The Raman Fingerprint of Graphene

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“Cut…. Get graphene”
Eklund-Sensei NT06

“Press (50GPa)…Get Diamond-like Carbon!”

S. Saito-Sensei CCNT06
Graphene

...big hype recently...

• Electron transport described by the (relativistic-like) Dirac equation. Access to the rich and subtle physics of quantum electrodynamics in a relatively simple condensed matter experiment.

• Scalability of graphene devices to true nanometre dimensions makes it a promising candidate for future electronic applications, because of its ballistic transport at room temperature combined with chemical and mechanical stability.

• Graphene is the two-dimensional (2d) building block for carbon allotropes of every other dimensionality.
Transistor: Graphene Ribbon
How to Make Graphene?

Drawing: (micro) mechanical cleavage of graphite
How to Make Graphene?

**GRAPHITE IS STRONGLY LAYERED**

SLICE DOWN TO ONE ATOMIC PLANE

**individual atomic sheets: do they exist?**
Free-Standing Graphene

AFM

Key: Visual Identification

single layer of atoms visible by “naked” eye only on 300 nm SiO$_2$

OPTICS

SEM
However

Need Extremely Good Eye To Spot!!!

Single Layer
Two Layers
One Comment…
Mechanical cleavage is nice and simple

However…
Low yield, messy, not scalable

Better to grow graphene directly on substrate

This can be done…

But…not the subject of this talk
Another Comment

AFM thickness of single layer is 0.5-1.5 nm! Due to chemical contrast

We want to be 150% sure

TEM
Free-Hanging graphene sheets

1 layer of graphene!
Preparation

1. Graphene sheet on substrate

2. Metal grid patterned onto the flake
3. Etching of substrate

4. TEM and electron diffraction analysis

Flake remains in metal grid
Electron diffraction:

Highly crystalline samples

Number of layers?
Diffraction tilt series!
One-layer graphene

Sheets fold back at the edges, and sometimes show a wrinkle within the sheet. HRTEM analysis of the folding allows to verify the layer count.
Two-layer graphene

2nm
Two-Layer Graphene

2 Layers

Stacking A/B

Intensity [a.u.]

11\bar{2}0
2 layers (g)

01\bar{1}0
1 layer (f)
8 layers
We Need
High Throughput
Non Destructive
Quick
Substrate Independent
Identification Technique

Raman Spectroscopy
514nm

Graphene

Graphite

Intensity

Raman shift (cm$^{-1}$)
Graphene

Intensity (a. u.)

Raman shift (cm\(^{-1}\))

514 nm

Graphite

G’ Peak

(2D peak)

Clear Fingerprint
D peak intensity
NOT related to Number of Layers
Disorder (in the widest possible meaning)

See Tuinstra Koening 1970…
Graphene

On Substrate

Suspended

Intensity (A.U.)

Raman Shift (cm\(^{-1}\))
2-Layers

514 nm

Intensity (A.U.)

Raman Shift (cm\(^{-1}\))

2600 2640 2680 2720 2760 2800

Intensity (A.U.)

Raman Shift (cm\(^{-1}\))
Slight Upshift ~ $5\text{cm}^{-1}$
The images show Raman spectroscopy results for graphite with different numbers of layers (1, 2, 5, 10) under 514 nm and 633 nm excitation wavelengths. The intensity is plotted against the Raman shift (cm$^{-1}$) for each layer configuration.
E) 2 Layer

514.5 nm

633 nm

D) 1 Layer

514.5 nm

633 nm

2D1B 2D1A 2D2A 2D2B

D1 D2

D

Edge

Graphite

Edge

1 Layer

Raman Shift (cm$^{-1}$)

Intensity (A. U.)

20000

15000

10000

5000

1000

500

0

2550 2600 2650 2700 2750 2800

Raman Shift (cm$^{-1}$)

Intensity (A. U.)
The Origin of G’ (2D) Peak

Named G’ since it is one of the 2 biggest peaks in graphite.

BUT it is the second order of D peak

Nothing to do with G peak

D forbidden in perfect crystal By
Raman Fundamental Selection Rule q~0

However 2\textsuperscript{nd} order always allowed: q+(-q)=0
D Peak Dispersion

Pocsik et al. (1998)

Vidano et al. (1981)
D peak comes from LO phonons
(Ferrari Robertson 2000)

Active by double resonance
(Baranov 1988, Thomsen-Reich 2000)

Strongly dispersive due to Kohn Anomaly at K
(Piscanec et al. 2004)
However...

Second order no defect scattering necessary

In principle ALL phonons active

BUT

Double resonant phonons enhanced
due to resonance and strong
electron-phonon coupling
Previous double resonance models predict multiple D peaks for graphene in contrast with experiments.

Double structure of 2D peak in graphite never explained.

Traditional interpretation (1980)
2 Maxima in graphite
Phonon Density of States at K and M WRONG since 2D disperses with excitation.

KEY: Evolution of Electron Bands with number of layers
Three Possible Processes

However: only 1 contributes
Three Possible Processes

However: only 1 contributes

Small: Trigonal Warping

Forbidden: EPC=0

Monolayer: $q = \text{ exchanged phonon momentum}$

$\varepsilon_L = \text{Laser energy}$  $\pi$  $\pi^*$

Fermi level

Monolayer: $q = \text{ exchanged phonon momentum}$

$\varepsilon_L = \text{Laser energy}$  $\pi$  $\pi^*$

Fermi level
Trigonal Warping Effect

- $q > K \rightarrow$ Strong EPC and large portion of the phase-space
- $q < K \rightarrow$ Strong EPC but small portion of the phase-space
- $q \sim K \rightarrow$ EPC $\sim 0$

1 Component D and 2D peaks

![Graphene Raman spectrum with D and 2D peaks](image)

- **Graphene**
  - Intensity (A.U.)
  - Raman Shift (cm⁻¹)
  - 514 nm

- **D**
  - Edge
  - 1 Layer
  - Raman Shift (cm⁻¹)
  - 514.5 nm

- **2D**
  - Intensity (A.U.)
  - Raman shift (cm⁻¹)
  - 514 nm
Two-layer Graphene

Two possibilities:

1) Phonon Splitting

2) Band splitting

Phonon Splitting
K-M is Minor

PRL 93, 185503 (2004)
Band Splitting Main Effect

<table>
<thead>
<tr>
<th></th>
<th>514.5</th>
<th>2 Layers</th>
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<tbody>
<tr>
<td>Experimental</td>
<td>-44</td>
<td>-10</td>
</tr>
<tr>
<td>Theory</td>
<td>-44</td>
<td>-11</td>
</tr>
<tr>
<td>633</td>
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<td>-10</td>
</tr>
<tr>
<td>Experimental</td>
<td>-44</td>
<td>-9</td>
</tr>
</tbody>
</table>

4 components
2 Most intense
Origin of Small Upshift of G peak

\[ \sim 5 \text{ cm}^{-1} \text{ Upshift} \]

IR
Raman Graphene
Raman Graphite
Kohn Anomaly

PRL 93, 185503 (2004)
Phonon-Linewidths and EPC

In a perfect crystal, phonon linewidths determined by interaction with other elementary excitations:

$$\gamma = \gamma^{an} + \gamma^{EPC}$$

$\gamma^{an}$: anharmonic contribution, due to interaction with other phonons. Determined by anharmonic terms in interatomic potential.

$\gamma^{EPC}$: interaction with electron-hole pairs. Determined by EPC and present in systems with null electron gap.
\( \Gamma - E_{2g}^{LO} \) Phonon Decay Processes

From the Fermi Golden Rule:

\[
\gamma_{\Gamma - E_{2g}^{LO}}^{EPC} \propto \frac{EPC(\Gamma)^2}{\beta^2}
\]
\( \Gamma - E_{2g}^{LO} \): Graphite Raman G Peak

- No D Peak
- No extra broadening due to disorder
- No FWHM(G) increase with temperature
- \( \gamma^{an} \leq 1.5 \text{ cm}^{-1} \) (spectrometer resolution)
- \( \text{EPC}(\Gamma) = 45.5 \text{ (eV/A})^2 \)
And... Single layer graphene...

Similar EPC

PRB 73, 155426 (2006)
Implications for Nanotubes

Single 2D peak graphene ⇒
Single 2D peak in Single Wall CNT

Curvature and confinement
give diameter dependence

2D(SWNT)~2D (graphene)- A/d

2D position in Graphite
should not be used to scale

Distribution of SWNTs of different diameters,
distribution of 2D peaks
What about Multi-Wall?

First approximation each wall gives a 2D peak

**DWNT two 2D peaks**  
(inner and outer wall)

** HOWEVER, inter-wall interactions**  
Can change simple picture  
Further splitting, Less peaks!

**Details to follow…**
Conclusions

Identified unique features of Raman spectrum, which fingerprints graphene amongst all other carbon allotropes.

The Raman spectrum evolution with increasing number of layers reflects the evolution of the electronic structure and electron-phonon interactions.

Raman spectroscopy is a quick, high-throughput, non-destructive technique for the unambiguous identification of graphene layers.

Raman+Graphene is Good Fun!
The Raman Fingerprint of Graphene

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Graphene is the two-dimensional (2d) building block for carbon allotropes of every other dimensionality. It can be stacked into 3d graphite, rolled into 1d nanotubes, or wrapped into 0d fullerenes. Its recent discovery in free state has finally provided the possibility to study experimentally its electronic and phonon properties. Here we show that graphene’s electronic structure is uniquely captured in its Raman spectrum that clearly evolves with increasing number of layers. Raman fingerprints for single-, bi- and few-layer graphene reflect changes in the electronic structure and electron-phonon interactions and allow unambiguous, high-throughput, non-destructive identification of graphene layers, which is critically lacking in this emerging research area.