Mater. Res. Soc. Symp. Proc. Vol. 1039 © 2008 Materials Research Society 1039-P15-03

Multi-wavelength Raman Spectroscopy of Nanodiamond Particles

Paul William May, Philip Overton, James A Smith, and Keith N Rosser
School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, United Kingdom

ABSTRACT

We have used Raman spectroscopy with 3 different laser excitation wavelengths (near infrared: 785 nm, green 514 nm, and ultraviolet 325 nm) to study diamond particles as a function of particle size, ranging from 5 nm to 100's of μm. We find that the position of the 1332 cm^{-1} diamond line varies with particle size as a direct result of heating by the laser. This effect is more significant for lower wavelengths, probably as a result of the increased absorbance by nanodiamond particles in the UV.

INTRODUCTION

Laser Raman spectroscopy is a powerful technique used to study various forms of carbon films, including diamond, diamondlike carbon, and nanodiamond particles [1]. For diamond particles of size >100 nm, the Raman spectra usually consist only of the zone-centre phonon line at 1332 cm^{-1} corresponding to symmetric vibrations of the sp^3 diamond lattice. However, for smaller diamond particles, Zhao *et al* [2] showed that the intense laser beam focused onto a small volume particle causes significant heating, and this shifts the diamond line to lower wavenumbers. Thus, the observed Raman line position is dependent upon laser power. Estimates for the temperature reached by the particles can be obtained by using results from Liu e*t al.* [3] and Borer *et al.* [4], who independently measured the position of the diamond Raman line from a single crystal diamond sample as a function of measured temperature, as shown in Fig.1.

Both sets of data can be fitted to an equation of the form:

$$\Delta\omega = \frac{-A}{(e^{B/T} - 1)} \qquad (1)$$

where A and B are constant fitting parameters and $\Delta\omega$ is the shift in peak position from a starting value of $\omega_0 = 1332.7$ cm^{-1} at 100 K. For Liu *et al*'s data, we found that values of $A = 10$ cm^{-1} and $B = 1222.1$ K^{-1}, and for Borer *et al*'s data $A = 11.5$ cm^{-1} and $B = 1527.6$ K^{-1}, gave the best fits to the experimental data. The two curves are reasonably consistent, which shows that the observed shifts down to ~1323 cm^{-1} occur when the diamond approaches temperatures ~750-900 K, which is close to the temperature at which diamond oxidises to graphite in air. Thus Raman may not be a completely non-destructive analysis tool for diamond unless low power lasers are employed. Other data for variation of the diamond Raman line with temperature include [5,6,7,8,9].

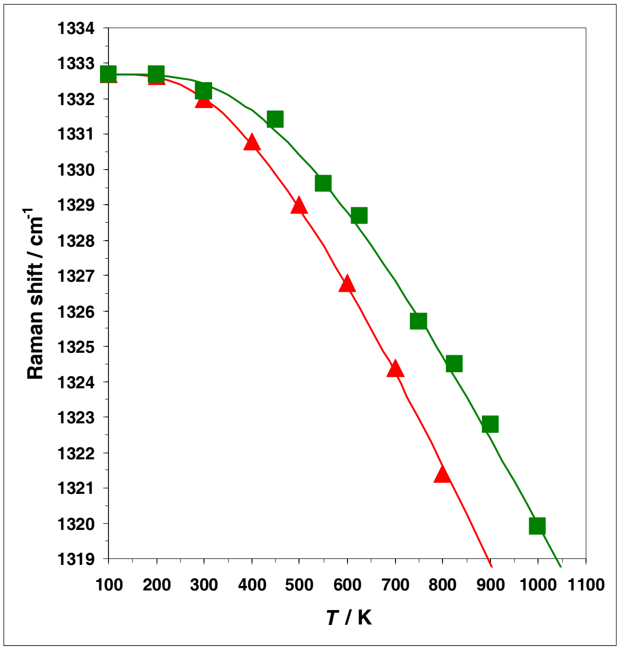

Figure 1. Values of Raman diamond line position from ref.[3] (red triangles) and ref.[4] (green squares) at different temperatures. The lines are fits from Equation (1) in the text.

Recently ultra-dispersed diamond (UDD) or detonation nanodiamond particles have become available, with particles sizes down to 5 nm. For UDD, Yushin *et al* [10] showed that the diamond line is not present when using green or infrared laser excitations due to a large background fluorescence. But the diamond peak was present when uasing ultra-violet excitation (325, 244 nm) and downshifted to 1320 cm^{-1}. In order to obtain these spectra, Yushin *et al* needed to use low laser powers, and dispersed the UDD in water to minimise laser heating and oxidation.

The purpose of the present paper is to extend the measurements of laser heating and peak shifts for nanoparticles into the UDD regime, as well as to determine the size of particle for which laser heating is no longer significant, as a function of excitation wavelength.

EXPERIMENTAL

Diamond powders were obtained from many commercial suppliers, and in a range of average particle sizes including: 5 nm, 30 nm, 100 nm, 500 nm, 1.25 µm, 5 µm, and 200 µm. For the larger 3 sizes, the particle size was checked by averaging the size of over 100 particles viewed by scanning electron microscopy (SEM). For the smaller four sizes, a high speed disk centrifuge was used to obtain the particle size distribution, and an example is shown in Fig.2. The distributions showed that the as-supplied nanopowders were far from being monodispersed, and had a wide size distribution around the mean.

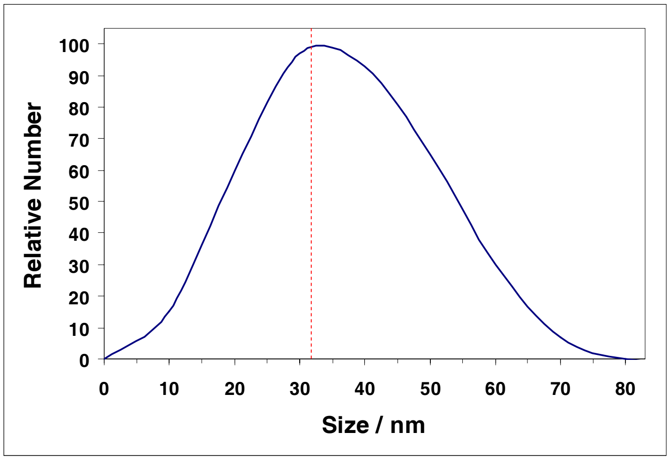

Figure 2. The size distribution from a nominally 30 nm size diamond powder, as measured by high speed disk centrifuge. The mean size is actually 33 nm (indicated by the dashed red line), but with a FWHM of 36 nm.

Laser Raman spectra were taken using a Renishaw 2000 spectrometer equipped with three laser wavelengths, and the power of each was measured at the sample surface: ultraviolet (325 nm, 0.25 mW), green (514 nm, 2 mW) and near infrared (785 nm, 4 mW). Each powder sample was packed tightly into a cone-shaped mould, and then tapped out onto a glass microscope slide such that the laser could sample an area of ~1 mm^2. The spot-size of the laser was ~1 µm, which meant that for the nanodiamond samples the laser was averaging the signal from many crystallites, whereas for the larger grained material the signal came from a few, or even one crystallite.

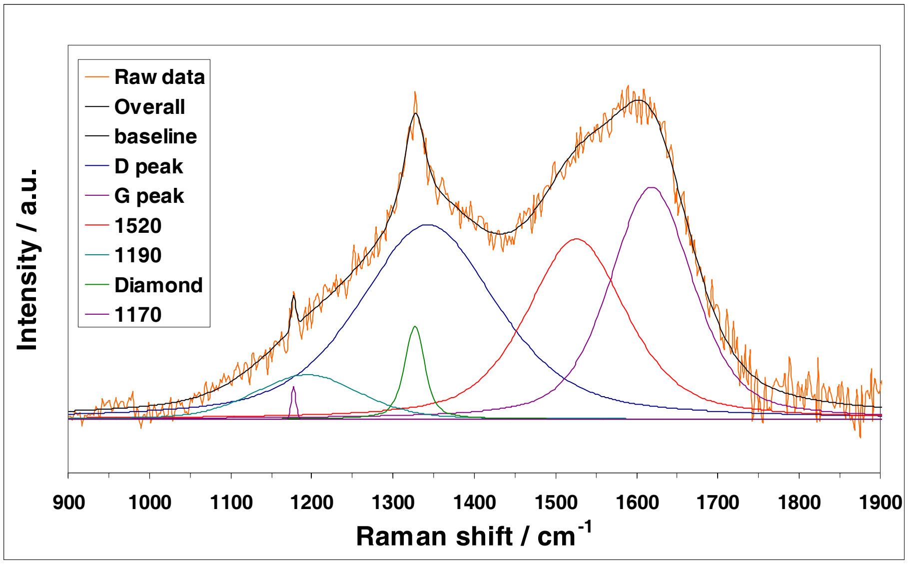

Figure 3. The Raman spectrum obtained from the 5 nm nanodiamond powder using 514 nm excitation, after subtraction of the PL background. The raw data have been deconvoluted into a number of peaks. These include the diamond zone-centre peak at 1324 cm^{-1}, the G (~1615 cm^{-1}) and D (~1339 cm^{-1}) peaks, and peaks at 1170, 1190 and 1520 cm^{-1} due to *sp*^{2} carbon structures at grain boundaries [11].

Most of the diamond powders gave a single sharp diamond line with all laser wavelengths. But problems occurred with the UDD powder, which gave a very small Raman signal and, except at 325 nm, the diamond line was hidden by the intense photoluminescent (PL) background. However, this PL background could be fitted to a quadratic function and subtracted to give a Raman spectrum of the nanoparticles, see Fig.3. These spectra showed not only the shifted diamond line, but also a number of features which could be deconvoluted using the Renishaw curve fitting software.

RESULTS

Using a series of neutral density filters, the laser power was varied from 100% to 1% of full power for all three lasers, and the results are shown in Fig.4. This figure shows that for 100 nm powder, laser heating can be a significant factor and greatly affects the position of the diamond Raman line.

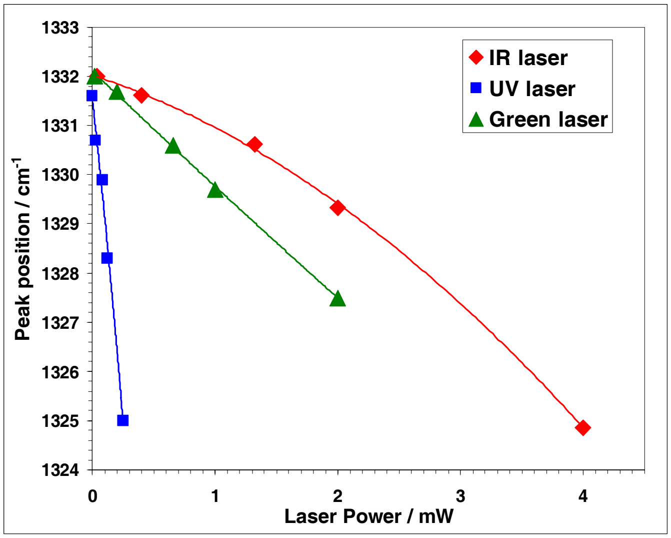

Figure 4. Diamond peak position as a function of laser power at the sample surface for the three excitation wavelengths, for 100 nm diamond powder. The curves through the points are lines of best fit to guide the eye.

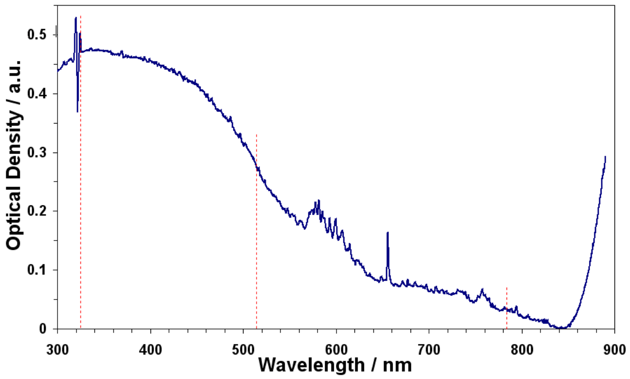

Figure 5. Optical density (absorbance) of 100 nm diamond particles as a function of wavelength. The dashed red vertical lines indicate the positions of the 325, 514 and 785 nm lasers used for Raman. The specific features in the spectrum have not been identified, however, the general trend is that the diamond powder absorbs significantly more energy at lower wavelengths than at higher ones.

The three curves show a near linear dependence of peak shift with laser power, but the gradients are very different for the three lasers. The UV laser affects the diamond line significantly more than the green or IR, with the IR laser the least perturbing (per mW power). This is probably a reflection of the amount of energy absorbed by the diamond, which varies since the absorbance of diamond is a function of wavelength, as shown in Fig.5.

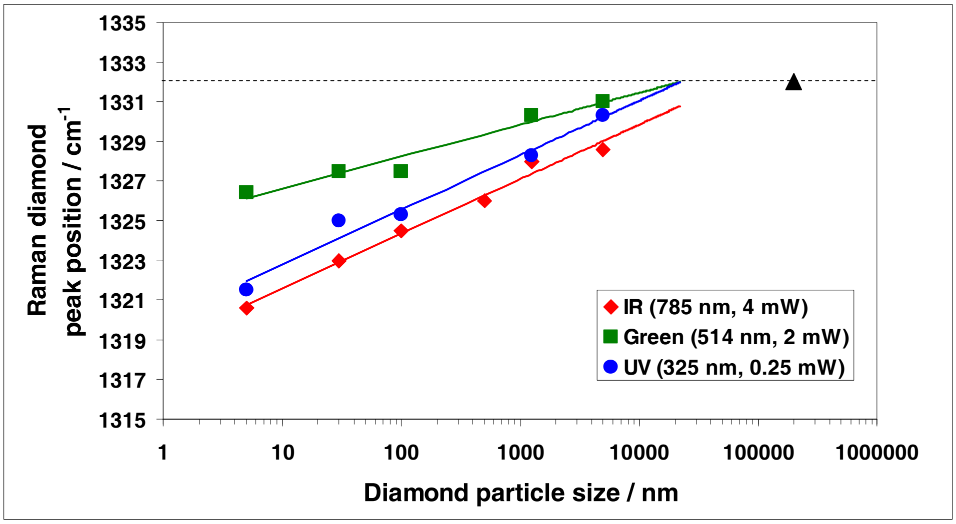

Figure 6. Position of the diamond Raman line as a function of particle size for the 3 different excitation wavelengths. The 1332 cm^{-1} position is indicated by the dashed black line, and the black triangle is the diamond Raman line position obtained with all three lasers for a particle size of 200 µm.

Fig.6 shows that on a log scale, there is a roughly linear relationship between particle size and the position of the diamond line. The maximum shift observed (for the IR laser at 4 mW and 5 nm particles) down to 1320.5 cm^{-1} corresponds to the particles achieving a temperature of 800-950 K (see Fig.1), which is only just below the temperature at which diamond graphitises in air. Thus, laser Raman spectroscopy cannot be considered to be a non-destructive test for these small particles. Indeed, many of the sp^2 features seen in the Raman spectrum of the UDD samples (Fig.3) may result from graphitisation of some fraction of the nanoparticles.

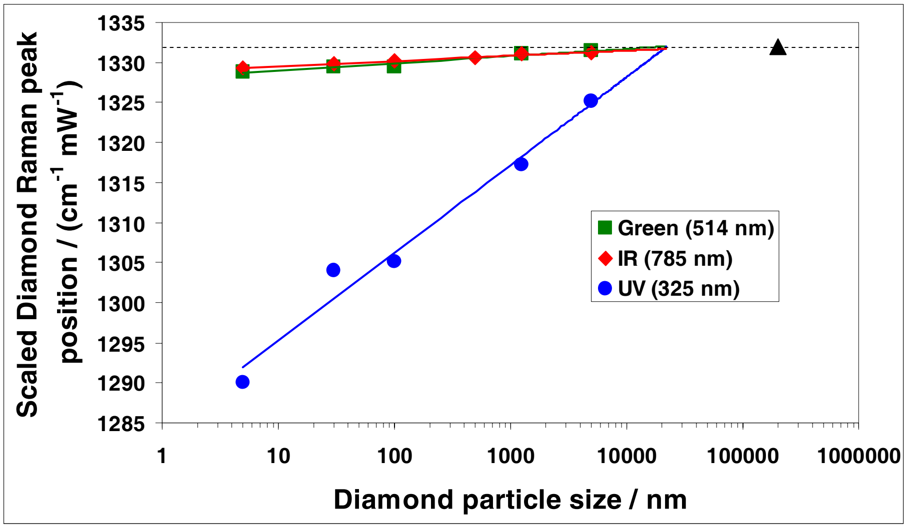

Figure 7. As Fig.6, but now scaled per mW power incident on the sample. Note that this plot serves purely to illustrate the *relative* effects of the 3 lasers. Shifts of ~40 cm^{-1} could never be achieved in reality since, from Fig.1, this would imply temperatures in excess of that at which diamond burns in air.

Fig.7 shows that, when scaled per mW laser power incident on the diamond powder, the UV laser shifts the Raman peak significantly more than the other lasers. Lines of best fit through the 3 sets of data converge at a particle size of ~22 μm. Thus, 22 μm is the minimum size for diamond particles that will not suffer a Raman peak shift due to laser heating, per mW laser power. This is a surprisingly large value, and serves as a cautionary warning to researchers using Raman spectroscopy as a quantitative analysis technique for diamond particles of size smaller than 22 μm.

CONCLUSIONS

It is clear from these results that the diamond Raman line for diamond powders is significantly shifted due to laser heating, and the smaller the size of the powder the greater the heating and resulting shift. The amount of shift is related to the amount of absorbance of the diamond at the laser wavelength, so UV has a bigger effect than visible light, which has a bigger effect than IR. Another important parameter is the laser power. The higher the laser power, the more heating, and therefore to avoid damage to the sample, it may be better to use lower powers but accumulate the spectrum for longer times. For very small size diamond, such as UDD, the localised laser heating may even be graphitising the crystallites to some extent, particularly when using UV excitation.

ACKNOWLEDGEMENTS

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

REFERENCES

1. J. Filik, *Spectroscopy Europe* **17**, (2005) 10.
2. X.-Z. Zhao, K.A. Cherian, R. Roy, W.B. White, *J. Mater. Res.* **13**, (1998) 1974.
3. M.S. Liu, L.A. Bursill, S. Prawer, R. Beserman, *Phys. Rev. B* **61** (2000) 3391.
4. W.J. Borer, S.S. Mitra, and K.V. Namjoshi, *Solid State Commun.* **9**, (1971) 1377).
5. H. Herchen and M. A. Cappelli, *Phys. Rev. B* **43**, (1991) 11740.
6. H. Herchen, M.A. Cappelli, M.I. Landstrass, M.A. Plano, M.D. Moyer, *Thin Solid Films* **212**, (1992) 206.
7. V. D. Andreyev, T. A. Nachalnaya, and E. V. Gabrusenok, *Sverkhtverdye Materialy* **15**, (1993) 11 (in Russian).
8. E. S. Zouboulis and M. Grimsditch, *Phys. Rev. B* **43**, (1991) 12490.
9. J.B. Cui, K. Amtmann, J. Ristein, and L. Ley, *J. Appl. Phys.* **83**, (1998) 7929.
10. G.N. Yushin, S. Osswald, V.I. Padalko, G.P. Bogatyreva, Y. Gogotsi, *Diam. Relat. Mater.* **14**, (2005) 1721.
11. A.C. Ferrari and J. Robertson, *Phil. Trans. R. Soc. Lond. A* **362**, (2004) 2477.