig. 2. A Raman spectrum (HeNe laser, 632.8 nm, 0.1 mW) of an amorphic diamond film prepared by laser ablation of a high purity graphite rod (Nd:YAG laser, 355 nm, 10 Hz repetition rate)

The 2260 cm^{-1} luminescence peak (1.68 eV) is often attributed to silicon defects in the diamond lattice [10, 16]. This peak is normally observed riding on the broad G band ($\approx$1580 cm^{-1}), and is strongest in the regions giving strong G signal [17]. The G band is closely related with bond-angle disorder between carbons in sp^2 sites with contributions from both disordered and crystalline graphite. In contrast, the diamond signal is normally observed riding on the D band ($\approx$1350 cm^{-1}), which is closely related with the disordered carbon in sp^3 sites. The 2260 cm^{-1} luminescence peak is strongest in regions of the grain boundary, which generally gives a strong G-band signal. It is possible that Si and other impurities (such as nitrogen) could diffuse more readily through the graphite planes in the G-band region than through the diamond grains. In Fig. 1, the 2260 cm^{-1} luminescence peak is more pronounced in the n-Si and Mo substrates than in the p-Si substrate. Both diamond films on p-Si and n-Si were prepared by bias-enhanced MWCVD without diamond powder abrasion. Therefore, it is suggested that during initial nucleation, more graphitic G material may be formed on n-Si than on p-Si, which results in faster silicon diffusion from the substrate, leading to a much stronger 2260 cm^{-1} luminescence signal. The diamond film on Mo was prepared by HFCVD with diamond powder abrasion, which may have been contaminated by repeated use on silicon wafers.

It is also interesting to notice the sharp luminescence peak at 2600 cm^{-1} (1.647 eV) which was only observed in HFCVD-produced diamond films and appeared stronger for films deposited on hard substrates such as Mo and W. Diamond films deposited on hard substrates such as molybdenum, alumina, tungsten carbide, and silica glass cannot relax through the plastic deformation which occurs in soft substrates. Therefore these films are expected to have significant stress within the bulk and interface due to the difference in thermal expansion coefficients and lattice mismatch between diamond and substrate. The 2600 cm^{-1} band could be the vibronic sidebands of the 2260 cm^{-1} zero-phonon line.

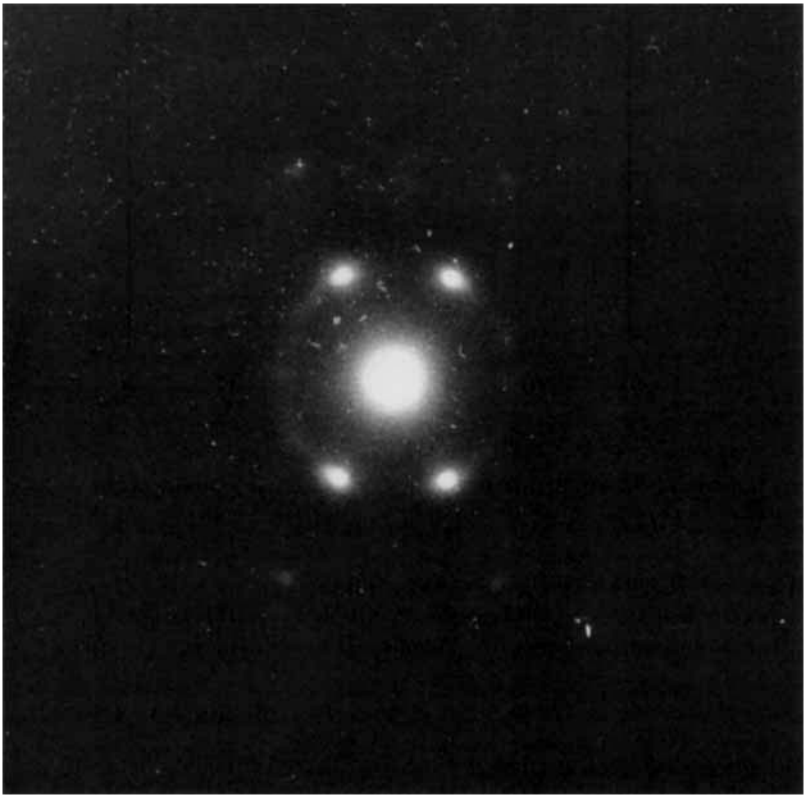

Fig. 3. Electron diffraction pattern of a single nanocrystalline diamond cluster embedded in the amorphic diamond film matrix (100 nm thickness) lifted from a silicon substrate by HF

However, its true origin is not clear. The stress induced cracks and microvoids in these diamond films, which were observed under high magnification SEM, and enhanced nitrogen intake through these defects, may be responsible for the luminescence at 2600 cm^{-1} [18]. If this is so, this band could serve as a qualitative indication for the presence of stress, defects, and impurities within a diamond film.

3.2 The presence of nanocrystalline diamond in amorphic diamond films

Fig. 2 shows a laser Raman spectrum (using an excitation wavelength of 632.8 nm) taken from an amorphic diamond film. It exhibits the general appearance characteristic of amorphic diamond, a broad band around 1500 cm^{-1} tailing down to lower wavenumber. The small shoulder is assigned to 1327.5 cm^{-1} after deconvolution of the spectrum, which might indicate the presence of small diamond clusters, or at least, clusters with some degree of sp^3 character. The electron diffraction pattern of one single cluster by TEM on a free-standing (HF-lifted) amorphic diamond thin film ($\approx$100 nm in thickness) with $d_{111} = 0.206$ nm and $d_{220} = 0.126$ nm (Fig. 3) confirmed the presence of nanocrystalline diamond. The small shift of 5 cm^{-1} from the normal position of the diamond Raman signal may be a result of stresses within the nano-sized crystallites.

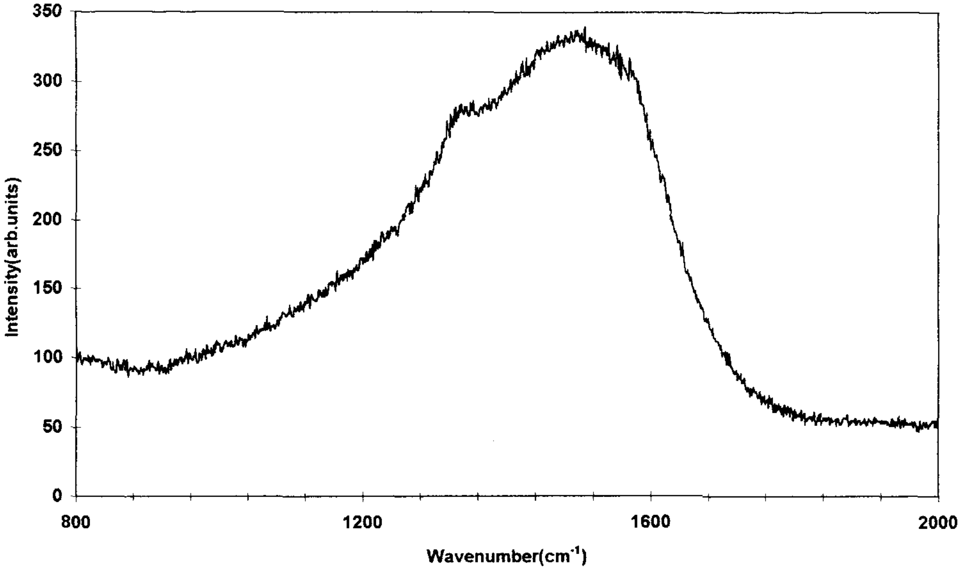

Fig. 4. A Raman spectrum of an amorphic diamond film prepared by laser ablation of a high purity graphite rod (Nd:YAG laser, 355 nm, 10 Hz repetition rate). The spectrum was taken from the centre of the film

Two possible explanations are offered to interpret the formation of diamond clusters in the amorphic diamond matrix. During laser ablation, the combination of the local pressure in the focal region on the substrate and the close distance between target and substrate ($\approx$0.6 cm) resulted in very energetic carbon particles being ejected from the graphite target to strike the substrate. In certain cases the impact energy was sufficiently high to cause local bond rupture followed by rapid recrystallisation. If the recrystallisation is rapid enough, the growing film does not have time to thermally equilibrate, and so crystallises into a dense, compacted structure – diamond. This is consistent with the observation that the deposited amorphic diamond films formed a concentric ring pattern evolving from the centre of the substrate, with diamond clusters only being found in the centre ring. This area was the closest to the target, received the highest flux of particles ablated normal to the target surface, and gave the strongest shoulder signal at 1328 cm^{-1} (Fig. 4). An alternative, but we believe less likely, explanation for diamond cluster formation within a DLC and amorphic diamond matrix is that it is catalysed by the presence of impurities, such as hydrogen, diffusing out of the grease used to attach the silicon substrate wafer to the manipulator [19]. We are presently looking at other ways to hold the substrate during deposition to rule out this possibility.

3.3 Comparison of Raman spectra of CVD diamond films obtained by using a 780 nm near-IR diode laser and a 632.8 nm red HeNe laser

Fig. 5 shows the Raman spectra of the a) front and b) back side of a polished free-standing HFCVD diamond film using HeNe (632.8 nm) laser excitation. A strong photoluminescence background can be seen, and the luminescence is much stronger from the front side than from the back side. A band located at around 2260 cm^{-1} in Fig. 5, curve b

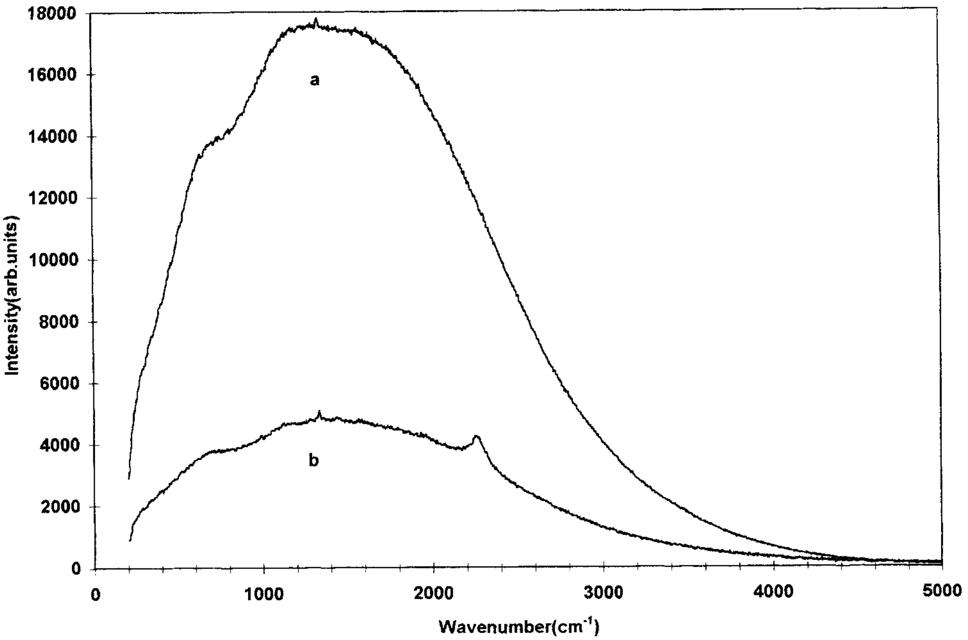

Fig. 5. Raman spectra (HeNe laser 632.8 nm, 0.1 mW) of (a) front and (b) back side of a free-standing HFCVD diamond film

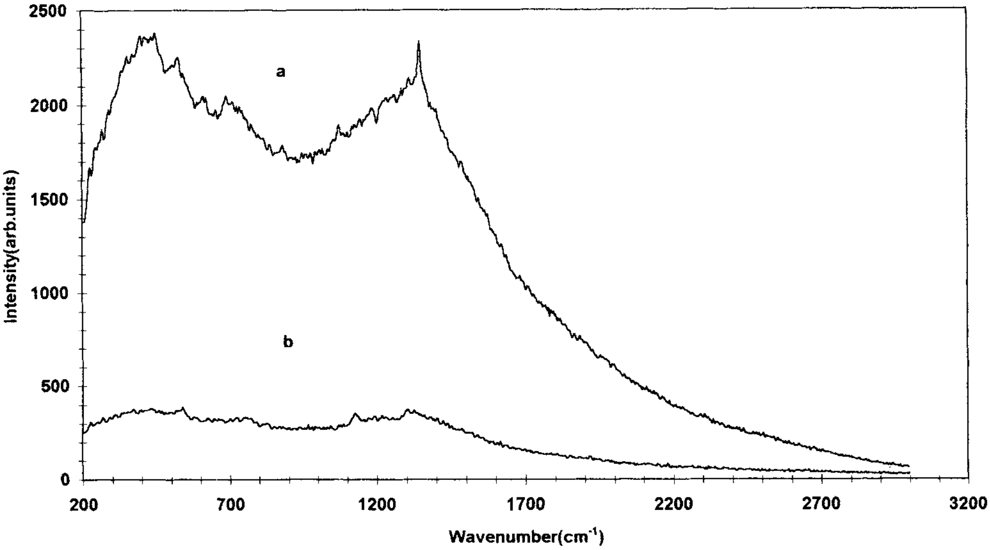

Fig. 6. Raman spectra (near-IR diode laser, 780 nm, 0.1 mW) of (a) front and (b) back side of a free-standing HFCVD diamond film

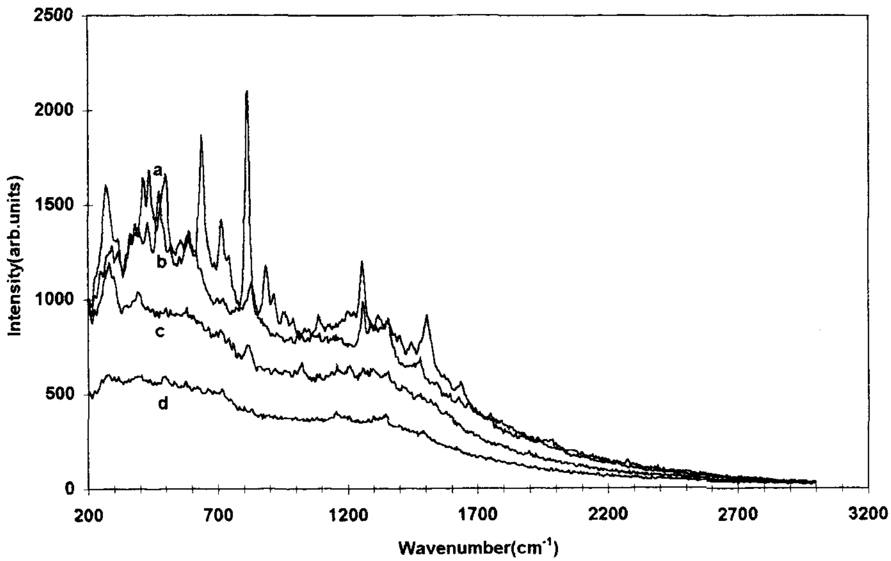

Fig. 7. Raman spectra (near-IR diode laser, 780 nm, 0.1 mW) of a bias enhanced MWCVD diamond film on n-Si with gradual increase of focal depth (10 μm increase each step) from (a) to (d)

attributable to silicon defects in the diamond lattice, clearly indicates that this is the side of the diamond film which was in contact with the silicon substrate. Fig. 6 shows the Raman spectra of the front (curve a) and the back side (curve b) of the same polished free-standing HFCVD diamond film obtained using a near-IR diode laser (780 nm). The main advantage of using this laser is the reduction of unwanted laser induced fluorescence, and hence the increased sensitivity and lower detection limit. As a result, more features can be seen in the spectra due to the near order of magnitude reduction in fluorescence. The difference is more significant in diamond films grown on n-Si prepared by bias enhanced MWCVD (compare Fig. 1 curve a with Fig. 7).

The Raman spectra in Fig. 7 were obtained by focusing the near-IR diode laser to different depths in the film, with the focusing depth increasing from curve a to d. It can be seen that the spectrum taken from close to the surface of the film contains a large number of well-resolved peaks which may provide abundant information related to the surface states of CVD diamond films. Detailed study is currently underway to assign these peaks. With increasing focusing depth, most of these peaks disappear, leaving us with the much simpler spectrum of the bulk film.

3.4 Third-order phonon peak observed in Ar laser excited Raman spectra

Bormett et al. [19] found that if a UV laser is used as the excitation source for Raman spectroscopy of diamond and CVD diamond films, the lack of unwanted fluorescence allows the carbon–hydrogen (C–H) stretching vibrations of the non-diamond components and the third-order phonon bands of diamond to be monitored. They carried out the experiment using a CW intracavity frequency-doubled Ar-ion laser with excitation wavelength at 228.9 nm. The third-order phonon band intensity and frequency maxima were found to be very sensitive to the diamond crystallite size.

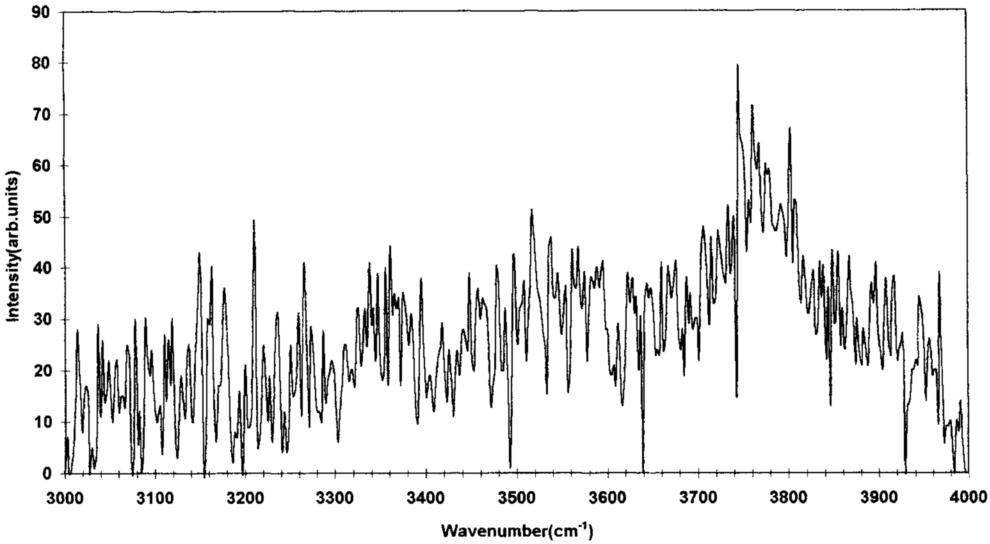

Fig. 8. A Raman spectrum of the third-order phonon band of a CVD diamond film obtained using an Ar ion laser operating at an excitation wavelength of 514.5 nm

We have performed similar work, and found that using the combination of a simple low power Ar^+ laser (operating at 0.1 mW) and a CCD multichannel detector, we could clearly observe (albeit at low signal-to-noise ratio) the third-order phonon signal (Fig. 8) in CVD diamond films ($3760\,cm^{-1}$) and natural type IIa single crystal diamond ($3820\,cm^{-1}$). This possibly resulted from the presence of complicated sub-bands induced by the presence of impurities as well as defects. A stronger signal of the third-order phonon band is readily obtainable using a higher laser power.

3.5 Raman studies of a diamond film damaged by electron emission burn-out

Fig. 9 shows the background corrected Raman spectra of a damaged diamond film cold cathode emitter with average particle size of 100 nm prepared by HFCVD. Field emission testing was performed in a UHV system (2×10^{-5} Pa) with anode–cathode spacing 100 μm. The threshold voltage for emission to occur was about $10\,V\,\mu m^{-1}$. The film broke down and ceased emitting after overnight operation at $10\,A\,cm^{-2}$, and a single damaged area of $\approx 100\,\mu m^2$ was selected for Raman study. Spectra were taken a) at the centre of the damaged area, b) 50 μm from the centre, and c) the edge of the damaged area (100 μm from the centre). A clear graphitisation was observed in areas a and b. Most of the diamond film was burnt away leaving a thin graphitic layer behind, which gave a very weak G-band signal. The diamond signal recovered at the edge of the damaged area but was accompanied by a strong graphite signal. It is proposed from these results that the failure mode of the diamond field emission cold cathode could result from the high resistivity and inefficient lateral thermal conduction through grain boundaries. This causes the diamond to overheat locally, at which point surface reconstruction occurs and the film graphitises.

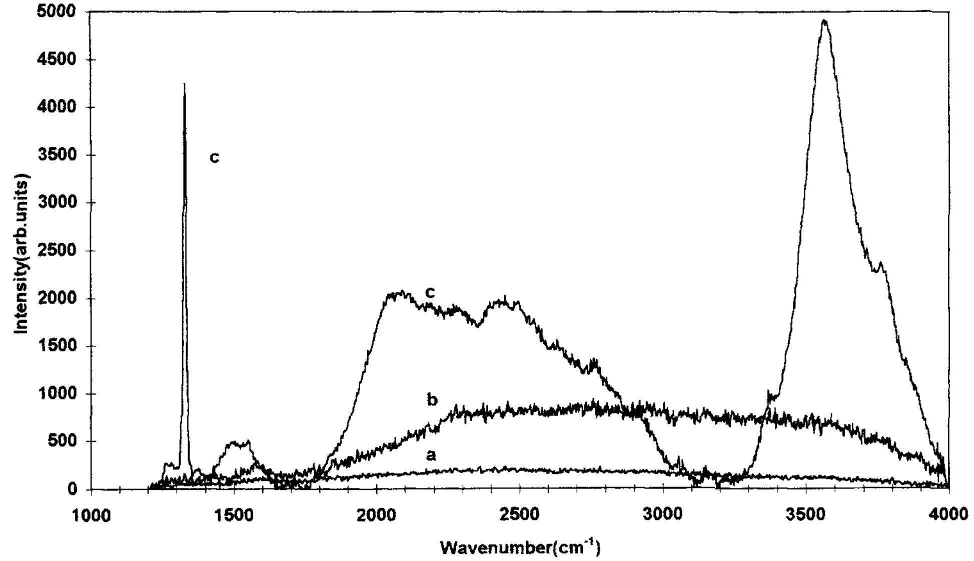

Fig. 9. Raman spectra (HeNe laser, 632.8 nm, 10 mW) of the (a) centre, (b) 50 µm from the centre, and (c) edge of the damaged area of a HFCVD diamond film cold cathode emitter

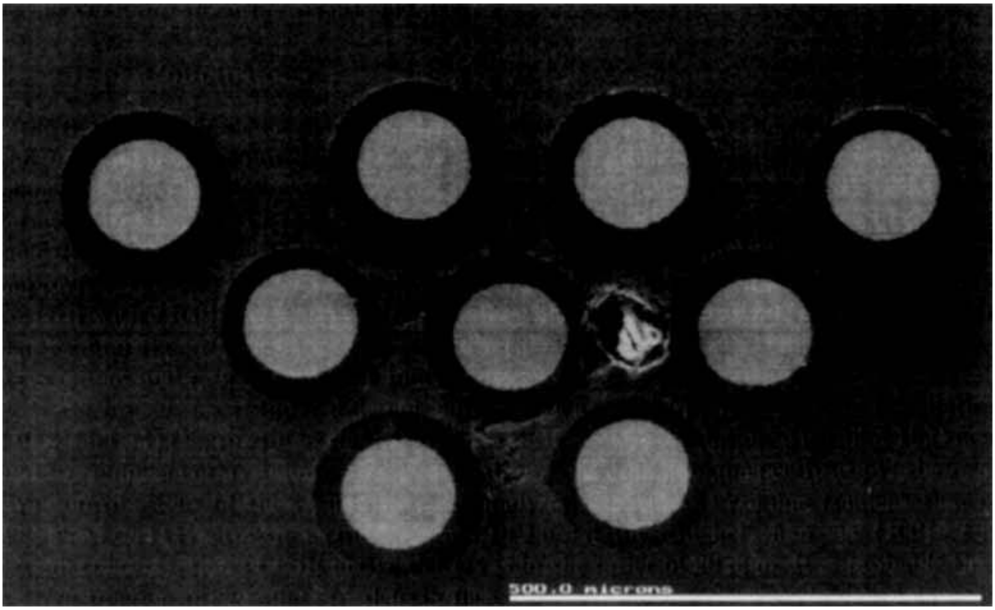

Fig. 10. SEM micrograph of a diamond fibre matrix composite. The matrix material is Ti–6Al–4V alloy, with diamond-coated W wires providing the reinforcement

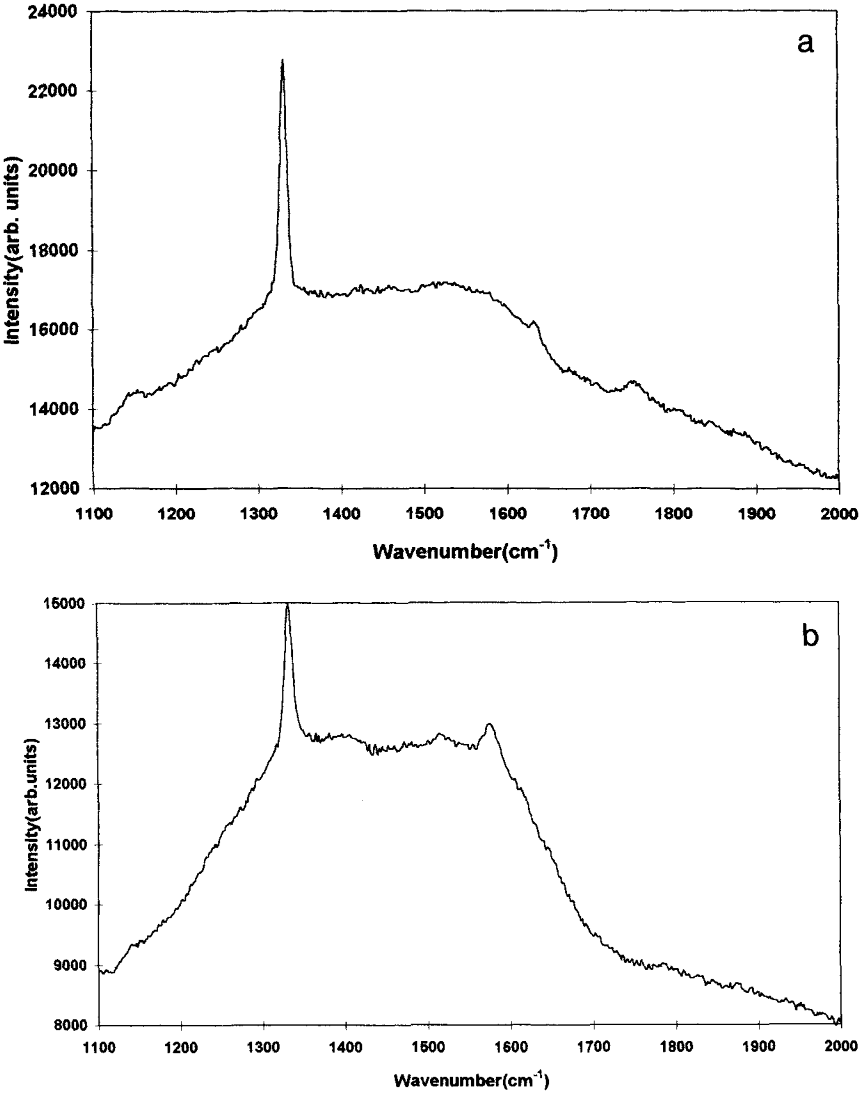

Fig. 11. Raman spectra of diamond-coated W wire used in the matrix composite, a) with no laser treatment, b) after laser cutting. After laser cutting there is a clear increase of the broad 1580 cm^{-1} G bands related to graphitic carbon

3.6 Direct Raman imaging of a diamond fibre metal matrix composite

The composite used was a Ti–6Al–4V alloy matrix with a number of diamond-coated W wires embedded within it. The SEM backscattered electron image of the diamond composite matrix (Fig. 10) shows that the cut surface was planar and very smooth across both the diamond and the core. However, a comparison of the Raman spectra of a single diamond fibre before and after the laser cutting (Fig. 11) indicated that graphitisation occurs on the irradiated diamond surface. Scanning Auger spectroscopy con-

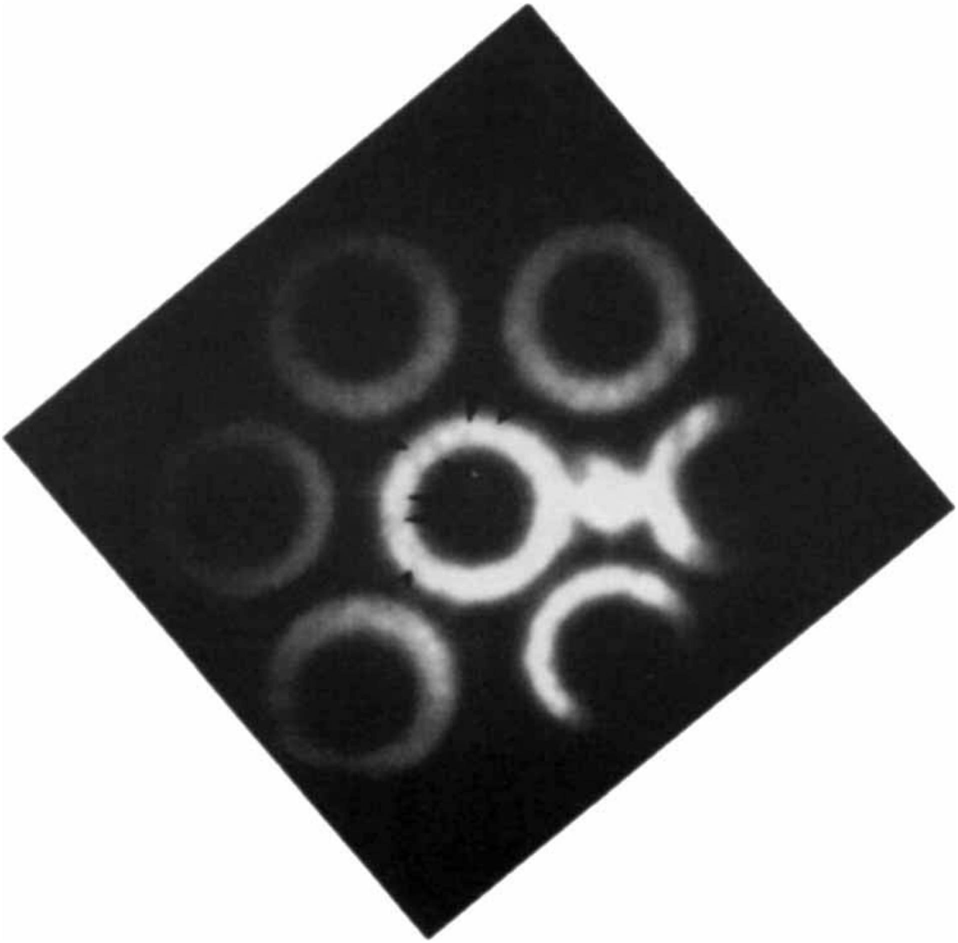

Fig. 12. Two-dimensional Raman image of a diamond fibre matrix composite, imaged via the characteristic diamond peak at $1332\,\mathrm{cm}^{-1}$. Grey areas marked by arrows are diamond fibres contaminated by ablated W metal

firmed this, and showed that the graphitisation occurred to a depth of less than 1 μm. A simple exposure of the graphitised diamond surface to a hydrogen plasma was effective in removing the non-diamond carbon species. After this treatment, the Raman image of the diamond composite showed some non-diamond grey areas (marked by arrows) in the diamond fibre (Fig. 12), which was confirmed by SEM-EDAX to be a thin tungsten film that had been redeposited onto the diamond fibre surface during ablation of the W core.

4. Conclusion

We have provided further demonstration of the fact that laser Raman spectroscopy can be a powerful analytical technique for studying CVD diamond and related carbon films. Proposed mechanical and electronic applications continually demand higher quality films, and so it will become increasingly important to obtain a better understanding of what exactly we mean by the term ‘quality’. Laser Raman spectroscopy is particularly well suited to this task, and its power and versatility will enable it to remain one of the critical diagnostic tools for diamond films, in whatever application they are used.

Acknowledgements The authors wish to acknowledge Renishaw plc Transducer Systems Division for kindly providing the three Raman systems for this research. P.W.M. would like to thank the Royal Society for financial support. N.A.F. gratefully acknowledges Smiths Industries and the Royal Commission for the Exhibition of 1851 for funding.

References

[1] M. N. R. Ashfold, P. W. May, C. A. Rego, and N. M. Everitt, Chem. Soc. Rev. **23**, 21 (1994).
[2] D. S. Knight and W. B. White, J. Mater. Res. **4**, 385 (1989).
[3] A. M. Bonnot, Phys. Rev. B **41**, 6040 (1990).
[4] S.-A. Stuart, S. Prawer, and P. S. Weiser, Appl. Phys. Letters **62**, 1227 (1993).
[5] P. K. Bachmann, H. D. Bausen, H. Lade, D. Leers, D. V. Wiechert, N. Heeres, R. Kohl, and P. Koidl, Diamond relat. Mater. **3**, 1308 (1994).
[6] N. S. van Damme, D. C. Nagle, and S. R. Winzer, Appl. Phys. Letters **58**, 2919 (1991).
[7] E. Gheeraert, A. Deneuville, and A. M. Bonnot, Diamond relat. Mater. **1**, 525 (1992).
[8] S. A. Stuart, S. Prawer, and P. S. Weiser, Appl. Phys. Letters **62**, 1227 (1993).
[9] M. Mitsuhashi, S. Karasawa, S. Ohya, and F. Togashi, Thin Solid Films **228**, 76 (1989).
[10] T. Feng and B. D. Schwartz, J. appl. Phys. **73**, 1415 (1993).
[11] C. B. Collins, F. Davanloo, D. R. Jander, T. J. Lee, H. Park, and J. H. You, J. appl. Phys. **69**, 7862 (1991).
[12] R. J. Nemanich and S. A. Solin, Phys. Rev. B **20**, 392 (1979).
[13] D. Beeman, J. Silverman, R. Lynds, and M. R. Anderson, Phys. Rev. B **30**, 870 (1984).
[14] P. G. Partridge, P. W. May, and M. N. R. Ashfold, Mater. Sci. Technol. **10**, 177 (1994).
[15] P. G. Partridge, G. Meaden, M. N. R. Ashfold, and E. D. Nicholson, presented at Diamond Films ’95, Barcelona (Spain), submitted to Diamond relat. Mater. (1995/6).
[16] C. D. Clark, H. Kanda, I. Kiflawi, and G. Sittas, Phys. Rev. B **51**, 16681 (1995).
[17] I. P. Hayward, K. J. Baldwin, D. M. Hunter, D. N. Batchelder, and G. D. Pitt, Diamond relat. Mater. **4**, 617 (1995).
[18] L. Bergman, M. T. McClure, J. T. Glass, and R. J. Nemanich, J. appl. Phys. **76**, 3020 (1994).
[19] R. W. Bormett, S. A. Asher, R. E. Witoski, W. D. Partlow, R. Lizewski, and F. Pettit, J. appl. Phys. **77**, 5916 (1995).