Raman Spectroscopy Optimizes Graphene Characterization

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Raman spectroscopy is an indispensable tool in laboratories conducting research of the nascent field of carbon nanomaterials.

Characterizing graphene is important because its unique properties make it a potential candidate for use in a variety of applications including electronics, heat transfer, biosensing, membrane technology, battery technology, and advanced composites. Graphene exists as a transparent, two-dimensional (2-D) network of carbon atoms. It can also exist as a single atomic layer-thick material, and it can be readily stacked to form stable, moderately thick samples containing millions of layers (a form generally referred to as graphite). Graphene properties include exceptionally large electrical and thermal conductivity, high mechanical strength, and high optical transparency.

However, graphene’s interesting properties are only observed for films containing just one, or a few layers. Therefore, developing technologies and devices based on these properties requires accurate determination of layer thickness. This article discusses the use of Raman spectroscopy to provide a fast, nondestructive means of determining layer thickness of graphene thin films.

The Raman spectrum of graphene exhibit a relatively simple structure characterized by three principle vibrational bands designated as the G, D, and 2D band. Even though the spectra of graphene is dominated by only three principle vibrational bands, they contain vital information about graphene and layer thickness, obtained by analyzing the band’s peak position, band shape, and intensity.

The G band

The G band is a sharp band that appears at around 1587 cm⁻¹ in the graphene spectrum. The band is an in-plane vibrational mode involving sp² hybridized carbon atoms that comprise graphene sheets. Because the position is highly sensitive to the number of layers present in the sample, its observation allows accurate determination of layer thickness. Figure 1 compares the G band position of single-, double-, and triple-layer graphene. These spectra are normalized to better reveal spectral shift information. The band position shifts to lower energy as layer thickness increases, representing a slight softening of bonds. The positions shown in Fig. 1 are in close agreement with the calculated positions for these band locations. Temperature, doping, and even small amounts of strain present in the sample can affect band position, so analysts must be cautious when using
band position to determine graphene layer thickness.

G band intensity also follows a predictable behavior, which can be used to determine graphene thickness. Figure 2 shows spectra of single-, double- and triple-layer graphene. The intensity closely follows a linear trend as the sample progresses from single to multilayer graphene. The method is less susceptible to the effects of strain, temperature, and doping, and can provide a more reliable measurement method of layer thickness when these environmental factors are present.

The D band

The D band is known as the disorder, or defect, band, and represents a mode from sp3-bonded carbon. The band is typically very weak in graphite and high-quality graphene. D band intensity is directly proportional to the level of defects in the sample and can also be used as a gauge of degree of functionalization when graphene is chemically modified.

The 2D band

The 2D band is the second order (often referred to as an overtone) of the D band. It is always strong in graphene, even when there is no D band present, and it does not represent defects. This band is also used to determine graphene layer thickness. In contrast to the G band position method, the 2D band method depends not only on band position, but also on band shape.

Figure 3 shows the differences in this band between single-, double-, and triple-layer graphene. For single-layer graphene, the 2D band is a single symmetrical peak with a full width at half maximum (FWHM) of ~30 cm⁻¹. Adding successive layers of graphene causes symmetry lowering, and as a result, the 2D band splits into several overlapping modes. These distinct band shape differences allow effective differentiation between single- and multilayer graphene for layer thickness of less than four layers.

Single-layer graphene can also be identified by analyzing the peak intensity ratio of the 2D and G bands (Fig. 4). The ratio I_{2D}/I_{G} of these bands for high-quality single-layer graphene is greater than, or equal to 2. This ratio is often used to confirm a defect-free graphene sample.

Instrument considerations

There are certain key considerations when selecting a Raman instrument for graphene characterization. Because graphene samples are usually very small, it is important to select an instrument with microscopy capabilities. While graphene measurements can be made successfully using any of the readily available Raman lasers, it is also important to consider the substrate on which graphene will be deposited. The most common substrates are Si and SiO₂, both of which can exhibit fluorescence with near infrared (NIR) lasers such as 780 and 785 nm. For this reason, visible lasers are usually recommended, typically a 633 or 532 nm laser. In addition, it is necessary to control the laser power and adjust it in small increments. In that way, temperature-related effects can be monitored and the Raman signal can be maximized while avoiding sample heating or damage.

Because relatively small wavenumber shifts can significantly impact interpretation of the Raman spectra, it is essential to have robust wavelength calibration across the entire spectrum. For example, multipoint wavelength calibration used with Thermo Scientific DXR Raman instruments is regularly refreshed, providing 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 representative of alterations rather than of measurement.

Fig. 3 — The 2D band exhibits distinct band shape differences with the number of layers present.

Fig. 4 — Single-layer graphene can be identified by the intensity ratio of the 2D to G band.
variability. Increased wave-number precision provides a high level of confidence in results, even when evaluating band shifts from low levels of strain or doping. The ideal Raman microscope should also feature an automated stage and associated software to generate detailed point maps. Raman point mapping, or imaging, extends single-point measurements to allow assessment of a sample’s layer thickness uniformity.

Raman mapping of graphene

Raman maps, or images, can be obtained from a sample if an automated stage is integrated into the Raman microscope. Raman mapping entails the coordinated measurement of Raman spectra with successive movements of the sample by a specified distance. Raman microscopes can generate chemical images of graphene samples with submicron spatial resolution. This allows characterizing a graphene sample with regard to whether it is composed of one layer across its entirety or whether it contains areas of differing thicknesses.

Figure 5 shows the results of Raman mapping measurement. An image of a graphene sample is visible on the right side. The light and dark areas indicate regions that differ in layer thickness. On the left side is the Raman map, or chemical contour map, of the sample, obtained by taking a series of Raman point measurements in the area de-
picted in the image. The chemical contour map is based on an intensity-based color scale; red represents low intensity and blue represents high intensity referenced to a particular Raman shift in this example (single layer Laurentian peak centered at 2663 cm\(^{-1}\)).

A wealth of information is contained in this chemical image, and further processing of the map is necessary to extract this information. Thermo Fisher’s OMNIC Atlas software contains powerful processing tools (namely discriminant analysis found in Thermo Scientific TQ Analyst software) that can determine the presence and distribution of regions in the map that differ in graphene layer thickness. Discriminant analysis can be based on a band or region where distinct differences exist in the material being investigated. In this case, the 2D band with its band shape differences is used. Discriminant analysis uses standard spectra for different layer thicknesses as a calibration set. Figure 6 shows the results of applying this analysis to the map presented in Fig. 5; the sample under investigation was composed of single-, double-, triple-, and multilayer graphene regions across the sample.

**Conclusion**

Raman spectroscopy is an ideal tool to characterize graphene, providing comprehensive information about the structure and layer thickness of graphene samples. The technique achieves high levels of stability, control, and sensitivity needed to produce confident results.

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