Impact of Raman Spectroscopy On Technologically Important Forms of Elemental Carbon

Pure carbon can occur in many forms reflected by the nearest neighbour bonds, and by mid-range and long-range ordering of the solid. Different forms of carbon are being exploited in newly engineered applications. For example, diamond can be doped and used as the substrates for integrated circuits with properties superior to silicon, and hard carbon films are being used to coat computer discs. Raman spectra have been shown to be uniquely diagnostic of the many forms of carbon, even when the material is present in small quantities or thin films. The following discussion should provide an aid to the use of Raman spectroscopy for characterising carbons in the design, monitoring, and control of manufacturing processes. The carbon atom has four valence orbitals, which can hybridise to form sp2 and sp3 orbital combinations. The sp2 orbital forms planar structures with 3-fold symmetry at the carbon atom, and is found in aromatic molecules and in crystalline graphite. The sp3 orbital forms the basis for 3-dimensional, tetrahedrally bonded carbon as in methane (CH_4) and in diamond. The most well-known forms of elemental carbon found in nature are graphite and diamond. In recent years exotic sp2 forms known as Fullerenes, and including the carbon nanotubes, have also drawn interest. Raman spectra of some of the common forms of carbon are shown in Figure 1. The salient features of these spectra will be discussed below.

Diamond

Diamond **(D)** is formed by an infinite extension of sp3 carbon-carbon bonds.

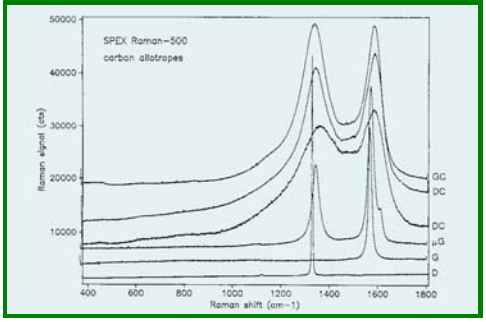


Figure 1.

While diamond is the hardest substance in nature, it is actually a metastable form that precipitates from high pressure, high temperature melts. Diamond is a unique material because of its physical properties, which include:

. high strength
. optical transparency
. electrical insulation (when pure)
. semi-conductivity (when doped)
. high thermal conductivity
. corrosion resistance.

Because of these properties there has been interest in utilising diamond in engineered materials. Diamond fibres (and graphite fibres, as well) are used in metal or polymer matrix composites for reinforcement. The high thermal conductivity and the robustness of diamond makes it an ideal candidate for heat sink substrates which are used for the dissipation of heat generated by high power micro or opto-electronics devices such as laser diodes. Diamond doped with nitrogen, boron, or phosphorous becomes the semi-conducting material of choice for electronic devices such as transistors. Due to its high reflectivity in the UV range, diamond could be used in the future for realisation of UV optics (gratings, mirrors).

However, as long as the only method to grow diamond requires high temperatures and pressures, this is not an economically feasible material for most applications.

Over the last 10 years many workers have demonstrated the ability to grow diamond films in CVD (chemical vapour deposition) reactors under conditions close to ambient. However, since diamond is not a thermodynamically stable phase, much sp2-bonded carbon often accompanies the diamond deposition. The sensitivity of Raman spectroscopy to even very small amounts of sp2 carbon makes it the technique of choice to study these films.

Aside from the ability of Raman spectroscopy to demonstrate the presence of diamond in CVD films, there is also information in the Raman band of the diamond itself. The Raman line appears at 1332 cm-1 in single crystal diamond. Under compressive and tensile stress in the film, the diamond line will shift respectively to lower and higher frequency. In these films the line can additionally broaden due to heterogeneity of the sample. Workers using Raman spectroscopy to characterise these films can develop a quality index that measures the following characteristics:

. Diamond frequency
. Diamond linewidth
. Sp2 carbon background

Figure 2 shows a typical Raman spectrum of a diamond film containing substantial amounts of non-diamond carbon. The spectrum has been band-fit to quantify the contributions of the various components. It is also useful to note that Yarbrough and Roy (MRS 1988 Symposium, Diamond and Diamond-like Material Synthesis, ed. Johnson, et.al, pp.33-38) have noted that under CVD conditions that are marginal for the deposition of diamond, a new phase is detected. XRD (x-ray diffraction) in this article indicates **nanocrystalline diamond (nD)**, but the Raman spectrum is completely different from anything that has been seen in other carbons. These materials show new diffuse bands at ca. 1140 and 1450 cm-1.

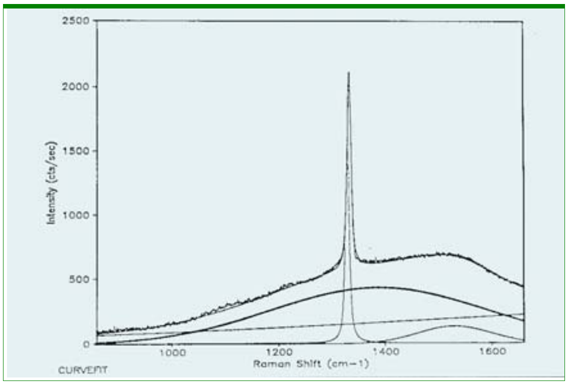


Figure 2.

Graphite

Graphite **(G)** is formed from stacks of infinitely extended planes of fused aromatic rings. The π electrons in the planes provide for high electrical conductivity and a 0eV bandgap. Van der Waals bonding between the planes is weak which is why the planes can lip, and the material can be used as a solid lubricant or as an additive to an oily lubricant (for valves, mechanical seals, sliders...)

Figure 1 shows the graphite first order phonon at about 1580 cm-1 which is fairly sharp, although not as sharp as that of diamond. This line has been documented to move with stress and temperature, and because of the potential for heating by laser absorption, stress- and temperature- induced effects can be difficult to separate.

When the long-range order of the graphite lattice is disrupted, a second line appears at about 1360 cm-1. In a grinding study Tuinstra and Koenig (J. Chem. Phys. 53, 1126, 1970) showed that the intensity of the peak at 1360 cm-1 scaled with the size of the crystal, as derived from XRD (x-ray diffraction). Material with shorter range order will be denoted **microcrystalline graphite (pG)**. A typical spectrum is shown in Figure 1.The relative peak intensities of these two lines at 1580 and 1360 cm-1, denoted respectively as G and D lines in the literature (graphite and defect), can vary enormously.

In addition, the D band will shift with excitation wavelength, appearing at lower frequencies with longer wavelength excitation lasers (Wang, Alsmeyer, and McCreery, Raman Spectroscopy of Carbon Materials: Structural Basis of Observed Spectra, Chemistry of Materials **2**, 557- 563 (1990). Since the relative intensity is determined by the degree of long range order of the lattice, it is not surprising that the linewidths of these lines also vary. Consequently, it has in recent years, been deemed more appropriate to calculate the ratio of the integrated intensities of the lines, using bandfitting algorithms to separate the components (LabSpec and DiskSpec softwares, Jobin Yvon).

The Raman spectrum of many carbon materials, including some films and graphitized fibres. exhibits such extensive broadening and overlap between the two bands that only band-fitting would permit appropriate use of the data.

Carbons showing this behaviour will be denoted **disordered carbon (DC)**. Spectra of two samples are shown in Figure 1.

In addition, it has been shown (Rouzaud, et.al., Thin Solid Films, 105, 75-96, 1983) that some carbon films require a second defect band at about 1500 cm-1 to flatten the residual of the band-fitted Raman spectra. These authors attribute this band to the presence of interstitial defects between the graphitic layers or between structural units in the layers. In contrast the D band at 1360 cm-1 is attributed to in-plane defects between basic structural units.

When band-broadening and overlap in carbon films is so extensive that separate bands are not discernible before the band-fit, the material is called **"diamond-like carbon" (DLC)**. This material was originally termed "diamond-like" because of its relative transparency and electrical insulation, properties that result from the limited size range of the graphitic structural units and their π systems. DLC films can be used as passivation layers in magnetic storage devices.

A material called **"Glassy Carbon" (GC)** has the intensity ratio of the D and G bands reversed (D band higher), with the bands fairly sharp. Ironically this material is composed of highly crystalline regions, but with very small dimensions (private communication, Wm. White, Penn State U.). A spectrum of glassy carbon is shown in Figure 1.
It is worthwhile to make another comment on the dependence of these spectra on excitation wavelength. Because the D and G bands are related to different sizes of graphitic structural units, enhancement of the two Raman bands that depends on the proximity of the laser wavelength to electronic transitions, is expected to behave differently as the excitation wavelength is changed. Yoshikawa, et.al. (Appl. Phys. Lett., 52, 1639-1641, 1988) show spectra of films with 0 and 30% hydrogen acquired with laser wavelengths between 647 and 458 nm. For both types of films, the D band is enhanced relative to the G band when excited with a red laser. At any one wavelength, the D band is more intense in the spectrum of the pure carbon film than that of a film with 30% hydrogen.

Engineered Carbons

Raman spectra can be used to quantify the degree of structural order as well as orientation in technologically important carbons. Spectra of carbon **fibres** manufactured from pitch and PAN (polyacrylonitrile) showed not only a difference in long range order but polarisation-dependent intensities related to the orientation of the graphitic planes in the fibers (Adar and Noether, in Microbeam Analysis-1 983, 269-273).

Hard carbon films are being used universally in the manufacture of hard discs in the computer industry and on read-write heads. Engineering the parameters of the deposition equipment is controlling the physical and tribological properties of the films. Raman spectra are being used in this industry as a rapid confirmation of the properties of the film because the spectra have been correlated with the tribological properties of interest (J. Ager, IEEE Trans. Magn, 1992).

Such hard films can also be used to improve the wear properties of cutting tools and surgical/scalpel blades, as well as to passivate medical implants. Indeed, their chemical inertness makes them bio-compatible.

Figures 3a and b exhibit spectra of carbon films that require a fit with 2 and 3 bands respectively. The film whose spectrum is shown in Figure 3b has some interstitial defects as discussed above.

Buckeyballs or Fullerenes, Nanotubes

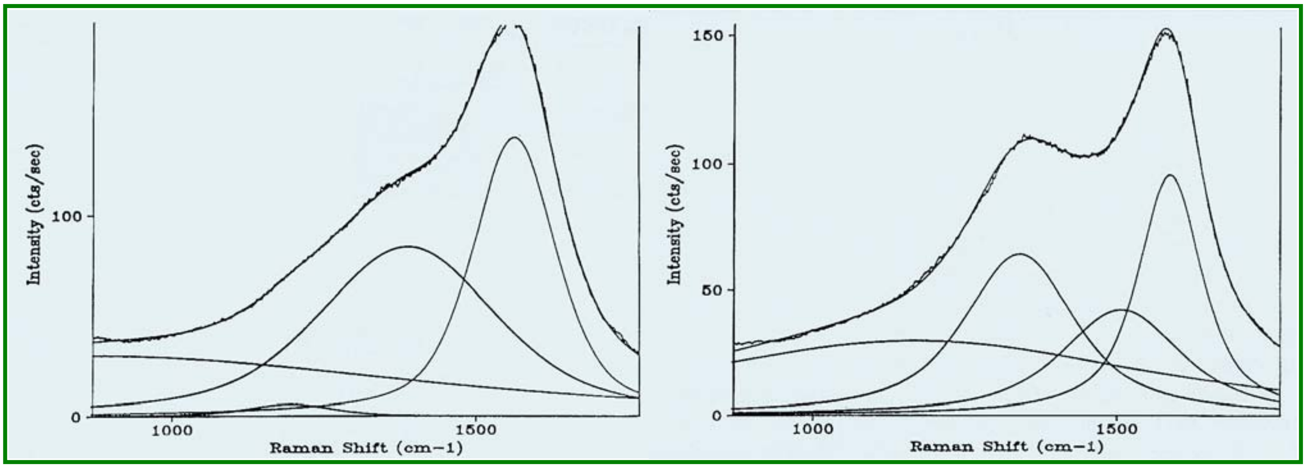
After the theoretical proposal that 60- and 70-atom clusters of carbon might exist in nature, fullerenes were isolated from carbon soot (Kroto; et al., Nature 318, 162, 1985). Actually, it is possible to construct balls, tubes and capsules of graphitic-like fused aromatic rings. The Raman spectra of some of these materials have been recorded from films of pure materials (Bethune, et al., Chem.Phys.Lett, 174, 219, 1990). In contrast to the Raman spectra of the other forms of carbon, which contain at most 3 bands in the fingerprint region of the spectrum (100- 1800 cm-1), some of which can be broad, the Raman spectra of these materials contains many bands that are quite sharp.

The spectra of carbon nanotubes reflect the structure of the tubes. That is, the diameter and chiral angle (which is related to how a graphite plane would be rolled into the tubular structure). An excellent review of Raman scattering in all types of carbons includes a detailed discussion of nanotubes (Dresselhaus, Pimenta, and Eklund, Raman Scattering in Carbon Materials, Chapter 9 in Analytical Applications of Raman Spectroscopy, ed. M. Pelletier, (Blackwell, Oxford, 1999).

Because the structure of the carbon nanotubes is recognized to determine the semiconducting/ metallic properties of these materials, they have been recognised as potential candidates to be used in nanoelectronics and in many functional devices such as field emitters.

Conclusion

The Raman spectra of the various forms of elemental carbon are very sensitive to the type of nearest neighbour bonding, and to intermediate and long range order. In many cases Raman spectroscopy is the technique of choice for characterisation of carbon materials. Correlation of Raman spectral features with tribological properties can facilitate the deposition of carbon films.



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