

Tip Enhanced Raman Spectroscopy for high power laser target applications

E. Crane

ECE Paris, 37 Quai de Grenelle, 75015, Paris, FRANCE

D. Haddock, C. Spindloe, M. K. Tolley

Central Laser Facility, Rutherford Appleton Laboratory,
Science and Technology Facilities Council, Harwell Oxford,
Didcot, Oxon OX11 0QX, UK

A. Parker

Research Complex, Rutherford Appleton Laboratory, Science
and Technology Facilities Council, Harwell Oxford, Didcot,
Oxon, OX11 0QX, UK

Abstract

The Target Fabrication group is responsible for the delivery of high specification microscale targets for irradiation in high power laser experiments. Targets vary in composition depending on the experimental aims and their production and delivery requires extensive expertise in thin-film coating, and characterization as well as a range of other techniques. Thin foil targets are amongst the most widely used target types but the chemical and structural information of such targets on the nanometer scale is not well understood. Collaboration between Target Fabrication (TF), Ultra and Octopus has enabled the development of the capacity to carry out Tip Enhanced Raman Spectroscopy (TERS). On the cutting edge of scanning probe microscopy science, TERS provides the powerful chemical and structural characterization of Raman spectroscopy combined with the high spatial resolution achieved through Atomic Force Microscopy (AFM). The prime aim for the technique is to gain a better understanding of Diamond-Like Carbon (DLC) which has been used successfully as a target material down to a few nanometers in thickness; a regime for targets that is completely unachievable with most materials. A better understanding of the chemical and structural nature of DLC has the potential to lead to even thinner foils.

Introduction

There has been considerable scientific interest in TERS over the last five years due to the combined chemical and structural characterisation information (which is unobtainable by other methods). The technique is usually performed at ambient temperature giving a spatial resolution of less than 30nm on a wide range of materials (including organic nanostructures, thin films, inorganic nanostructures and biological samples).

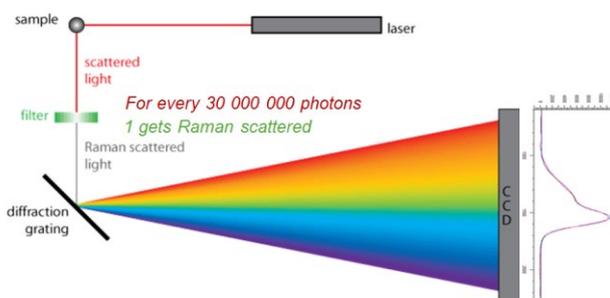


Figure 1 [1]: Graphical representation of the principle of Raman Spectroscopy.

In Raman spectroscopy a laser beam irradiates a sample to deduce its chemical content and molecular structure. Every molecule has a unique set of vibrational energy levels; the laser light probes the vibrational energy levels and different compositions give their own unique spectra. When photons interact with materials most of them come away with the same energy (Rayleigh scattering), however, one in approximately 30 million is inelastically scattered (Raman scattering) resulting in a wavelength shift which is specific to each molecule.

In figure 1 the Raman scattered light is isolated from the background by a filter and the wavelengths are separated by a diffraction grating. The Tip Enhanced Raman effect can increase the Raman signal coming from the molecules surrounding the tip by up to a million times allowing access to very fine spatial resolution (as illustrated in figure 2).

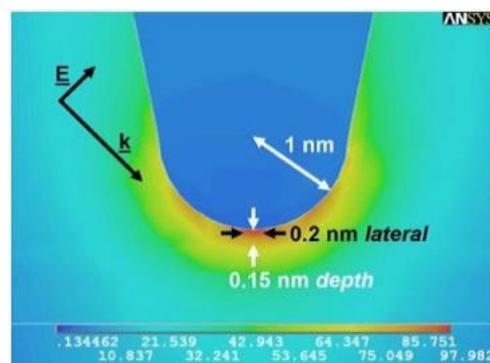


Figure 2: Pictorial representation of enhancement of the Raman Signal from the molecules surrounding the tip. It is in contrast to normal Raman Spectroscopy where the signal is received from the size of the laser spot, typically half a millimeter.

Raman spectra of Diamond-Like Carbon

DLC is an amorphous carbon material that possesses a significant fraction of sp^3 bonds. The usefulness of the coating comes from the diamond-like properties that it exhibits. Ultrathin DLC films have been used as target materials in laser experiments at the CLF with applications in particle acceleration and, potentially, in hadron therapy. The increased demand for such foils has naturally led to the need for increasingly detailed characterisation of the material.

Structurally speaking sp^3 hybridized carbon has theta bonds and sp^2 hybridized carbon has pi and theta bonds. Due to the preferential excitement of pi bonds by a 514nm laser the sp^2 sites are resonantly enhanced giving an overwhelming signal peak from the sp^2 sites which overshadows the sp^3 peak [3].

Due to the enhancement, the concentration of sp^3 bonds is indirectly derived by comparison of Raman spectra taken from known sp^3/sp^2 data in literature. Different peaks in the spectrum correspond to different Raman excitations. The Disorder (D) peak is present around 1370 wavenumbers and the Graphitic (G) peak is present around 1580 wavenumbers. If the sp^2 sites are in chains the D peak is absent. If the sp^2 sites are in disordered rings there is a residual D peak [2]. From this information we can deduce that the clustering is the height of the D peak relative to the G peak (see figure 3). Plotting the Raman data from DLC we obtained a typical spectrum as shown in figure 3. Fitting Gaussian peaks allowed us to compare the spectra for different amorphous carbons.

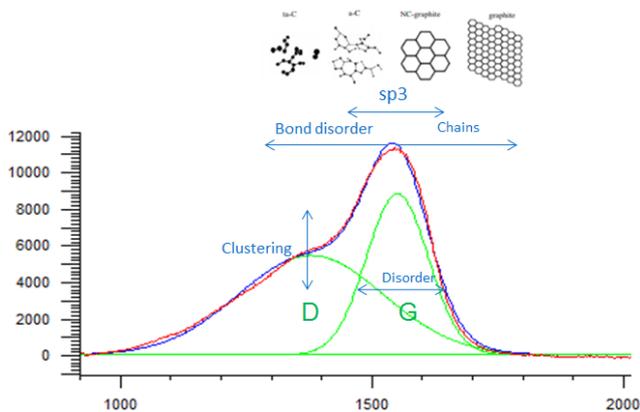


Figure 3: An example Raman spectra taken of Diamond-Like Carbon. The x-axis is wavenumber in cm^{-1} and the y axis is signal intensity. The red line is the taken data and the blue line is the result of the two Gaussian fitted peaks.

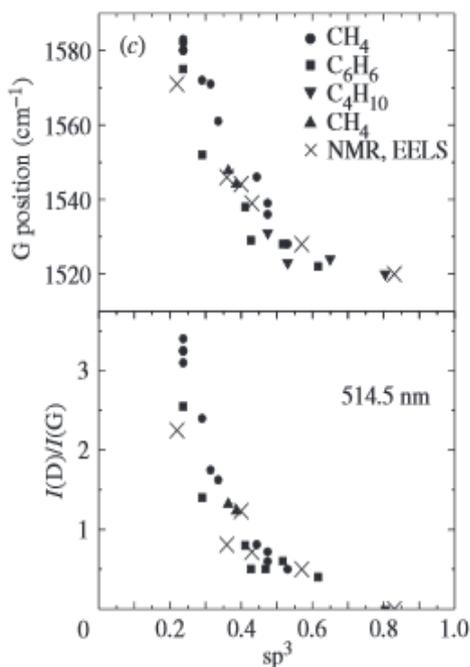


Figure 4^[2]: Recorded sp^3 content for Diamond-Like Carbon with corresponding G peak position and the ratio of D to G peak intensity. It can be seen that the G peak position and $I(D)/I(G)$ decrease with increasing diamond content.

With the information in figures 3 and 4 it is possible to reliably infer the diamond content of the DLC foils made in the Target Fabrication Plasma Enhanced Chemical Vapour Deposition (PECVD) coating plant.

Tip Enhanced Raman Spectroscopy (TERS)

In standard Raman analysis a CCD camera collects data indicating how many photons have been Raman scattered enabling characterisation of the sample and giving a unique footprint for each different molecule. The laser light for a normal measurement is incident on a large area of the sample, equal to the size of the laser focal spot. A normal Raman measurement will collect an averaged spectrum from about $1mm^2$ which, in practice, is suitable for most applications because samples are often homogeneous.

However, in an amorphous carbon sample, the diamond molecules are dispersed in small clusters and a normal Raman measurement gives data from a large area and many clusters, which is unsuitable for detailed characterisation of DLC.

The Surface Enhanced Raman (SERS) effect uses elements such as silver or gold to enhance the Raman signal of the molecules around them. The molecules of the sample which are in contact with the silver or gold exhibit a higher intensity signal, and are preferentially detected. The increase arises because metals, nanostructures and nanotubes produce plasmon resonances enhancing the electric field from an optical beam.

By using an AFM tip coated with silver or gold TERS combines the topographical capability of an atomic force microscope with the chemical and structural characterization of Raman spectroscopy. Shining a laser on the coated tip it is possible to obtain a signal coming only from the region of the sample in the very near vicinity of the tip. Rastering the tip over the surface, therefore, creates a very precise map showing the nuances of bonding between adjacent very small regions on the surface of the sample.

An Atomic Force Microscope consists of a cantilever with a sharp tip on its end having a tip radius of the order of nanometres. When brought into contact with a sample surface the cantilever deflects and gives height measurements reliably achieving resolutions of a few nanometres (several hundred times smaller than the optical diffraction limit). Figure 5 shows images obtained of an SPM reference sample. The AFM was able to resolve a topography of 3nm in the x and y axes and 10nm in the z axis.

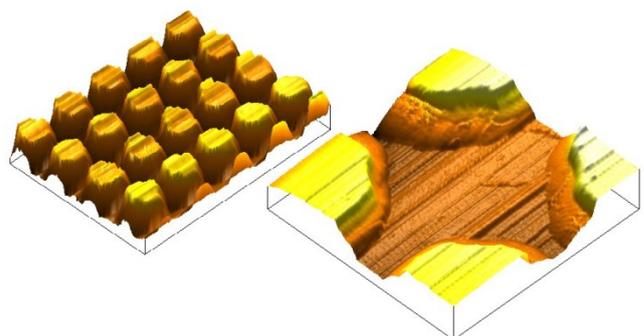


Figure 5: Images from the AFM of an AFM calibration sample consisting of 100nm high cylinder structures.

Rhodamine 6G (R6G)

To develop the ability to perform TERS, we examined several samples which are expected to show large TERS signals. The expectation was that the signal from single 100nm polystyrene spheres dispersed on a glass surface would have been too low to detect using normal Raman. After coating them in Rhodamine 6G (a pigment which gives off a very clear Raman signal) the aim was to use a TERS tip to obtain signals coming from single spheres.

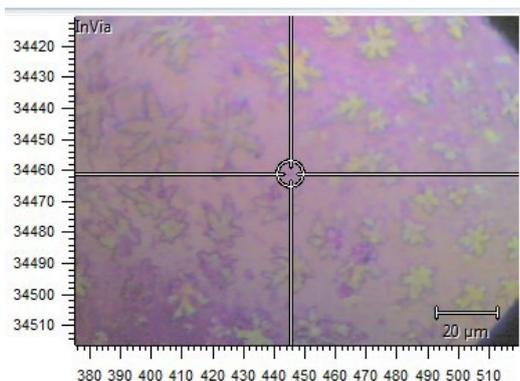


Figure 6: Rhodamine 6G sample viewed through the Raman Spectrometer microscope.

Rhodamine 6G (although aesthetically pleasing, as shown in figure 6) did not give reliable results. It was suspected that it was photosensitive because the Raman signal decayed after as little a tenth of a second exposure at 5% laser power. Consequently it was not possible to repeat the experiment to confirm the result. Ideally the signals need to be taken from the same area to disambiguate the TERS effect from variations in the sample.

Strained Silicon

In an attempt to demonstrate the SERS effect with the coated tip strained silicon was used. The sample consisted of bulk silicon covered by a thin layer of strained silicon. To prepare the sample; on one half the strained silicon was removed by plasma etching to reveal the bulk silicon for comparison of Raman signals from the two silicon types. It was anticipated [6] that the signal coming from the strained silicon would be enhanced by the presence of the gold nanoparticle at the end of the tip and the signal should increase when the tip is in contact as shown in figure 7.

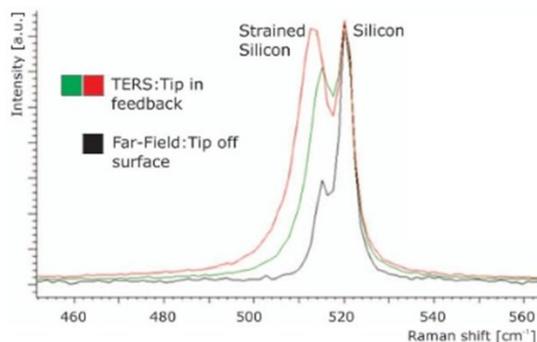


Figure 7^d: What should have been observed; the published spectrum of the TERS effect on strained silicon.

Although no enhancement was witnessed the signals obtained were all about 10 wavenumbers lower than expected. Not having the detailed knowledge of how the strained silicon samples were manufactured, it was proposed that the sample contained some germanium which is known to disrupt the Raman signal of samples in this manner. When the suppliers were consulted it was confirmed that germanium had been added during the manufacturing process.

HCM Rotaxane

Finally HCM Rotaxane was tried; a hexayne chain threaded through a phenanthroline macrocycle.

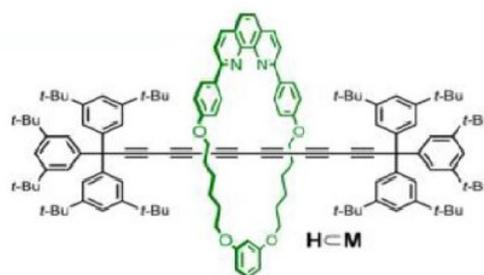


Figure 8: Structure of HCM Rotaxane; a molecule trialed to test TERS.

As with the other samples it was essential to take a spectrum of the sample without the tip and then another of exactly the same place with the tip in contact in order to ascertain whether the tip was enhancing the signal from the surface molecules. To do this we decided to check whether there was any enhancement near the tip by creating a Raman map of the tip on and off the surface and comparing them. The software is able to take one complete Raman spectrum for each point on a map. If the user chooses the peak wavenumber it can also make a map comparing the intensity of each spectrum at that specific wavenumber.

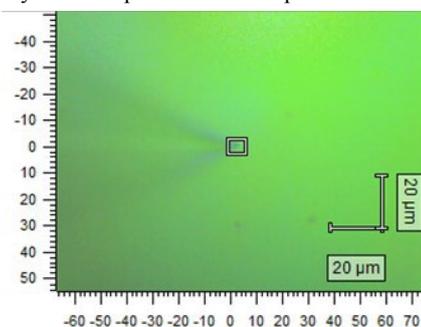


Figure 9: Image of tip from above. The white square shows the area in which a Raman map was produced.

Figure 10 shows the intensity at the peak wavenumber for each spectrum at each point on the map. It shows clearly that the spectra taken near the center have enhanced peak wavenumber intensities compared with the ones around the edges. This proves that the TERS effect is obtained.

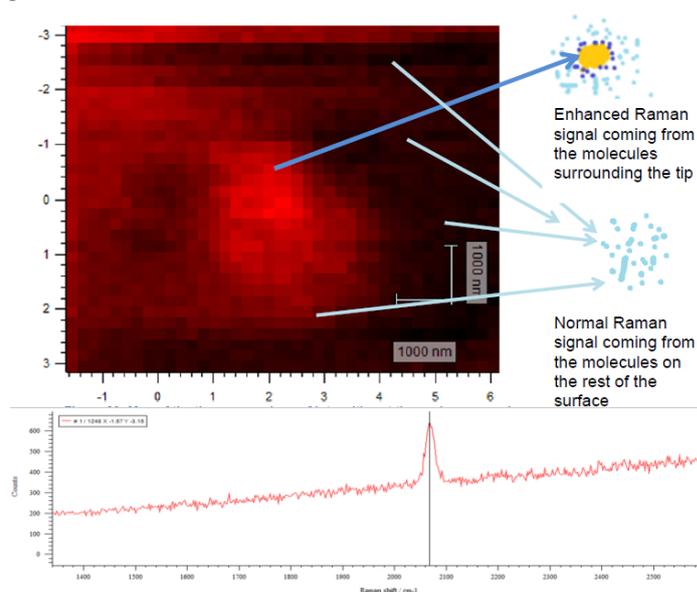


Figure 10: Surface map with tip in contact - comparison of intensities at peak wavenumber. The brighter red area showed a greater Raman signal at the wavenumber specified.

However, it was necessary to compare the intensities at a peak wavenumber for each point on a map, not only for the tip on the surface. To do this the map of the tip off the surface was subtracted from the map of the tip on the surface. The result is plotted in figure 11.

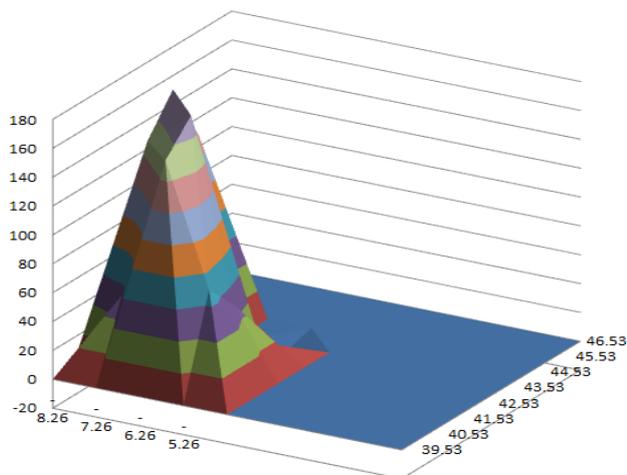


Figure 11 Map of Raman signal from the tip in contact minus the signal from the tip out of contact for an area surrounding the tip.

As shown in figure 11 the TERS effect was demonstrated using HCM Rotaxane on a gold substrate. It can be seen that there is a large enhancement of the Raman signal around the tip. The automated technique will allow future users to find the enhancement easily for use on other samples. (The coordinates of the best enhancement were: 7.26; 40.53)

PEDOT.PSS (Polymer bilayer)

Another way of aligning the laser with the tip is to move the tip around on the sample surface under a fixed laser beam. It is possible to compare in real time the signal obtained with the tip off the surface (in blue in figure 12) with the signal obtained in contact (in red in figure 12). The red spectra keeps changing every time a new measurement is made, and it should be possible to see the signal intensity significantly augment as the tip moves into the laser focus. The graph again proves that it was possible to obtain the TERS effect.

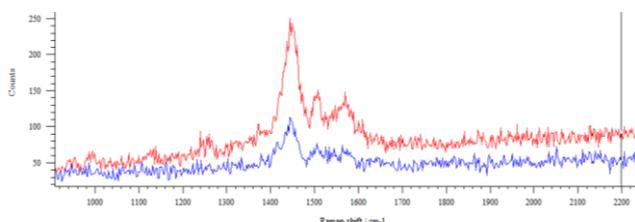


Figure 12: Enhancement of Raman spectra on the polymer bilayer PEDOT.PSS (red – with tip in contact; blue – tip out of contact)

Conclusion

This project has demonstrated and developed the cutting edge characterisation capability TERS. As part of the development work an automated mapping system was created which subtracts the Raman map of the tip out of contact with the surface from the Raman map of the tip in contact and compares the two for as many characteristic peak wavelengths as the user desires, taking into account variations around the tip, and creating a new map of the results. This goes a very long way towards automating the alignment of the laser on the tip, saving a significant amount of time for users also thereby reducing the number of times the AFM probes have to be replaced. TERS is a powerful and informative tool and the technique can now be used for a range of research studies for example in the characterisation of high power laser targets; for seeking detailed information about DNA, pigments, live cells or ancient wines; or for user groups wanting to examine nanowires in photovoltaic cells.

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