

Characterizing Graphene with Raman Spectroscopy

Introduction

Interest in graphene has been growing rapidly over the past several years. This interest is primarily driven by its potential as a material with which to manufacture nano electric devices – although this is far from its only application. Raman spectroscopy is used extensively to characterize graphene, as the material is composed almost entirely of symmetric sp^2 bonded carbon, which is represented in great detail in the Raman spectrum.

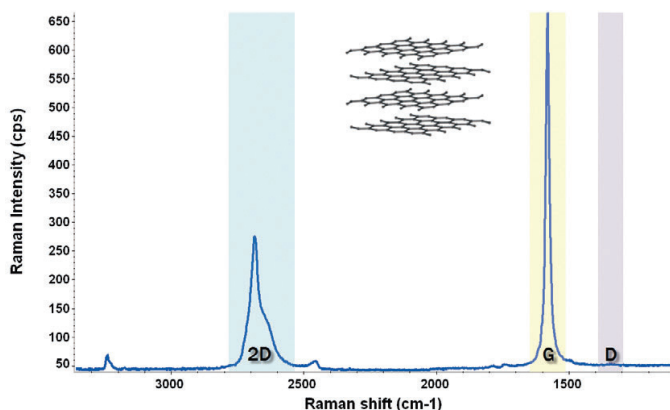


Figure 1. Raman spectrum of highly ordered pyrolytic graphite (HOPG). 633 nm excitation laser.

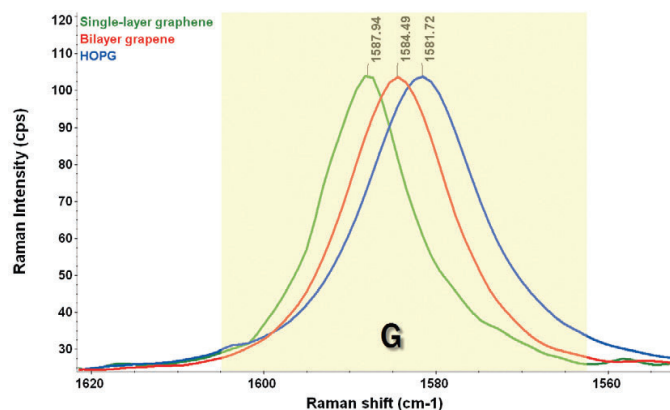


Figure 2. Shifting of G-band as graphene layer thickness increases. 633 nm excitation laser.

The Raman spectrum of graphene

A great deal of detail about the fine structure of graphene can be extracted from the Raman spectrum if you know where to look. At first glance, the Raman spectrum of graphene or graphite can appear fairly simple – usually consisting of only two main bands and a few more very small bands. However, these bands actually tell us quite a bit about the material. Figure 1 shows a typical Raman spectrum of graphite. The Raman spectrum of graphene is very similar, as we would expect, since graphite is composed of multilayer graphene. (The differences will be explained a little later in this note.) The two main bands in the graphite spectrum are known as the G-band at $\sim 1582 \text{ cm}^{-1}$ and the 2D-band at $\sim 2685 \text{ cm}^{-1}$. A third band known as the D-band at $\sim 1350 \text{ cm}^{-1}$ is also worth some discussion, although it is usually very weak in graphite. Now we will take a closer look at each of these bands.

The G-band

The G-band is the primary mode in graphene and graphite. It represents the planar configuration sp^2 bonded carbon that constitutes graphene. The band is resonant, which means it is much more intense than we would expect it to be otherwise. The band position is mostly independent of excitation laser frequency, making it different from the other graphene bands that will be discussed. The position of the band and, to a certain extent, the shape can provide you with more information. One common application for the G-band is to determine graphene layer thickness. Figure 2 demonstrates the effect that layer thickness has on the position of the G-band. As the layer thickness increases, the band position shifts to lower

energy representing a slight softening of the bonds as the layer thickness increases. The positions of the bands shown here are in very close agreement with calculated positions for these band locations. It is also worth noting that the position of the G-band is quite sensitive to doping and even very minor strain. Take this into consideration when you attempt to use the band position to determine graphene layer thickness.

The D-band

The D-band is known as the disorder band or the defect band. It represents a ring breathing mode from sp^2 carbon rings, although the ring must be adjacent to a graphene edge or a defect to be active. The band is the result of a one phonon lattice vibrational process. The band is typically very weak in graphite and also is typically weak in graphene. If the D-band is significant, it indicates numerous defects in the material. The intensity of the D-band is directly proportional to the level of defects in the sample. The last thing to note about the D-band is that it is a resonant band that exhibits what is known as dispersive behavior. This means that there are a number of very weak modes underlying this band, and the excitation laser used will enhance different modes. Consequently, both the band's position and its shape can vary significantly with different excitation laser frequencies, making it important to use the same excitation laser frequency for all measurements when characterizing the D-band.

The 2D-band

The 2D-band is the final band discussed here. The 2D-band is sometimes referred to as the G-band when discussing similar materials such as carbon nanotubes. However, it is more commonly referred to as the 2D-band for spectra of graphene. The 2D-band is the second order of the D-band, sometimes referred to as an overtone of the D-band. It is the result of a two phonon lattice vibrational process, but unlike the D-band, it does not need to be activated by proximity to a defect. As a result, the 2D-band is always a strong band in graphene even when no D-band is present, and it does not represent defects.

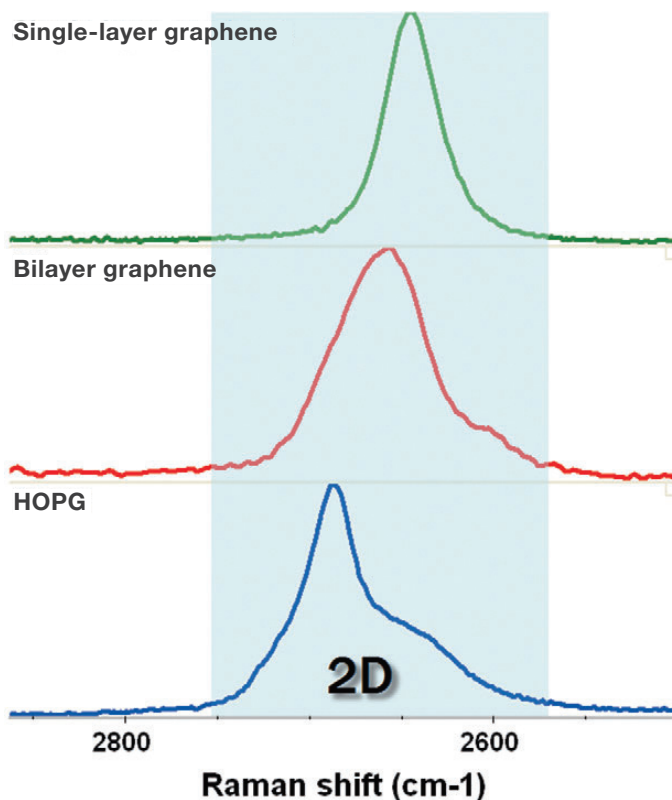
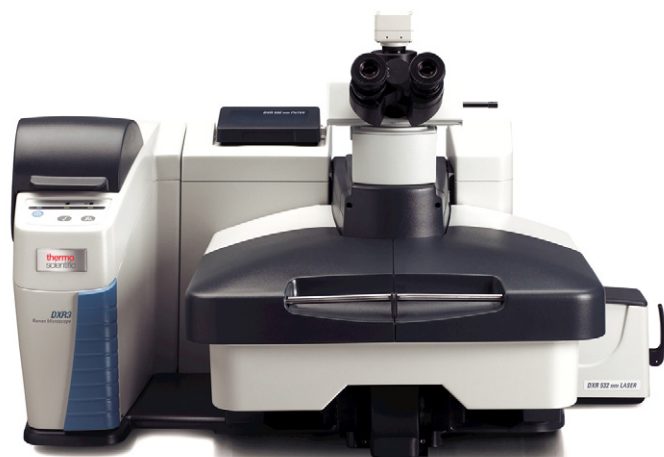


Figure 3. Changes within 2D-band structure as graphene layer thickness increases. 633 nm excitation laser.

This band is also used to determine graphene layer thickness; however, the differences between single and bilayer graphene in this band are more complex than a simple band shift, as was observed with the G-band. Figure 3 demonstrates the effect of increasing layer thickness on the 2D-band. Note that while there is a general shifting to higher wavenumbers as the layer thickness increases, the more noticeable changes have to do with the band shape. The changes in band shape have to do with changes to the active components of the vibration. With single layer graphene, there is only one component to the 2D-band, but with bilayer graphene, there are four components to the 2D-band. This is why the shape of the band is so different. Just like the D-band, the 2D-band is resonant. It exhibits strong dispersive behavior so the position and shape of the band can be significantly different with various excitation laser frequencies. Again, it is important to use the same excitation laser frequency for all measurements when doing characterization with the 2D-band. Finally, it is also worth noting that the 2D-band is very sensitive to graphene folding, which you need to consider when using this band to determine layer thickness in graphene samples.



Thermo Scientific DXR3 Raman Microscope

Instrumental considerations

A few things should be considered when you choose a Raman instrument for graphene characterization. First, since graphene samples are usually very small, it is important to select a Raman instrument with microscopy capabilities.

The next issue to consider is which excitation laser to select. While graphene measurements can be made successfully with any of the readily available Raman lasers, it is also important to consider what substrate the graphene will be deposited onto. It is common for graphene to be deposited on either Si or SiO₂ substrates. Both of these materials can exhibit fluorescence with NIR lasers such as 780 nm or 785 nm, so for this reason visible lasers are usually recommended, such as a 633 nm or 532 nm laser.

Next, since relatively small wavenumber shifts can significantly impact the interpretation of the Raman spectra, it is important to have a robust wavelength calibration across the entire spectrum. With some other applications, it may be sufficient to use a single point wavelength calibration, but this really only ensures that one wavelength is in calibration and leaves room for a large margin of error. A multipoint wavelength calibration that is regularly refreshed, such as the standard calibration routine used with the Thermo Scientific™ DXR™ Raman Microscopes, will give you considerably more confidence in the results. It is also necessary to have an instrument with high wavenumber precision to ensure that small wavenumber shifts observed when altering the sample are in fact representative of changes in the sample rather than of measurement variability from the instrument. A common myth states that it is necessary to use high resolution to achieve high wavenumber precision. Not only is this incorrect, but high resolution will also add considerable noise to the spectrum, which will add to wavenumber variability. It has been previously demonstrated¹ that a Thermo Scientific

DXR3 Raman microscope configured with a 5 cm⁻¹ resolution grating will provide wavenumber precision of at least 0.066 cm⁻¹. This level of wavenumber precision will give you a high level of confidence even when evaluating band shifts from low levels of strain or doping.

Finally, it is important to have exact control of your laser power at the sample and to be able to adjust that laser power in small increments. This is important to control temperature-related effects and to provide flexibility to maximize Raman signal while still avoiding sample damage from the laser. Thermo Scientific DXR3 Raman systems are equipped with a unique device called a laser power regulator, which maintains laser power with unprecedented accuracy and provides an exceptional ability to fine-tune laser power and optimize it for each experiment.²

Conclusions

Raman spectroscopy is a great tool for the characterization of graphene. Few techniques will provide as much information about the structure of graphene samples as Raman spectroscopy, and any lab performing graphene characterization without a Raman instrument would be at a significant disadvantage. The DXR3 Raman Microscope is an ideal Raman instrument for graphene characterization providing the high level of stability, control, and sensitivity needed to produce trustworthy results.

References

1. Guide to Evaluating Spectral Resolution on a Dispersive Raman Spectrometer, Thermo Scientific technical note, 2009.
2. The Importance of Tight Laser Power Control When Working with Carbon Nanomaterials, Thermo Scientific application note, 2010.

Author

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

Keywords

2D-band, D-band, G-band,
Graphene, Layer Thickness,
DXR3 Raman Microscope

Learn more at thermofisher.com/energy

thermo scientific

For research use only. Not for use in diagnostic procedures. For current certifications, visit thermofisher.com/certifications

© 2022 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries unless otherwise specified. AN51946-EN-03-2022