The Raman Spectroscopy of Graphene and the Determination of Layer Thickness

Introduction

Currently, a tremendous amount of study is being directed toward graphene. This interest is driven by the novel properties that graphene possesses and its potential use in a variety of application areas that include but are not limited to electronics, heat transfer, bio-sensing, membrane technology, battery technology and advanced composites. Graphene exists as a transparent two-dimensional network of carbon atoms. It can exist as a single atomic-layer thick material, or it can be readily stacked to form stable, moderately thick samples containing millions of layers—a form generally referred to as graphite. However, the interesting properties exhibited by graphene (substantial electrical and thermal conductivity, high mechanical strength, and high optical transparency) are only observed for graphene films that contain only one or a few layers. Therefore, developing technologies and devices based upon graphene's unusual properties requires accurate determination of the layer thickness for materials under investigation. Raman spectroscopy can be employed to provide a fast, non-destructive means of determining layer thickness for graphene thin films.

Raman spectroscopy and the Raman spectrum of graphene

Raman spectroscopy is a vibrational technique that is extremely sensitive to geometric structure and bonding within molecules. Even slight differences in geometric structure lead to significant differences in the observed Raman spectrum of a molecule. This sensitivity to a geometric structure is beneficial to study different allotropes of carbon such as diamond, carbon nanotubes, Buckminsterfullerenes, carbon nanoribbons, and more. The various forms of these carbon allotropes differ only in the relative position of their carbon atoms and how they bond to one another. Indeed, Raman techniques have evolved into indispensable tools for laboratories pursuing research into the nascent field of carbon nanomaterials.

The Raman spectra of graphene and graphite (composed of millions of layers of graphene stacked together) are shown in **Figure 1**. The spectra exhibit a relatively simple structure characterized by two principle bands designated as the G and 2D-bands. Sometimes, a third band, the D-band may also be apparent in graphene when defects in the carbon lattice are present. Although these differences may appear subtle, they supply crucial information when scrutinized closely. There are differences in the band positions and the band shapes of the G-band and 2D-bands and the relative intensity of these bands is also significantly different.

Clearly, these Raman spectra demonstrate the ability to differentiate between single-layer graphene and graphite. However, the utility of Raman techniques lies in the ability to differentiate single, double, and triple-layer graphene. In other words, Raman techniques can determine layer thickness at atomic layer resolution for graphene layer thicknesses of less than four layers (i.e., at thicknesses that are of interest to the present field of graphene research).
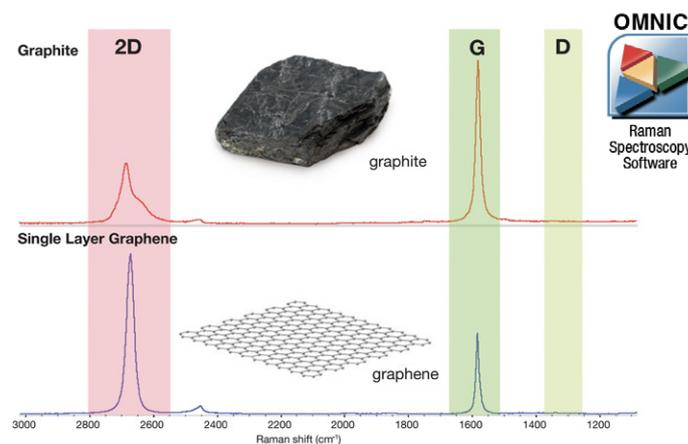

Figure 1. The Raman spectra of graphite and angle layer graphene, collected with 532 nm excitation.

Let's now take a closer look at the vibrational bands of graphene and how analyzing these bands can give insight into the thickness of a graphene sample.

The G-band

The G-band is a sharp band that appears around 1587 cm^{-1} in the spectrum of graphene. The band is an in-plane vibrational mode involving the sp^2 hybridized carbon atoms that constitute the graphene sheet. The G-band position is highly sensitive to the number of layers present in the sample and is one method for determining layer thickness; it is based upon the observed position of this band for a particular sample. To demonstrate this behavior, Figure 2 compares the G-band position of a single layer, double layer, and triple layer graphene. These spectra have been normalized to better reveal the spectral shift information. As the layer thickness increases, the band position shifts to lower energy representing a slight softening of the bonds with each addition of a graphene layer. Empirically, the band position can be correlated to the number of atomic layers present by the following relation

$$\omega_G = 1581.6 + 11/(1 + n^{1.6})$$

Where wG is the band position in wavenumbers, and n is the number of layers present in the sample. The positions of the bands shown in Figure 2 are in close agreement with calculated positions for these band locations. It is worth noting that the band position can be affected by temperature, doping, and even small amounts of strain present on the sample, so this must be applied with caution when attempting to use the position of this band to determine graphene layer thickness. Not only can the band position of the G-band give insight into the number of layers present but the intensity of the G-band also follows a predictable behavior that can be used to determine graphene thickness. Figure 3 shows spectra of single, double and triple layer graphene. The intensity of this band closely follows a linear trend as the sample progresses from single to multilayer graphene. The G-band intensity method will be less susceptible to the effects of strain, temperature, and doping. It may also provide a more reliable measurement of layer thickness when these environmental factors are present.

$$\omega_G = 1581.6 + 11/(1 + n^{1.6})$$

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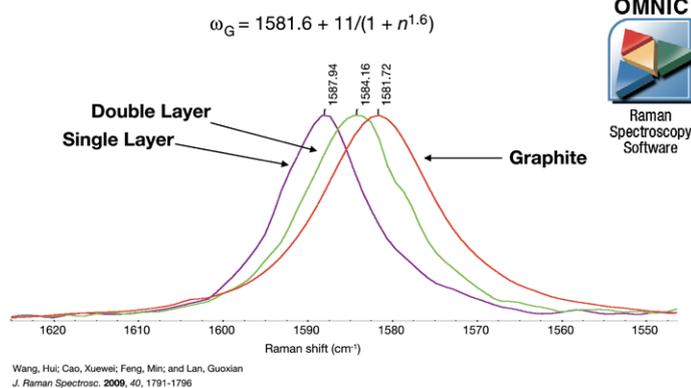*J. Raman Spectrosc.* **2009**, *40*, 1791-1796

Figure 2. The G-band position is a function of layer thickness. As the number of layers increase, the band shifts to lower wavenumber, collected with 532 nm excitation.

The D-band

The D-band is known as the disorder band or the defect band, and it represents a ring breathing mode from sp^2 carbon rings, although to be active, the ring must be adjacent to a graphene edge or a defect. The band is typically very weak in graphite and is typically weak in high-quality graphene. If the D-band is significant, it means that there are many defects in the material. The intensity of the D-band is directly proportional to the level of defects in the sample. The last thing to note about the D-band is that it is a resonant band that exhibits what is known as dispersive behavior. This means that there are a number of very weak modes underlying this band, and depending on which excitation laser is used, different modes will be enhanced. The consequence of this is that both the band's position and the shape can vary significantly with different excitation laser frequencies, so it is important to use the same excitation laser frequency for all measurements if you are doing characterization with the D-band.
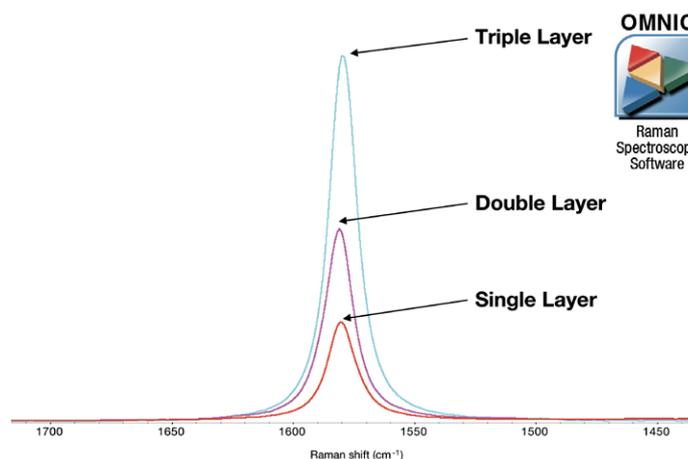

Figure 3. There is a linear increase in G-band intensity as the number of graphene layers increases, collected with 532 nm excitation.

The 2D-band

The 2D-band is the final band that will be discussed here. The 2D-band is the second order of the D-band, sometimes referred to as an overtone of the D-band. It results from of a two phonon lattice vibrational process, but unlike the D-band, the 2D-band does not need to be activated by proximity to a defect. As a result, the 2D-band is always a strong band in graphene, even when there is no D-band present; 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. The differences in this band between single, double, and triple layer graphene can be seen in Figure 4.

For single layer graphene, the 2D-band is observed to be a single symmetric peak with a full width at half maximum (FWHM) of ~30 cm^{-1}. Adding successive layers of graphene causes the 2D-band to split into several overlapping modes. The band splitting of the 2D-band going from single layer graphene to multilayer graphene arises from symmetry lowering when increasing the layers of graphene in the sample. These distinct band shape differences allow the 2D-band to be used to effectively differentiate between single and multilayer graphene for layer thickness of fewer than four layers. Just like the D-band, the 2D-band is resonant and exhibits strong dispersive behavior, so the position and shape of the band can be significantly different with different excitation laser frequencies. Again, it is crucial to use the same excitation laser frequency for all measurements when doing characterization with the 2D-band.

It is worth pointing out that single layer graphene can also be identified by analyzing the peak intensity ratio of the 2D and G-bands, as seen in **Figure 5**. The ratio I_{2D}/I_G of these bands for high quality or defect-free, single layer graphene will be seen to be equal to two. This ratio or lack of a D-band with a sharp symmetric 2D-band is often used to confirm a high-quality, defect-free graphene sample.

Instrument considerations

There are a few specifications that should be considered when selecting a Raman instrument for graphene characterization. First, since graphene samples are usually very small, selecting a Raman instrument with microscopy capabilities is imperative.
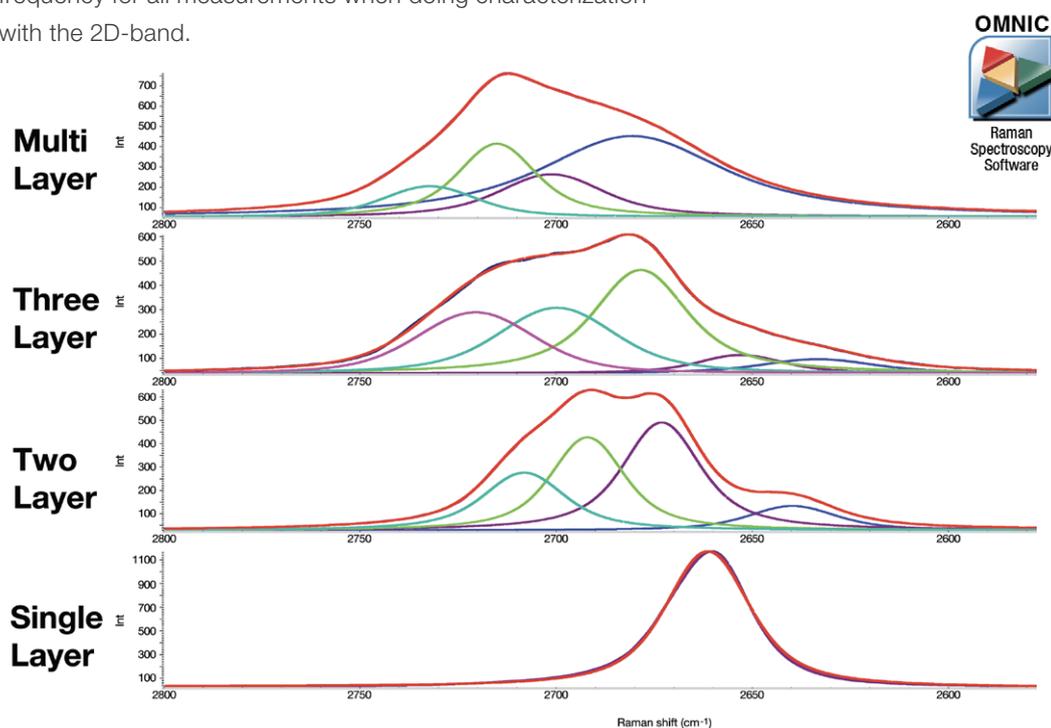

Figure 4. The 2D-band exhibits distinct band shape differences according to the number of layers present.
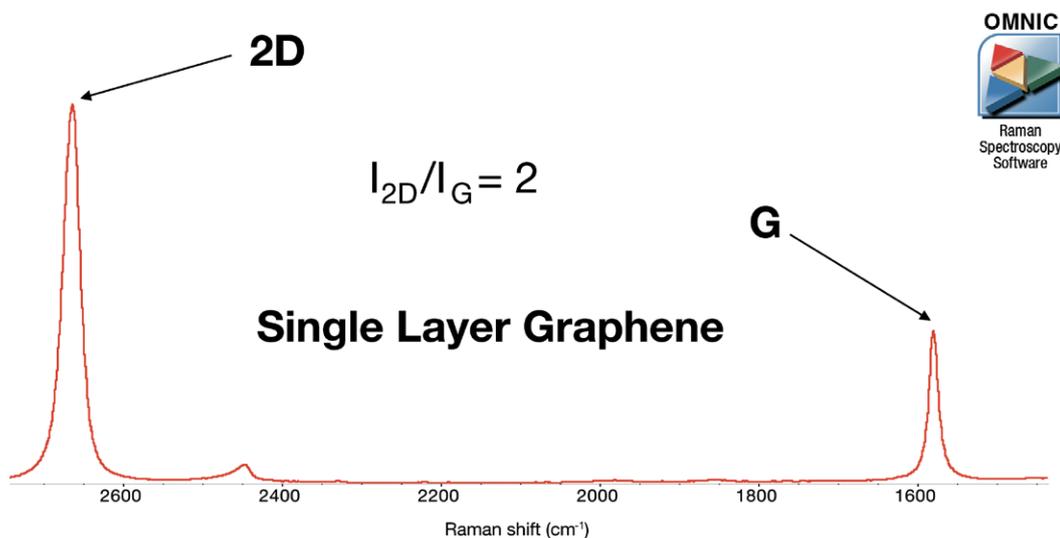

Figure 5. Single layer graphene can be identified by the intensity ratio of the 2D-band to G-band.

The next issue to consider is which excitation laser to select. While graphene measurements can be made successfully with any of the readily available Raman lasers, it is also important to consider the substrate that the graphene will be deposited onto. It is common for graphene to be deposited on on either Si or SiO_2 substrates, and both of these materials can exhibit fluorescence with near-infrared (NIR) lasers such as 780 nm or 785 nm. For this reason, visible lasers are usually recommended, typically a 633 nm or 532 nm laser.

Next, since relatively small wavenumber shifts can significantly impact the interpretation of the Raman spectra, it is crucial to have a robust wavelength calibration across the entire spectrum. Using a single point wavelength calibration with some other applications may be sufficient, but this only ensures that one wavelength is calibrated and leaves room for a large margin of error. A multipoint wavelength calibration that is regularly refreshed, such as the standard calibration routine used with Thermo Scientific DXR3 Raman instruments, will provide considerably more confidence in the results. It is also necessary to have an instrument with high wavenumber precision to observe small wavenumber shifts when altering the sample. In fact, small wavenumber shifts can represent changes in the sample rather than represent the variability from the instrument. There is a common myth that it is necessary to utilize high resolution in order to achieve high wavenumber precision. Not only is this incorrect, but a high resolution will actually add considerable noise to the spectrum, which will add to the wavenumber variability. A high degree of wavenumber precision, such as that provided by the Thermo Scientific™ DXR™3 Raman Microscope, will significantly improve data confidence even when you are evaluating band shifts from low levels of strain or doping. It is also important to have exact control of your laser power at the sample and be able to adjust that laser power in small increments. This is important to

control temperature-related effects and to provide flexibility to maximize Raman signal while still avoiding sample heating or damage from the laser. The DXR3 Raman systems are equipped with a unique device called a laser power regulator, which maintains laser power with unprecedented accuracy and provides exceptional ability to fine-tune laser power and optimize it for each experiment.[1]

Lastly, the Raman microscope must have an automated stage and associated software to generate detailed Raman point maps. As will be seen in the next section, Raman point mapping or imaging extends the single point measurement to assess a sample's layer thickness uniformity. The Thermo Scientific OMNIC™ Software suite contains powerful mapping and processing tools that diminish the complexity of collecting highly detailed maps and interpreting their results.

The Raman mapping of graphene

We have taken a detailed look at the Raman spectroscopy of graphene and how a Raman measurement can identify a particle with a particular thickness at a specific point. Now we turn to multipoint Raman mapping. Raman mapping entails the coordinated measurement of Raman spectra with successive movements of the sample by a specified distance. Raman maps or images can be obtained from a sample if an automated stage is integrated into the Raman microscope. Raman microscopes, such as the DRX3 Microscope, can generate chemical images of graphene samples with submicron spatial resolution. This capability allows a graphene sample to be characterized regarding whether the sample is composed entirely of one layer across the whole sample or whether it contains areas of differing thicknesses. Figure 6 shows the results of a Raman map measurement using Thermo Scientific OMNIC Atlμs™ Mapping Software. Seen on the right of this slide is the video image
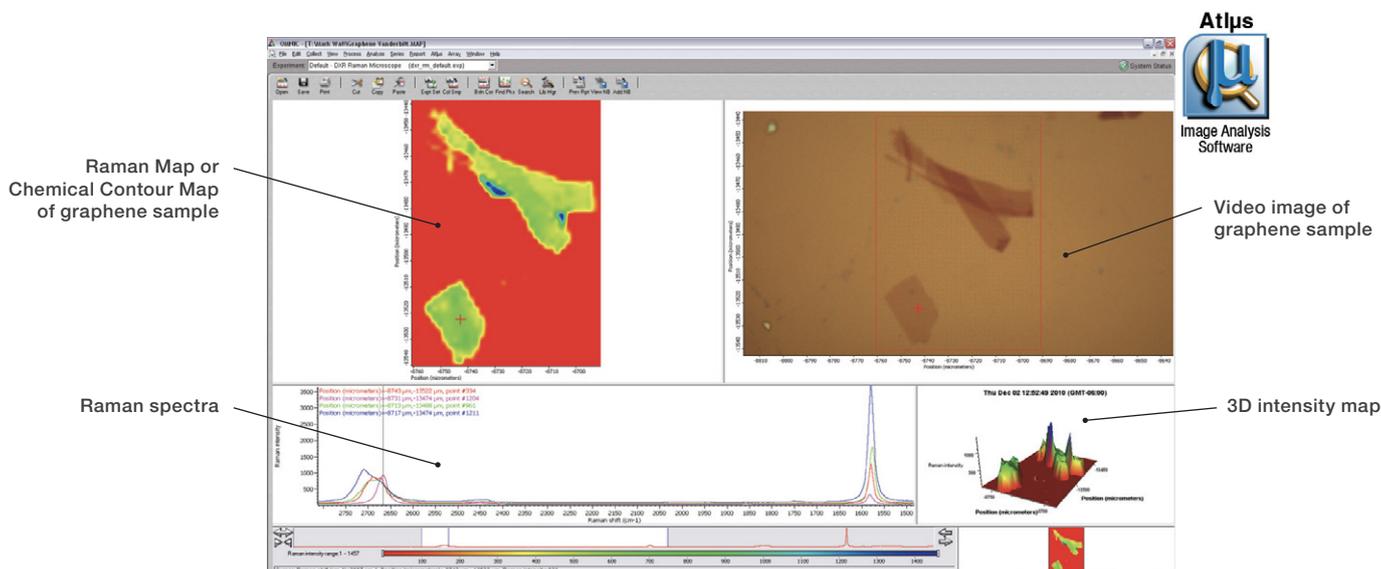

Figure 6. Raman spectra of graphene at specific locations exhibiting differences in layer thickness.

of a sample of graphene that contains areas that differ in graphene thickness. It can be readily seen that the light and dark areas of this image give a hint that there are regions that differ in graphene layer thickness. On the left-hand side is the Raman map or chemical contour map taken of the graphene sample. This was obtained by taking a series of Raman point measurements in the area depicted in the video image. The chemical contour map uses an intensity-based color scale with red representing low intensity and blue representing high intensity referenced to a particular Raman shift (in this case, the 2658 cm^{-1} associated with the 2D-band of single layer graphene). In this case you can see some indication of the distribution of single layer graphene in the sample. A wealth of information is contained in this chemical image, and further processing of this map is necessary to extract this information. OMNIC Atlµs Software contains some very powerful processing tools, namely discriminant analysis, also found in the Thermo Scientific TQ Analyst™ Pro Edition Software, that can determine the presence and distribution of regions in the map that differ in graphene layer thickness. The discriminant analysis can be based on a band or region where distinct differences exist in the investigated material. The 2D-band with its band shape differences is used. The discriminant analysis employs standard spectra for the different layer thicknesses as a calibration

set. The discriminant analysis results applied to this map are presented in Figure 7. The results show that the sample under investigation was composed of single, double, triple, and multi-layer graphene regions across the sample.

Conclusions

Raman spectroscopy is an excellent tool for the characterization of graphene and layer thickness. Few techniques will provide as much information about the structure of graphene samples as Raman spectroscopy, and any lab doing graphene characterization without Raman would be at a significant disadvantage. The DXR3 Raman Microscope is an ideal Raman instrument for graphene characterization because it can provide the high level of stability, control, and sensitivity needed to produce confident results.

References

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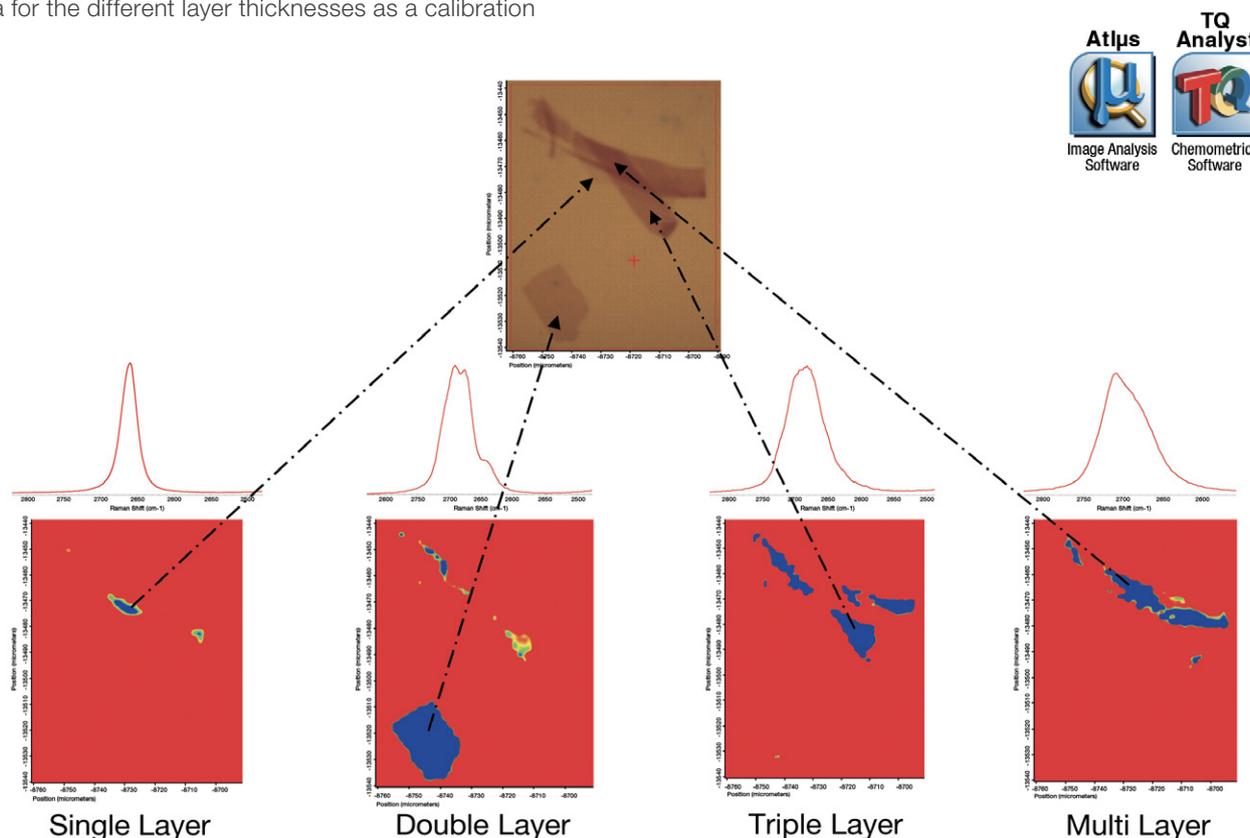
Figure 7. Discriminant analysis applied to the graphene Raman Atlµs Software image shown in Figure 6. The analysis gives the distribution of the different layer thicknesses contained in the sample.

Thermo Scientific DXR3 Raman Microscope

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Keywords

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