

## High Temperature Raman Scattering Behaviour in Diamond

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### Introduction

The Raman spectrum of synthetic carbon films is now routinely used as an identification of the phase or measure of the quality of such films, when compared to that of natural diamond or natural and synthetic graphite.<sup>1</sup> Since the development of CVD diamond technology, the width and relative shift of the first-order Raman transition of polycrystalline diamond has been used to qualitatively ascribe the amount of disorder<sup>2</sup> (inhomogeneous strain) or homogeneous strain<sup>3</sup> in these new materials. In diamond, the lattice dynamics that give rise to the Raman effect are also responsible for determining the thermal properties such as specific heat and thermal conductivity. The variation with temperature of the first-order Raman mode in polycrystalline diamond in comparison to that of natural diamond can therefore be used as an additional qualitative check on the high temperature behaviour of the thermal properties of these films.

The temperature variation of the first-order Raman spectrum in natural diamond was first investigated by Nayar<sup>4</sup> in 1941 in an attempt to better understand the relationship between the observed shift and measured thermal expansion coefficients. A similar but more extensive study was performed by Krishnan.<sup>5</sup> In both cases, the highest temperature achieved (about 1100 K) was limited by diamond contamination and thermal emission, which contributed to background interference. Recently, Herchen and Cappelli<sup>6</sup> extended these measurements to about 1900 K, using gated photon counting and either modulated or pulsed laser excitation sources. In this paper, similar data is presented for free standing 100  $\mu\text{m}$  thick diamond film. The Stokes to anti-Stokes ratio of the first-order Raman spectrum is used to infer the sample temperature. It is found that this temperature is consistent with temperatures measured by optical pyrometry, provided a diamond emissivity of close to unity is used in the analysis. These temperatures are then employed to deduce the variation in the shift and width of the Raman feature with temperature. The results are compared to similar measurements on type IIa natural diamond.

### Experiment

The experimental facility is similar to that used in previous studies,<sup>6</sup> and is only briefly described here. The Raman spectra were obtained by exciting the free standing polycrystalline diamond samples with the 457.94 nm output from an argon-ion laser that was mechanically chopped at 2 kHz. The backscattered light from near-normal incidence was collected with  $f/5$  optics and imaged onto the entrance slit of a 1-m scanning monochromator. The dispersed light at the exit slit was detected with a photomultiplier tube and analyzed with photon counting electronics. The spectral resolution was approximately 0.1-nm, and all spectral width measurements were corrected for instrument broadening.

The free-standing polycrystalline diamond used to obtain the results described here was provided by Crystallume Inc.<sup>7</sup> The thickness of the sample studied was approximately 100  $\mu\text{m}$  and was grown by microwave plasma deposition. It was translucent and grey in appearance partly resulting from the scattering of light at the grain boundaries. The sample was treated for one hour by boiling in 96% sulphuric acid at atmospheric pressure prior to inserting it into a

high vacuum chamber where it was sandwiched between two electrically heated tungsten ribbons (Fig. 1). The chamber had optical access permitting laser excitation and direct measurement of the tungsten and diamond brightness temperatures.

The diamond was not expected to be in thermal equilibrium with the tungsten ribbons, and so each brightness temperature was monitored independently. A disappearing filament pyrometer with a filter centered at 655 nm was used in the measurement of the brightness temperatures. These temperatures can be corrected to the actual temperatures provided that emissivities of the two materials at 655 nm are known. The emissivity of tungsten at that wavelength is well known, however there is no available data on the emissivities of polycrystalline diamond films. Indeed, the values will be highly dependent on surface and growth conditions. Consequently, the Raman Stokes to anti-Stokes intensity ratio was used to arrive at the true diamond temperature, and this together with the measured brightness temperature provided an experimental determination of the sample emissivity.

## Results and Discussion

Typical Stokes and anti-Stokes first-order Raman spectra of the free-standing polycrystalline diamond samples at approximately 1200 K brightness temperature are shown in Fig. 2. The nearby argon plasma transition from the laser discharge ( $\text{Ar}^+ 4s^2P \rightarrow 4p^2D^o$  line at 487.986 nm) appears at a shift of  $1344.7 \text{ cm}^{-1}$  and acts as an accurate calibrant for the Stokes shifted diamond component which appears here at  $1309 \text{ cm}^{-1}$ . The argon plasma spectral line at 433.12 nm is sufficiently close to the anti-Stokes component to provide a similar reference at  $-1251.2 \text{ cm}^{-1}$ . It is evident that both the Stokes and anti-Stokes components are significantly broadened to about  $10 \text{ cm}^{-1}$  after correction for the instrument broadening. Their widths are nearly twice that observed for natural type IIa diamond at the same temperature.<sup>6</sup>

The Raman Stokes to anti-Stokes intensity ratio

$$\frac{I_{St}}{I_{a-St}} = \left( \frac{\omega_\ell - \omega_s}{\omega_\ell + \omega_s} \right)^4 e^{h\omega_s/kT}$$

can be a direct measure of the sample temperature. Here  $\omega_s$  is the phonon frequency,  $\omega_\ell$  is the line center frequency of the laser excitation source,  $T$  is the sample temperature, and  $h$  and  $k$  are the Planck and Boltzmann constants, respectively. Figure 3 compares the sample temperature derived from the Stokes to anti-Stokes ratio to the tungsten ribbon temperature as measured by optical pyrometry. It is clear from this figure that the sample does not come to thermal equilibrium with the tungsten heaters and is usually 200 to 300 K cooler over the range tested. This difference can be attributed to the thermal contact resistance between the diamond sample and tungsten ribbon heaters and to significant radiative losses due to the high emissivity of this diamond sample. This result further emphasizes the need to directly measure the diamond temperatures during vapor deposition, so as to have a more accurate assessment of the deposition conditions.

The emissivity can be estimated from the temperatures derived from the Stokes to anti-Stokes ratios and the measured diamond brightness temperatures. These are given in Fig. 4. The results suggest emissivities at 655 nm of close to unity, consistent with the visual appearance of the sample. These results are intriguing in that they suggest that polycrystalline diamond coatings may be very useful as high temperature radiative surfaces in circumstances where other properties of such diamond are also advantageous.

The variation in the observed Raman shift with diamond temperature for both the Stokes and anti-Stokes components is shown in Fig. 5. The diamond temperature is found from its brightness temperature and an emissivity of unity. The error in the shift is  $\pm 0.3 \text{ cm}^{-1}$  which is less than the size of the symbols used to represent the data points. Also shown in the figure is

a solid line summarizing previously measured values for natural diamond.<sup>6</sup> The values for the polycrystalline diamond are found to be in excellent agreement with that of natural diamond over the range of temperature studied here. Furthermore, these results are in general agreement with the theoretical molecular dynamics predictions of Wang et al<sup>6</sup>, a fit through which is shown by a dashed line in Fig. 5.

The variation in the full width at half maximum intensity (FWHM) of the Raman spectrum with temperature (again using the diamond brightness temperature and an emissivity of unity) is shown in Fig. 6. The spectra were corrected for instrument broadening. The spectral lineshapes were found to be well represented by a Voigt profile. The Lorentzian Raman profile was obtained by deconvolving the Gaussian instrument broadening from the measured profiles. The instrument contribution to the FWHM amounted to  $3.7 \text{ cm}^{-1}$  and  $4.7 \text{ cm}^{-1}$  for the Stokes and anti-Stokes components, respectively. The solid line in Fig. 6 is a fit to the results obtained for natural diamond.<sup>6</sup> The high temperature FWHM for the polycrystalline samples are 4 to  $6 \text{ cm}^{-1}$  greater than that for natural diamond, consistent with room temperature data. Both results however are in reasonable agreement with the predicted FWHM values of Wang et al.<sup>8</sup> The difference between the measured values of the FWHM for the polycrystalline and natural diamond samples can be attributed to slight disorder in the carbon-carbon bond length (inhomogeneous strain).<sup>2</sup> An accurate and unambiguous identification of the source of broadening in the first-order Raman spectra requires further experimental and theoretical investigation.

### Summary

The data presented here suggest that one can grow polycrystalline CVD diamond that has high temperature Raman scattering characteristics comparable to that of natural diamond. The usefulness of Raman scattering as a possible unambiguous measure of the sample temperatures has been demonstrated. Furthermore, this independent temperature measurement provided the opportunity to make one of the first direct measurements of CVD diamond emissivity. Emissivities approaching unity were obtained, suggesting that CVD diamond could be quite useful as a high temperature radiative coating in chemically harsh environments.

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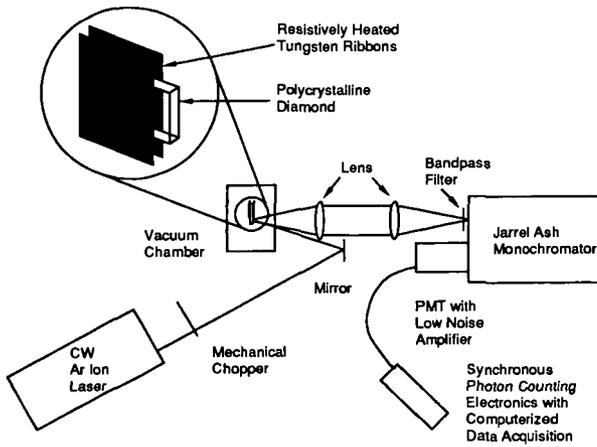


Figure 1. Schematic of the experimental setup for Raman backscattering studies of polycrystalline diamond at high temperature. The inset illustrates the mechanism used to heat and hold the sample.

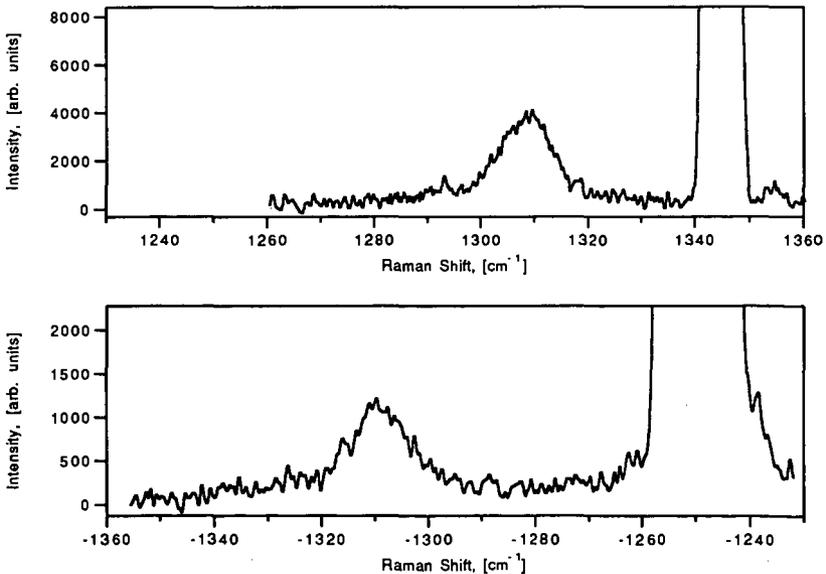


Figure 2. Stokes, top, and anti-Stokes first-order Raman spectra with argon ion emission calibration lines. The diamond temperature was 1200 K.

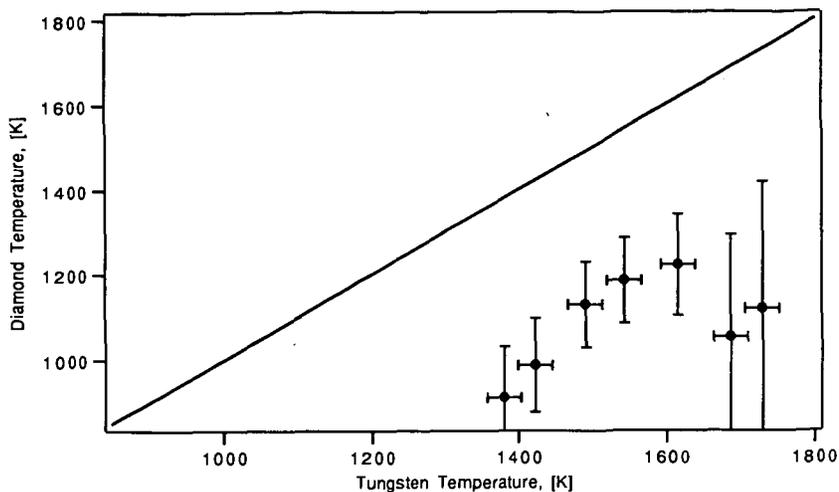


Figure 3. Polycrystalline diamond temperature based on the Stokes to anti-Stokes intensity ratio as a function of the tungsten ribbon temperature. The solid line corresponds to equal diamond and tungsten temperatures.

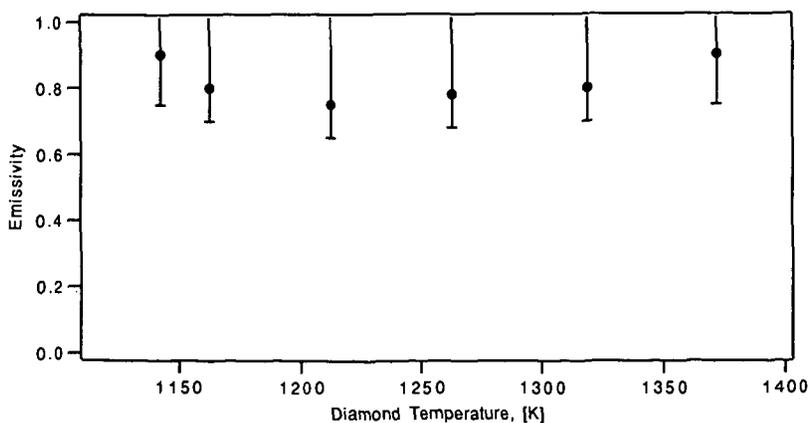


Figure 4. Polycrystalline diamond emissivity at 655 nm determined from the measured brightness temperature and the diamond temperature found from the Stokes to anti-Stokes intensity ratio.

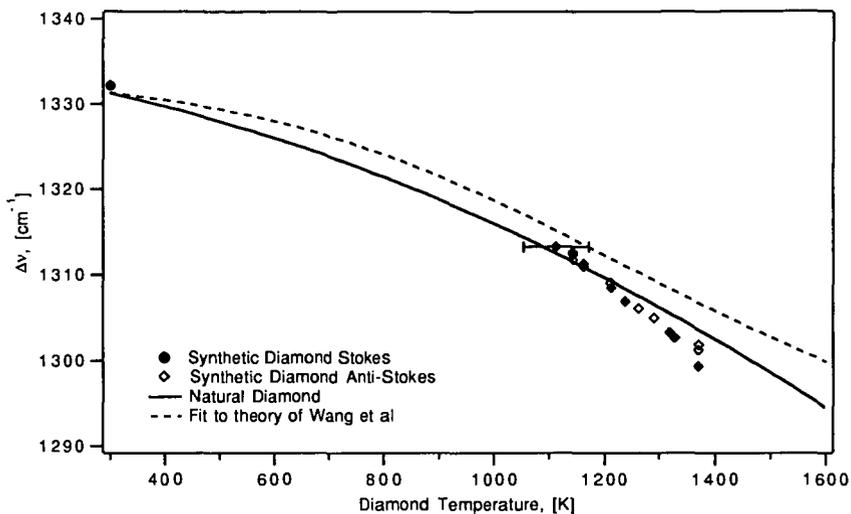


Figure 5. Variation of the first-order Raman shift in polycrystalline diamond with temperature. The diamond temperature is found using an emissivity of unity. The solid line is a fit to the first-order Raman shift for natural diamond (Ref. 6). The dashed line is a fit to the results of molecular dynamics simulation of Wang et al (Ref 8).

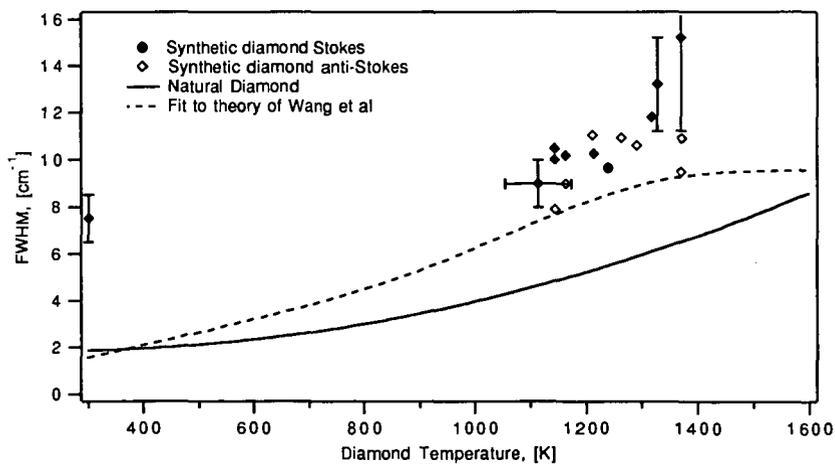


Figure 6. Variation of the full width at half maximum (FWHM) of the first-order Raman spectrum in polycrystalline diamond with temperature. The diamond temperature is found using an emissivity of unity. The solid line is a fit to the FWHM for natural diamond (Ref. 6). The dashed line is a fit to the theoretical results of Wang et al (Ref 8).