

785 nm Raman spectroscopy of CVD diamond films

P.W. May*, J.A. Smith, K.N. Rosser

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

Received 27 June 2007; received in revised form 16 November 2007; accepted 4 December 2007

Available online 14 December 2007

Abstract

Raman spectroscopy is a powerful technique often used to study CVD diamond films, however, very little work has been reported for the Raman study of CVD diamond films using near-infrared (785 nm) excitation. Here, we report that when using 785 nm excitation with 1 μm spot size, the Raman spectra from thin polycrystalline diamond films exhibit a multitude of peaks (over 30) ranging from 400–3000 cm^{-1} . These features are too sharp to be photoluminescence, and are a function of film thickness. For films >30 μm thick, freestanding films, and for films grown in diamond substrates the Raman peaks disappear. This suggests that the laser is probing the vibrations of molecular units at the grain boundaries of the disordered crystallites present at the interface between the diamond and substrate.

© 2007 Elsevier B.V. All rights reserved.

Keywords: CVD diamond films; Laser Raman spectroscopy; Microstructure; Nanodiamond

1. Introduction

Raman spectroscopy is a powerful technique often used to study CVD diamond films [1,2]. Excitation using laser wavelengths in the UV and visible regions are most commonly used, and for diamond films these typically produce spectra with a limited number of characteristic peaks, including the diamond peak ($\sim 1332 \text{ cm}^{-1}$), the D and G bands from graphitic impurities, and sometimes the 1150 and 1450 cm^{-1} bands from sp^2 carbon impurities at the grain boundaries of nanophase diamond. Very little work has been reported, however, for the study of CVD diamond films using near-infrared (785 nm, 1.58 eV) excitation, which is exceptionally sensitive to sp^2 carbon. A few groups have used 785 nm excitation to study carbon films, but these have usually concentrated on studies of non-diamond carbon, such as measuring the dispersion of the G band in amorphous carbon films [3,4], carbon nanotubes and onions [5], or the graphitic residues following polishing of diamond [6]. It has also been used in combination with excitation from other wavelengths to study diamondoid molecules [7], revealing a multitude of peaks in the range 400–1500 cm^{-1} corresponding to the numerous different

vibrations of the carbon framework in each molecule. It was suggested that the Raman spectrum from a sufficiently large diamondoid molecule would eventually resemble that seen for nanocrystalline diamond particles or films [8].

For CVD diamond films, however, the only Raman spectra reported using 785 nm excitation concerns the shift of the diamond line and Fano resonance effects during heavy boron doping [9], and some simple characterisation [10]. Recently, Veres et al. [11] reported 785 nm Raman spectra from nanocrystalline diamond films with varying grain sizes, and found that samples with larger grains (>125 nm) exhibited spectra with a number of well distinguished sharp peaks. They suggested that this was due to the increased band gap of the larger crystals, which reduced the amount of resonantly enhanced sp^2 carbon structures allowing the remaining stronger peaks to become visible above the background. Even more recently, the same group reported that the 785 nm Raman spectra from ultrananocrystalline diamond (UNCD) films produced a large number of peaks in the range 1000–2000 cm^{-1} sitting on the broad composite background in the 850–1700 cm^{-1} range [12]. These peaks were specific to 785 nm excitation, and were thought to be due to the selective excitation of different structural units present at the grain boundaries. The intensity and appearance of these sharp peaks was a function of laser spot size on the sample—for spot sizes

* Corresponding author.

E-mail address: Paul.May@bris.ac.uk (P.W. May).

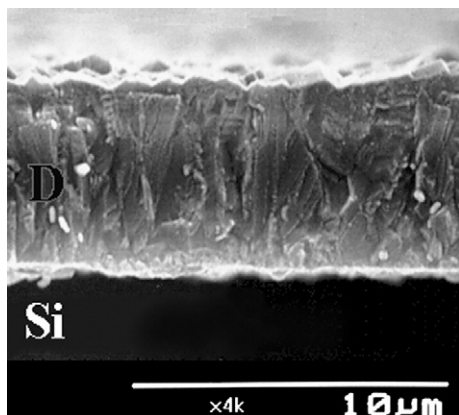


Fig. 1. An electron micrograph cross-section through a 6 μm -thick HFCVD diamond film grown on Si. The diamond film (shown as 'D') has a columnar structure with an interface to the Si substrate consisting of a large number of disordered grains, small defective crystallites, and possibly SiC. Nearer the surface the film is predominantly microcrystalline diamond with relatively large crystallites and fewer grain boundaries.

>5 μm only the broad background was present. As the diameter of the spot size decreased, the sharp peaks began to appear, until by the smallest size ($\sim 1 \mu\text{m}$) the spectrum shows numerous sharp, well resolved peaks. The authors concluded that the peaks appear when the excitation volume is small enough that the sampled grain surface area is comparable to that of the grain. Previously [13], we reported that since the intensities of the diamond and non-diamond components in CVD diamond films vary as a function of excitation wavelength, multi-wavelength Raman studies could be used as a selective probe to the study of different constituents in the deposited films. In that paper we noted that – unlike the other excitation wavelengths which gave the expected D, G and diamond peaks – the spectra obtained using 785 nm excitation gave a large number of well-defined peaks, and that the positions and intensities of these peaks changed in an unpredictable manner. This behaviour is unusual and unexpected, and we now report a series of experiments to attempt to elucidate the reasons behind this observation.

2. Experimental

The CVD diamond films were taken from a variety of sources, however most were deposited using a conventional hot filament CVD reactor using a 1% CH_4/H_2 process gas mixture at 20 Torr. The substrate temperature was constant at $\sim 900 \text{ }^\circ\text{C}$ while the tantalum filament temperature was maintained at 2300 K (monitored by 2-colour optical pyrometer). The substrate was usually single crystal (100) silicon pre-abraded either manually or ultrasonically using 1–3 μm diamond grit. The diamond growth rate was $\sim 0.5 \mu\text{m h}^{-1}$ and the film morphology was microcrystalline with the standard columnar growth structure typical of CVD diamond (see Fig. 1).

The films were analysed using a Renishaw 2000 Raman spectrometer equipped with 3 laser wavelengths, the one of interest here being a 785 nm near-infrared diode laser. The resolution of the laser spot is $\sim 1 \mu\text{m}$ and the sampling depth is

estimated to be around a few μm depending upon the transparency and clarity of the diamond film. The accuracy of the calibration and run-to-run repeatability of the line positions was $\pm 0.2 \text{ cm}^{-1}$ over the range 400–3000 cm^{-1} .

3. Results

Fig. 2 shows a series of Raman spectra using different laser excitation wavelengths, taken from a standard 2 μm -thick CVD diamond film grown on Si. Most of the spectra show the expected peaks and bands from CVD diamond, but with varying intensities due to the different resonance efficiencies of the laser light with sp^2 or sp^3 carbon structures. However, the spectrum taken with 785 nm excitation shows substantially more structure than the other spectra, with upwards of 30 distinct peaks/features visible in the range shown. A listing of these peaks is given in Table 1. Thus, 785 nm excitation seems to be quite special in terms of its interaction of the diamond film compared to the other wavelengths – even those only 100 nm higher or lower in wavelength (as noticed by Veres et al. [12] for UNCD films) – and it appears to substantially enhance features that are normally too small to see.

Fig. 3 shows the 785 nm Raman spectra for a series of HFCVD films of varying thicknesses. For films $< 1 \mu\text{m}$ thick, there are few peaks and little structure in the spectrum, which is dominated by the large peak from the Si substrate. As the film thickness increases above 1 μm , the spectra become more complicated, with a multitude of peaks appearing. These peaks and features behave in an unpredictable way: some appear in all spectra, some only in a few of the spectra, and most change

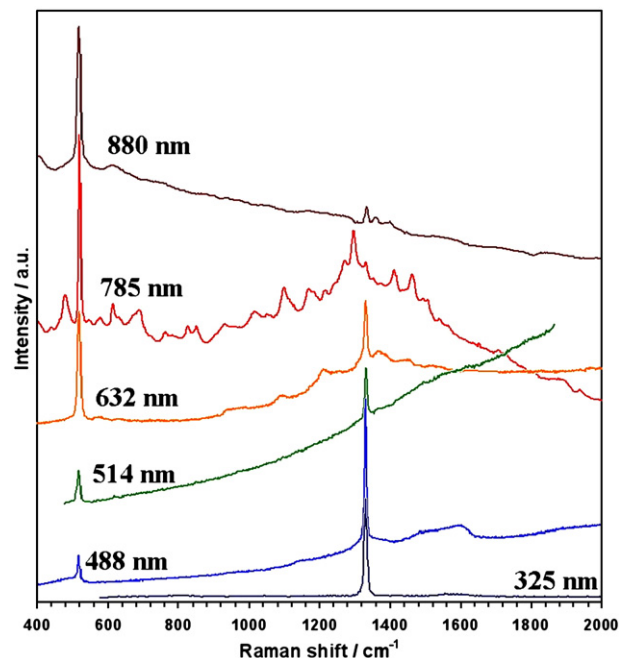


Fig. 2. Raman spectra of a CVD diamond film grown for 4 h ($\sim 2 \mu\text{m}$ thick) on Si using different laser excitation wavelengths. The spectra have been scaled and offset vertically for ease of comparison. The peak at 520 cm^{-1} is due to the Si substrate, and other obvious features are the diamond line at 1332 cm^{-1} , the D band at $\sim 1380 \text{ cm}^{-1}$ and the G band $\sim 1580 \text{ cm}^{-1}$.

Table 1

The following is a list of 785 nm Raman peak positions obtained from various CVD diamond films on Si substrates

Peak positions (cm^{-1}): 2223, 2210–2213, 2172, 2134, 2056, 2017, 1940, 1901, 1877, 1756, 1711, 1675, 1654–1658, 1630, 1620, 1568, [1576, 1540–1542] (G band?), 1507, 1500, [1467–1472, 1459–1465, 1449, 1433–1436] (*trans*-polyacetylene?), 1420, 1412–1416, 1400, [1356–1359, 1350–1352] (D band?), [1331–1333] (diamond), [1323, *1311–1314*] (lonsdaleite?), 1296–1299, 1271–1275, 1262–1264, 1243–1245, 1212–1220, 1185, 1169–1175, 1125–1134 (*trans*-polyacetylene?), 1116, 1098–1105, 1050, 1045, 1034, 1021–1026, 1009–1015, 1000, 976–985, 929–934, 897, 890, 878–883, 852–853, 835–841, 828, 783–785, 760–764, 744–746, 713–718, 689–693, 655, 645–649, 630–634, 625, 613–616, 597, 577, 570, 561–563, 547–549, 537, 521–523, 495, 481–485, 465, 457, 438–443, 423, 405–407.

The first-order (520 cm^{-1}) and second-order ($950\text{--}1000 \text{ cm}^{-1}$) Si peaks are not included. Unless stated otherwise, these peaks are unassigned, but they probably originate from sp^2 carbon structures, defective diamond or nanophase carbon species present at the interface. Peaks shown with a range of positions (e.g. 2210–2213 cm^{-1}) indicate that a sharp peak was seen at different positions within this range from a number of spectra taken from different samples, and so we have assumed that this is the same peak that shifts by a few cm^{-1} . Values enclosed in square brackets have been given the same tentative assignment. The values which are underlined are those which have a superficial correspondence (within a few cm^{-1}) to Raman features reported in the literature (and collated in Zaitsev's book [15]) and, therefore, may have a tentative assignment. Values in italics were seen in UNCD films using 785 nm excitation [12].

relative intensities between spectra in a seemingly random way. The peaks reach a maximum in terms of quantity and complexity at a film thickness of between 2–5 μm . For films thicker than 5 μm , the number of distinct peaks decreases until by a thickness of $\sim 50 \mu\text{m}$ they have disappeared altogether, and the spectrum just consists of a few broad humps (centred ~ 1200 , ~ 1330 , and $\sim 1420 \text{ cm}^{-1}$) on a large photoluminescent background.

A series of experiments were performed to try to pin down the cause of these Raman lines. First, 2- μm -thick diamond films

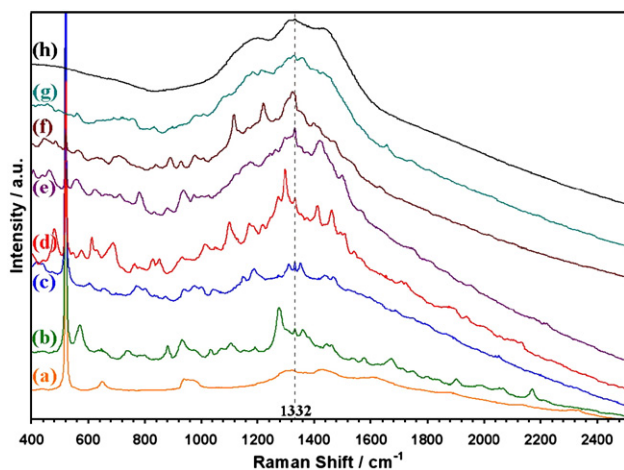


Fig. 3. Raman spectra (785 nm excitation) of CVD diamond films grown on Si using the HF reactor (Ta filament) for varying deposition times, and hence thicknesses. (a) 20 min, 0.17 μm , (b) 45 min, 0.38 μm , (c) 1.5 h, 0.75 μm , (d) 4 h, 2 μm , (e) 10 h, 5 μm , (f) 17 h, 8.5 μm , (g) 32 h, 16 μm , (h) 100 h, 50 μm . The feature at 950–1000 cm^{-1} in (a) is the second-order peak from the Si substrate. The spectra have been scaled and offset vertically for clarity. The dashed vertical line marks the position of the diamond line at 1332 cm^{-1} .

were grown in the same reactor under identical conditions using filaments made from tungsten and rhenium. The 785 nm Raman spectra from each of these films was identical to the spectrum from the film grown with a tantalum filament (Fig. 2). This indicates that the origin of the peaks is unlikely to be contamination in or on the diamond surface from filament material. To be certain, these films were then treated with concentrated 10% nitric acid/sulphuric acid mixture for 24 h, which should dissolve away any metallic residues on the surface. After this treatment the spectra were unchanged. We used similar conditions in a microwave plasma reactor to grow a CVD diamond film of similar thickness and morphology to the ones grown under HFCVD. The Raman spectrum from this MW film also exhibited the Raman features (as was noted previously [11]), which rules out contamination effects from our HF system as being the origin of the peaks.

To rule out substrate effects, films were grown on a variety of substrate materials using identical conditions to before. 2- μm -thick films were grown on tungsten, tungsten carbide, aluminium nitride, quartz, molybdenum, n-type Si, p-type Si, and undoped (intrinsic) Si, and these all exhibited 785 nm Raman spectra containing a multitude of peaks, although as before, the relative intensities of the peaks were variable. The exception to this was for films grown on HPHT single crystal (100) diamond substrates. Since the films were not grown under optimum homoepitaxial growth conditions, deposition formed a polycrystalline layer, although since the substrate was diamond there was no nucleation layer consisting of nanocrystalline diamond. The 785 nm Raman spectrum from this film gave only the diamond zone-centre line, with no other features present in the spectrum (see Fig. 4).

One possibility was that the peaks could be due to SiC layers or nanocrystals at the diamond/Si interface. This is because 785 nm excitation has been shown to enhance the Raman scattering from nitrogen defects in SiC [14] giving rise to extra peaks. Fig. 4 shows the 785 nm Raman spectrum of single crystal SiC taken with our system under identical conditions to before. The spectrum is dominated by two peaks at 777 and

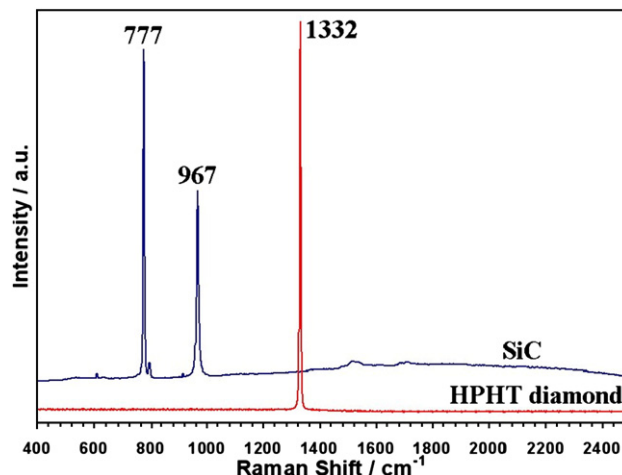


Fig. 4. 785 nm Raman spectrum of single crystal silicon carbide, and that of a 2 μm CVD diamond polycrystalline film grown on a HPHT single crystal diamond substrate.

967 nm, with only a few very minor features elsewhere. Thus, if the features seen in the diamond spectra were due to SiC, we should also observe these two intense characteristic peaks. Since these 2 peaks are not present, we can conclude that the features are not due to SiC—and this is confirmed by the fact that the features are present when using non-Si substrates.

An interesting observation was that freestanding diamond films that had delaminated from the substrate did not show any of the Raman features, and just gave a broad PL hump, similar to that seen in Fig. 3 (h). This was true for thick (150 μm) and thin (4 μm) freestanding films, and indicates that the Raman peaks we see require the presence of a diamond film bonded directly onto a substrate surface.

The effect of nucleation was then studied by performing a series of experiments with different abrasion/pre-treatment methods. For ‘perfect’ nucleation (as occurs on a diamond substrate), the sharp Raman peaks were not present. Manual abrasion of a Si substrate using 0.1 μm diamond powder (compared to 1–3 μm powder) made no significant difference to the type of diamond film that was grown, or to the 785 nm Raman spectrum it exhibited. Similarly, ultrasonic abrasion using either 1–3 μm or 0.1 μm diamond/water slurry gave the same results. However, seeding the surface (but with no abrasion) with a sub-monolayer of 0.1 μm diamond powder followed by 4 h growth produced a film with very high nucleation density and a highly structured Raman spectrum (see Fig. 5 (a)). Smearing hydrocarbon rotary-pump oil onto the Si wafer, followed by 4 h growth produced isolated islands of diamond growth (with no residue remaining of the hydrocarbon oil). The Raman spectra from these islands gave rise to Raman spectra with an extremely large enhancement for some peaks (see Fig. 5 (b)). Note that the positions of many of these enhanced peaks in Fig. 5 (b) are significantly different to the ones observed in Fig. 4 (a), which means that different peaks are being enhanced in each case.

We observed that if the same area of a sample was analysed repeatedly over a period of a few hours, the relative intensities of some of the peaks would fluctuate from spectrum-to-spectrum. This fluctuation would sometimes be substantial,

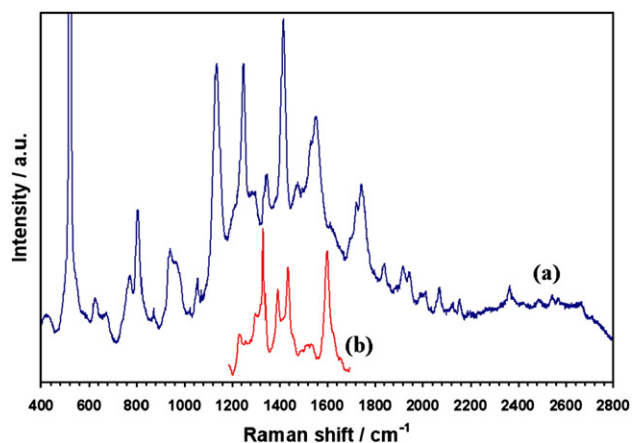


Fig. 5. 785 nm Raman spectrum of diamond film grown for 4 h ($\sim 2 \mu\text{m}$ thick) on Si with different surface pre-treatments prior to deposition: (a) seeded with 0.1 μm diamond powder, (b) smeared with hydrocarbon oil.

with peaks disappearing, and sometimes reappearing again (‘blinking’) or new peaks emerging. Sampling from several different positions that were only a few 100 μm apart on the same film also gave rise to spectra that were very different from each other. Some peaks would be common to all spectra, and some peaks would appear in some, or only one of the spectra. Peaks often appeared to have shifted by as much as 5 cm^{-1} in either direction, although it was unclear whether this was the same peak or a new one that had emerged while the previous one had disappeared.

4. Conclusions

We have seen that the Raman spectra of thin diamond films obtained using 785 nm excitation appear very different to those obtained using other wavelengths, and that the spectra consist of a multitude (at least 30 in the range $400\text{--}3000 \text{ cm}^{-1}$) of sharp, well-defined peaks which fluctuate greatly in intensity (‘blink’) as a function of time and position on the substrate. These features are too sharp to be photoluminescence [15], and are a function of film thickness. For films $>30 \mu\text{m}$ thick, for freestanding films, and for films grown on a diamond substrate, these Raman peaks disappear. Since the peaks are independent of substrate material, metals, SiC and other metal carbides or impurities can be discounted, leaving sp^2 and sp^3 carbon structures as prime candidates. The peaks probably originate from vibrations of molecular units that are positioned at the grain boundaries of the disordered material (a mixture of small crystallites embedded in an amorphous matrix) near to the interface between the diamond and substrate. This is entirely consistent with the findings of Veres et al. [12] for UNCD films.

The differences in the spectral features of Raman scattering measured by visible (514 nm, 632 nm), IR (785 nm) and far IR (833 nm) are caused by the different scattering cross-sections of the amorphous matrix for the resonant Raman process when changing the excitation energy. The visible wavelengths resonantly enhance the scattering from the amorphous matrix, and the intense bands from this phase will overlap the scattering arising from minor structures present at the grain boundary. Far IR excitation does not enhance the amorphous matrix as much, but also does not enhance the surface structures of interest. 785 nm excitation is ideal, in that it has exactly the correct energy to enhance the scattering from the vibrations of molecular units in the grain boundaries, while having little enhancement of the unwanted bands from the amorphous matrix.

Possible structures responsible for some of these peaks include:

- (i) Polymorphs of diamond, such as lonsdaleite (or hexagonal diamond), which is reported to exhibit a sharp Raman peak appearing between 1315 cm^{-1} and 1326 cm^{-1} [16]. Such features are reported to have been observed on cut (polished) diamond surfaces, on diamond surfaces prepared using thermochemical polishing with hot transition metals, and around indentations made on diamond surfaces [17].

- (ii) Isolated diamond nanocrystals of varying sizes (1 nm–100 nm) can exhibit a zone-centre phonon line ranging from 1332 cm^{-1} down to 1315 cm^{-1} as the crystal size decreases as a result of heating by the laser to temperatures as much as 700 K [18,19]. It is highly likely that these nanocrystals such as these would be present at or near the interface, however, the high thermal conductivity of the surrounding diamond film should efficiently spread the heat away maintaining the local temperature at near ambient. Alternatively, stress is known to shift the position of the diamond line or split it into 2 or 3 components in the range $1328\text{--}1370\text{ cm}^{-1}$ [13]. So the peaks we observe could be due to a variety of diamond nanocrystals experiencing varying amounts of compressive or tensile stress. Again, we feel this is unlikely, as stress effects tend to shift the diamond line by only a few cm^{-1} , whereas we observe peaks hundreds of cm^{-1} away from 1332 cm^{-1} .
- (iii) Diamondoid molecules may also be present at the interface, and these are known to exhibit a multitude of Raman peaks between 400 and 3000 cm^{-1} [7,8].
- (iv) Defects and impurities (nitrogen, silicon) often give rise to Raman peaks in diamond, and these peaks are comprehensively catalogued in the book by Zaitsev [13]. Some of the peaks observed in this work can be matched (within a few cm^{-1}) with some of those reported in Zaitsev's book, and a tentative assignment suggested. However, we would treat such assignments with caution until corroborating evidence can be found.
- (v) Resonant Raman scattering from a variety of sp^2 and sp^3 carbon structures present at the grain boundaries is another possibility.

Option (v) is the most likely, and this would be consistent with the findings of Veres et al. [12] for UNCD films. Our laser spot size is sufficient to achieve a sampling volume small enough that the sampled grain surface area may be comparable to that of the grain. This creates a substantial enhancement of the Raman signal from those grain boundary structures which are at or near the surface/interface. The instability of the peaks with time and position is probably a function of the extreme sensitivity of the sampled structures to this enhancement. Movements of the position of the spot by fractions of a micron – which may occur with time due to thermal drift – would alter the sampling volume enough that different species are excited giving rise to large changes in peak intensities, and apparent 'blinking'. Such enhancement of Raman signals is not unknown – indeed, it is the basis of the surface enhanced Raman spectroscopy (SERS) technique [20]. SERS spectra taken from diamond nanoparticles [21] and films [22–25] involve many preparation steps and are difficult to perform, but yield spectra that look very similar to ours, with a plethora of sharp peaks in the range $400\text{--}3000\text{ cm}^{-1}$ that have been assigned as various types of unspecified sp^2 carbon species. Adding gold nanoparticles to UNCD films has also been shown to increase the intensities of these Raman peaks

further [12], and similar experiments will be attempted with our microcrystalline diamond films.

We have shown that 785 nm Raman can be a useful tool to study CVD diamond films, and especially the diamond/surface interface. Using this technique, information about the plethora of molecular units present at the grain boundaries can be obtained readily, without the need for difficult preparation steps or SERS analysis. However, assignment of these peaks to individual molecular structures or vibrations will not be an easy task, and will provide a challenge to both experimentalists and theoreticians.

Acknowledgements

The authors would like to thank Jacob Filik for many useful discussions.

References

- [1] J. Filik, *Spectroscopy Europe* 17 (2005) 10.
- [2] S. Praver, R.J. Nemanich, *Phil. Trans. R. Soc. Lond. A* 362 (2004) 2537.
- [3] M. Koós, M. Veres, S. Tóth, M. Füle, in: G. Messina, S. Santangelo (Eds.), *Carbon: The Future Material for Advanced Technology Applications*, Springer Series Topics in Applied Physics, 100, Springer, Berlin, 2005, p. 423.
- [4] A.C. Ferrari, J. Robertson, *Phil. Trans. R. Soc. Lond. A* 362 (2004) 2477.
- [5] D. Roy, Manish Chhowalla, H. Wang, N. Sano, I. Alexandrou, T.W. Clyne, G.A.J. Amaratunga, *Chem. Phys. Lett.* 373 (2003) 52.
- [6] J.R. Hird, M. Bloomfield, I.P. Hayward, *Phil Mag* 87 (2007) 267.
- [7] J. Filik, J.N. Harvey, N.L. Allan, P.W. May, J.E.P. Dahl, S. Liu, R.M.K. Carlson, *Spectrochimica Acta A: Mol. Biomol. Spect.* 64 (2006) 681.
- [8] J. Filik, J.N. Harvey, N.L. Allan, P.W. May, J.E.P. Dahl, S. Liu, R.M.K. Carlson, *Phys. Rev. B* 74 (2006) 035423.
- [9] M. Pedroza-Montero, V. Chernov, B. Castañeda, R. Meléndrez, J.A.N. Gonçalves, G.M. Sandonato, R. Bernal, C. Cruz-Vázquez, F. Brown, E. Cruz-Zaragoza, M. Barboza-Flores, *Phys. Stat. Sol. (A)* 202 (2005) 2154.
- [10] N.M. Balzaretti, A. Feldman, E.S. Etz, R. Gat, *J. Mater. Res.* 14 (1999) 3720.
- [11] M. Veres, S. Tóth, M. Füle, M. Koós, Abstract Book from 'New Diamond and NanoCarbons' conference, Osaka Japan, 2007.
- [12] M. Veres, S. Tóth, M. Koós, *Appl. Phys. Lett.* 91 (2007) 031913.
- [13] S.M. Leeds, T.J. Davis, P.W. May, C.D.O. Pickard, M.N.R. Ashfold, *Diamond Relat. Mater.* 7 (1998) 233.
- [14] J.C. Burton, F.H. Long, I.T. Ferguson, *J. Appl. Phys.* 86 (1999) 2073.
- [15] A.M. Zaitsev, *Optical Properties of Diamond: A Data Handbook*, Springer, Berlin, 2001.
- [16] D.S. Knight, W.B. White, *J. Mater. Res.* 4 (1989) 385.
- [17] Y.G. Gogotsi, A. Kailer, K.G. Nickel, *J. Appl. Phys.* 84 (1998) 1299.
- [18] X.-Z. Zhao, K.A. Cherian, R. Roy, W.B. White, *J. Mater. Res.* 13 (1998) 1974.
- [19] P.W. May, P. Overton, J.A. Smith, K.N. Rosser, *MRS Symp. Proc.* (Fall 2007), in press.
- [20] M. Kerker (Ed.), *Selected Papers on Surface-enhanced Raman Scattering*, SPIE Milestone Series MS, 10, SPIE, Billingham, Wa, USA, 1990.
- [21] E. Perevedentseva, A. Karmenyan, P.-H. Chung, C.-L. Cheng, *J. Vac. Sci. Technol. B* 23 (2005) 1980.
- [22] M. Veres, M. Füle, S. Toth, M. Koos, I. Pocsik, *Diamond Relat. Mater.* 13 (2004) 1412.
- [23] D.S. White, R. Weimer, L. Pilione, W.B. White, *Appl. Phys. Lett.* 56 (1990) 1320.
- [24] D. Roy, Z.H. Barber, T.W. Clyne, *J. Appl. Phys.* 91 (2002) 6085.
- [25] T. López-Ríos, É. Sandré, S. Leclercq, É. Sauvain, *Phys. Rev. Lett.* 76 (1996) 4935.