

## Application Note AN R535

# Analysis of Graphene with Raman-Spectroscopy

### About Graphene's remarkable properties

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.

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

In many cases, layer thicknesses below  $4 \text{ \AA}$  were measured, indicating the presence of a monoatomic carbon layer. 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 of Graphene

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 small graphene units with high lateral resolution, drawing conclusions about the number of layers, defects, dopants and the edge-type of graphene-samples.

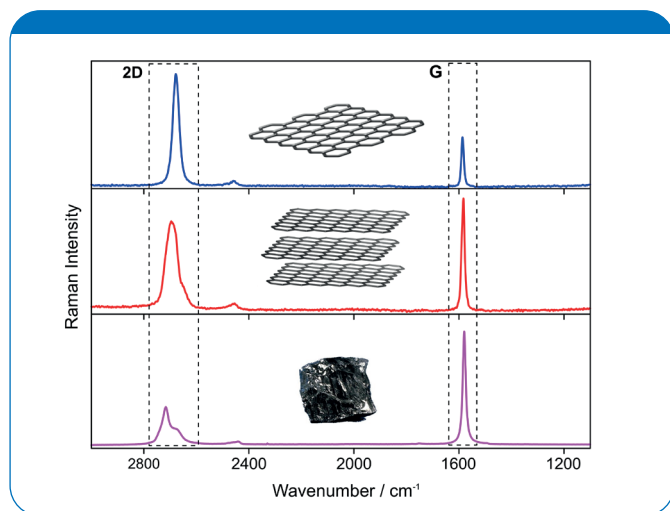


Figure 1: Raman spectra of graphene (blue), three-layer graphene (red) and graphite (magenta).

Raman spectroscopy can also be used to differentiate other carbon nanomaterials like carbon nanotubes, fullerenes and different types of graphite. 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.

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  $I_{2D}/I_G$ .

For single-layer graphene this value is 2, further values are listed in Table 1. It becomes clear that the differentiation of the individual layer thicknesses becomes more difficult with increasing number of layers.

The spectrum of graphite (Figure 1, bottom) has the same intensity ratio as 5-layer graphene and is barely distinguishable from it. However, the intensity ratio is not only dependent on the number of layers but can also be changed by doping the graphene. 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> The formula given in the original article applies only to ideal cases and may be affected by temperature effects, doping and lattice strains.

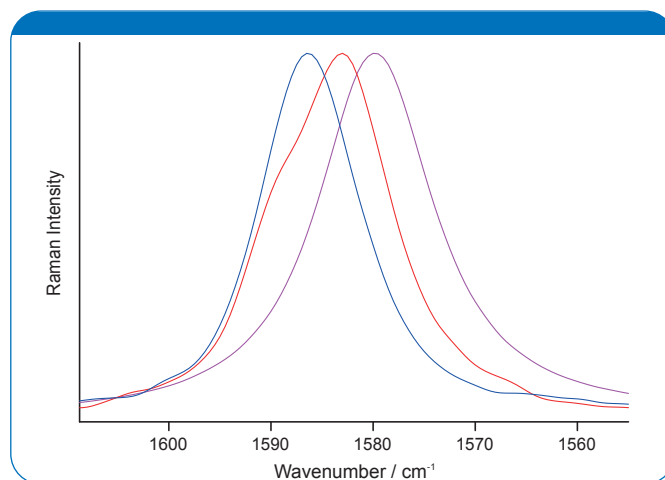


Figure 2: Normalized G-band of monolayer- (blue), three-layer graphene (red) and graphite (magenta).

Figure 2 qualitatively shows the shift for single-layer (blue) and 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  $532\text{ nm}$ .

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  $532\text{ nm}$ .

## Instrumentation

The Raman measurements were performed with the SENTERRA II microscope (see Figure 3). It features automatic an switch of excitation lasers, apertures, brightfield, darkfield and grating, without manual adjustments or need for recalibration.

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.

The high sensitivity of the SENTERRA II enables performing an analysis with very low laser power so that even sensitive samples such as carbon nanotubes or other carbon modifications can be investigated.

High wavenumber precision and accuracy are guaranteed at any time by Bruker's SureCal™ technology of the SENTERRA II achieving wavenumber stability of better than  $0.1 \text{ cm}^{-1}$  with each measurement. This ensures that observed band shifts have its cause in the sample and not in misalignment of the device. This 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.

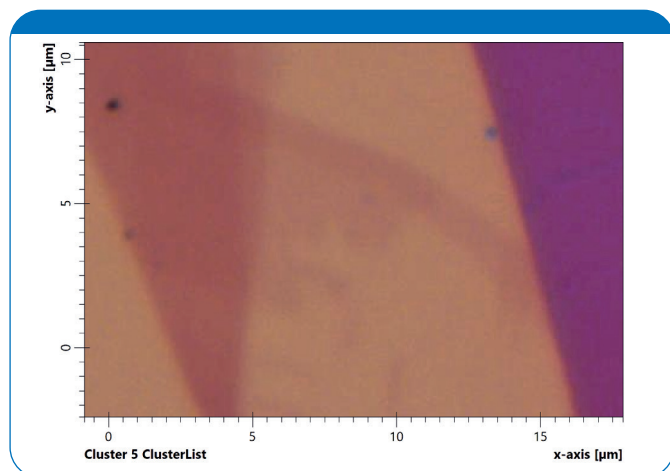


Figure 4: Visual image of various graphene layers on a silicon substrate. Visual contrast of the sample is limited, but single sheets can be vaguely recognized.

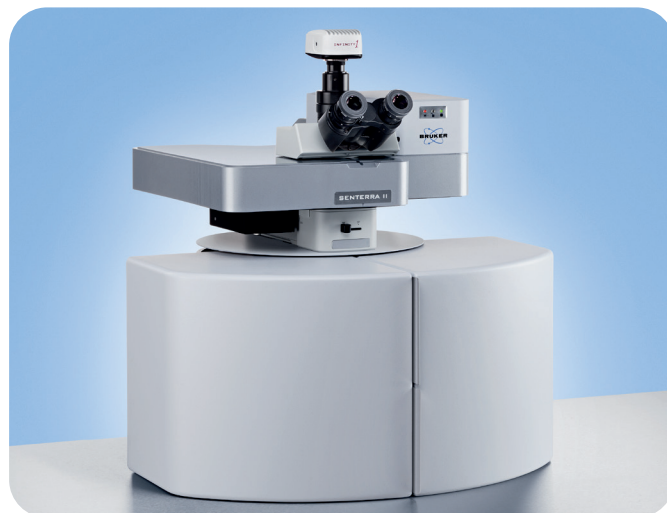


Figure 3: SENTERRA II Raman-microscope.

## Application Example: Analysis of a Graphene-Sample

The following example shows the analysis of a graphene sample that exhibits different kinds of layer thicknesses. For the analysis, 1200 Raman spectra were measured with an excitation wavelength of 532 nm. The evaluation of the results was performed via the Cluster Analysis function of the OPUS spectroscopy software, that forms groups of spectra according to their similarity.

The resulting chemical image is about  $17 \times 8 \mu\text{m}$  in size and shown in figure 5. The chemical information is color coded: The silicon substrate is shown in black, a monolayer is colored white, two layers are magenta, green represents a few layers and orange multiple layers. When compared to the visual image (figure 4), the contrast of the chemical image is far superior and allows direct conclusions about the number of layers.

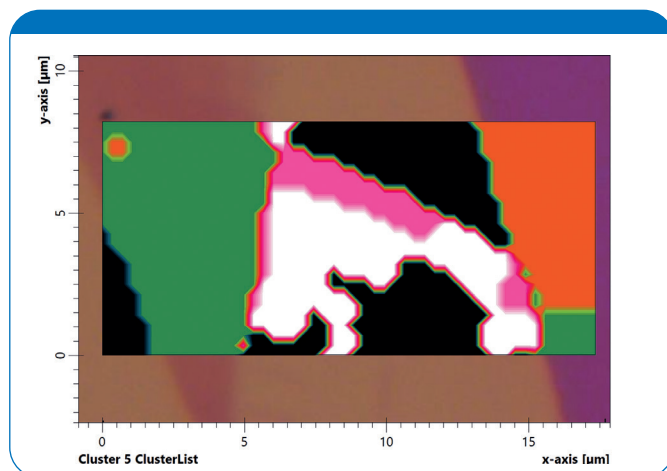


Figure 5: Chemical image of the graphene layers in Figure 4. Silicon substrate (black), mono-layer (white), double-layer (magenta), few layers (green) and multiple layers (orange) are color coded.

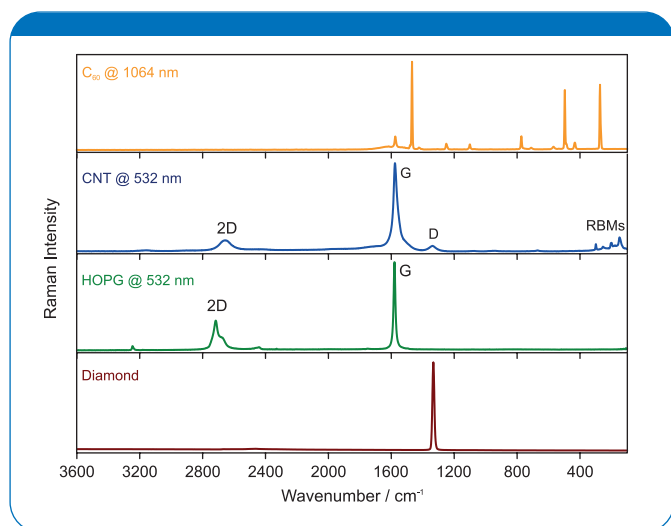


Figure 5: Raman spectra of diverse carbon allotropes.

### 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>[9]</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 wave number (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.

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