Hunting monolayer graphene: How does the thickness affect the raman spectra of graphene?

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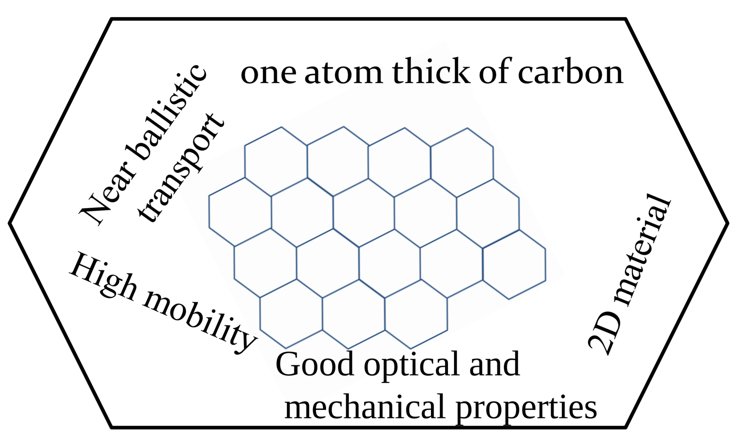
Abstract

Producing a monolayer graphene has been the target of many researches since its discovery. This leads to better use of Raman spectroscopy technique in terms of thickness determination of graphene due to its relatively easy and non-destructive set-up. Various studies were done to correlate the number of layers to the Raman spectra of graphene and suggest that layer thickness identification is based on the appearance, peak position and the intensity ratio of the G and 2D peaks. In this paper, we review the basic theory of Raman spectroscopy and discuss some fundamental principles regarding the effect of thickness to the Raman spectra of graphene such as the change in shape, position and relative intensity of G and 2D peaks as the graphene layer changes. For verification, we conducted mechanical exfoliation experiment and relate the spectra of graphene of few layers with the single layer. The result showed prominent peaks of G and 2D bands with wide peak difference between the monolayer and few layered graphene. The G and 2D bands in monolayer graphene appears to be upshifted and downshifted as compared to the few layered graphene, respectively, and has intensity ratio (I_{2D}/I_G) of ~ 4.04. These results are in good agreement with the previously reported studies which suggest that hunting monolayer graphene can be effectively done using Raman spectroscopy.

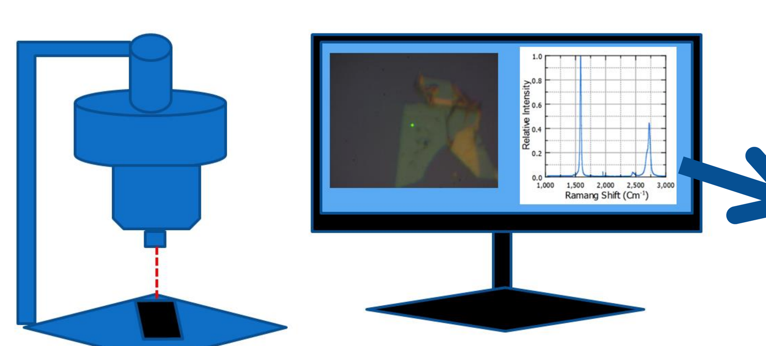
Introduction

Why care about graphene?

Graphene



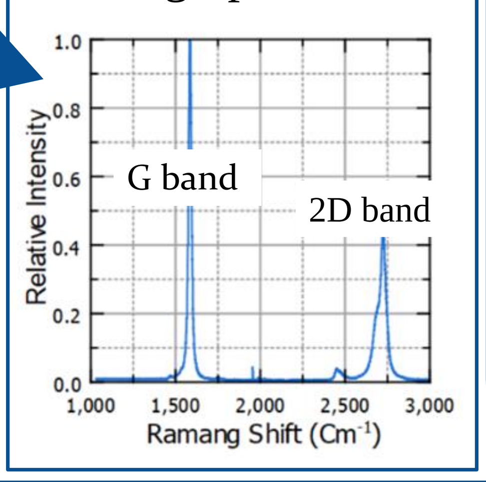
Ideal characterization for graphene thickness identification.



Raman spectroscopy

Pros of Raman spectroscopy [1]
- Fast and non-destructive.
- Offer high resolution.
- Provide structural and electronic information.

Raman peaks used for thickness identification of graphene.

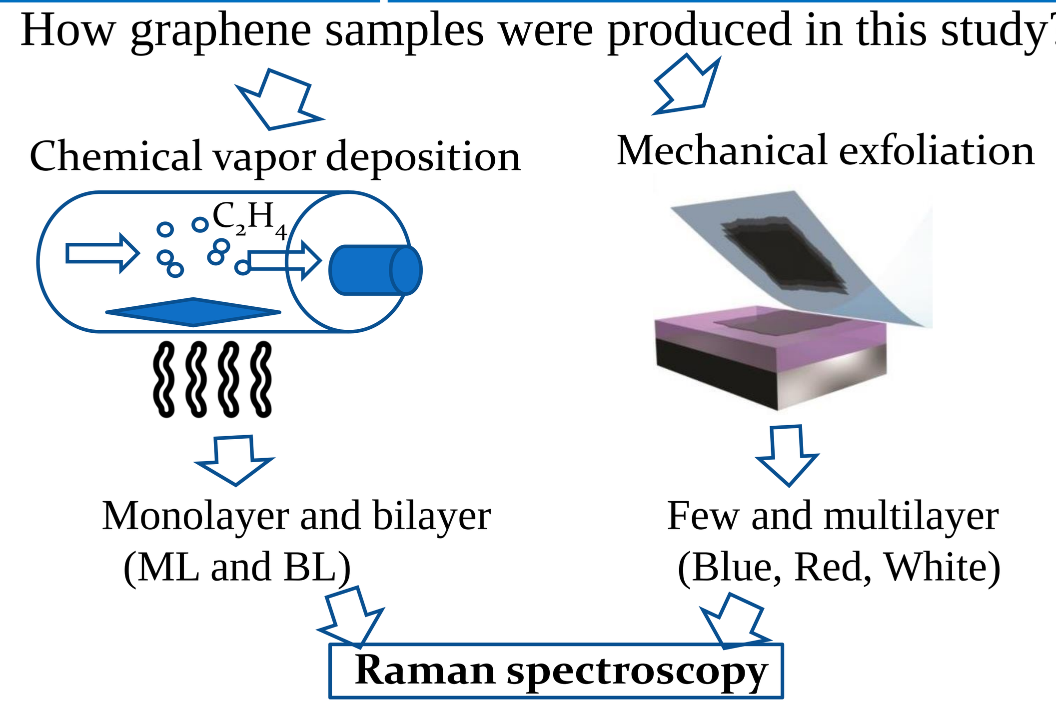


In this study....

→ We examine the Raman spectra of few layer, multi-layer, bilayer and monolayer graphene and discuss how the Raman spectra of graphene changes with layer thickness.
→ Aside form the intensity ratio ($I2_D/I_G$), consideration on the individual properties of G and 2D peaks is crucial.
→ Here, the the peak positions (G and 2D), FWHM and shape of the peak with respect to the thickness were analyzed.

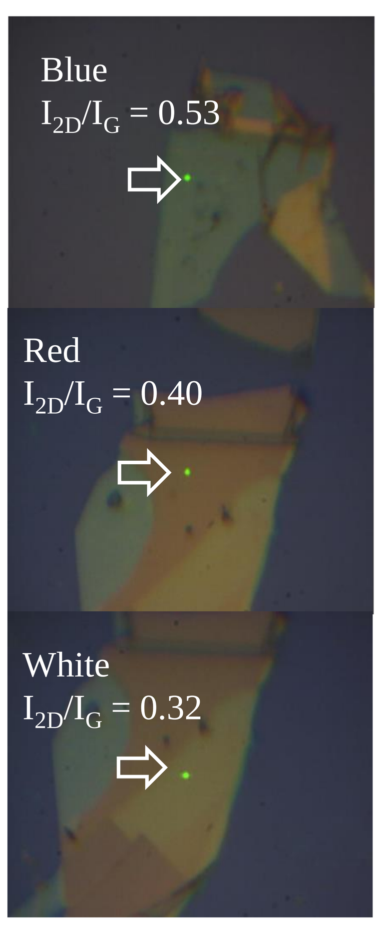
Experimental

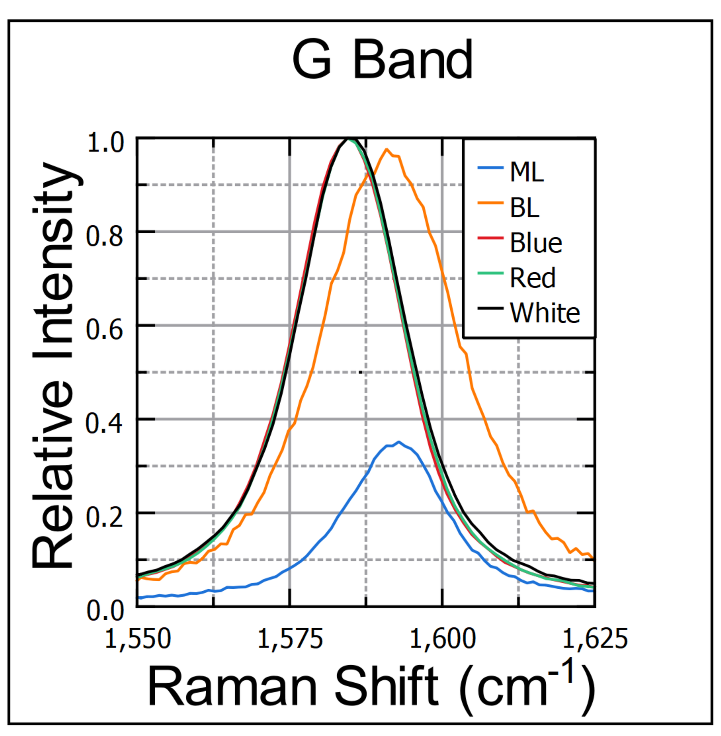
How graphene samples were produced in this study?



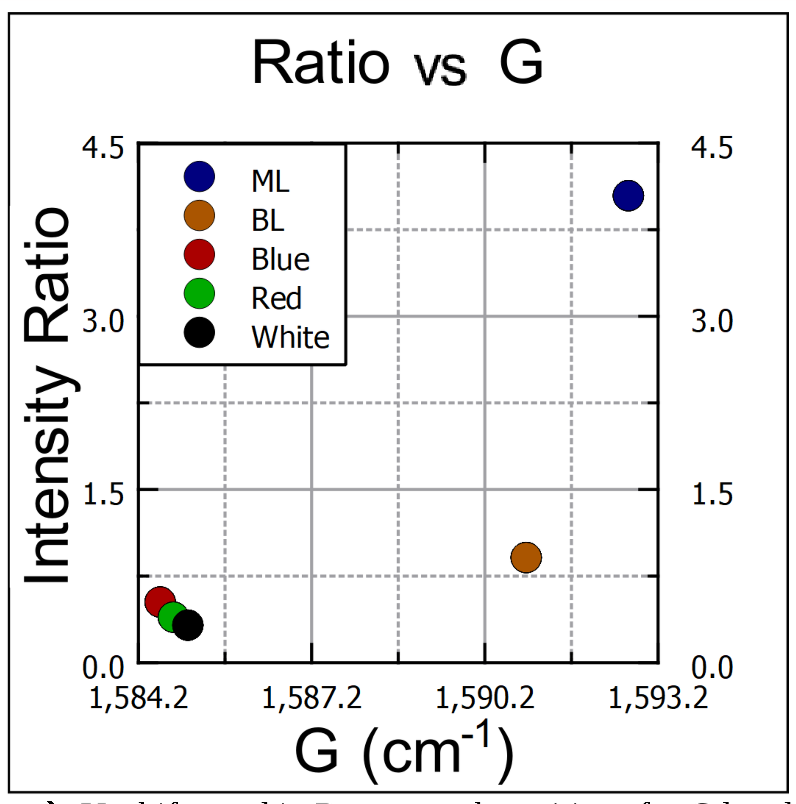
Results

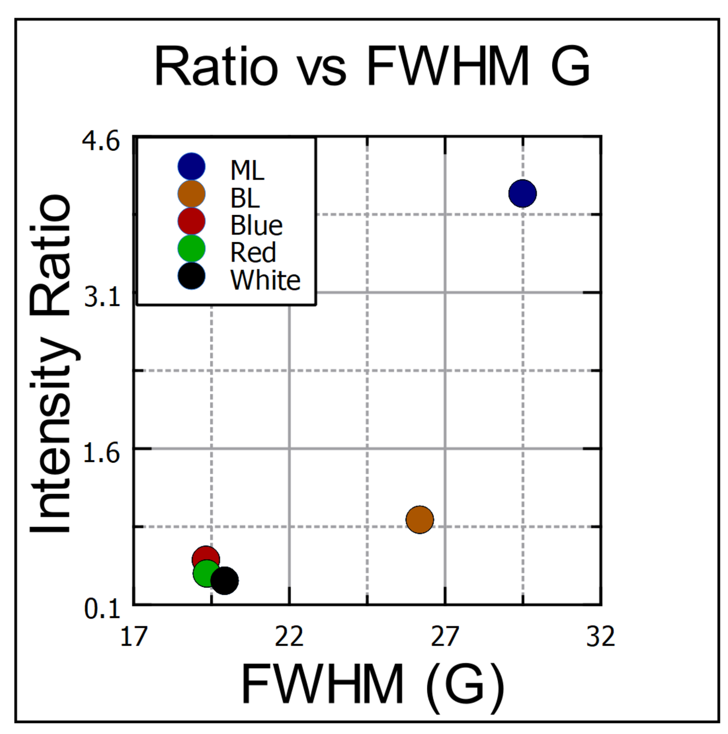
Micrograph images and locations of multi-layer and few-layer graphene.



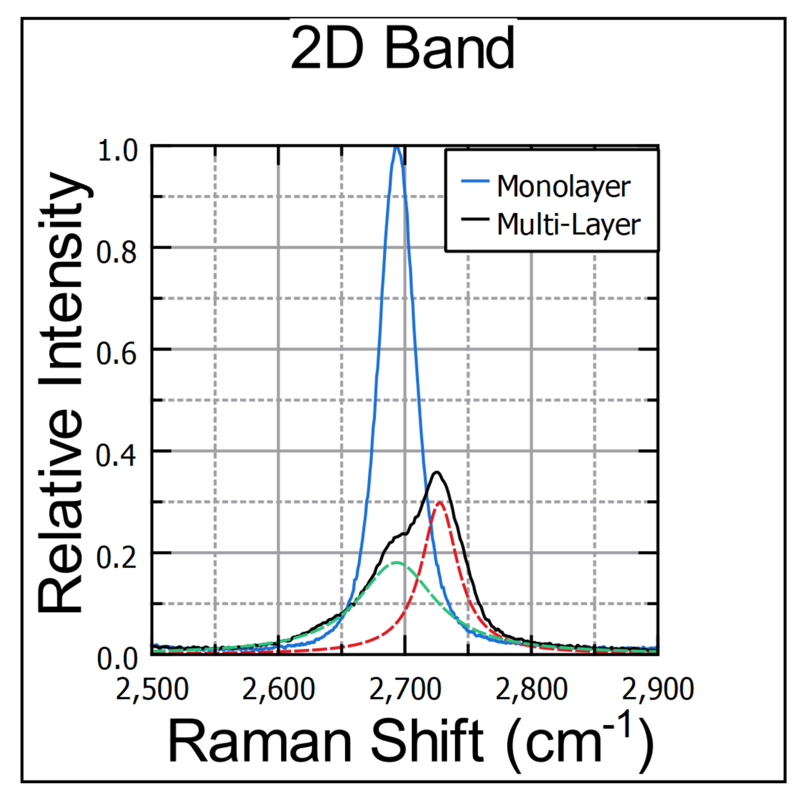


G band intensity for monolayer (ML), bi-layer (BL), few layer (Blue), and multi-layer (Red and White) graphene.





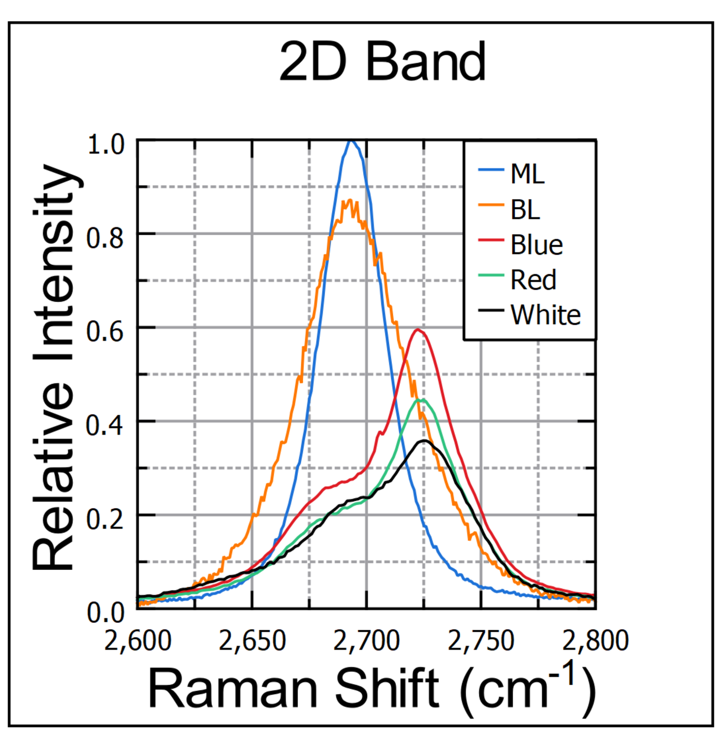
→ Upshift trend in Raman peak positions for G band.
→ Increasing trend in FWHM for G band.
→ No significant trend in FWHM for 2D band between few and multi-layer graphene.
→ No significant trend in peak position for G band between few and multi-layer graphene.
→ For ML, the FWHM value of ~ 30cm^{-1} [2] while the G peak position ~ 1592 cm^{-1}[3].



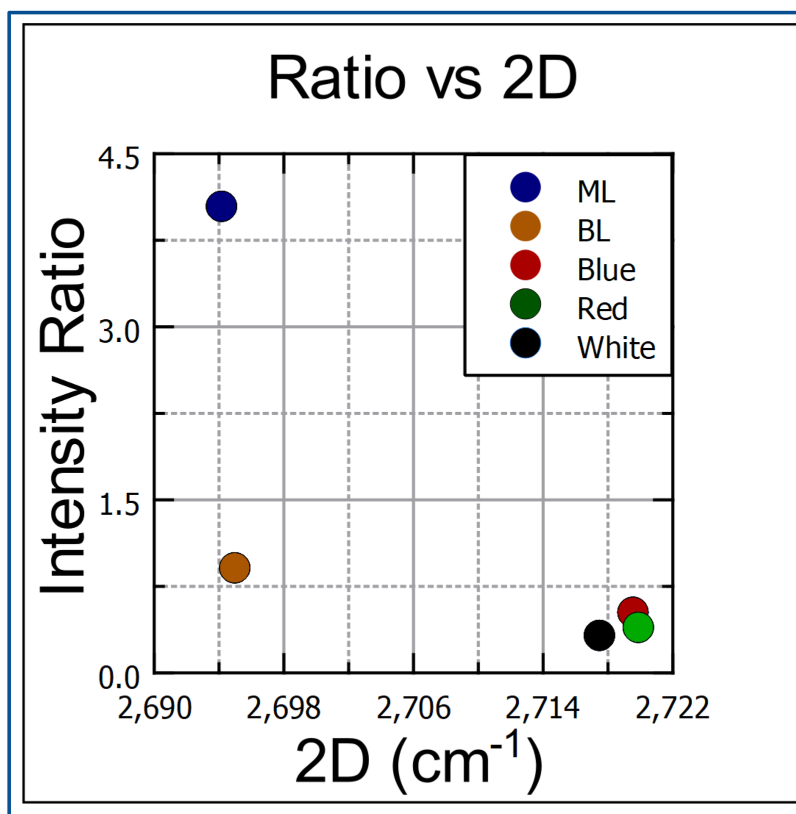
2D band for monolayer graphene has one peak while the multilayer graphene has two peaks. One de-convoluted peak from multilayer has similar position with the monolayer.

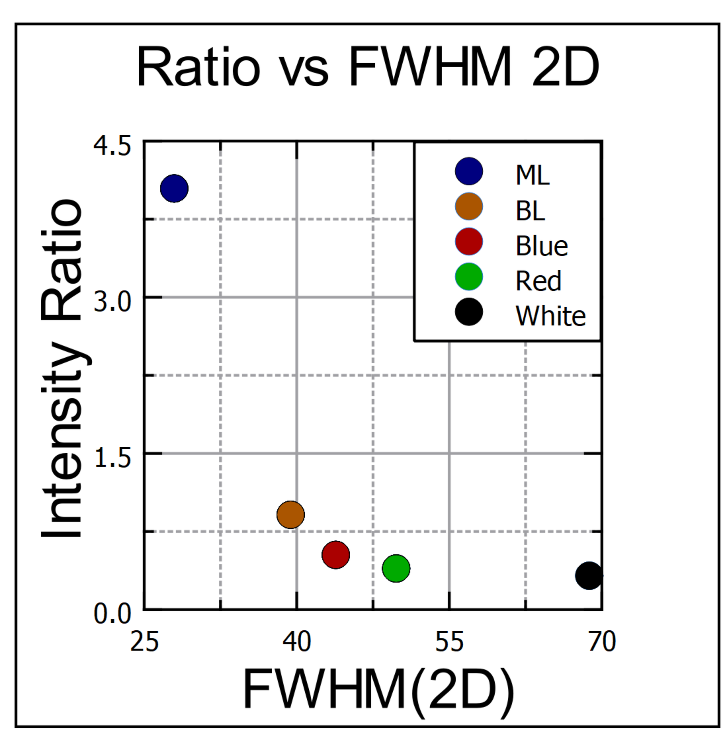
Calculated intensity ratio from 2D and G band

Sample	I2D/IG
ML	4.04
BL	0.999
Blue	0.53
Red	0.40
White	0.32



2D band intensity for monolayer (ML), bi-layer (BL), few layer (Blue), and multi-layer (Red and White) graphene.





→ Downshift trend in Raman peak positions for 2D band.
→ Decreasing trend in FWHM for 2D band.
→ Decreasing trend in FWHM for 2D band between few and multi-layer graphene.
→ No significant trend in peak position for 2D band between few layer and multilayer graphene.
→ For ML, the FWHM value of ~ 28 cm^{-1} while the 2D peak position ~ 269 cm^{-1}[10].

Discussion

→ The results are in agreement with the previous reported studies for the Raman signature of monolayer graphene [4,5,6].
→ 2D band is much more sensitive to layer stacking of graphene and significant trend is observed in its FWHM with respect to layer thickness [8].
→ FWHM for 2D bands appear to decrease exponentially with respect to the increasing intensity ratios.
→ This is because the 2D peaks are from the intervalley scattering at the K point in the brillouin zone which is highly affected by the change in band structure as the layer increases [2].
→ The change in band structure could also be the reason for the evolution of two peaks in the few layer and multilayer graphene [7].
→ Equations reported by Wang X. et al. could explain the effect of layer thickness to the FWHM and the shifting of 2D band[8].

Phonon energy (cm⁻¹)

$$\frac{1}{2}\omega_{2D} \approx \omega_{D_0} + \frac{v_{ph}}{v_F} \cdot \left(\frac{E_L}{hc} - \omega_{D_0}\right)$$

(FWHM) linewidths (cm⁻¹)

$$\delta\omega_{2D,io} \approx 4\left(\frac{v_{ph}}{v_F}\right)_{i,o} \frac{\gamma_{i,o}}{hc}$$

where: v_F= Fermi velocity, v_{ph} =phonon velocity

→ Chuang K-H et al. reported that as the graphene thickness decreases the Fermi velocity increases[9]. Therefore, the Fermi velocity (v_F) can affect the peak position and FWHM of the 2D band
→ The change in Fermi velocity resulted to the downshift in the peak position of 2D and decreases the value of its FWHM.

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Conclusion

→ Mechanical exfoliation offers cheap and easy method to produce graphene for advanced research.
→ Thickness determination in graphene could be easily done using Raman spectroscopy.
→ 2D band analysis is reliable counterpart for layer identification since it is more sensitive to layer stacking.
→ G band and 2D band peak positions are not sensitive to the variations of layer thickness between few layers and multi-layers.
→ FWHM for G band in few layer and multi-layer graphene showed no significant trend.
→ Hence, using Raman spectroscopy for thickness determination between few-layers and multi-layers is challenging. Raman spectroscopy can only distinguish efficiently the graphene layers of not more than 5 [2].
→ The Fermi velocity relationship with graphene thickness is partly the reason for the shift of the 2D band peak and the decreasing trend of its FWHM.

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