Evolution of Raman Spectrum of Graphene with Thickness of SiO_2 Capping Layer on Si Substrate

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Outline

I. Background and Motivation

II. Method and Result

III. Summary

Graphene, an ideal 2D material with high mobility, transmittance, good mechanical properties, and anomalous quantum Hall effect.

The physical property of graphene is very sensitive to its number of layers

Methods used to identify number of layers of graphene:

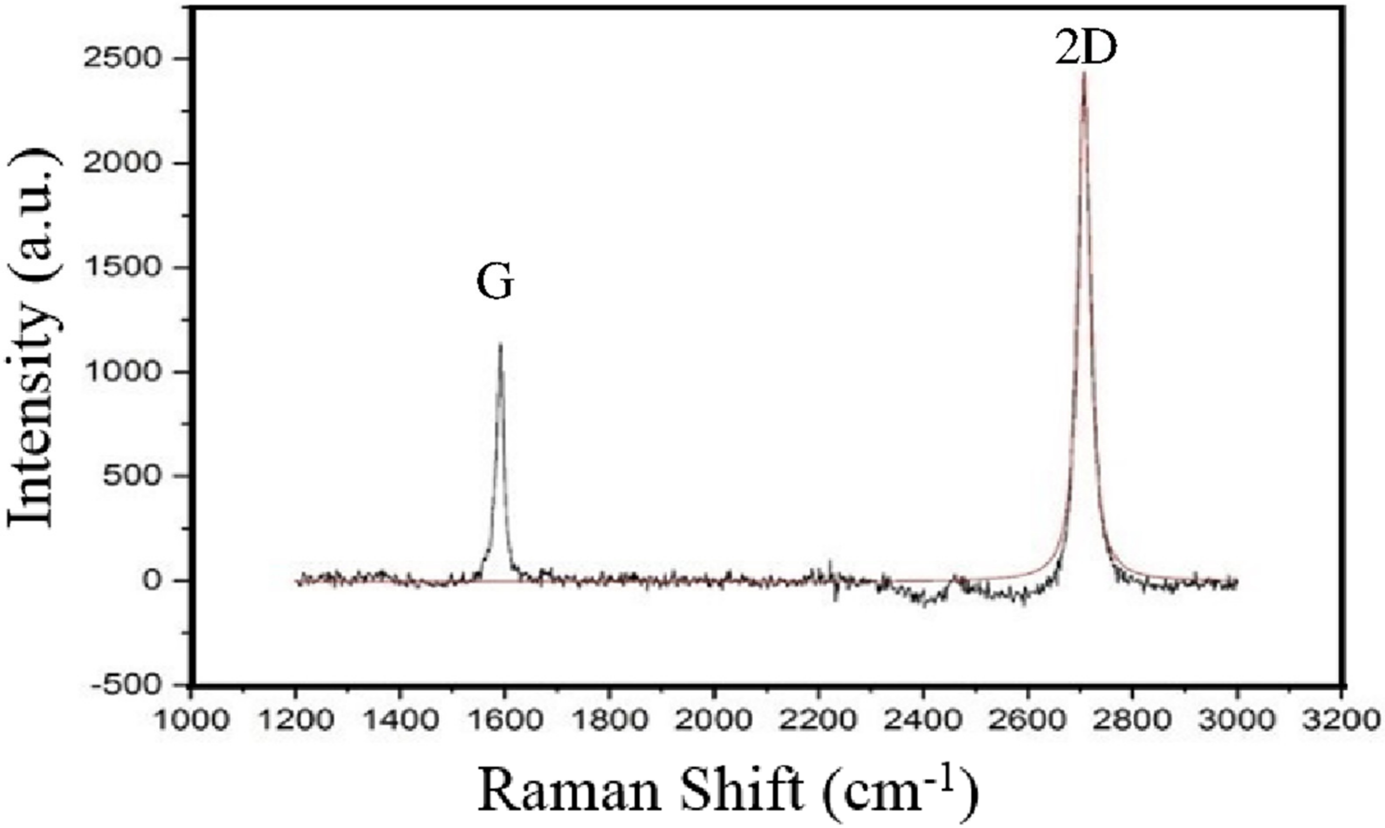
- AFM

Not so accurate, because of the existence of an air gap between the transferred graphene (grown by CVD) and the substrate, low throughput.

- TEM

destructive, low throughput.

Raman spectrum: in-situ non-destructive, high-throughput



the G band:1580.8 cm^{-1}, originating from the doubly degenerate zone center E_{2g} mode;
2D band: 2676.6 cm^{-1}, originating from second order of zone-boundary phonons

Using: (1) the shape, position, and width of 2D band;

(2) the intensity ratio of 2D to G bands (I_{2D}/I_G)

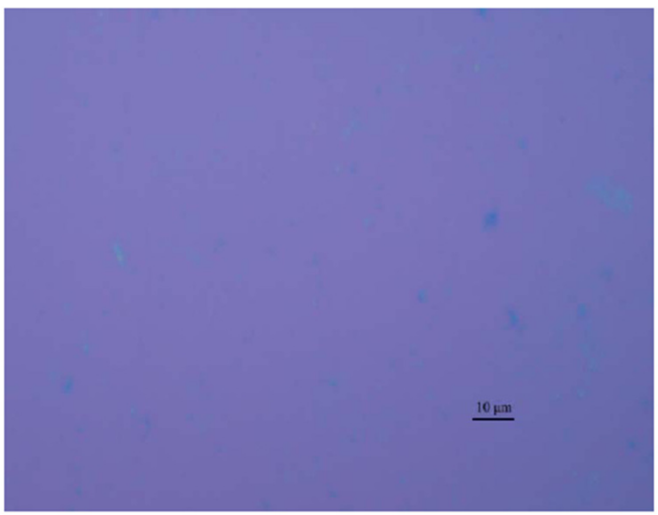
for monolayer, $I_{2D}/I_G \geq 2$; for bilayer, $I_{2D}/I_G \sim 1$

(A. A. Green, et al., Nano Lett. 9, 4031 (2009); X. Ding, et al., Carbon 49, 2522 (2011).)

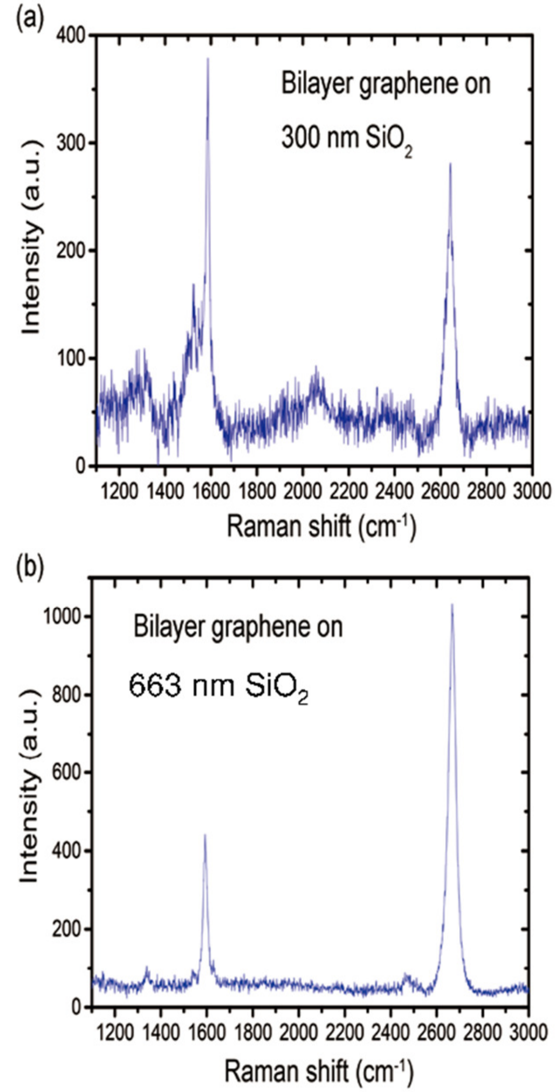
The latter is more common and convenient to be used, because it is less sensitive to measurement condition, such as equipment alignment etc.

However,

CVD equipment



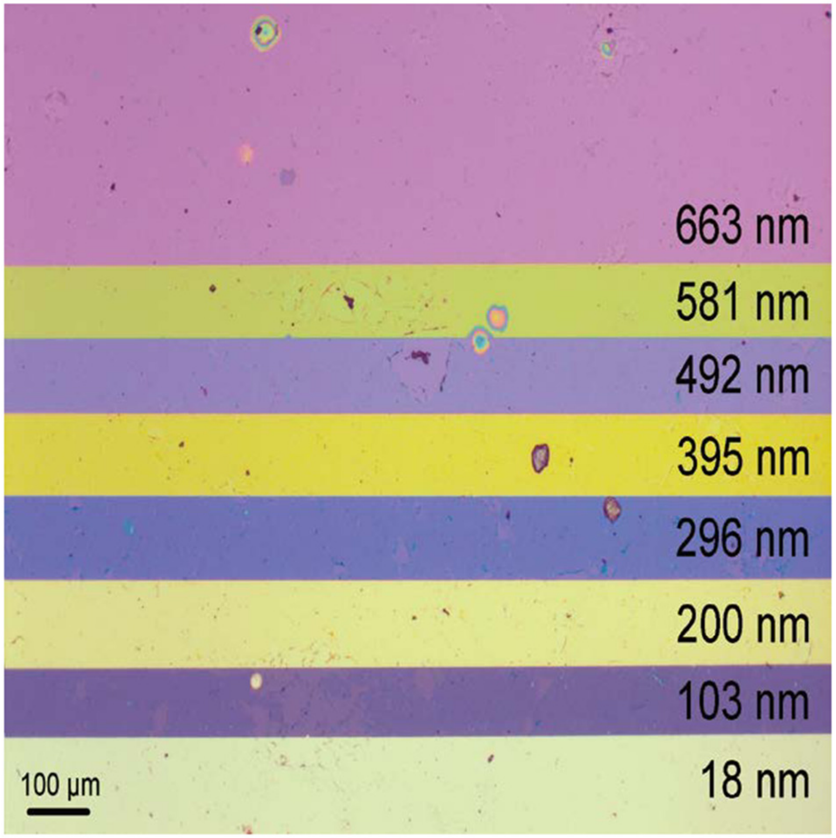
Optical image of graphene



The Raman spectra of bilayer graphene.

The effect of thickness of SiO_2 Capping Layer on the Raman Spectrum of Graphene

Chu Liu, and Lun Dai* *et al*, *Applied Physics Letters* 103, 213103 (2013).



The optical microscope image of a monolayer graphene on A SiO_2/Si substrate with various SiO_2 thicknesses

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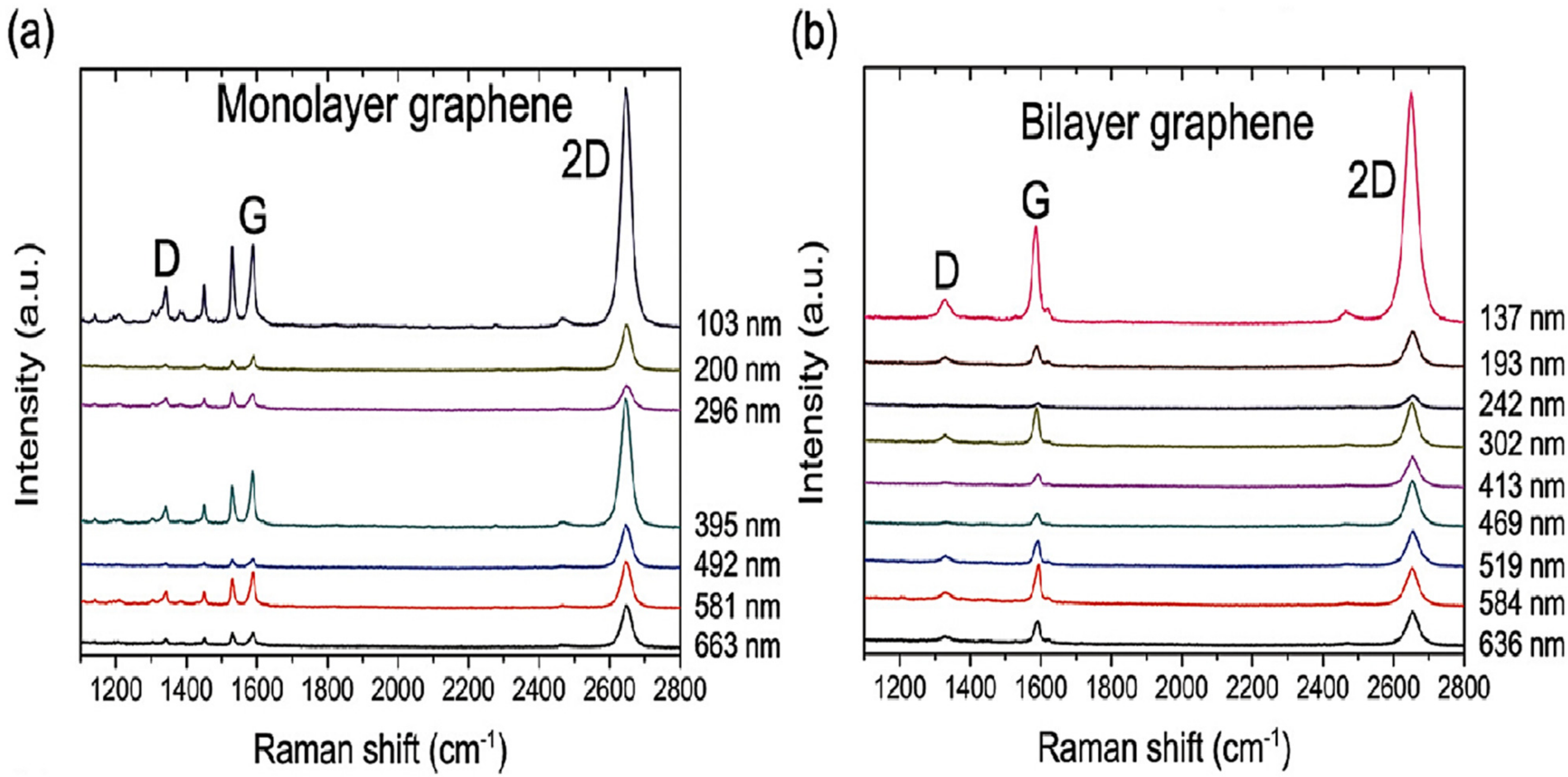
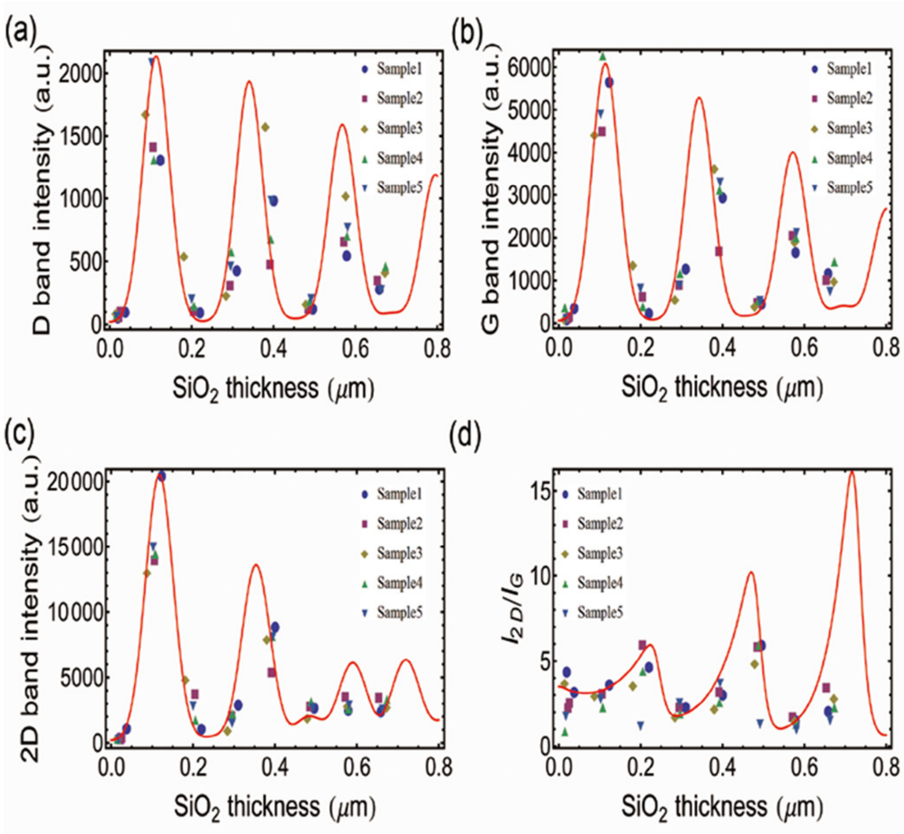


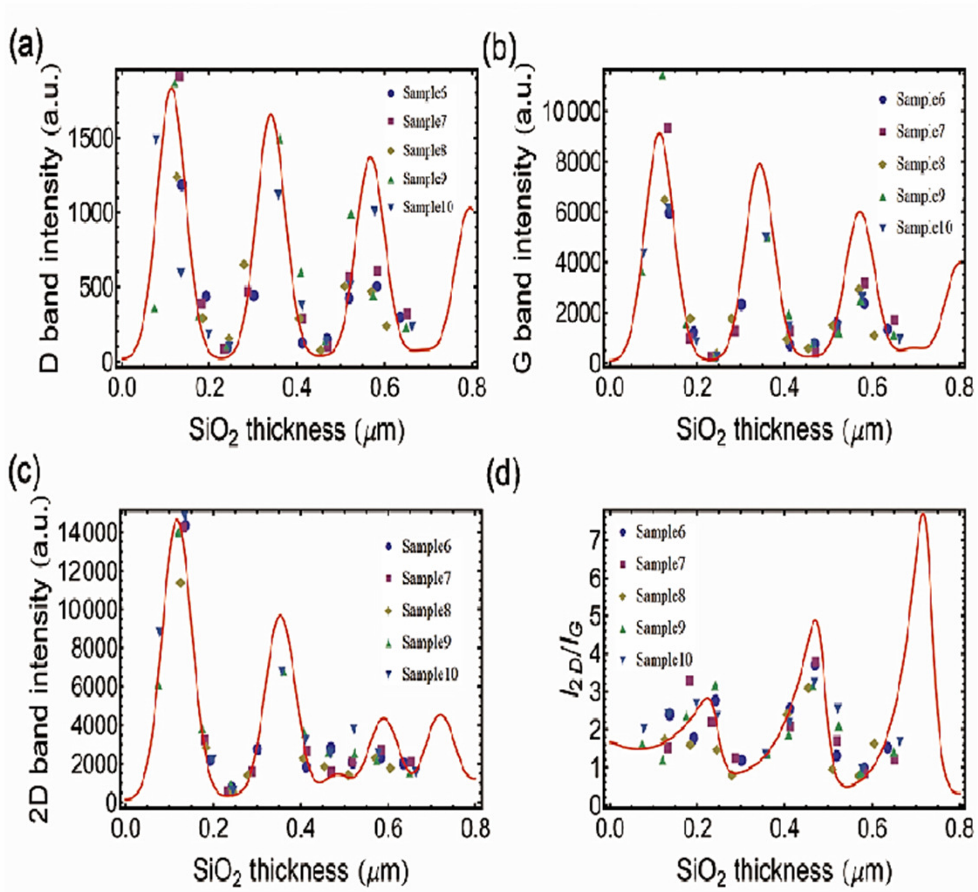
The evolution of Raman spectra with the thickness of SiO_2 for (a) monolayer and (b) bilayer graphenes, under 632.8 nm laser excitation. The two additional signals (1450 cm^{-1} and 1530 cm^{-1}) in (a) are the Raman signals of PMMA.



I_D、I_G、$I_{2D,}$ and I_{2D}/I_G oscillate with SiO_2 thickness.

Their amplitudes change with SiO_2 thickness .

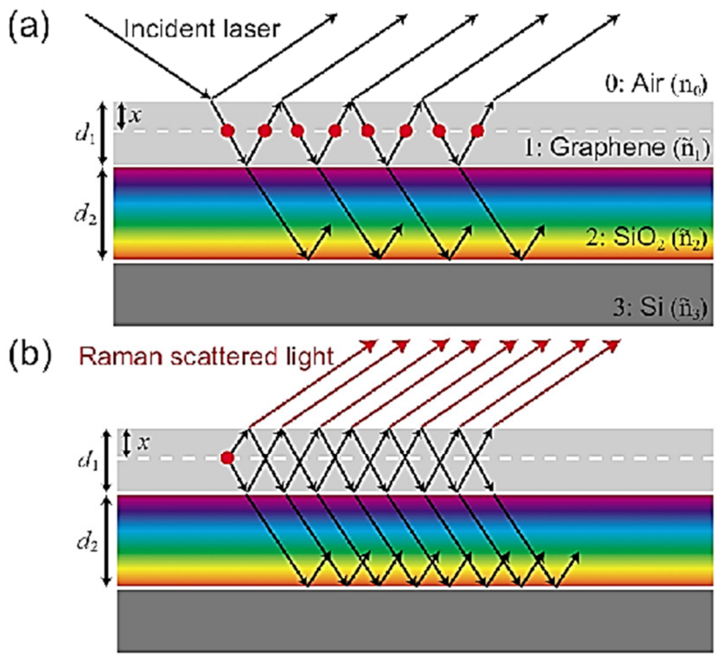
(a)–(d) The I_D, I_G, I_2, and I_{2D}/I_G of monolayer graphene as functions of SiO_2 thickness, respectively. The scattered data are the experimental results. The red lines are the theoretical results.



(a)–(d) The I_D, I_G, I_2, and I_{2D}/I_G of bilayer graphene as functions of SiO_2 thickness, respectively. The scattered data are the experimental results. The red lines are the theoretical results.

Y. Wang, et al., "Interference enhancement of Raman signal of graphene", Appl. Phys. Lett. 92, 043121 (2008).

Deducing a theoretical equation based on the Fresnel's equations (multireflection model (MRM)), by considering the interference of both incident light and Raman scattering light.



Schematic diagrams of MRM in the (a) absorption and (b) scattering processes

D. Yoon, et al., "Interference effect on Raman spectrum of graphene on SiO_2 /Si", Phys. Rev. B 80, 125422 (2009).

Modifying the MRM equation by taking account of the different wavelengths of the incident light and Raman scattering light.

- Mechanically exfoliated monolayer graphene;
- SiO_2 thicknesses: 240~380 nm.

$$F_{ab} = t_1 \frac{\left[1 + r_2 r_3 e^{-2i\beta_2}\right] e^{-i\beta_x} + \left[r_2 + r_3 e^{-2i\beta_2}\right] e^{-i(2\beta_1 - \beta_x)}}{1 + r_2 r_3 e^{-2i\beta_2} + (r_2 + r_3 e^{-2i\beta_2}) r_1 e^{-2i\beta_1}}$$

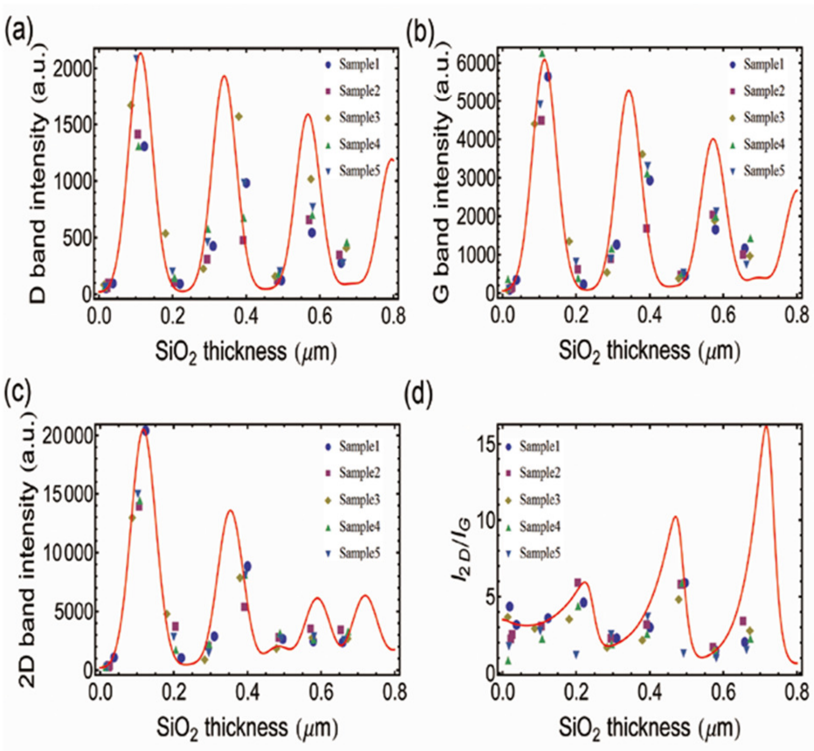
$$F_{sc} = t_1' \frac{\left[1 + r_2 r_3 e^{-2i\beta_2}\right] e^{-i\beta_x} + \left[r_2 + r_3 e^{-2i\beta_2}\right] e^{-i(2\beta_1 - \beta_x)}}{1 + r_2 r_3 e^{-2i\beta_2} + (r_2 + r_3 e^{-2i\beta_2}) r_1 e^{-2i\beta_1}}$$

$F = N \int_0^{d_1} |F_{ab} F_{sc}|^2 dx$, N: normalization factor

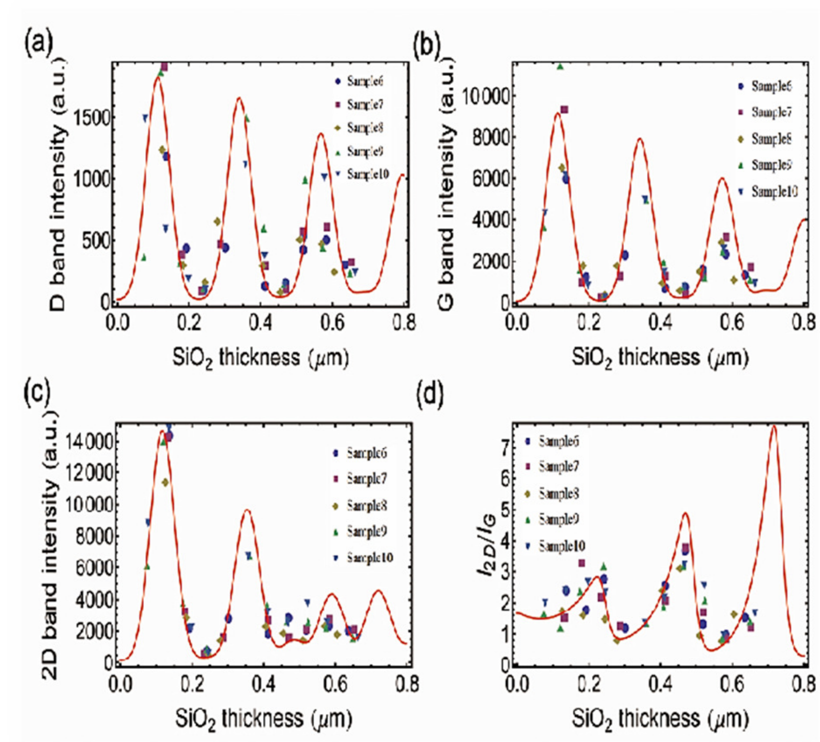
$I = I_i \cdot F$, F: total enhancement factor， I: measured Raman intensity, I_i:

- $\beta_x = \frac{2\pi x \widetilde{n_1}}{\lambda}$
- $\beta_1 = \frac{2\pi d_1 \widetilde{n_1}}{\lambda}$
- $\beta_2 = \frac{2\pi d_2 \widetilde{n_2}}{\lambda}$
- $t_1 = \frac{2 n_0}{\widetilde{n_1} + n_0}$, $t_1' = \frac{2 \widetilde{n_1}}{\widetilde{n_1} + n_0}$
- $r_1 = \frac{n_0 - \widetilde{n_1}}{n_0 + \widetilde{n_1}}$, $r_2 = \frac{\widetilde{n_1} - \widetilde{n_2}}{\widetilde{n_1} + \widetilde{n_2}}$, $r_3 = \frac{\widetilde{n_2} - \widetilde{n_3}}{\widetilde{n_2} + \widetilde{n_3}}$
- n_0=1, $\widetilde{n_1}$, $\widetilde{n_2}$, $\widetilde{n_3}$ **:** refractive indices

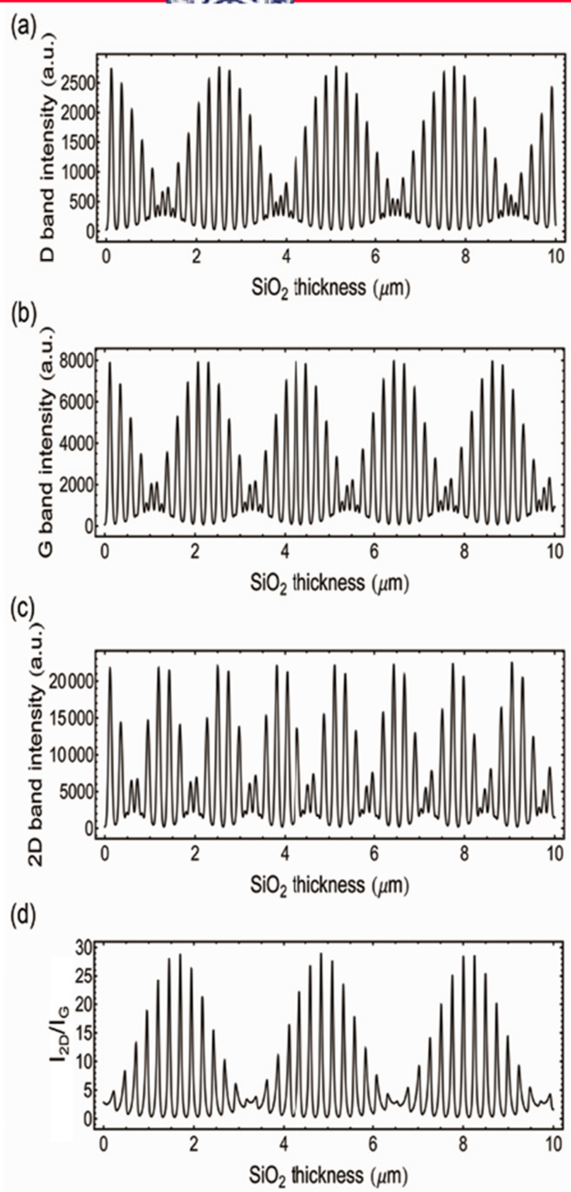
monolayer graphene



bilayer graphene



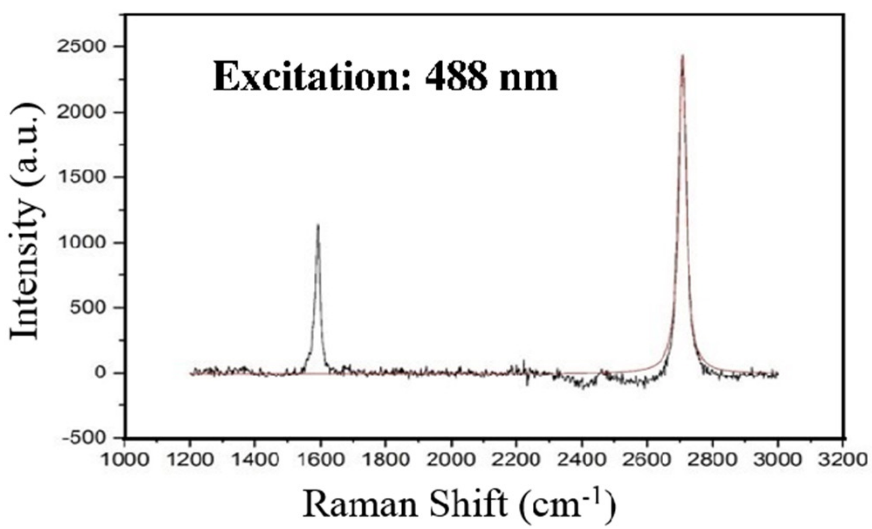
The criterion: monolayer: $I_{2D}/I_G \geq 2$; bilayer, $I_{2D}/I_G \approx 1$, is only correct for 300 nm SiO_2 capping layer.

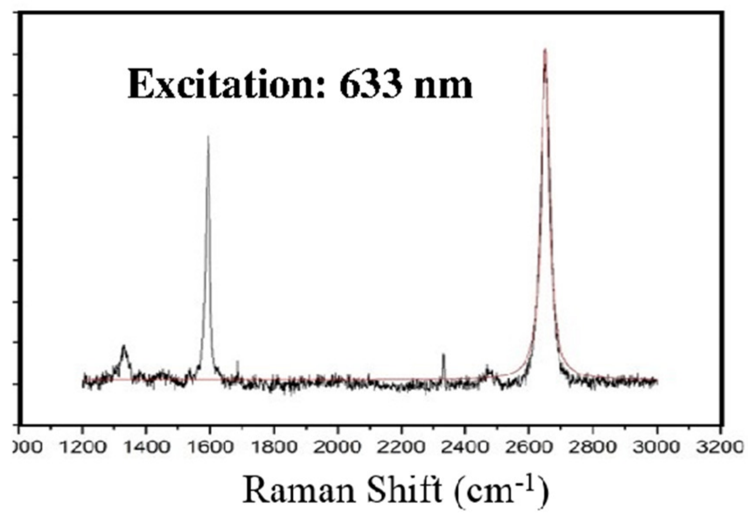


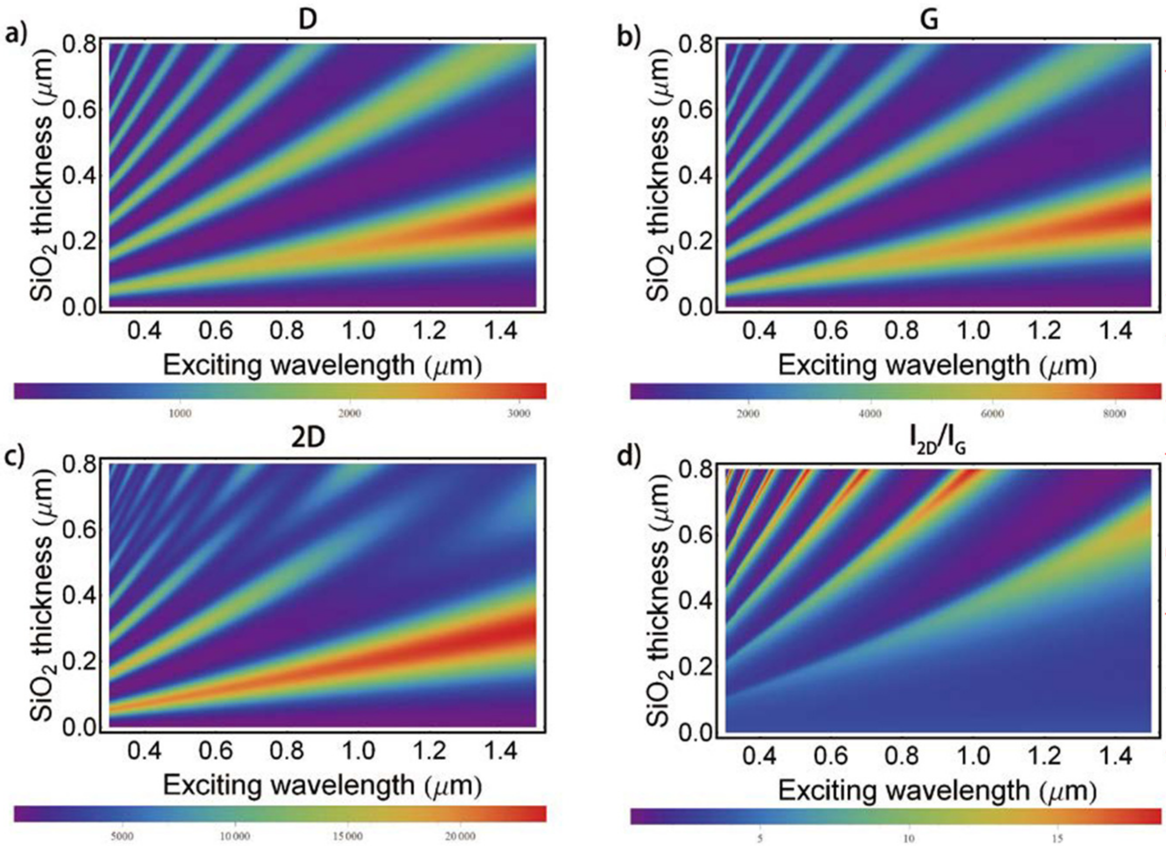
The calculated I_D (a), I_G (b), I_{2D} (c), and I_{2D}/I_G (d) of monolayer graphene as functions of SiO_2 thickness.

Their amplitude show a beat frequency behavior as a result of the wavelength difference between the incident light and Raman scattering light.

How about the effect of the excitation wavelength on the Raman signature of monolayer or bilayer graphene?







I_D、I_G、I_{2D}, and I_{2D}/I_G oscillate with excitation wavelength.

As the excitation wavelength increasing, the oscillation period becomes larger.

Their amplitudes show a beat frequency behavior with the excitation wavelength.

The color contour plots of I_D (a), I_G (b), I_{2D} (c), and I_{2D}/I_G (d) of monolayer graphene as functions of both SiO_2 thickness and excitation wavelength.

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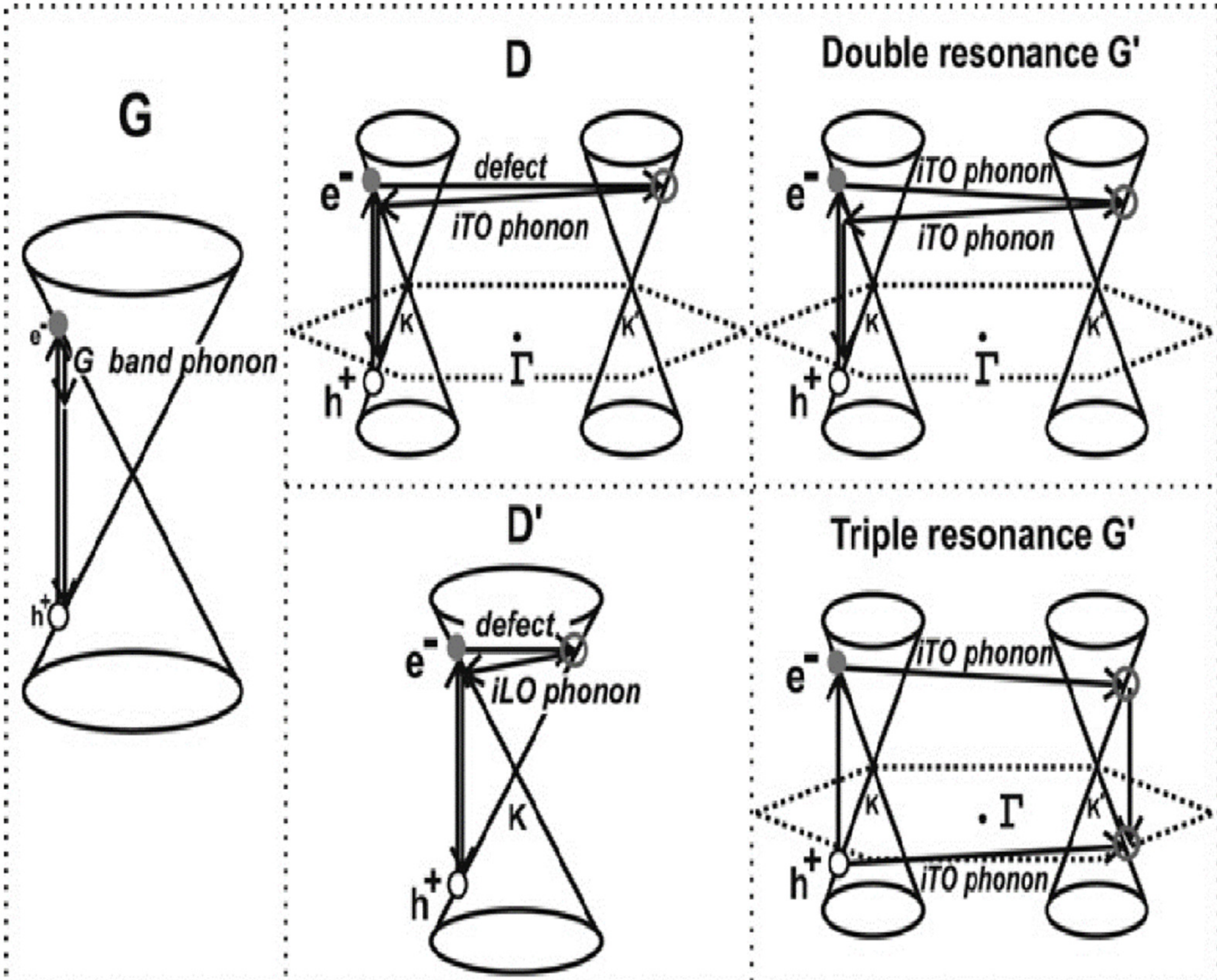
- **We have investigated the effect of SiO_2 thickness, as well as the incident light wavelength, on the Raman spectra of both monolayer and bilayer graphenes, which were grown by CVD and transferred onto the SiO_2/Si substrates.**
- **When the SiO_2 thickness or excitation wavelength increases, I_D、I_G、I_{2D}, and I_{2D}/I_G oscillate, and their amplitudes show a beat frequency behavior.**
- **One must pay enough attention to the SiO_2 thickness, as well as the excitation wavelength, when using the commonly used I_{2D}/I_G criterion to identify the number of layers of graphene.**

Thanks!



G
e-
G band phonon
h+
D
defect
iTO phonon
e-
K
K'
Γ
h+
Double resonance G'
iTO phonon
iTO phonon
e-
K
K'
Γ
h+
D'
defect
e-
iLO phonon
K
h+
Triple resonance G'
iTO phonon
e-
K
Γ
K'
h+
iTO phonon