Spatially resolved Raman spectroscopy on single- and few-layer graphene

D. Graf, F. Molitor, and K. Ensslin

Solid State Physics Zürich

C. Stampfer, A. Jungen, and C. Hierold, Micro and Nanosystems, ETH Zürich
L. Wirtz, Institute for Electronics, Microelectronics, and Nanotechnology, Lille

Raman on graphene
Spectral resolution
Spatial resolution
Phonon spectrum of graphite

- does the phonon spectrum depend on the number of layers?

Raman spectrum of graphite

- does the phonon spectrum depend on the number of layers?

$E_L = 2.33 \text{eV}$
Raman spectrum of graphite

- **Single-resonant**
  - at Γ point, $k \approx 0$
  - $\rightarrow G$, overtone $G'$
    - $(1582 \text{ cm}^{-1})$
  - $\omega_{\text{phonon}}$
  - $EL = 2.33 \text{ eV}$

- **Double-resonant**
  - close to $K$ point, $k > 0$
  - elastic scattering $\rightarrow D$
    - $(\sim 1350 \text{ cm}^{-1})$
  - $2\omega_{\text{phonon}}$
  - $EL = 2.33 \text{ eV}$
  - close to $K$ point, $k > 0$
  - $\rightarrow D'$ ($\sim 2700 \text{ cm}^{-1}$)

**Intensity (a.u.)**
- G
- D'
- G'
- (D)
Spatial resolution: AFM

Optical microscope

2 μm

Scanning force microscope

SiO₂

SFM height (nm)

Lateral position (μm)

→ Raman spectroscopy: characterize by optical means (# layers and structural quality)
Raman spectra of single-
and double layer graphene

Scanning force microscope

Scanning confocal Raman spectroscopy:
- Laser excitation of 532 nm/2.33 eV
- Spot size:
Raman mapping: intensity of G-line

Scanning confocal Raman spectroscopy:
- Laser excitation of 532 nm/2.33 eV
- Spot size: 1 μm

two layers have higher G-line intensity, slightly different peak position
Raman mapping:
intensity of G-line

Scanning confocal Raman spectroscopy:
- Laser excitation of 532 nm/2.33 eV
- Spot size: 1 μm

Scanning force microscope

Raman: Integrated G line intensity

Intensity (a.u.)
Lateral position (μm)

2-layer  1-layer  SiO₂
Raman mapping: position of G-line

HOPG reference: 1582 cm\(^{-1}\)
Raman spectra of single- and double layer graphene

Scanning force microscope

Scanning confocal Raman spectroscopy:
- Laser excitation of 532 nm/2.33 eV
- Spot size:

![Graphene Raman Spectra](image-url)
Raman mapping: FWHM of the D' line

Scanning force microscope

Scanning confocal Raman spectroscopy:
- Laser excitation of 532 nm / 2.33 eV
- Spot size: 1 μm

Raman: D' line intensity

Intensity (a.u.)

Raman shift (cm⁻¹)

1  ~ 30 cm⁻¹
2  ~ 60 cm⁻¹

two layers have broader G-line, different peak position
Raman mapping: 
FWHM of the D' line

Scanning force microscope

Raman: FWHM of D' line

Scanning confocal Raman spectroscopy:
- Laser excitation of 532 nm/2.33 eV
- Spot size: 

two layers have broader G-line, different peak position
D' line for single layer graphene

Related work: A.C. Ferrari et al., cond-mat/0606284
D’ line for double layer graphene

Related work: A.C. Ferrari et al., cond-mat/0606284
Detecting single layer graphene

Scanning force microscope

SFM height (nm)

Raman: FWHM of D' line

D' FWHM (cm⁻¹)

Lateral position (μm)
What about the D-line?

Scanning force microscope

Scanning confocal Raman spectroscopy:
- Laser excitation of 532 nm/2.33 eV
- Spot size:

![Graphene Raman Spectroscopy](image)

- Double-layer graphene
- Single-layer graphene

Raman shift (cm⁻¹)

Intensity (a.u.)
Raman mapping: intensity of the D line

Double-resonant

1) Crystallite grain size, symmetry breaking
   [Tuinstra and Koenig, 1970]
2) Defects, disorder in general
   [Y. Wang et al, 1990]

Momentum restoring: elastic scattering → D

Scanning force microscope

Raman: Integrated D line intensity

Symmetry breaking and defects
at edges and boundaries,
not within the flake.
Raman mapping: position of D-line

Scanning confocal Raman spectroscopy:
- Laser excitation of 532 nm/2.33 eV
- Spot size:
Raman mapping: intensity of G-line
Raman mapping: relative intensity of G/D'-line

- Height sensitivity for few-layer graphene
- Proportional to # of layers, but saturation above ~ 6 ML
Conclusions

- Raman spectroscopy: an alternative to scanning force microscopy
- Monolayer sensitivity (single to double layer)
- Defects/symmetry breaking at the edge (not within the flakes)

D. Graf et al., cond-mat/0607562, submitted
Related work: A.C. Ferrari et al., cond-mat/0606284, A. Gupta et al., cond-mat/0606593

Experiment:
Davy Graf, Françoise Molitor, and Klaus Ensslin
Solid State Physics, ETH Zürich, Switzerland

Christoph Stampfer, Alain Jungen, and Christofer Hierold
Micro and Nanosystems, ETH Zürich, Switzerland

Theory:
Ludger Wirtz
Institute for Electronics, Microelectronics, and Nanotechnology (IEMN), 59652 Villeneuve d'Ascq, France