

Raman spectroscopy: a simple, non-destructive way to characterise diamond and diamond-like materials

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Introduction

There was a point in time when diamond was considered merely as an exotic material, the principle use for which was decorating the necks, wrists and fingers of the wealthy and the famous. Wars were fought, and paid for, by the wealth generated from what is essentially just a regular tetrahedral arrangement of carbon (Figure 1), the sixth most abundant element in the universe.

Nowadays, this precious crystal is not only found flaunted at film premières, it's found on cutting blades, in thermal management systems and even producing the high frequency sound in high-end stereo speakers. What happened to turn this much-coveted gem into a versatile engineering material?

Throughout the 20th century, several methods of "growing" diamonds synthetically were developed. One of the more important of these methods, chemical vapour deposition (CVD), is commonly used in micro-fabrication of semiconductor devices. The growth of diamond films by this method¹ is straightforward and simple; although very slow (micrometres per hour).

Depending on the conditions used, this film could be a single crystal (if grown epitaxially on a diamond substrate) or consist of diamond micro- or nanocrystallites bound together by amorphous carbon grain boundaries (Figure 1).

A limitation of the CVD process is the relatively high substrate temperature (900°C), that is required for diamond

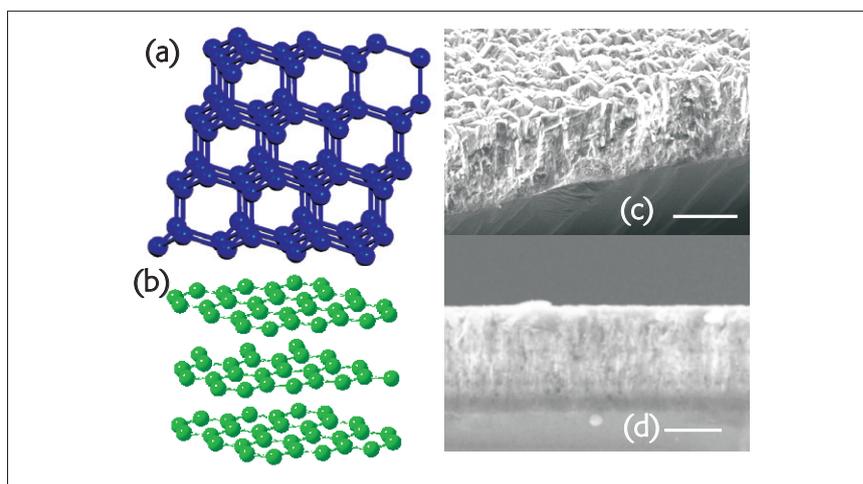


Figure 1. Illustrations of (a) the diamond lattice structure, (b) the graphite lattice structure and scanning electron microscope images of cross-sections through (c) microcrystalline diamond (10 μm scale bar) and (d) nanocrystalline diamond films (5 μm scale bar).

growth, which precludes the use of many important low melting materials, such as glass, plastic, GaAs etc. A crystalline diamond coating cannot, therefore, be deposited onto these materials. Instead, a coating of "amorphous carbon" may be used. These amorphous carbon films have properties similar to those of diamond, but can be deposited at room temperature, and are often called diamond-like carbon (DLC) films. As I write this article, the word processor is regularly saving a back-up copy to my hard-drive. The hard-drive is protected from damage by the read/write head by a nanometre thin coating of amorphous carbon. Uses of DLC films are not just restricted to high-tech electron-

ics, however. Chances are, if you had a shave this morning your razor blade was coated in a thin amorphous carbon layer to keep it sharper for longer.

Whether your chosen form of carbon is crystalline or amorphous, its properties are dependent on the structure. Amorphous carbon films are smoother and softer than nanocrystalline diamond films which, in-turn, are smoother and less transparent than microcrystalline films—the requirements of the application determine which type of film is used.

After producing your thin film the question that arises is, "How do I know what form of carbon I have made?" Common techniques such as X-ray diffraction and

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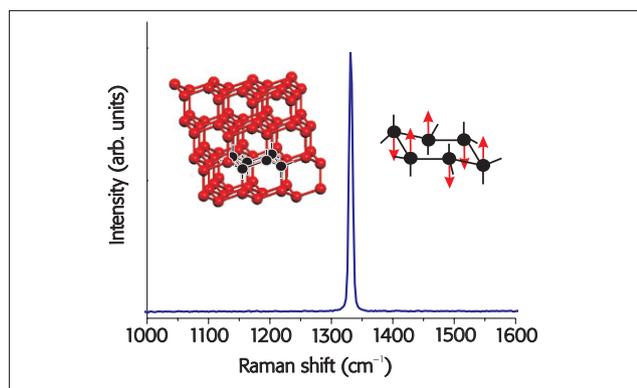


Figure 2. Raman spectrum of a diamond single crystal, inset shows a cartoon of the nuclear displacements associated with this vibration. In the bulk crystal the vibration propagates throughout the lattice.

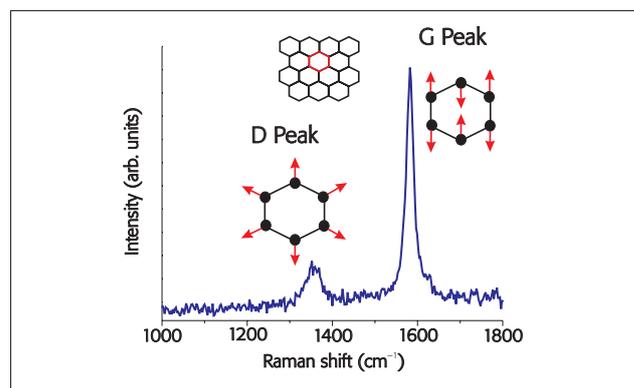


Figure 3. 514nm Raman spectrum of highly orientated pyrolytic graphite, with inset cartoons of the nuclear displacements associated with each vibration.

transmission electron microscopy will allow you to identify diamond crystals in a sample, but these methods are time consuming and may require the destruction of the sample. What's really needed is a fast, non-destructive method of unambiguously characterising a variety of thin carbon films. Raman spectroscopy is now the method of choice for this. A laser is focused through a microscope onto the sample surface, and the scattered light is passed into a spectrometer, which disperses the light onto a charge coupled device (CCD) detector. The choice of laser wavelength can be varied depending upon the required application. Common choices are visible light (e.g. 632nm red from a HeNe laser or 514.5nm green from an argon ion laser), ultraviolet (e.g. 325nm from a He:Cd laser) or near infrared (e.g. 785nm from a diode laser).

Single crystal diamond

The identification of pure diamond by Raman spectroscopy is trivial, so men bear that in mind if your fiancée is a spectroscopist and you are thinking of passing off cheap cubic zirconia as expensive diamond! The characteristic fingerprint of diamond is a single sharp Raman line at 1332cm^{-1} , see Figure 2.

As mentioned above, most CVD diamond films consist of small diamond crystallites surrounded by graphitic/amorphous carbon grain boundaries. These boundaries produce extra signals in the Raman spectrum that can help diagnose the crystallite size and overall "qual-

ity" of the diamond sample. Before we can understand these peaks we need to understand the Raman spectra of graphite and amorphous carbon.

Crystalline graphite

It was not until the advent of the laser that Raman spectroscopy could be used to analyse black materials like graphite. Tuinstra and Koenig first took the Raman spectrum of graphite in 1970.² They discovered that a single crystal of graphite produces a single peak at 1575cm^{-1} whereas in all other graphite materials (activated charcoal, carbon black etc.) a second feature appears at 1355cm^{-1} . The intensity of this second peak increases relative to the first peak as (a) the amount of "disorganised" carbon increases and (b) the graphite crystal size decreases. The 1575cm^{-1} peak (called the "G" peak, after crystalline graphite) is the only Raman active mode of the infinite lattice. The other peak (the "D" peak from disordered graphite) is caused by breakdown of the solid-state Raman selection rules, which prevent its appearance in the spectrum of the perfect crystal (Figure 3).

Amorphous carbon

Amorphous carbon (a-C) films are unstructured mixtures of sp^3 (as in diamond) and sp^2 (as in graphite) hybridised carbon. The properties of these films are strongly dependent on the ratio of these two types of carbon. Films with high sp^3 content (called tetrahedral amorphous carbon, ta-C) are generally harder,

more transparent and have a higher resistivity than those of high sp^2 content, although they are also highly stressed and more likely to delaminate from the substrate. It is also common for amorphous carbon films to contain hydrogen, by virtue of the way they are prepared. Hydrogenated a-C films are softer, more stable and tend to have higher transparency than the hydrogen-free films.

The sp^2/sp^3 ratio of a carbon film is determined by the deposition conditions.³ Unlike diamond, a-C films are generally deposited by methods that involve carbon ions being accelerated towards the substrate (e.g. RF glow discharge or pulsed laser deposition). The impact of the carbon ions onto the substrate permits the formation of the less thermodynamically stable sp^3 structure by a mechanism called "subplantation". To maximise the sp^3 content the substrate should be maintained at room temperature as excess heating can induce graphitisation (see Figure 4).

When studying a two-component sample, such as amorphous carbon, by Raman spectroscopy, it is important to consider the relative polarisability of each component. The π bonds formed by the sp^2 hybridised carbons are more polarisable than the σ bond formed by the sp^3 hybridised carbon, and so have a larger Raman cross-section. Also, when using visible lasers for excitation, the π states are resonantly enhanced, whereas the σ states are not. As a result the visible Raman spectrum of even high (~80%) sp^3 content films is dominated by the sp^2



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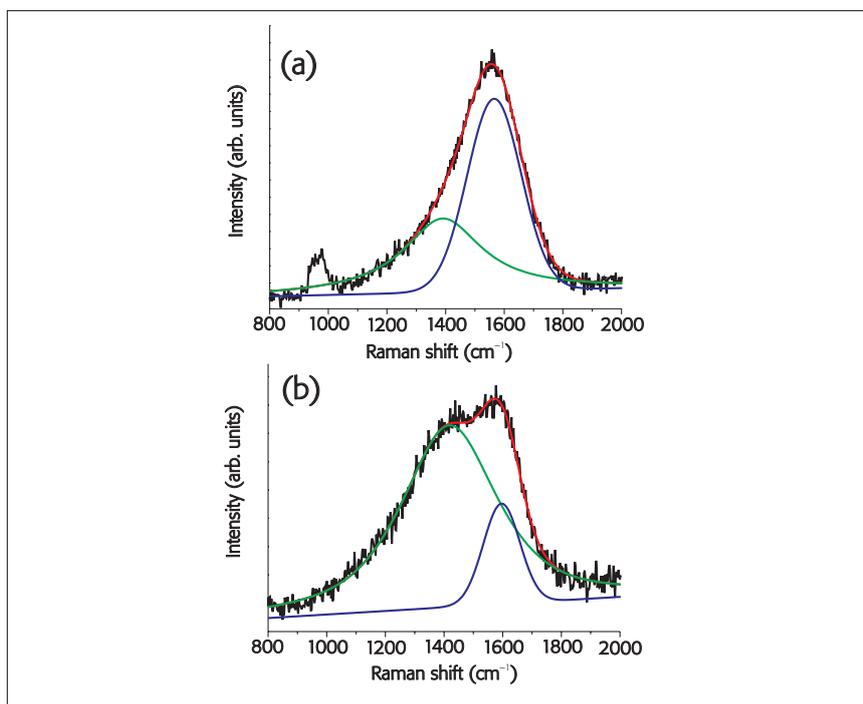


Figure 4. Raman spectra of two a-C films, deposited on Si substrate maintained at (a) 25°C and (b) 400°C. Red line is the sum of the two components used to fit the measured spectrum (black). Small peak around 1000 cm^{-1} in (a) is the second order silicon signal.

signal. Therefore, the Raman spectrum of a-C appears similar to that of graphite, displaying both the G and D signals, but with much larger peak widths, depending on the ordering of the sample. In the case of amorphous carbon, "G" does not just mean graphite—the G mode arises from stretching of any pair of sp^2 sites, whether in rings or chains. The D mode is the breathing mode of sp^2 sites in rings not chains.

The ratio of the intensity of the D peak to the intensity of the G peak [$I(D)/I(G)$] can provide a useful measure of the disorder in an a-C sample. Starting with a pure graphite single crystal, the Raman spectrum contains only a sharp G peak and no D peak, because there is no disorder. As the crystallite size is reduced and the long-range periodicity is broken, the D peak appears and increases in intensity. The $I(D)/I(G)$ ratio reaches a maximum for a nanocrystalline graphite sample which contains the maximum disorder while still only containing sp^2 rings. To increase the disorder further, from nanocrystalline graphite to a-C, sp^2 chains and sp^3 network replace some of the ring structure. The disorder is still high

so the D peak is still present, but the relative proportion of sp^2 rings to sp^2 chains is decreasing; so too does the $I(D)/I(G)$ ratio. This continues until there is no sp^2 ring structure in the a-C film, and then only a single broad G peak remains. Figure 4 shows the Raman spectra of two a-C films grown by pulsed laser ablation under the same conditions except for the temperature of the substrate. The spectra have been fitted with two Gaussians corresponding to the G (blue) and D (green) peaks. It is clear that the higher temperature has produced an increase in the $I(D)/I(G)$ ratio implying an increase in the ordering of the π bonds.

More information can be derived from the peak position changes but this is beyond the scope of this article. A fuller description can be found in a definitive review of all aspects of a-C by Robertson.³

It is possible to observe vibrations produced by the sp^3 network in the Raman spectrum of a-C but only by using UV excitation, which excites the σ states into resonance. The signal produced is broad and very weak and appears at around 1050 cm^{-1} . Referred to as the "T"

peak (for tetrahedral), it is only observable in samples with very high sp^3 content (such as ta-C).

Microcrystalline diamond

Now that we've discussed the non-diamond features that are likely to be seen in the Raman spectrum of carbon materials, we shall use this knowledge to help us characterise CVD diamond. The Raman spectrum of microcrystalline CVD diamond can generally be deconvoluted into separate contributions from the 1332 cm^{-1} diamond phonon and the D and G modes of amorphous carbon. The relative intensity of the diamond-to-non-diamond signals is strongly dependent on the excitation wavelength.⁴ Whether this is due to resonance enhancement of the sp^3 component, a decrease in the resonance enhancement of the sp^2 component, or some other process, is as yet not fully understood.

The Raman spectra displayed in Figure 5 are of the same sample but taken with different laser excitation wavelengths. These spectra clearly show the increase in the $I(\text{diamond})/I(G)$ ratio with decreasing excitation wavelength. This emphasises that the laser wavelength has to be chosen very carefully depending on what the experiment is trying to determine. For example, research into nanocrystalline diamond is becoming popular due to the smooth surface, film homogeneity and high Young's modulus of this material, making it ideal for micro-electronic mechanical devices. Analysis of a nanocrystalline sample by Raman spectroscopy using near infrared (NIR) excitation would not produce a diamond line; the signal from the amorphous carbon grain boundaries would be far too strong. UV excitation, on the other hand, would reveal a small diamond signal indicating that the sample was indeed nanocrystalline diamond, rather than simply amorphous carbon. Conversely, differentiating two high quality CVD diamond samples would be much easier with NIR excitation than UV, since the sp^2 impurities would be enhanced.

The relative intensity of the diamond line to the intensity of the G peak is often used as a crude measure of the phase purity of CVD diamond. This can



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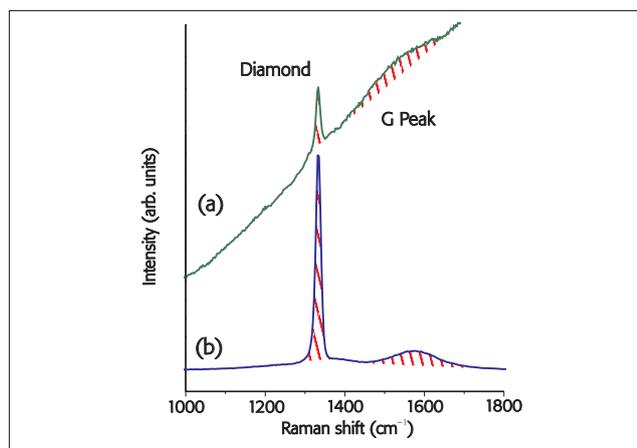


Figure 5. Raman spectra of microcrystalline diamond taken with (a) 514 nm [$I(\text{diamond})/I(\text{G})=2.2$] and (b) 325 nm excitation [$I(\text{diamond})/I(\text{G})=11.7$]. The rising background in the 514.5 nm spectrum is due to strong photoluminescence from nitrogen-vacancy defects.

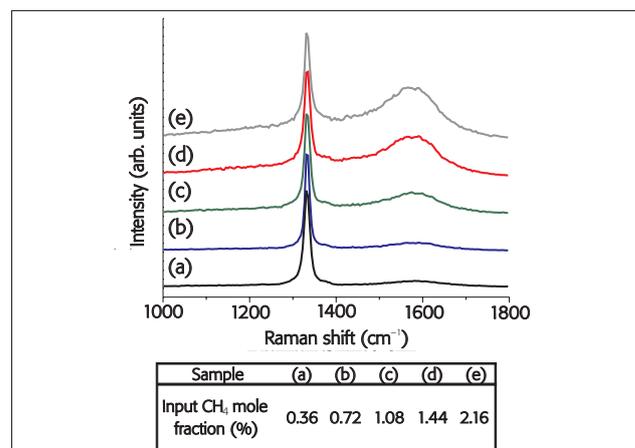


Figure 6. Raman spectra of microcrystalline diamond films grown by CVD using CH₄/H₂ gas mixtures,⁵ taken at 244 nm. Increasing the CH₄ mole fraction on the gas mixture during growth decreases the quality of the diamond film, as evidenced by the increasing G band around 1550 cm⁻¹.

be extremely useful when empirically relating deposition conditions to sample quality (Figure 6).

Nanocrystalline diamond

As the diamond crystallites reduce in size from micrometres to nanometres, analysis of the Raman spectrum becomes considerably more complicated. When dealing with a large perfect crystal, where the lattice size is effectively infinite, only certain phonons are Raman active and the spectra are quite simple. In nanocrystalline or highly disordered samples, the selection rules break down, allowing many more vibrational modes to become Raman active. The effects of this appear in two ways: (a) shifting and asymmet-

ric broadening of existing peaks and (b) the appearance of new signals activated by disorder. The activation of the D peak with disorder in graphite is an example of (b). Peak shifting and asymmetric broadening has been observed in the 1332 cm⁻¹ mode of shock-synthesised nanodiamond powders, but in diamond thin films any change in peak position is generally taken as a sign of compressive or tensile stress in the film.

The appearance of new signals activated by disorder in nanodiamond films is still a subject of some controversy.⁶ Figure 7 shows a 325 nm Raman spectrum of a film grown under typical nanodiamond conditions. The diamond line and the G and D peaks are present,

but there is also a small broad signal at ~1150 cm⁻¹ which is not observed in the spectrum of microcrystalline diamond. The presence of this peak is often taken as direct evidence for nanosized diamond crystals, since at first it was thought that it was a disorder-activated peak. It is now believed that this peak arises from an *sp*² hybridised structure, such as polyacetylene-type molecules that may be present on the surface and in grain boundaries.

Diamondoid hydrocarbons

If the size of the diamond crystallites is reduced even further then the resulting material is closer to a hydrocarbon molecule than a diamond crystal. This class of molecules, which have a structure that is

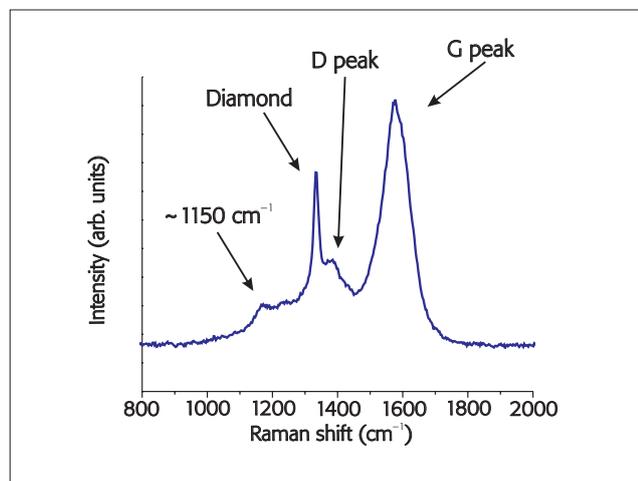


Figure 7. Raman spectrum of nanocrystalline diamond taken with 325 nm excitation.

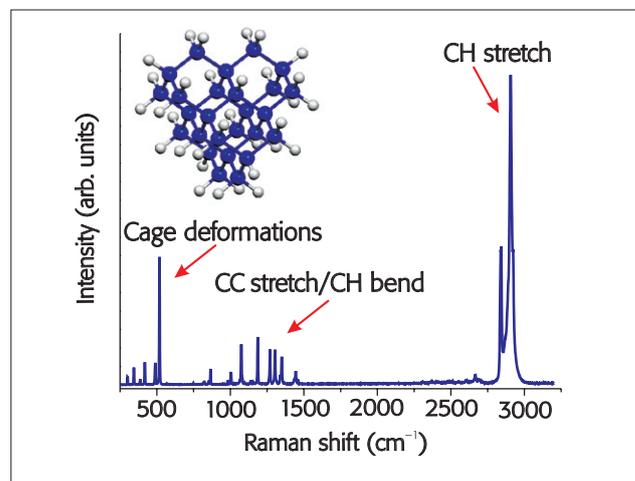


Figure 8. Raman spectrum of a diamondoid hydrocarbon, [1(2,3)4] Pentamantane with its structure shown in the inset.

partially or wholly superimposable on the diamond lattice, are called "diamondoids". Diamondoids are found in petroleum but only exist in minute concentrations making them difficult to isolate.⁷ Figure 8 shows the Raman spectrum of one such diamondoid hydrocarbon, [1(2,3)4] pentamantane. The spectra of diamondoid molecules contain many lines and are closer to those of hydrocarbons, such as cyclohexane, than that of diamond. The small size of these structures permits the use of computational chemistry (*ab initio* and density functional methods) to calculate the vibrational frequencies and Raman intensities, greatly aiding the peak assignment.⁸

Conclusions

When analysing carbon thin films, whether crystalline or amorphous, Raman spectroscopy is a powerful

diagnostic tool permitting simple, non-destructive characterisation. Its versatility is greatly improved if a range of excitation wavelengths can be used, especially if at least one is in the UV, where the sensitivity to sp^3 hybridisation is strongest. Many companies now sell multi-wavelength Raman systems that allow the user to switch between IR, visible and UV lasers in a matter of minutes. This article provides only a brief review of this long-studied, yet still rapidly-growing, field and with the advent of new variations such as surface- and tip-enhanced Raman spectroscopy, there is little sign of it slowing down.

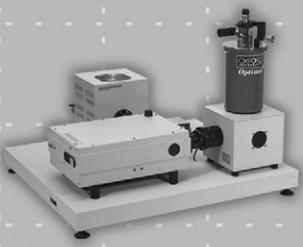
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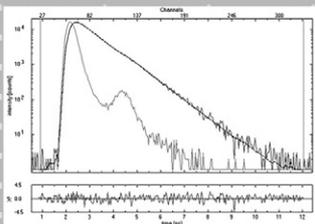
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