

Perspectives on Raman spectroscopy of Graphene

The novel advanced material, Graphene, first report 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 at the Department of Physics, University of Manchester, UK and the Institute for Microelectronics Technology Chernogolovka, Russia. Graphene exhibits excellent electron transport properties which make it a potential material for future nanoelectronic devices. Electronic mobilities in excess of $15\,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature have been reported.

Its mechanical strength is excellent, at least 200 times better than steel and it has 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 characterisation tool in the fast growing field of graphene.

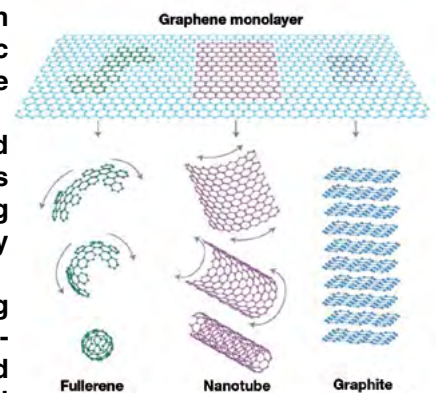


Figure 1: Graphene is the basic structural element of carbon allotropes such as fullerenes, nanotubes or graphite.[1]

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 characterised 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] (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]

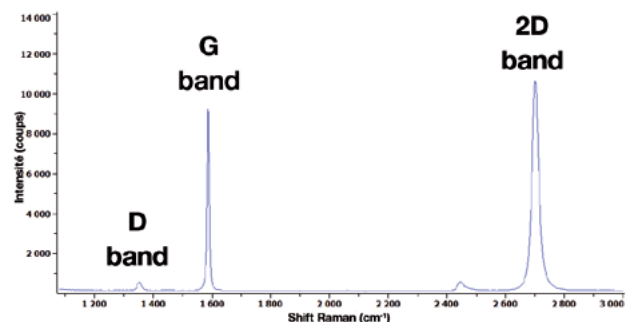


Figure 2: Raman spectrum of graphene

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.

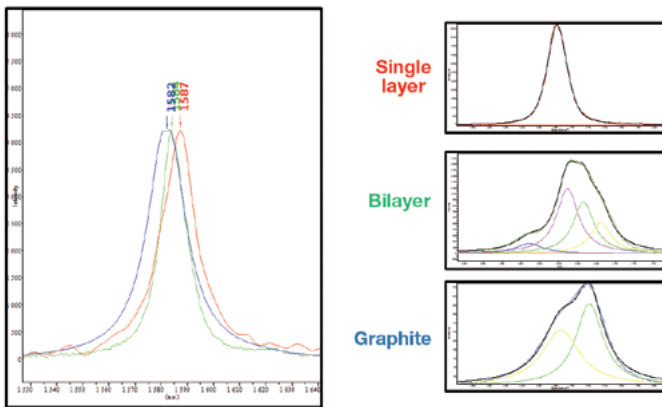


Figure 3: G band and 2D band are commonly used to determine the number of graphene layers

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 2700cm^{-1} for a 514nm laser excitation (Figure 2), and can also be used for the determination of the number of graphene layers. However its behaviour 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 bilayer 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 $0.5\mu\text{m}$), 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 532nm laser excitation. Two different routes for processing the data, namely multivariate modelling and peak-fitting treatments are described here below.

Modelling

The distribution of the bilayer (in green) and a multilayer (in red) are easily obtained using the modelling function of Labspec 5 which in this case used a form of classical least squares 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).

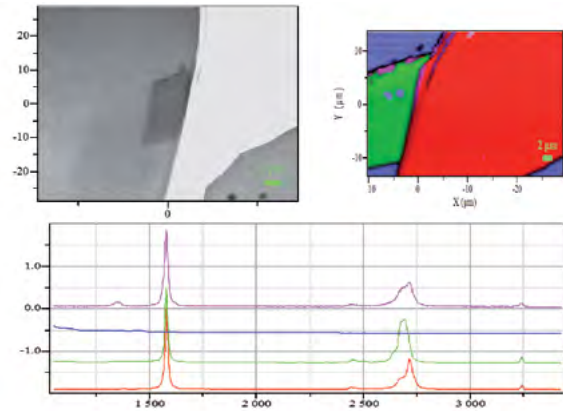


Figure 4: Optical micrograph (top left), Raman image of graphene bilayer (in green), multilayer graphene (in red), edges (in pink) and SiO_2/Si substrate (in blue) (top right) based on the modelling algorithm using "pure" spectra of the different regions (bottom).

Bandfitting

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

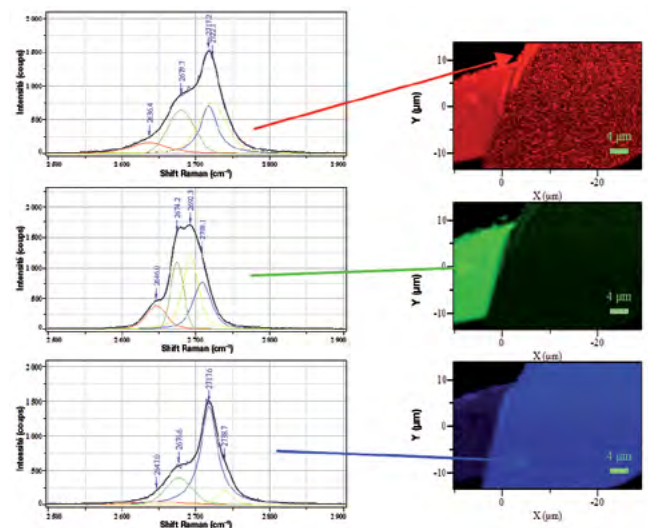


Figure 5: Raman image (right) are based on band-fitted parameters: the intensity of the color in each image is based on the integrated intensity of the spectrum at each point. The band-fitted spectra for selected points are shown on the left.

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).

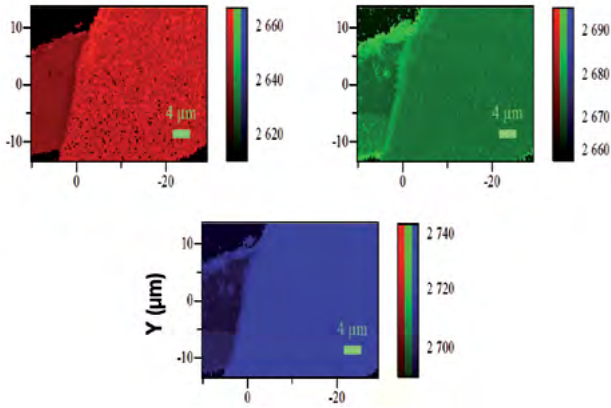


Figure 6: Raman images are based on band-fitted parameters: the intensity of the color in each image is based on peak position of the Lorentzian line at each point.

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 μm^2 area are acquired and the distribution of monolayer and multilayers of graphene, which are barely visible in the video image, is clearly revealed.

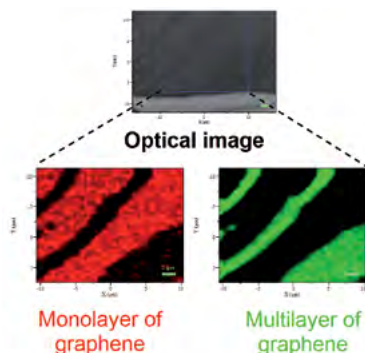


Figure 7: Raman map of a graphene sample using the SWIFT mode. Monolayer and multilayer area are perfectly discriminated with only 20ms acquisition time per point.

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

Graphene as a Raman substrate

Recent studies from Xi Ling (from the College of Chemistry and Molecular Engineering of Peking University) have revealed that graphene could be an interesting Raman substrate for the analysis of difficult samples. Indeed, it has been shown that it can help suppress strong intrinsic fluorescence. Moreover, a Raman enhancement effect could be observed when depositing a sample on to a graphene layer. These two effects are illustrated below.

Fluorescence suppression

Figure 8 shows the comparison of Raman spectra of Rhodamine 6G (R6G) in solution and deposited on graphene.

The R6G fluorescence background is clearly weaker on the graphene substrate than in solution, and even than on the SiO₂/Si substrate. These preliminary results, if confirmed on other samples, will certainly draw additional attention from Raman spectroscopists to graphene.

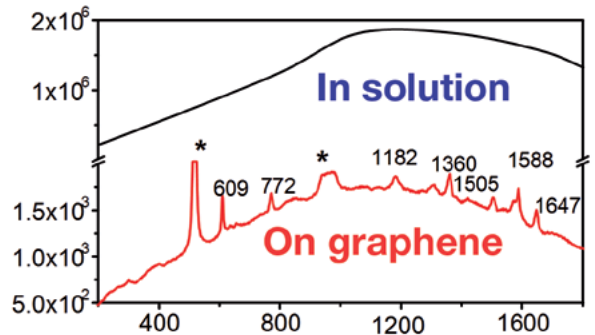


Figure 8: Raman spectra of R6G in water (10 μM) (blue line) and R6G on a graphene monolayer at 514 nm excitation. The spectrum integration time is 10s for the blue line and 50s for the red line. The Raman peaks labelled as * are from the SiO₂/Si substrate. The 1588 cm^{-1} peak is from graphene.

Graphene Enhanced Raman Scattering

Because Raman scattering is by nature sometimes very weak, the use of enhancement techniques has become very popular. These are mainly based on resonant Raman scattering (RRS) and surface enhanced Raman scattering (SERS).

Despite a strong enhancement, the SERS effect, based on a noble metal such as Au, Ag or Cu still suffers from the limitations of stability and reproducibility. The need for a substrate capable of Raman enhancement that is low cost, chemically inert and biocompatible is an important technological objective and graphene seems to be an ideal candidate.

To prove the Graphene Enhanced Raman effect, a comparison of the signal obtained on a graphene substrate or a SiO₂/Si substrate has been carried out[7]. Molecules of Phthalocyanine (Pc) have been deposited on the sample by vacuum evaporation and Raman spectra have been collected with the same acquisition parameters. The Raman signal is much stronger on the graphene substrate than that on the SiO₂/Si substrate (Figure 9).

This result seems to indicate a Raman enhancement effect on graphene.

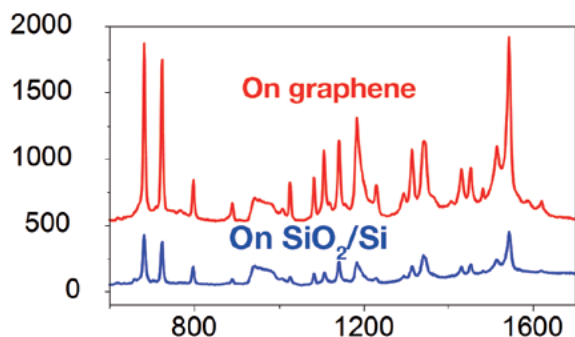


Figure 9: Comparison of the Raman spectra of Pc collected on graphene (red line) and on the SiO₂/Si substrate (blue line) at 632.8nm.

In order to investigate the dependence of the Raman enhancement efficiency on the number of graphene layers, Raman spectra on graphene consisting of a variable number of layers have been collected.

The comparison in Figure 10 shows the enhancement efficiency is quite different depending on the number of graphene layers. It actually decreases with the increase of the number of graphene layers.

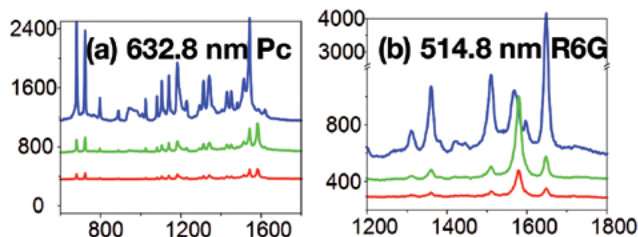


Figure 10: The Raman spectra of Pc (a) and R6G (b) on different numbers of graphene layers. The blue trace is for spectra obtained on a graphene monolayer, the green one for graphene multilayers (up to about 5), and red trace for graphite.

In summary, these results show that the use of a graphene monolayer as a Raman substrate can help to reduce the fluorescence background as well as enhance the sample spectrum by a factor ranging between 2 and 15 (spectral feature dependant).

Instrumental specifications

As seen for the different examples given in this application note, an efficient characterisation of graphene samples by Raman spectroscopy calls for some specific instrumental features. A high spectral resolution is recommended to detect small frequency shifts or to effectively decompose the 2D band in order to determine the number of layers. A reliable wavelength calibration is thus needed to compensate for any potential variations and to ensure correct frequency labeling. As mentioned, there is a strong frequency dependence on the excitation wavelength and the use of many lasers is required in order to collect the maximum information.

In addition, the power density has to be carefully selected to avoid any photo-damage of the sample. A Raman imaging capability is very useful to localise the different graphene layers and detect edge defects. The fast imaging options recently developed (SWIFT™, DuoScan™) allows efficient mapping of very large surfaces efficiently and with considerable saving in acquisition times. It is worth noting that AFM and Raman systems can be combined to access structural, mechanical and electrical properties of graphene simultaneously. Tip Enhanced Raman Spectroscopy (TERS) on graphene can also be considered for revealing the nano-scale properties of this material as well as for characterising the existence of localised defects.

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. It has also enabled the discovery of some unexpected and very attractive properties of graphene as a Raman substrate for the suppression of fluorescence and its enhancement of weak Raman signals.

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