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Carbon Nanotubes – What Information Does Raman Microscopy Bring?

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Carbon nanotubes, a relatively new allotropic form of sp^2-type carbon, has attracted a great deal of interest because of its many engineering possibilities. Single-walled carbon nanotubes are of the greatest interest, and Raman microscopy has been shown to be the technique of choice for characterizing these materials.

Background

One can conceptualize the structure of a single-walled carbon nanotube by imagining a single layer of graphite that is rolled into a tube. The orientation of the graphite plane relative to the axis of the tube, as well as the diameter of the tube, will determine many physical properties; tubes can be insulating, semiconducting, or metallic. When multiple layers of graphite are rolled into a single tube, the resulting structure is called a multi-wall carbon nanotube.

The large variety of SWNTs is defined by a pair of integers (n,m) from which their diameter, chirality and semiconducting/metallic behaviour can be determined (1). Chirality defines the orientation of the rolled Graphite sheet relative to the main axis of the tube.

There are limitless ideas of how to take advantage of the tubes' properties in engineered materials. Composites will have strength derived from of the tensile strength of the tubes, metallic tubes have already been in integrated circuits (2), and tubes are being considered for drug delivery devices.

Raman spectra of these tubes are quite interesting because of resonance phenomena and sensitivity to tube structure. That is, there is very strong excitation wavelength dependence of the spectra resulting from the electronic band structure. And features in the Raman spectra are diagnostic of the CNT type.

The characteristic Raman spectrum of SWNT

The most important feature in the Raman spectrum of CNT's is the Radial Breathing Mode (RBM), which is usually located between 75 and 300 cm^{-1} from the exciting line; an illustration of the spectrum resulting from this mode is displayed in the figure. The frequency of the RBM is directly linked to the reciprocal of the nanotube diameter (d_t). In the case of an isolated Single Wall NanoTube (SWNT) this relation is [1]:

$\omega_r = 224/d_t$

However, non isolated SWNTs are subject to inter-tube interactions which increase the frequency of the RBM.

The D mode (the disorder band is located between 1330-1360 cm^{-1} when excited with a visible laser) is expected to be observed in Multi Wall NanoTubes (MWNT). However when it is observed in SWNT's, one assumes that it is due to defects in the tubes.

The G mode or (TM- Tangential Mode) corresponds to the stretching mode in the graphite plane. This mode is located around 1580 cm^{-1}.

The figure shows the spectrum of a preparation of nanotubes, in which the same deposit was excited at four laser wavelengths. It is clear that the spectra are highly dependent on the excitation which follows from the resonance behaviour mentioned above. These spectra indicate that the spectrum generated from a sub micron spot were acquired from tubes of varying diameters that come into resonance at different wavelengths. There is actually a theoretical relationship between the electronic energy separation (that determines resonance conditions), and the tube diameter and chirality which is displayed in a "Kataura" plot. When the Resonant Raman spectrum of one SWNT has been recorded, the Kataura plot allows one to determine its semiconducting or metallic behaviour, and to estimate its diameter and chirality (n,m). Inspection of the figure indicates the possibility that it will not be unexpected for there to be closely spaced lines, so adequate spectral resolution will be important.

This last point is illustrated in the following figure where the RBM was recorded using 2 different gratings producing different spectral resolutions. It is clear that the higher resolution spectrum reveals more information on this sample.

Conclusion

The configuration of the Raman system will determine how much information one can extract about the Carbon Nanotubes. A multiexcitation, low frequency, high spectral and spatial resolution system is the best solution to collect the maximum information. In addition, by adding an InGaAs array, a system can be configured to record photoluminescence as well which will provide the bandgap energy directly.

References

1. Dresselhaus and Eklund, Phonons in Carbon Nanotubes, Advances in Physics 2000 **49** 705-814
2. M. Jacoby, Nanoscale Electronics, C&Enews 80 39, pp38-43, Sept 30, 2002

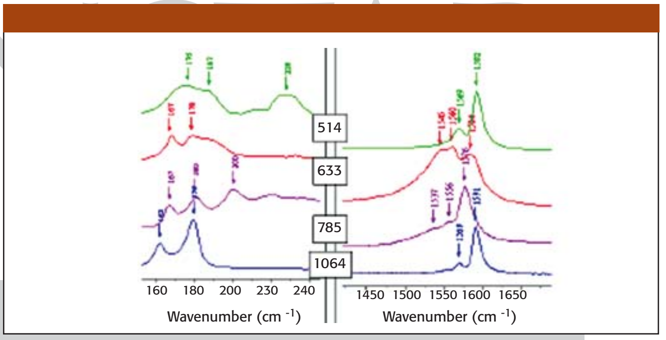

Figure 1. Exciting at different wavelengths allows us sweep several resonance conditions to show the existence of various CNTs

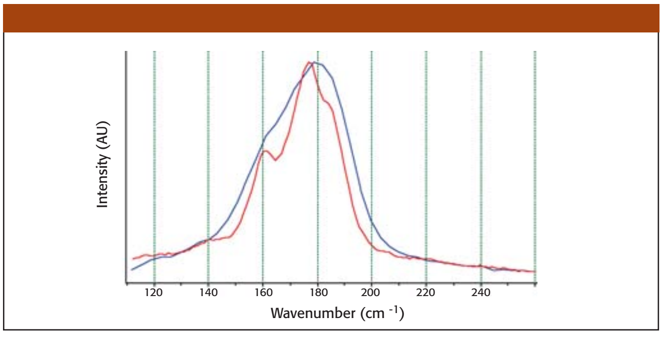

Figure 2.

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