Characterizing Carbon Materials with Raman Spectroscopy

Joe Hodkiewicz, Thermo Fisher Scientific, Madison, WI, USA

Introduction

Carbon nanomaterials have revolutionized the field of material science in recent years. Individual carbon nanomaterials offer a wide range of useful properties pertaining to electrical conductance, thermal resistance, and exceptional strength, making them very interesting materials to a broad range of industries. The high-level of interest in the processing, modification, and customization of these materials has created a strong demand for techniques that can be used to characterize carbon nanomaterials. Raman spectroscopy is one technique that has proven to be very well suited to many of the characterization needs with these materials.

Raman spectroscopy is most sensitive to highly symmetric covalent bonds with little or no natural dipole moment. The carbon-carbon bonds that make up these materials fit this criterion perfectly and as a result Raman spectroscopy is highly sensitive to these materials and able to provide a wealth of information about their structure. As we shall see, Raman spectroscopy is capable of discerning even slight changes in structure making it a very valuable tool in the characterization of carbon nanomaterials.

Carbon Nanomaterials Defined

There are a wide variety of different carbon nanostructures, however they all have a few basic things in common. First, all of these materials are predominantly made up of pure carbon, and as such can be called carbon allotropes. The range of these materials starts with the well known allotropes of diamond and graphite, and continues on to encompass fullerenes, graphene and more complex structures such as carbon nanotubes. From a molecular perspective, these materials are all entirely composed of C-C bonds, although the orientation of these bonds is different in the different materials and therefore, to characterize their molecular structure in a meaningful manner, it is necessary to have a technique which is highly sensitive to even slight changes in orientation of C-C bonds.
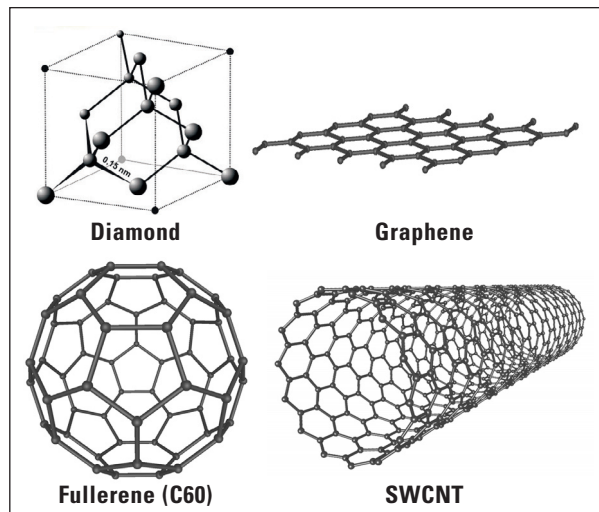

Figure 1: Structure of some representative carbon allotropes

Raman Highly Sensitive to Morphology

Raman spectroscopy is particularly well suited to molecular morphology characterization of carbon materials. Every band in the Raman spectrum corresponds directly to a specific vibrational frequency of a bond within the molecule. The vibrational frequency and hence the position of the Raman band is very sensitive to the orientation of the bands and weight of the atoms at either end of the bond. Figure 2 shows an example in which the Raman spectrum of diamond is compared to the Raman spectra of crystalline silicon and germanium. These spectra show us several things. First, note that in the case of diamond, where the material consists of highly uniform C-C bonds in a tetrahedral crystal structure, the Raman spectrum is very simple. It consists of only a single band because all of the bonds in the crystal are of the same orientation and strength resulting in a single vibrational frequency. We also see that the spectrum of diamond is easily distinguished from the spectra of silicon and germanium by the frequency (cm^{-1} position) of the band even though they share the same tetrahedral crystal configuration. The heavier atoms of silicon and germanium slow the vibrational frequency and shift the corresponding Raman band to lower frequency as well.
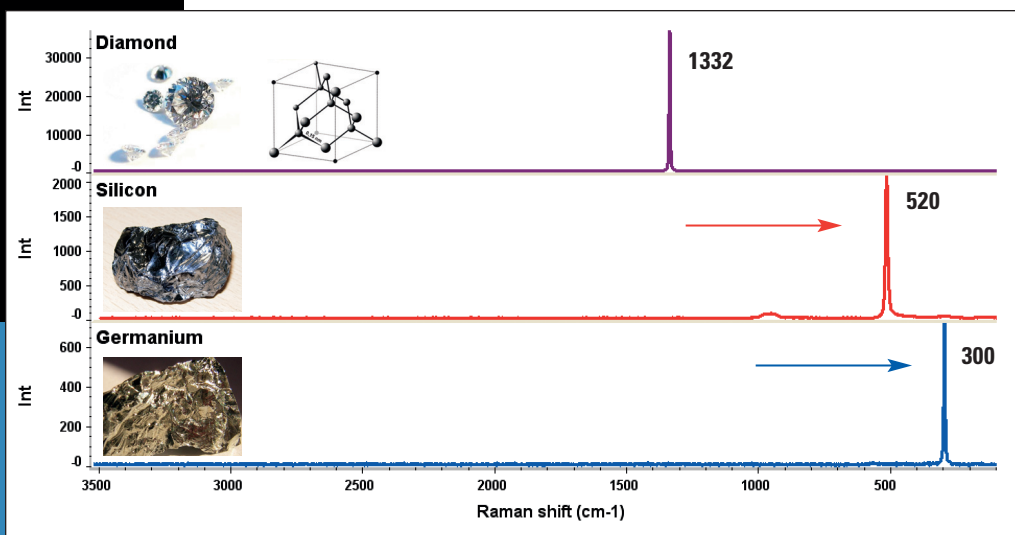
Figure 2: Raman spectra of diamond, crystalline silicon, and crystalline germanium
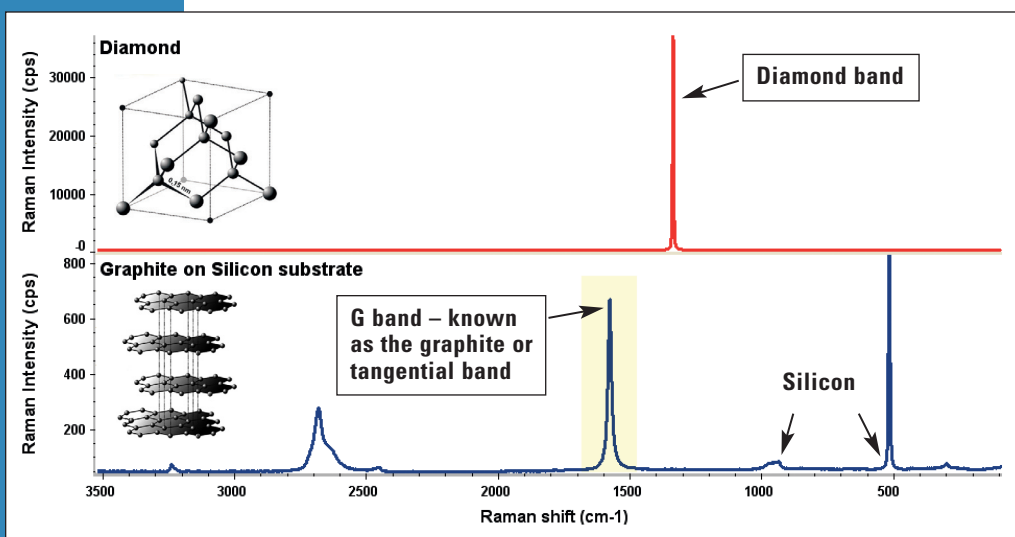

Figure 3: Raman spectra of diamond and of a sample of graphite on a silicon substrate
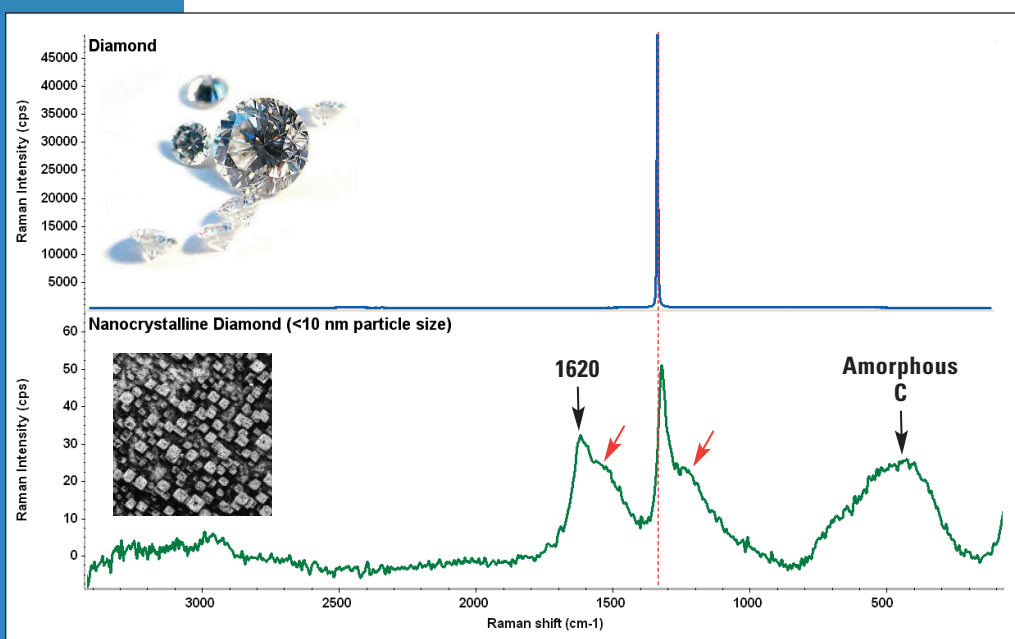

Figure 4: Raman spectra of diamond and nanocrystalline diamond

Similarly in Figure 3, when we compare the Raman spectra of two carbon allotropes – diamond and graphite – again we can easily distinguish the two materials by their Raman spectrum even though both are composed entirely of C-C bonds. The graphite spectrum has several bands in the spectrum and the main band has shifted from 1332 cm^{-1} in diamond to 1582 cm^{-1} in graphite. The reason for this is that graphite is composed of sp^2 bonded carbon in planar sheets in which the bond energy of the sp^2 bonds is higher than the sp^3 bonds of diamond. The higher energy of the sp^2 bonds in graphite pushes the vibrational frequency of the bonds and hence the frequency of the band in the Raman spectrum to higher frequency. The 1582 cm^{-1} band of graphite is known as the G band. The presence of additional bands in the graphite spectrum indicate that there are some carbon bonds with different bond energies in the graphite sample and this is in fact the case, as graphite is not quite as uniform in structure as diamond.

Another good example to show the remarkable sensitivity of Raman to molecular morphology is to compare the Raman spectra of diamond with that of nanocrystalline diamond as can be seen in Figure 4. The small crystal size of nanocrystalline diamond results in a finite-size effect in which the lattice is somewhat distorted. This is manifested in the Raman spectrum by a slightly downshifted tetrahedral sp^3 band. The additional band at 1620 cm^{-1} and the shoulders on the 1620 cm^{-1} and tetrahedral sp^3 band are also indicative of sp^2 bonded carbon that represents surface defect modes, which would be insignificant in larger diamond crystals. Finally, the very broad band around 500 cm^{-1} is indicative of some amorphous sp^3 bonded carbon. This example illustrates just how sensitive Raman spectroscopy is to even very slight differences in molecular morphology.

What Raman Can Reveal About More Complex Carbon Structures

Fullerenes: Fullerenes are essentially hollow carbon shells of various sizes. The most well known of these is a 60-carbon unit called Buckminster fullerene or C60. There are many other fullerenes, from a few to many hundreds of carbon atoms. Figure 5 compares the Raman spectra of C60 and C70. The main feature in the C60 spectrum is a relatively sharp line at around 1462 cm^{-1}, known as the pentagonal pinch mode. This tells us several things. Firstly, it tells us that C60 is composed of sp^2 bonded carbon. The sharpness of the band also tells us that the bonds are for the most part very uniform in nature. In fact, the carbon atoms in C60 are equivalent and indistinguishable. In contrast, the spectrum of C70 is littered with numerous bands. This is due to a reduction in molecular symmetry which results in more Raman bands being active. Additionally Raman can also be very sensitive to doping and stress due to temperature or pressure.

Graphene: Graphene is the fundamental building block of many important carbon materials including graphite. Graphite consists of stacks of sp^2 bonded planar graphene sheets. When comparing Raman spectra of graphene and graphite, at first glance the spectra look very similar. This is not too surprising as graphite is just stacked graphene. However, there are some significant differences as we can see in Figure 6. The most obvious difference is that the band at 2700 cm^{-1}, which is known as the G' band, is much more intense than the G band in graphene compared to graphite. You may have heard the G' band referred to as the 2D band; both 2D
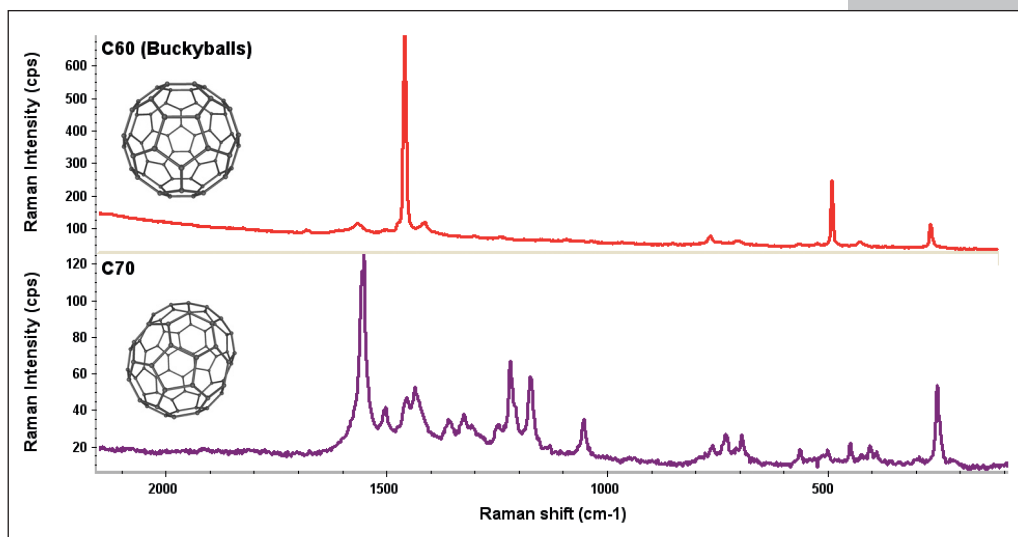

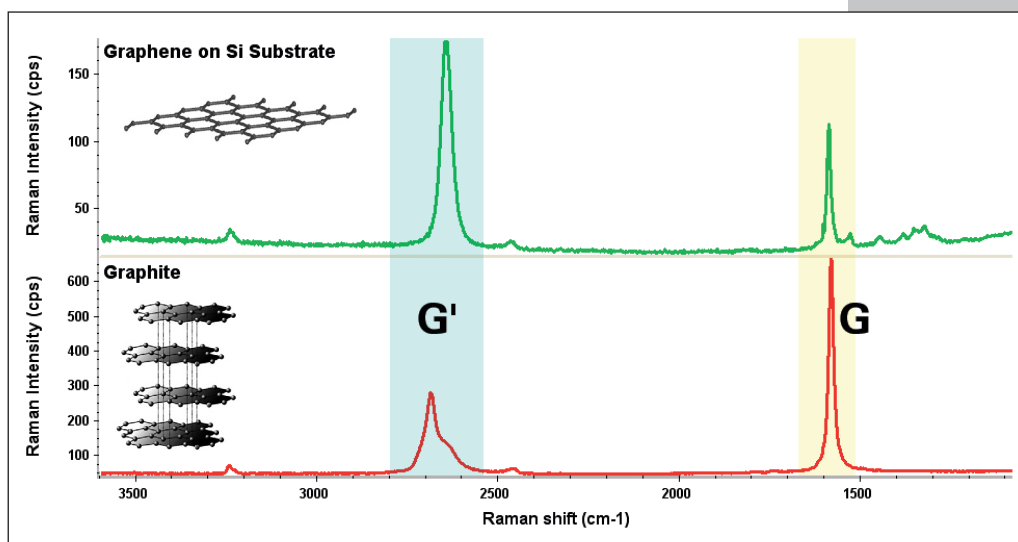Figure 5: Raman spectra of two fullerenes – C60 and C70

Figure 6: Comparison of Raman spectra of graphene and graphite

and G' are accepted names for this band. Figure 7a allows us to take a closer look at the G' band of these two materials where we can see that both the shape of the band and the position are different and both tell us something. The peak shift in graphite is a result of interactions between the stacked graphene layers which has a

tendency to shift the bands to higher frequency. Figures 7b and 7c show the same spectra as in 7a with the addition of curve fitting that has been used to provide a better picture of the underlying structure of these bands. The G' band in a single layer graphene spectrum fits to a single band whereas curve fitting reveals several
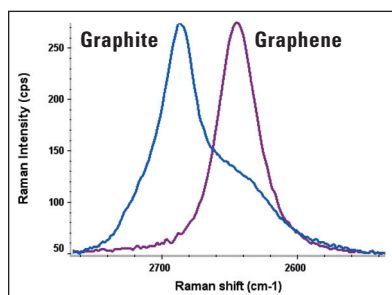

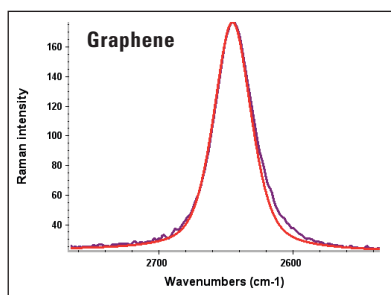Figure 7a: G' band of graphite and graphene

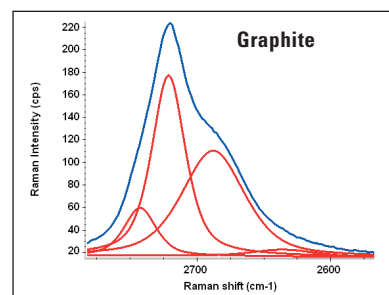Figure 7b: G' band of graphene with curve fitting results overlaid in red

Figure 7c: G' band of graphite with curve fitting results overlaid in red

underlying bands in the graphite spectrum. These bands are a result of the different interlayer interactions that occur at different depths within the graphene.

Carbon Nanotubes:

Carbon nanotubes are essentially rolled up graphene sheets that have been sealed to form hollow tubes. Single-wall carbon nanotubes (SWCNT) are cylindrical tubes with a single outer wall with diameters that are usually only 1 – 2 nm. There are also double-wall carbon nanotubes (DWCNT) which have a second layer of graphene wrapped around an inner single-wall carbon nanotube. These are a subset of the larger category of multi-wall carbon nanotubes (MWCNT) that have many layers of graphene wrapped around the core tube. Refer to Figures 8a and 8b. Due to their unique mechanical, electrical and thermal properties, carbon nanotubes are one of the most active areas in the field of carbon nanotechnology today.
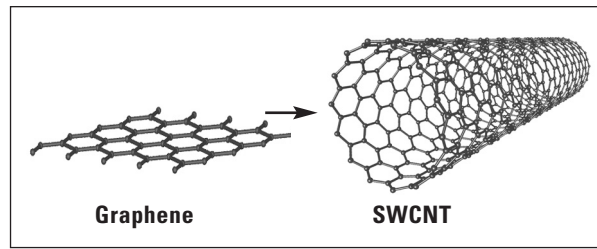

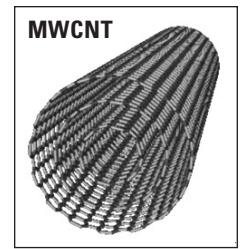Figure 8a: Diagram depicting the structure of graphene and a SWCNT

Figure 8b: Diagram depicting the structure of a MWCNT

The Raman spectrum of a SWCNT bears a lot of similarity to graphene, which is not too surprising as it is simply a rolled up sheet of graphene. Figure 9 shows us a Raman spectrum of a SWCNT in which we can see well defined G and G' bands as there were in graphene and graphite. We also see a prominent band around 1350 cm^{-1}. This band is known as the D band. The D band originates from a hybridized vibrational mode associated with graphene edges and it indicates the presence of some disorder to the graphene structure. This band is often referred to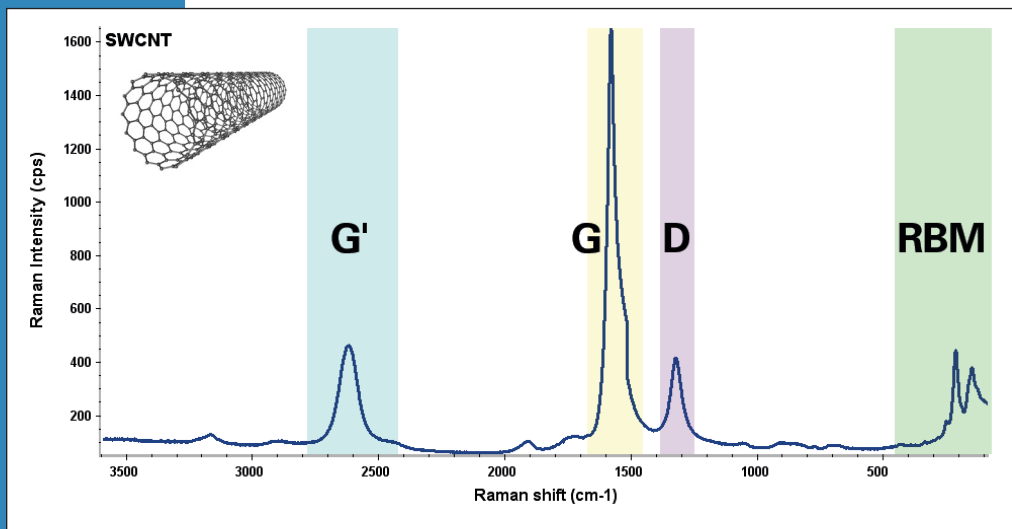 as the disorder band or the defect band and its intensity relative to that of the G band is often used as a measure of the quality with nanotubes. There is another a series of bands appearing at the low frequency end of the spectrum known as Radial Breathing Mode or RBM bands. The RBM bands are unique to SWCNTs and as their name suggests, correspond to the expansion and contraction of the tubes. The frequency of these bands can be correlated to the diameter of SWCNTs and they can provide important information on their aggregation state.

MWCNTs have very similar spectra to those of SWCNTs, as is apparent from Figure 10. The primary differences are the lack of RBM modes in MWCNTs and a much more prominent D band in MWCNTs. The RBM modes are not present because the outer tubes restrict the breathing mode. The more prominent D band in MWCNTs is to be expected to a certain extent given the multilayer configuration and indicates more disorder in the structure. Figure 10 compares the spectra of samples of SWCNTs, DWCNTs, and MWCNTs. Notice that the RBM mode completely disappears as we go to a double-wall tube and that the D bands and G' bands get proportionately larger as we add layers to the walls of the tubes.

Figure 9: Raman spectrum of SWCNTs with prominent bands labeled
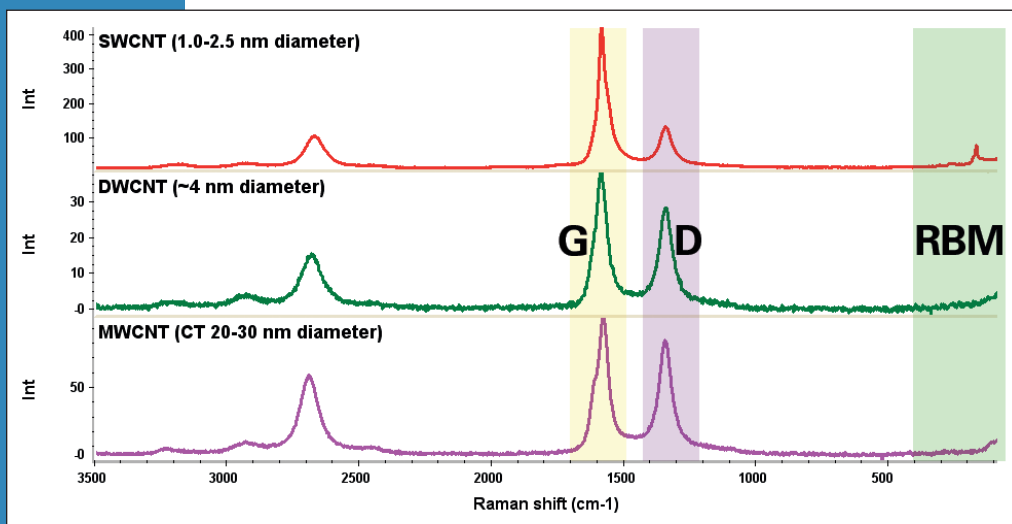
Figure 10: Comparison of Raman spectra of SWCNTs, DWCNTs, and MWCNTs

What is Involved in Recording a Raman Spectrum

It is relatively easy to collect a Raman spectrum of a carbon nanomaterial. The materials are generally recorded neat under standard atmospheric conditions which make for very easy sampling and provide a lot of flexibility as to what can be sampled. Although if samples are in the form of a loose powder, then the powder is usually compressed to provide a denser sample. This can be done by simply pressing a small amount of sample between two microscope slides. If the powders are loose, the density is often too low to get a measureable spectrum. Many times CNTs are cast onto slides within a surfactant. This works well as the density is generally much higher than the powdered form of the material, although it is worth noting that there may be some bands present from the surfactant. These can be easily identified by measuring a blank sample of the surfactant. Films are typically measured in their native state on whatever substrate they happen to be on.
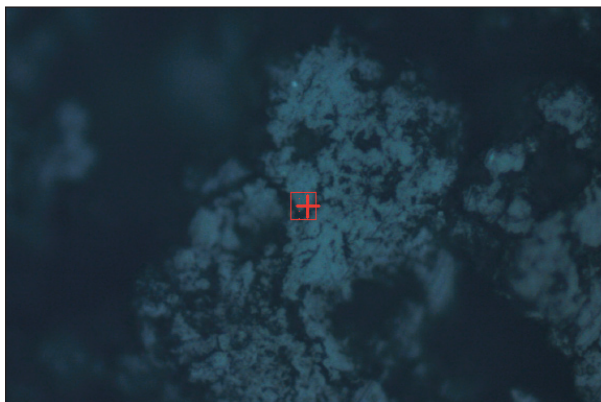

Figure 11: View of compressed CNTs on a microscope slide (500× magnification)

In terms of time of analysis, Raman measurements are generally short compared to other techniques. The measurement time typically ranges anywhere from a few seconds to five minutes depending primarily on the density of the sample and on the laser power at the sample. The denser a sample, the shorter the necessary measurement time will be; and the higher the laser power, the shorter the necessary measurement time will be. Note that when we talk about laser power – it is the laser power at sample and really the optical density of the laser power at the sample that is most critical. If a lot of laser energy is dispersed over a large area it will not have the same impact as a lesser amount of energy tightly focused on the area of interest. It is also worth noting that many carbon nanomaterials are sensitive to laser power, so the amount of laser power you can use is often limited by the samples and it is important to have good control of the laser power to insure reproducible measurements.

Figure 12: Thermo Scientific DXR Raman Microscope

Figure 13: Thermo Scientific DXR SmartRaman Spectrometer

Conclusions

Raman is a very powerful and valuable technique that can be of great benefit to characterization of carbon nanomaterials. Raman is particularly well suited to detect small changes in structural morphology of carbon nanomaterials making it an indispensable tool for many material scientists working with carbon nanostructures. Raman instruments are very fast and provide a great deal of flexibility in samples that can be accommodated. Every lab that is characterizing carbon nanomaterials will benefit from having access to Raman instrumentation.

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