Raman spectroscopy as a probe of graphene and carbon nanotubes

By M. S. Dresselhaus[1,2,*], G. Dresselhaus[3] and M. Hofmann[2]

[1]*Department of Physics,* [2]*Department of Electrical Engineering and Computer Science, and* [3]*Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA*

Progress in the use of Raman spectroscopy to characterize graphene samples for the number of graphene layers and doping level they contain is briefly reviewed. Comparisons to prior studies on graphites and carbon nanotubes are used for inspiration to define future promising directions for Raman spectroscopy research on few layer graphenes.

Keywords: Raman; graphene; carbon nanotubes; double resonance

1. Introduction

In the brief history of experimental studies of few layer graphene, Raman spectroscopy has already emerged as an important structural characterization tool, following in the footsteps of other related forms of carbon, such as graphite, on one hand, containing an infinite number of graphene layers, and carbon nanotubes, on the other hand, representing a seamless rolled-up graphene layer (Jorio *et al.* 2007). Study of the special characteristics of the Raman spectra of carbon nanotubes has significantly enriched our understanding of phonons in graphite, as well as the Raman spectroscopy in one-dimensional systems. Likewise, prior studies of Raman spectra in carbon nanotubes and graphite are likely to yield new insights into the richness expected for the Raman spectra of graphene. In this short paper, we summarize a few of the early findings about the Raman spectra of few layer graphene (figure 1), what we have learned from these early findings, and some thoughts about the future of this field.

Two prominent features appear in the Raman spectra of graphene (Ferrari *et al.* 2006; Jorio *et al.* 2007) both of which are strongly connected to graphite, as shown in figure 1. The first, the so-called G-band (for graphite) in the first-order Raman spectrum (figure 1a), corresponds to the optical mode vibration of two neighbouring carbon atoms on a graphene layer, occurring in graphite at $1582 \, \text{cm}^{-1}$, but upshifted by approximately $5 \, \text{cm}^{-1}$ in single-layer graphene. In fact, the upshifts in ω_G follow a $1/n$ dependence on the number of layers n

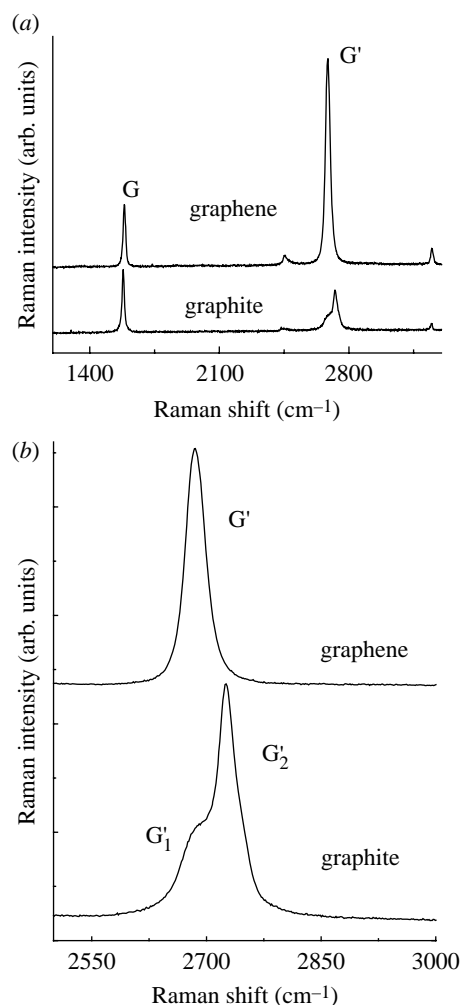* Author and address for correspondence: MIT Room 13-3005, Cambridge, MA 02139-4307, USA (millie@mgm.mit.edu).

Figure 1. (*a*) Comparison of the Raman spectra of graphene and graphite measured at $E_{laser} =$ 2.41 eV (514.5 nm). The two unidentified lower intensity peaks are associated with the second-order Raman scattering. (*b*) Comparison of the G′-band peaks of graphene and graphite (also measured with 2.41 eV radiation). Adapted from Jorio *et al.* (2007).

without significant change in lineshape (figure 2*a*; Ferrari *et al.* 2006; Jorio *et al.* 2007). This dependence can be used to characterize the number of graphene layers *n* in few layer graphene samples (Ferrari *et al.* 2006; Jorio *et al.* 2007).

The second feature appearing at approximately 2700 cm^{-1} for $E_{laser} = 2.41$ eV is usually called the G′-band in the graphite literature because this feature is also found in all sp^2 carbon materials (figure 1). This feature occurs in the second-order Raman spectrum and is due to a double-resonance process involving two phonons of opposite wavevector, as shown in figure 2*c*. The scattering process shows an electron from a *K* point (where the graphene electronic valence and conduction bands are degenerate at what is called the Dirac point in the recent graphene literature) being scattered to an adjacent *K*′ point and then scattered back to a *K* point, thereby creating two phonons with opposite wavevectors. The
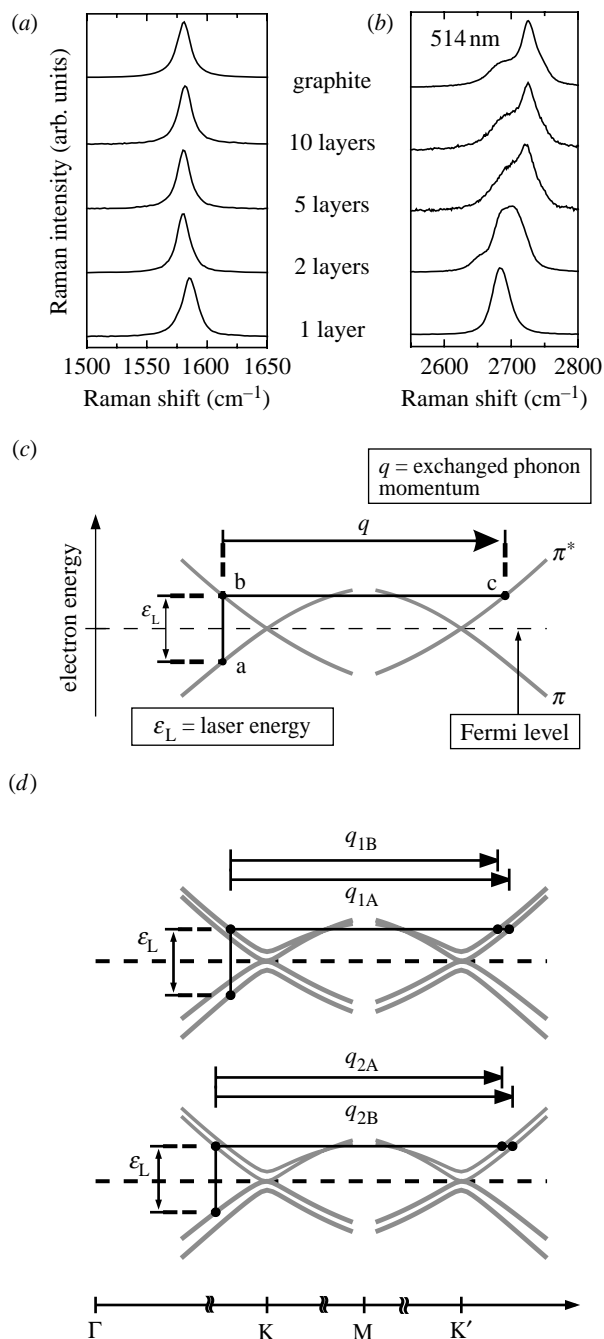
Figure 2. Raman spectra at $E_{laser} = 2.41$ eV for (*a*) the G-band and (*b*) the G′-band of graphene for various numbers of graphene layers. The double-resonance process for the G′ feature for (*c*) monolayer graphene (1GL) and (*d*) bilayer graphene (2GL). Adapted from Jorio *et al.* (2007).

large intensity for the G′ feature arises from the resonance of the laser excitation with the intermediate state, and with either the incident or scattered photons. For monolayer graphene, only one strong peak in the Raman spectra is seen,

whereas for graphite two distinct peaks, G'_1 and G'_2, are resolved (figure 1b). Furthermore, the intensity for the G' feature $I_{G'}$, is very large with an intensity ratio to the G-band $I_{G'}/I_G = 4$ at $E_{laser} = 2.41$ eV, in sharp contrast to the situation in graphite where the G-band is stronger than the G'-band (figure 1a), as is also the case for single-walled carbon nanotubes (SWNTs; Dresselhaus *et al.* 2005).

For the case of monolayer graphene (1GL), only one peak is seen (figure 2c), but for bilayer graphene (2GL) the double-resonance process can occur with one of four possibilities as indicated in figure 2d.

From figure 2b, it is clear that the detailed spectra for n-layer graphene (nGL) is distinct for each n, and for this reason the G'-band Raman spectra has become an important tool for characterizing the number of graphene layers n in a sample. When doing this characterization it is important to stress the strong dependence of the lineshape on the laser excitation energy E_{laser} (Ferrari *et al.* 2006). Whereas for monolayer graphene, the lineshape is simply a single Lorentzian line with a linear dependence of $\omega_{G'}$ on E_{laser} with $(\partial\omega_{G'}/\partial E_{laser} = 96\ \text{cm}^{-1}\ \text{eV}^{-1})$ reflecting the linear wavevector dependence of the electron and hole energies near the K point (Ferrari *et al.* 2006), each of the four peaks for bilayer graphene, for example, depend somewhat differently on E_{laser}. Therefore, it is necessary to develop a metrology standard for specifying the laser excitation energy at which the G' spectra are taken for the n-layer characterization process.

The richness of the combination mode spectra for graphene provides further tools for distinguishing the various n-layer graphenes from one another. For example, the use of the $G + G'$ combination mode, occurring at approximately $4270\ \text{cm}^{-1}$ for $E_{laser} = 2.41$ eV, has been shown to exhibit a dependence of $\omega_{G+G'}$ on $1/n$ which can also be used to distinguish the various n-layer graphenes (nGL) from one another up to $n = 5$ (P. H. Tan *et al.* 2007, unpublished data).

Most of the quantitative studies on graphene have been carried out on monolayer and bilayer graphenes. Of particular interest have been the carrier doping studies where a gate was used to move the Fermi level E_F (with $E_F = 0$ at the Dirac point) into the conduction (valence) band to dope the graphene n-type (p-type) and both transport and Raman measurements have been carried out as a function of E_F for monolayer graphene samples on a SiO_2/Si substrate. Both calculations and experiments on undoped monolayer graphene show a small downshift in the Raman G-band frequency ω_G as the sample becomes n-type for $E_F < \hbar\omega_G/2$ and reaches a minimum $\omega_{G_{min}}$ at $E_F = \hbar\omega_G/2$. As the gate voltage V_g and E_F continue to increase, calculations and experiment both show that ω_G increases, in contrast to the situation in three-dimensional graphite where ω_G monotonically *decreases* with n-type doping as in alkali metal intercalated graphite (Dresselhaus & Dresselhaus 2002). This difference in behaviour is attributed to both strong electron–phonon coupling via the Kohn anomaly process, and a breakdown in the Born–Oppenheimer approximation in the case of monolayer graphene (1GL), where the electron and phonon energies are comparable. Further study of physical phenomena in this interesting limit will be a future direction for graphene research.

Fruitful comparisons have been made between Kohn anomaly behaviour and the effect of continuum doping by variation of the V_g in monolayer graphene and in metallic SWNTs. These successes inspire a follow-on joint study of transport and Raman spectroscopy in bilayer graphene and double-walled carbon

nanotubes (DWNTs). For bilayer graphene, the electronic energy bands exhibit a quadratic (k^2) dependence about the degenerate Dirac point and the two layers exhibit an AB layer stacking arrangement as in three-dimensional graphite, where the stacking order affects both the electronic and phonon dispersion relations. Placing bilayer graphene on a substrate is one way to break the mirror symmetry between the valence and conduction bands of bilayer graphene (Berger 2007), and to manipulate their electronic dispersion relations. Recent Raman experiments (Souza Filho *et al.* 2007) have revealed a related phenomenon occurring in DWNTs especially when one constituent is metallic (M) and the other is semiconducting (S), leading to a charge transfer interaction between the inner and outer nanotubes when they form a DWNT. Such charge transfer effects can be studied by measurement of the same (n, m) nanotube when it is an isolated SWNT or when part of a DWNT. Furthermore, the Raman spectra of M/S and S/M configurations on DWNTs are qualitatively different. For M inner/S outer, the inner tube is strongly affected by exohedral doping with Br_2 or H_2SO_4, whereas for the S inner/M outer configuration, the S inner tube is hardly affected by doping with a dopant species such as Br_2 or H_2SO_4. By analogy, substrates should be important in controlling the electronic properties of (2GL) graphene, and Raman spectroscopy would be expected to provide a sensitive probe of such interactions.

Furthermore, the Raman effect would be expected to provide a sensitive probe of stacking defects in bilayer graphene, which can be identified using a Raman confocal scan to locate disorder-induced D-band features (at approx. $1350 \, \text{cm}^{-1}$ for $E_{\text{laser}} = 2.41 \, \text{eV}$). At these locations a dependence of the normalized D-band intensity $I_{\text{D}}/I_{\text{G}}$ on E_{laser}^{-4} could be used to identify such stacking faults (Cançado *et al.* 2006). Since the D-band is dependent on wavevector $\boldsymbol{k}$ measured from the K point, the anisotropy of the phonon dispersion in graphene can be measured using nGL graphene ribbons based on a similar study using SWNT Raman spectroscopy (Samsonidze *et al.* 2003). Comparative measurements of the TO+LA combination mode at $2450 \, \text{cm}^{-1}$ (figure 1) should provide interesting comparisons between graphene and nanotubes regarding the Kohn anomaly and doping effects (Barros *et al.* 2007). It is expected that cross-comparisons between graphene, carbon nanotubes, graphite and sp^2 carbons will cross-fertilize these fields and lead to interesting advances in all in the near future.

References

Barros, E. B. *et al.* 2007 Raman spectroscopy of double-wall carbon nanotubes treated with H_2SO_4. *Phys. Rev. B* **76**, 045425. (doi:10.1103/PhysRevB.76.045425)

Berger, C. 2007 Invited talk. American Physical Society Meeting, Denver, Colorado. March 2007.

Cançado, L. G. *et al.* 2006 General equation for the determination of the crystallite size L_{a} of nanographite by Raman spectroscopy. *Appl. Phys. Lett.* **88**, 163106. (doi:10.1063/1.2196057)

Dresselhaus, M. S. & Dresselhaus, G. 2002 Intercalation compounds of graphite. *Adv. Phys.* **51**, 1–186. (doi:10.1080/00018730110113644) [Reprinted from ibid vol **30**, 1981.]

Dresselhaus, M. S., Dresselhaus, G., Saito, R. & Jorio, A. 2005 Raman spectroscopy of carbon nanotubes. *Phys. Rep.* **409**, 47–99. (doi:10.1016/j.physrep.2004.10.006)

Ferrari, A. C. *et al.* 2006 Raman spectrum of graphene and graphene layers. *Phys. Rev. B* **97**, 187401. (doi:10.1103/PhysRevLett.97.187401)

Jorio, A., Dresselhaus, M. S. & Dresselhaus, G. 2007 *Carbon nanotubes: advanced topics in the synthesis, structure, properties and applications. Springer series in topics in applied physics*, vol. 111. Berlin, Germany: Springer.

Samsonidze, G. G., Saito, R., Jorio, A., Souza Filho, A. G., Grüneis, A., Pimenta, M. A., Dresselhaus, G. & Dresselhaus, M. S. 2003 Phonon trigonal warping effect in graphite and carbon nanotubes. *Phys. Rev. Lett.* **90**, 027403. (doi:10.1103/PhysRevLett.90.027403)

Souza Filho, A. G. *et al.* 2007 Selective tuning of the electronic properties of coaxial nanocables through exohedral doping. *Nano Lett.* **7**, 2383–2388. (doi:10.1021/nl0710351)