

# Introduction to Raman Spectroscopy as a Characterization Tool for Carbon Nanotubes, Graphene, and other Carbon Nanostructures

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## ABSTRACT

While there have been many publications produced in which Raman spectroscopy has been used to characterize various aspects of carbon nanostructures, there have only been a few works published which provide an overview of what the technique can offer to the field of carbon nanostructures, and works which discuss optimization of analysis parameters and the variation that is observed as those parameters are varied are still lacking. This work will provide an overview of the information that Raman spectroscopy can provide on carbon nanostructures with emphasis placed on carbon nanotubes and graphene. This work will go further to demonstrate the impact that varying key analysis parameters such as laser power and laser excitation will have on the measurements. The goal of this work is to provide people who are looking to characterize carbon nanostructures with an understanding of what Raman spectroscopy can offer and with some insight on how to optimize measurement conditions.

**Keywords:** raman, d-band, g-band, nanotube, graphene

## 1 EXPERIMENTAL

All Raman microscopy characterization was performed with a Thermo Scientific DXR Raman microscope. All bulk Raman spectroscopy characterization was performed with a Thermo Scientific DXR SmartRaman spectrometer. Both instruments were configured with 532 nm, 633 nm, and 780 nm lasers and data is labeled with the excitation laser that was used.

## 2 RESULTS AND DISCUSSION

### 2.1 Raman Highly Sensitive to Morphology

Raman spectroscopy is one technique which 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 1 shows an example in which the Raman spectrum of

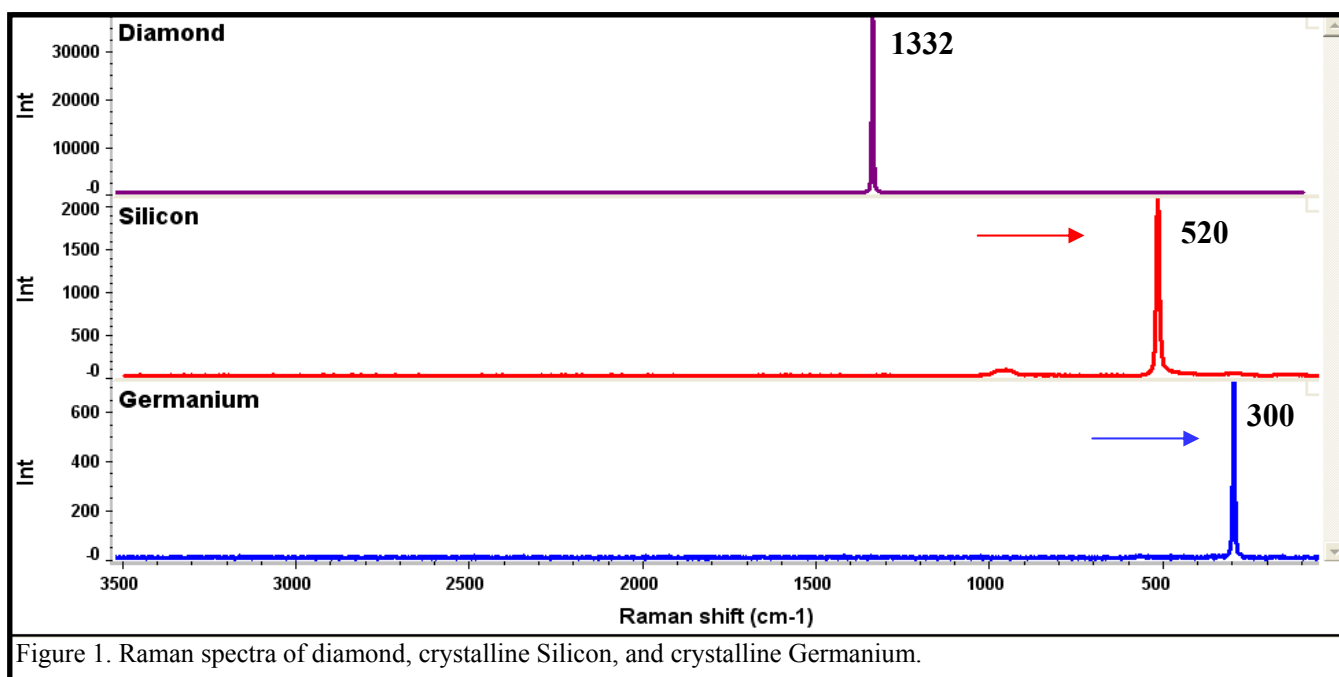


Figure 1. Raman spectra of diamond, crystalline Silicon, and crystalline Germanium.

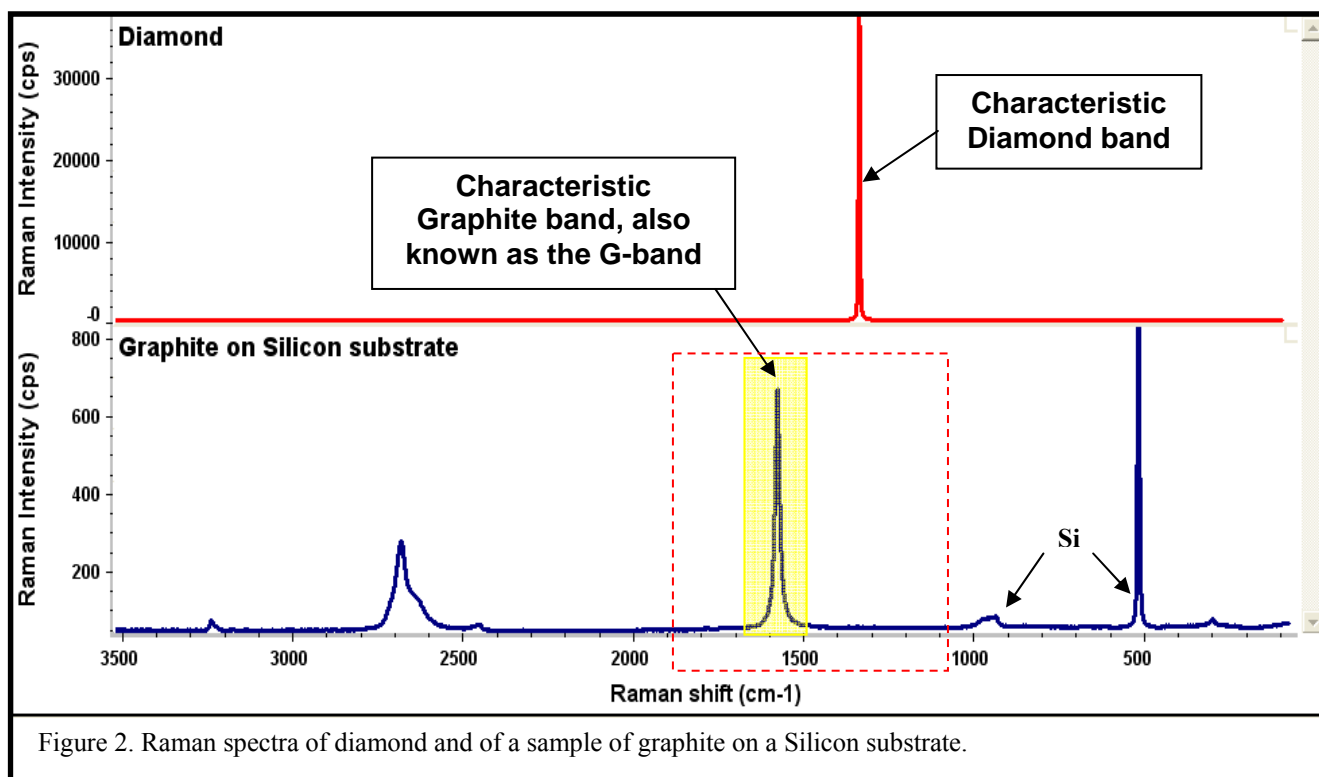


Figure 2. Raman spectra of diamond and of a sample of graphite on a Silicon substrate.

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 that 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 ( $\text{cm}^{-1}$  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.

Similarly in figure 2, 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  $1332 \text{ cm}^{-1}$  in diamond to  $1582 \text{ cm}^{-1}$  in graphite. The reason for this is that graphite is composed of  $\text{sp}^2$  bonded carbon in planar sheets in which the bond energy of the  $\text{sp}^2$  bonds is higher than the  $\text{sp}^3$  bonds of diamond. The higher energy of the  $\text{sp}^2$  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  $1582 \text{ cm}^{-1}$  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.

## 2.2 What Raman Can Reveal About More Complex Carbon Structures

We will start out by taking a look at 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 3 compares the Raman spectra of C60 and C70. The main feature in the C60 spectrum is a relatively sharp line at around  $1462 \text{ cm}^{-1}$ , known as the pentagonal pinch mode. This tells us several things. Firstly, it tells us that C60 is composed of  $\text{sp}^2$  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

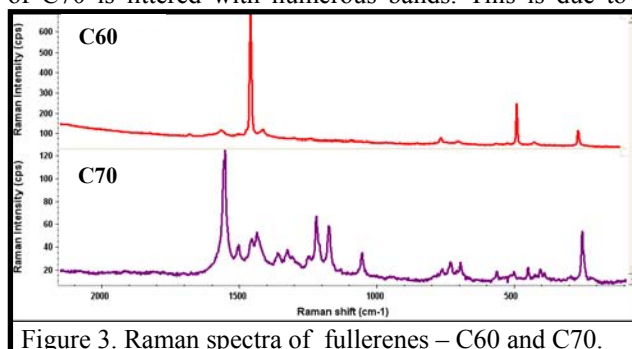


Figure 3. Raman spectra of fullerenes – C60 and C70.

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

Next we will take a look at 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. The most obvious difference is that the band at  $2700\text{ cm}^{-1}$ , which is known as the  $G'$  band, is much more intense than the G band in graphene compared to graphite. Figure 4 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. The  $G'$  band in a single layer graphene spectrum fits to a single band whereas curve fitting reveals a multitude of underlying bands in the graphite spectrum. These bands are a result of the different interlayer interactions that occur at different depths within the graphene.

Lastly, we will take a look at 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. 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.

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 5 shows us a Raman spectrum of a SWCNT in which we can see well defined G and  $G'$  bands as there are in graphene and graphite. We also see a prominent band around  $1350\text{ cm}^{-1}$ . This band is known as the D band. The D band originates

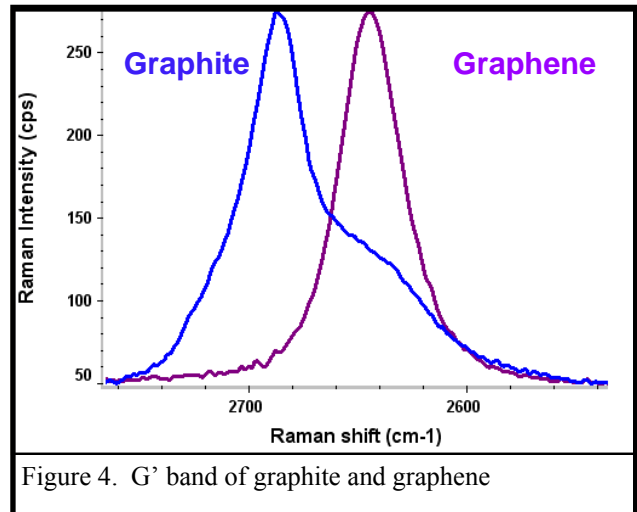


Figure 4.  $G'$  band of graphite and graphene

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 also 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. 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.

## 2.3 Recording a Raman Measurement

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 you measure the powders loose, the density is often too low to get a measureable spectrum. Many times CNTs are cast onto slides within a surfactant. This works quite 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 though. Films are typically measured in

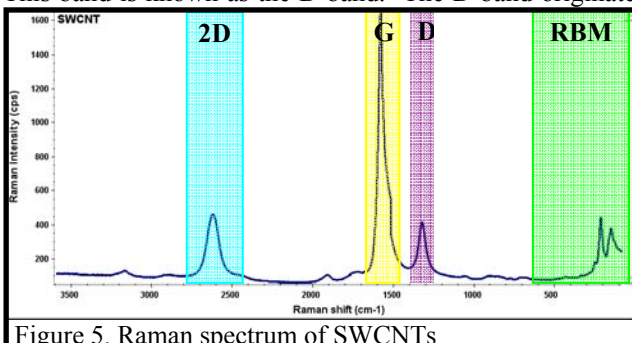


Figure 5. Raman spectrum of SWCNTs

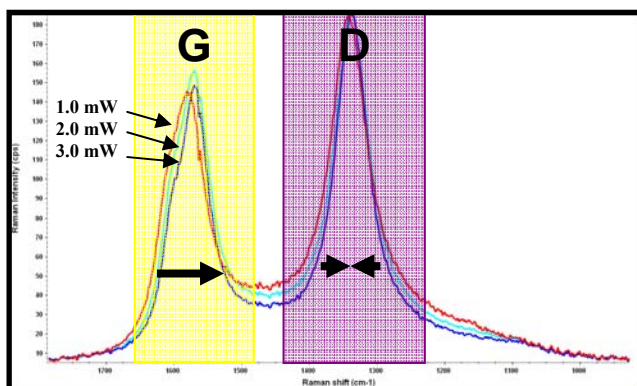


Figure 6. MWCNTs at different laser powers

their native state on whatever substrate they happen to be on.

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 you have a lot of laser energy 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.

It turns out that it is especially important that you have good laser power control when measuring carbon samples. This is for two reasons. The first is that some carbon materials are very sensitive to laser power and even low laser powers can damage the sample. It is important to understand the laser power tolerance of your samples before you start your experiments for this reason. The second reason that good laser power is important is that even when tolerant of the laser power, carbon nanotube samples will exhibit significant spectral differences depending on the laser power, so it is important that exactly the same laser power be used. Figure 6 provides an example of this. In this example you can see that the D-band contracts in width and the G-band shifts to lower frequency as you increase laser power. This is a reversible effect, but it is still important to control laser power tightly to avoid misinterpreting effects such as this.

We have not discussed this so far, but excitation laser frequency can also have a dramatic effect on the spectrum. Figure 7 provides us with an example of this. The reason for these differences is that several of the bands in the Raman spectrum of carbon nanotubes exhibit what is known as resonant dispersive behavior. Meaning that there

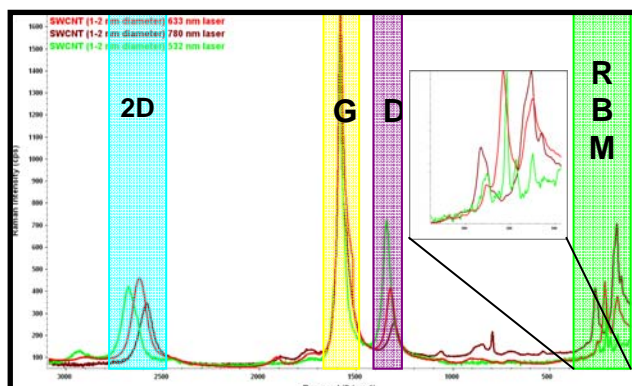


Figure 7. Effect of different excitation frequencies

are a number of very weak bands present, but the bands that are visible are those that are resonant at the excitation frequency. These bands are greatly enhanced and since each excitation frequency enhances different bands, you get significant differences when comparing the spectra obtained with different excitation lasers. For some applications it may be desirable to characterize the samples with multiple excitation frequencies, but often it is sufficient to use only one provided that you always use the same excitation frequency.

### 3 SUMMARY

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.