Perspectives on Raman Spectroscopy of Graphene

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Abstract
This application note explains what the Raman spectroscopy can bring into the analysis of graphene. The basics of analysis and some examples are presented.

Key words
graphene, raman spectroscopy, raman imaging.

Introduction

The novel advanced material, graphene, first reported in Science in 2004, consists of single molecular layers of highly crystalline graphite. It is the basic structural element of some carbon allotropes, including graphite, carbon nanotubes and fullerenes.
It was isolated for the first time by a collaborative team from the Department of Physics, University of Manchester, UK, and the Institute for Microelectronics Technology, Chernogolovka, Russia.
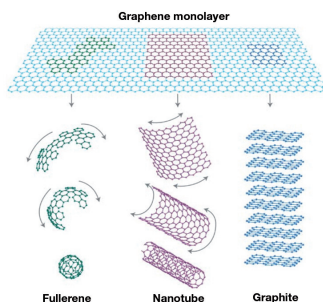

Figure 1: Graphene is the basic structural element of carbon allotropes such as fullerenes, nanotubes and graphite.[1]

Graphene exhibits excellent electron transport properties which make it a potential material for future nanoelectronic devices. Electronic mobilities in excess of 15,000 $cm^2V^{-1}s^{-1}$ at room temperature have been reported. Its mechanical strength is excellent electron transport properties which make it a potential material for future nanoelectronic devices. Electronic mobilities in excess of 15,000 $cm^2V^{-1}s^{-1}$ at room temperature have been reported. Its mechanical strength is excellent, at least 200 times stronger than steel, with a high thermal conductance. An exciting field of development for this material is for a new generation of ultra-fast nanoscale transistors operating in the THz region. Due to its scale and optical properties, graphene is hardly visible on most substrates. However, distinguishing the number of graphene layers, as well as quantifying the impact of disorder on its properties is critical for the study of graphene-based devices. Raman micro- spectroscopy has proven to be a convenient and reliable technique for determining both of these properties. The high structural selectivity of Raman spectroscopy, combined with both spectral and spatial resolution, as well as the non-destructive nature of this technique make it an ideal candidate as a standard characterization tool in the fast growing field of graphene.

Raman spectrum of graphene and graphene layers

As seen in figure 2 below, the Raman spectrum of graphene consists of a number of peaks which are well characterized and understood. Each is described below.

The G band

The main spectral feature of graphene is derived from in-plane motion of the carbon atoms and appears near 1580cm^{-1} (Figure 2): this is the G band. It is extremely sensitive to strain effects and is also a good indicator of the number of graphene layers. As the number of layers increases, the G band position shifts to lower frequencies, following a 1/n dependence on the number of layers n [2, 3] (Figure 3). There is no significant change in spectral shape. (However, despite this sensitivity to the number of layers, it is preferable to use the 2D band for reasons described below).
The G band is also sensitive to doping and both the frequency and the line width of this peak can be used to monitor the doping level. [3]
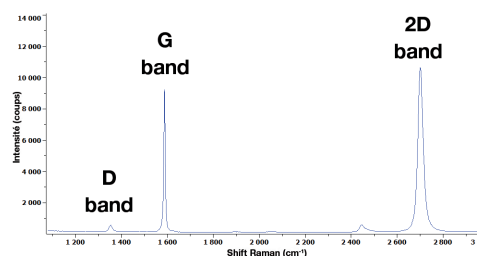

Figure 2: Raman spectrum of graphene

The D band

The D band, for historical reasons, is known as the disorder band. This peak is due to lattice motion away from the center of the Brillouin zone and its presence between 1270 and 1450 cm^{-1} (which depends on the excitation wavelength [4]) indicates defects or edges in the graphene sample (Figure 2). In fact, a definitive explanation of its origin and dependence on excitation wavelength is derived from the double resonance theory originally proposed by Thomsen [5]. In this theory, the intraband phonon scattering of the electron requires momentum that is easily taken up by defects, which is why this band was first observed in defective crystals.
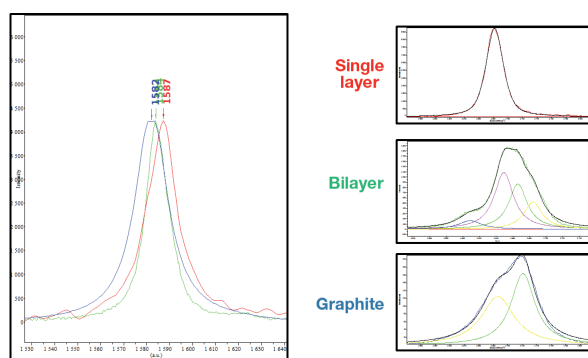

Figure 3: G band and 2D band are commonly used to determine the number of graphene layers

The 2D band or G'

The 2D band, also called G', is a second order two phonon process. It exhibits an unusually strong frequency dependence on the excitation laser due to a double resonance process which links the phonon wave vector to the electronic band structure [4]. This feature appears at approximately 2700 cm^{-1} for a 514 nm laser excitation (Figure 2), and can also be used for the determination of the number of graphene layers. However its behavior is more complex than the frequency shift observed for the G band. Figure 3 shows the dependence of the 2D band on the number of layers. While a graphene monolayer can be fitted by a single Lorentzian peak, a bi-layer requires four Lorentzians, which are related to the four possible double resonance scattering processes when only one is possible for the monolayer. When the number of layers increases, the number of double resonance processes also increases and the spectral shape converges to that of graphite, where only two peaks are observed. [6]

Raman imaging of graphene layers

Graphene is often difficult to localise optically and the number of graphene layers or defects cannot be determined using only an optical microscope. Raman imaging, with its high spatial resolution (better than 0.5 µm), is a fast and reliable technique to obtain such information.

A Raman map of a graphene sample on a SiO$_2$/Si substrate (courtesy of Kirill Bolotin, Vanderbilt University) has been performed using the XploRA Raman spectrometer with a 532 nm laser excitation. Two different routes for processing the data, namely multivariate modelling and peak-fitting treatments are described here below.

Multivariate analysis

The distribution of the bi-layer (in green) and a multi-layer (in red) are easily obtained using the Classical Least Squares (CLS) fitting function of LabSpec software, to fit the spectra to user-selected "pure" spectra. Because the D band was also detected at some edges, a third spectrum representing that species was also used to fit the map (in pink).
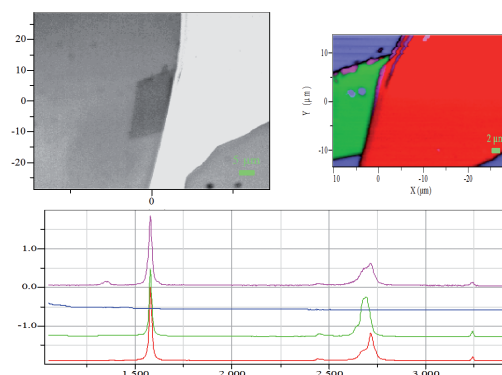

Figure 4: Optical micrograph (top left), Raman image of graphene bi-layer (in green), multi-layer graphene (in red), edges (in pink) and SiO$_2$/Si substrate (in blue) (top right) based on the modelling algorithm using "pure" spectra of the different regions (bottom).

Band-fitting

It is also possible to construct such maps based on band fitted parameters, such as peak position, amplitude, area, and/or bandwidth.

Figure 5 illustrates the power of mapping using the band-fitting algorithm. The images on the right of the figure were constructed using the integrated intensity of each of the lines in the spectra. However, careful inspection of representative spectra (left part of figure) indicates that the peak centroids to which the spectra have been fitted are changing. It may be that the peak position can be correlated with properties of the films, which would make a map of the peak positions quite meaningful.
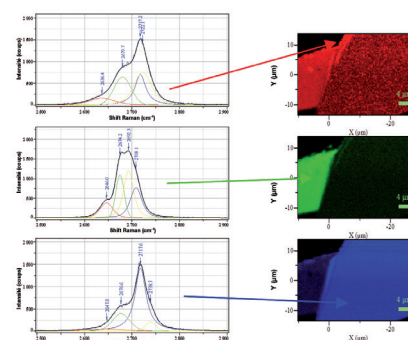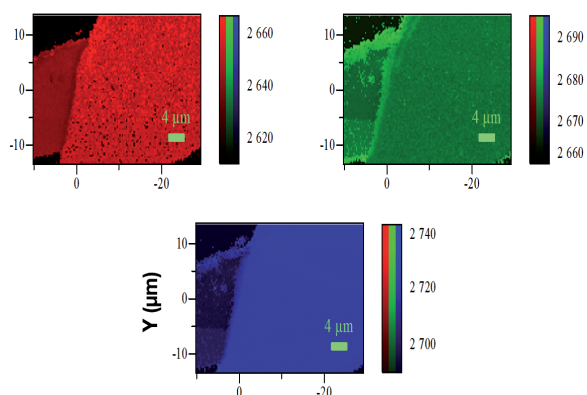

Figure 5: Raman image (right) are based on band-fitted parameters: the intensity of the color in each image is based on the integrated intensity of the spectrum at each point. The band-fitted spectra for selected points are shown on the left.

Figure 6 shows images of the sample obtained when plotting the peak frequency as a function of the spatial location for the three Lorentzian lines (2640 cm^{-1} in red, 2675 cm^{-1} in green, and 2720 cm^{-1} in blue) used in the peak fitting procedure. Note that the highest frequency band does not show texture (that is, it is homogeneous) but the other two do. In particular the 2675 cm^{-1} (in green) line shows edge effects and the lowest frequency band shows very large variations in spectral width as well (not shown).

Figure 6: Raman images are based on band-fitted parameters: the intensity of the color in each image is based on peak position of the Lorentzian line at each point.

This example clearly demonstrates the usefulness of Raman imaging for verifying the homogeneity of graphene layers.

Fast Raman imaging

The previous Raman image has been obtained using a traditional point-by-point imaging mode. However, graphene benefits from a strong Raman efficiency and can afford very short acquisition times making it a suitable application for SWIFT™ ultra-fast mapping. Based on an innovative acquisition and synchronisation process, mapping with acquisition times less than 5ms/point can be performed. This dramatically reduces the Raman image acquisition time.

A Raman map has been performed on a graphene sample (courtesy of C. Glattli, CEA Saclay, France) using the SWIFT mode (Figure 7). In less than one minute, about 1500 spectra over a 20 µm² area are acquired and the distribution of monolayer and multi-layers of graphene, which are barely visible in the video image, is clearly revealed.

Optical image

Monolayer of graphene

Multilayer of graphene
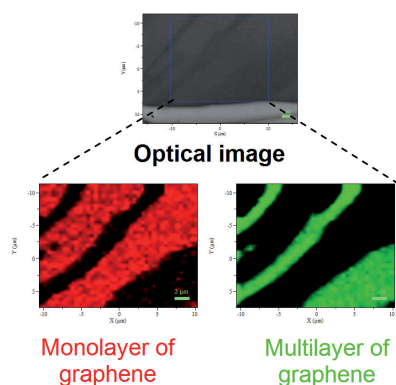
Figure 7: Raman map of a graphene sample using the SWIFT mode. Monolayer and multi-layer area are perfectly discriminated with only 20ms acquisition time per point.

Combining the SWIFT™ together with the unique DuoScanTM macro-spot feature, extremely large surfaces can be mapped in record times.

Conclusion

Graphene is a new nanomaterial which may partially replace silicon in microcircuits and computer chips in the future. In order to better understand its quality characteristics, fast reliable techniques that deliver the right property measures are needed. Raman spectroscopy has emerged as a key technique for studying this exceptional material.

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