

## Application Note AN R535

# Analysis of Graphene with Raman-Spectroscopy

Graphene is an allotropic form of carbon consisting of a single layer of graphite and thus of a monatomic layer of carbon atoms arranged in a honeycomb structure with a bond angle of  $120^\circ$ . Graphene has a variety of remarkable electronic, thermal and mechanical properties. These include, amongst others, an extremely high tensile strength which is significantly higher than that of steel and a white light absorption of more than 2% with only one atomic layer thickness. This results in numerous new application possibilities, for example in electronic components such as capacitors or transistors, optical components or in the manufacturing of sensors.

Based on earlier works, the first systematic analyses of Graphene were performed in the early sixties of the twentieth century by Boehm et al.<sup>[1,2]</sup> Graphite oxide was chemically reduced to graphene and subsequently the average number of layers was determined by X-ray powder diffraction and adsorption techniques (BET, phenol, methylene blue). Individual graphene flakes were measured with transmission electron microscopy. In many cases, layer thicknesses below 4 Å were measured, indicating the presence of a monatomic carbon-layer.

Keywords	Instrumentation and Software
Graphene	SENTERRA II Raman imaging microscope
Monoatomic layers	OPUS Spectroscopic software
Material science	RamanScope III FT-Raman microscope
Battery research	

Decades later, Novoselov and Geim et al. were able to produce much larger and chemically purer graphene units by exfoliation of graphite layers with adhesive tape.<sup>[3,4]</sup> Both scientists were awarded the Nobel Prize for Physics in 2010 for this method as well as for the detailed characterization of many unusual properties. This resulted in a rapid increase of research activity that continues until today. Graphene is of interest in many areas, such as materials research on nanocomposites or battery research.<sup>[5,6]</sup>

### Raman Spectroscopy

In contrast to many complex and costly analysis methods, like the aforementioned transmission electron microscopy,

Raman microscopy represents a simple and cost-efficient characterization method. It can be used to analyze very small graphene units with high lateral resolution and allows to draw conclusions about the edge-type of graphene-samples. Furthermore, Raman spectroscopy can be used to differentiate other carbon nanomaterials like carbon nanotubes, fullerenes and different types of graphite.

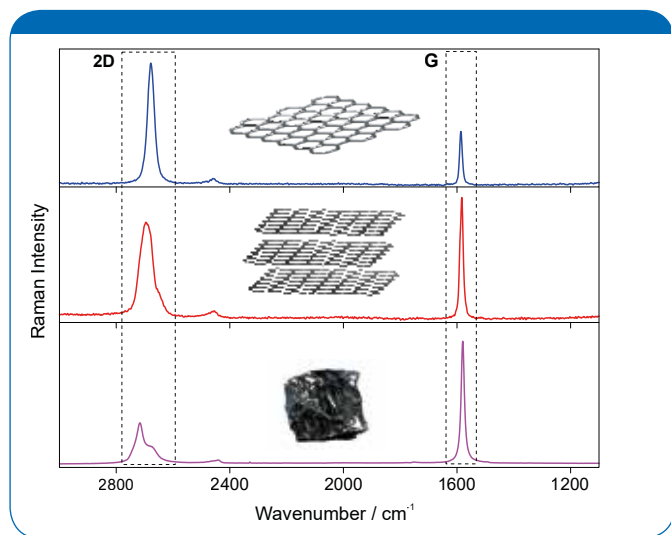


Figure 1: Raman spectra of graphene (blue), three-layer graphene (red) and graphite (magenta).

The upper blue spectrum in Figure 1 shows a typical Raman spectrum of single-layer graphene. Defect-free graphene has two bands which are approximately located at  $1590\text{ cm}^{-1}$  and  $2700\text{ cm}^{-1}$  and are usually named G and 2D. For 2D one finds less often also the designation G'. For low layer thicknesses of a few layers, the intensity ratio of these two bands ( $I_{2D} / I_G$ ) allows to determine the number of layers at atomic resolution. For single-layer graphene this value is 2, further values are listed in Table 1, whereby it becomes clear that the differentiation of the individual layer thicknesses becomes more difficult with increasing number of layers.

Number of layers	Approx. intensity ratio $I_{2D}/I_G$
1	2
2	1
3	0.8
4	0.5
5+	0.4

Table 1: The number of graphene layers can be determined via  $I_{2D}/I_G$

However, the intensity ratio is not only dependent on the number of layers but can also be changed by doping the graphene. The spectrum of graphite (Figure 1, bottom) has

the same intensity ratio as 5-layer graphene and is barely distinguishable from it. There are a variety of other methods for determining the number of layers from the position, shape or intensity of various graphene bands. An example is the layer thickness determination via the shift of the G band, which according to Wang et al. for single-layer graphene has a value of  $1587.1\text{ cm}^{-1}$  and asymptotically approaches  $1581.6\text{ cm}^{-1}$  as the number of layers increase.<sup>[7]</sup> However, the formula given in the original article applies only to ideal cases and may be affected by temperature effects, doping and lattice strains. Figure 2 qualitatively shows the shift for single-layer (blue) and three-layer graphene (red) and graphite (magenta).

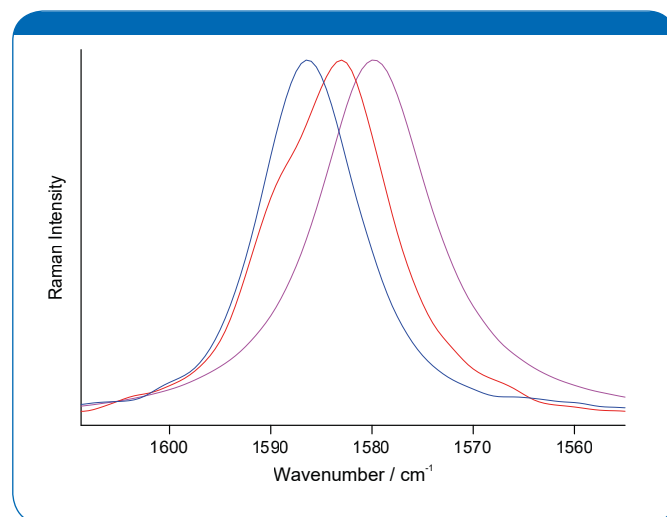


Figure 2: Normalized G-band of monolayer- (blue), three-layer graphene (red) and graphite (magenta).

In addition to the G and 2D bands, further bands can occur in the Raman spectra of graphene and other carbon allotropes. Predominantly, the bands D, D' and D+G, which are all coupled to the presence of defects, should be mentioned here. The position and shape of the D-band as well as the 2D band occurring at twice the wavenumber are also dependent on the wavelength of the excitation laser. Table 2 gives an overview of the most important bands and their approximate position at a laser wavelength of 532 nm.

Band	Wavenumber	Meaning
D	$1350\text{ cm}^{-1}$	Only with defects
G	$1585\text{ cm}^{-1}$	Graphite band, $sp^2$ -carbon
D'	$1620\text{ cm}^{-1}$	Only with defects
2D (G')	$2700\text{ cm}^{-1}$	Independent from defects. $\nu_{2D} = 2 \nu_D$
D+G	$2940\text{ cm}^{-1}$	Only with defects. $\nu_{D+G} = \nu_D + \nu_G$

Table 2: Typical bands of graphene with approximate wavenumbers for a excitation wavelength of 532 nm.

## Instrumentation

The Raman measurements were performed with the SENTERRA II microscope (see Figure 3). Thanks to the high level of automation of the SENTERRA II, excitation lasers or apertures change automatically, without manual modifications or adjustments. A few seconds after switching any components, the device is fully calibrated and ready to measure.



Figure 3: SENTERRA II Raman-microscope.

In addition to the typical excitation wavelengths of 532 nm and 785 nm, the system can also be extended by a third laser with 488 nm or 633 nm. With the FT-Raman extension „RamanScope III“, a fourth excitation line with 1064 nm is available in the near infrared. The wide selection of laser wavelengths makes it possible to adapt the measuring conditions to the sample with only a single mouse-click and to avoid problems with sample fluorescence in the first place. The high sensitivity of the SENTERRA II allows performing an analysis with very low laser power so that even sensitive samples such as carbon nanotubes or other carbon modifications can be investigated.

A high wavenumber precision and accuracy is guaranteed at any time by the unique SureCal™ technology of the SENTERRA II achieving wavenumber stability of better than  $0.1 \text{ cm}^{-1}$  with each measurement. This ensures that an observed band shift has its cause in the sample and is not due to a misalignment of the device. High wavenumber accuracy is of particular importance in the determination of graphene monolayers.

The SENTERRA II offers powerful confocal Raman imaging and mapping functionality that is easy to use. Measurements are started directly and without time-consuming

setting of parameters. Efficient data acquisition in conjunction with a high-precision sample stage enables Raman images to be measured quickly and at sub-micron spatial resolution. Even Raman images with high spectral resolution can be generated within seconds.

## Application Example: Analysis of a Graphene-Sample

The following example shows the analysis of a  $7 \times 17 \mu\text{m}$  sized graphene sample that shows different kinds of layer thicknesses. For the analysis  $10 \times 20$  Raman spectra were measured with an excitation wavelength of 532 nm. The evaluation of the results was performed by both integration as well as component regression. After vector normalization on the G-band the intensity of the 2D-band was integrated in the range between  $2752$  and  $2623 \text{ cm}^{-1}$ . The result of the integration is shown in figure 4 on the right of the visual image. A monolayer will appear very bright and multilayers darker according to the color scale shown on the right.

In order to achieve a direct assignment of the number of layers, a further evaluation was carried out by means of the so-called component regression. In the process, all measured spectra are automatically compared with reference spectra of a known number of layers and assigned to the best matching reference spectrum via color coding. Figure 4 shows the result of the component regression to the left of the visual image. The number of layers increases from white (monolayer) to yellow, red, light blue and dark blue.

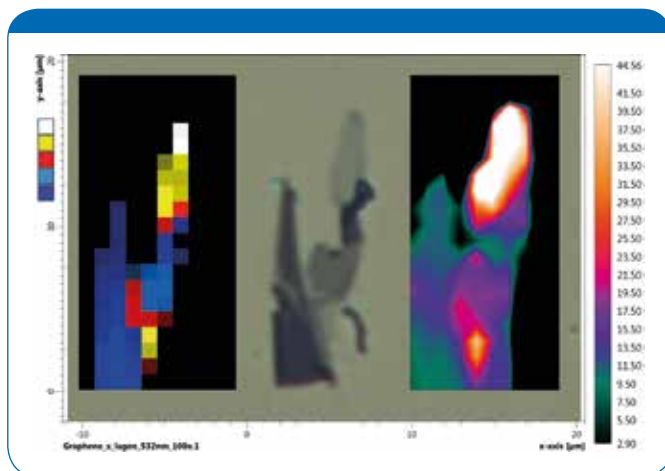


Figure 4: Visual image of graphene (middle) with component regression (left) and integration (right).

Both evaluation methods consistently show two areas with a low number of layers, where the point just below the upper right-hand tip represents the thinnest area.

## Application Example: Differentiation of carbon-allotropes

The SENTERRA II is also suitable for the differentiation and characterization of other carbon allotropes. For the class of fullerenes, the Raman spectrum of C<sub>60</sub> is exemplarily shown (Figure 5, top). In general, fullerenes have a large number of bands and can thus be distinguished easily. In the case of higher fullerenes it is also possible to differentiate isomers of different symmetry, e.g. C<sub>84</sub> in the point groups D<sub>2d</sub> and D<sub>2</sub>.<sup>[8]</sup>

Carbon nanotubes (CNTs, carbon nanotubes) constitute another form of carbon. Single-walled carbon nanotubes (SWCNT) CNTs typically have the G band split into two bands called G<sup>+</sup> and G<sup>-</sup>. Irrespective of the excitation wavelength, the more intense G<sup>+</sup> band is around 1590 cm<sup>-1</sup>. In contrast, the weaker G<sup>-</sup> band is wavelength dependent and located around 1570 cm<sup>-1</sup>. However, depending on the number of walls, the size distribution or functionalization, only one band might be recognizable. The blue spectrum in Figure 5 exemplifies the spectrum of a CNT sample. The spectrum shows only one G-band, but has well-visible **Radial Breathing Modes (RBM)** at lower wavenumbers, which allow the determination of the CNT's diameter.<sup>[8]</sup>

For comparison, Figure 5 shows the known spectrum of graphite (HOPG) as well as that of diamond in which the carbon atoms have sp<sup>3</sup> hybridization. Due to the high symmetry of the diamond lattice, the diamond spectrum has only one band, which is recognizable at a lower wavenumber (1332 cm<sup>-1</sup>) due to the weaker C-C single bond compared to the G band of graphite.

## Summary

The Raman imaging microscope SENTERRA II allows the spectroscopic analysis of graphene and other carbon-modifications with the highest measurement sensitivity and precision. Various carbon allotropes can be differentiated and characterized. Since Raman spectroscopy is very sensitive to the morphology of a sample, it is possible to draw conclusions about different characteristics like for instance the number of layers (graphene), the diameter (CNTs) and the symmetry. Furthermore, the SENTERRA II is able to

analyze the smallest samples with a high spatial resolution and to generate chemical images that allow to analyze the local morphology of a sample.

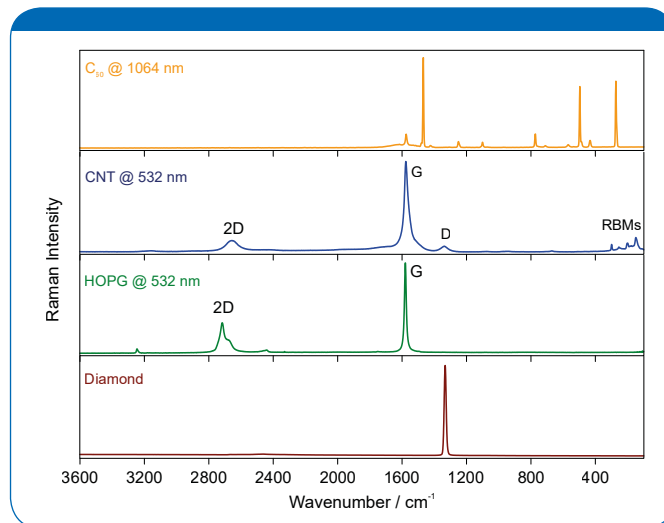


Figure 5: Raman spectra of diverse carbon allotropes.

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