Determining Graphene Stacking via Raman Spectroscopy

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Abstract

Graphene, a planar, atomically-thin layer of graphite exhibits outstanding electrical, mechanical, and thermal properties.[1] Multilayer graphene can be characterized by the relative stacking of its individual layers and the ability to expediently determine stacking registry is crucial to engineering around graphene's novel properties. While stacking registry is often determined via relatively technical procedures such as near-field spectroscopy, previous studies have found minor differences in the Raman spectrum of differently stacked graphene.[2] Therefore, Raman spectroscopy is an enticing tool for characterizing stacking. Our project seeks to determine the practical feasibility and limitations of such techniques in determining the stacking of trilayer graphene (3LG).

Background

The stacking of 3LG is characterized by the relative positions of the graphene layers, known as stacking registry. 3LG has three possible stacking registries: AAA, simple hexagonal; ABA, Bernal; and ABC, rhombohedral. (Image 1) Note, Bernal stacking is the most stable at room temperature and constitutes ~ 85% of exfoliated trilayer graphene while the metastable ABC stacking makes up ~ 15%.

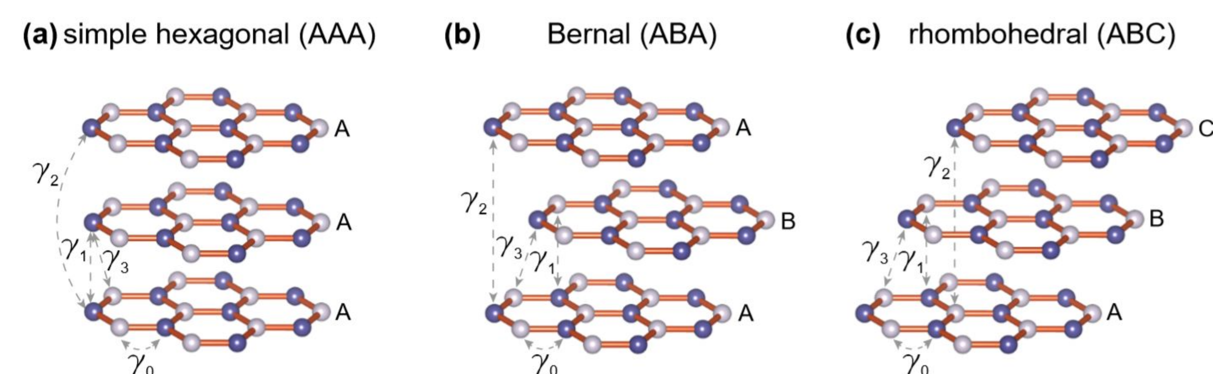

Image 1. Stacking registries of graphene, from *Stacking-dependent electronic structure of trilayer graphene resolved by nanospot angle-resolved photoemission spectroscopy,* Bao. et al.

Raman spectroscopy is a technique used to probe a material's vibrational states by measuring the energy shift of an exciting laser. The Raman spectrum of graphene is primarily characterized by two main peaks: the G (1580 cm^{-1}) peak of an in-plane vibrational mode, and the 2D (2690 cm^{-1}) second-order overtone of a different in-plane vibrational mode.[3] [4]

Recent literature suggests that Raman spectroscopy can differentiate stacking registries.[5] These experiments, in conjunction with theory, predict that ABC has a slightly lower (~ 5 cm^{-1}), or redshifted, G-mode peak than that of ABA. In addition, ABC was found to have a narrower G-mode peak width than that of ABA.[1] Our work seeks to corroborate these results and determine if Raman spectroscopy is an effective, and practical tool for measuring stacking registry.

Methods

3LG was prepared by mechanical exfoliation of graphite crystals onto a 90 nm SiO_2/Si substrate. An optical microscope was utilized to determine 3LG (Image 2) and the stacking of our graphene sheets were determined via near-field spectroscopy (Image 3). We would like to acknowledge Li Hongyuan for ultimately providing the 3LG sample and associated near-field spectroscopy image presented in this project as our attempts at producing a viable sample was unsuccessful in the limited time.

Raman spectroscopy of our 3LG sample was conducted by backscattering 532 nm (2.33 eV) laser radiation focused to a spot of ~1 μm.

Analysis

Having obtained the raw Raman spectrum, we averaged data of similar stacking into a single data points before conducting fruthur analysis in order to remove the effect of random noise. (Figures 1-2) Next, we focussed specifically on the Raman shifts corresponding to the local maximum of the G mode: ~ 1520-1540 cm^{-1}. (Figure 3) Having noticed a difference between the ABA* and ABC* samples, we plotted the residuals of our data in order to understand the significance of our observed variation. (Figure 4)

Results

We expect the G mode for ABC to be slightly red-shifted narrower as compared to the mode for the ABA sample.[5] This would correspond to a relatively flat (ABC*-ABA*) residual plot and a downward trend at the G-peak (red-shift). Instead, we observed the ABA sample to be narrower than the ABC sample - corresponding to a peak in our residual plot instead of a trough. This result contradicts previous predictions. However, an important point to note is that the ABA* confidence interval overlaps with that of ABC*. (Figure 3) This is an indication that our results may not be as significant as they appear. Instead, we can only definitively conclude that our attempt to use Raman to differentiate 3LG stacking has been unsuccessful.

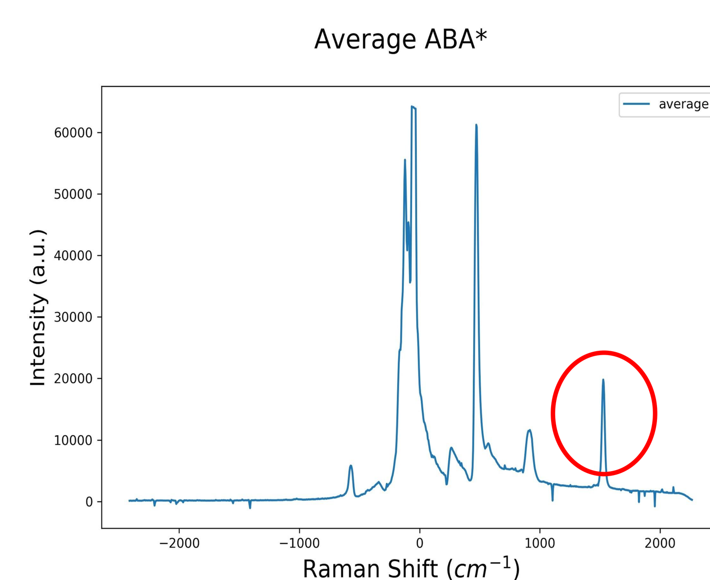

Figure 1. Average of three Raman spectra taken over sample regions predicted to be ABA.

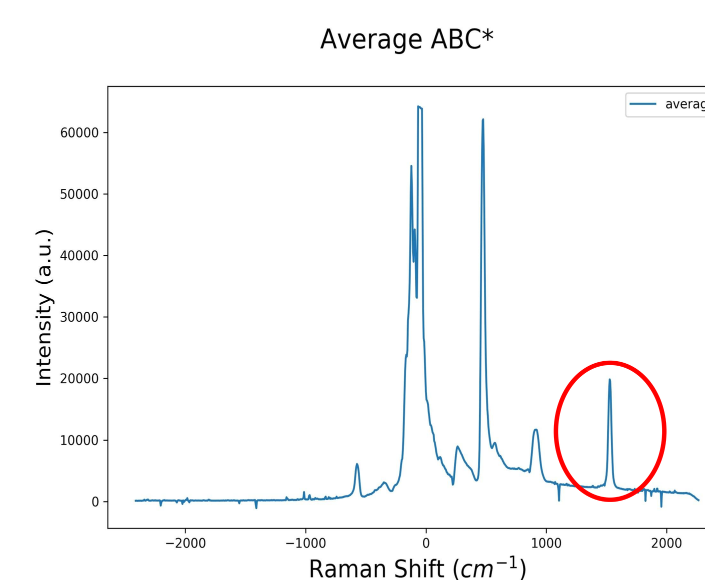

Figure 2. Average of three spectra taken over regions predicted to be ABC.

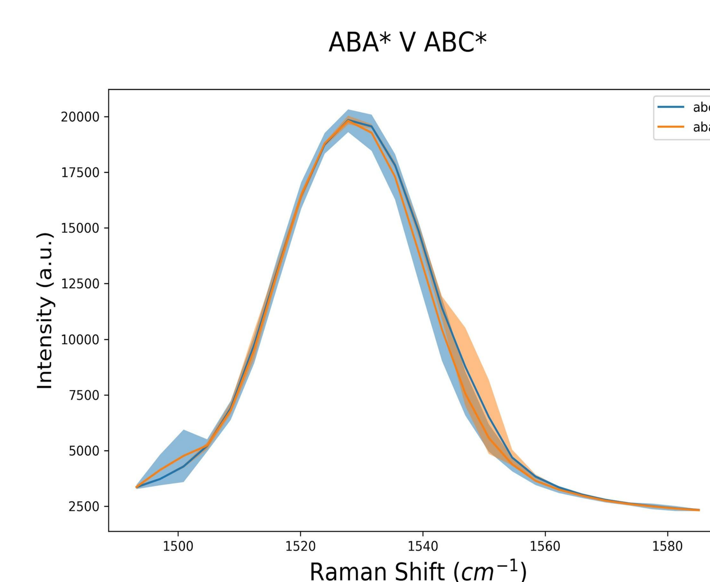

Figure 3. G-mode Raman spectrum of possible ABA* and possible ABC* sample with their 95% confidence intervals.

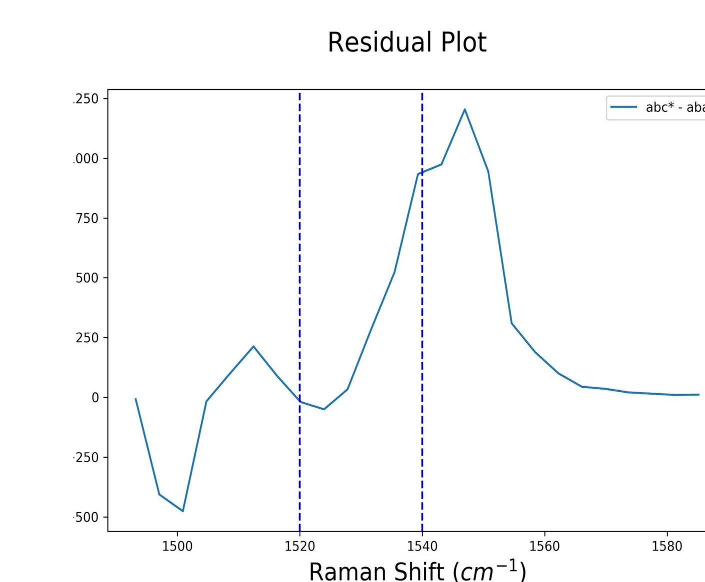

Figure 4. Residual of possible ABC* relative to possible ABA* at the G mode.

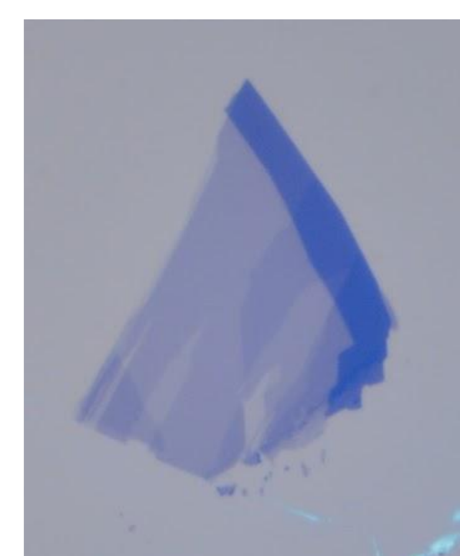

Image 2. Optical microscopy of 3LG on 90 nm SiO_2/Si substrate.

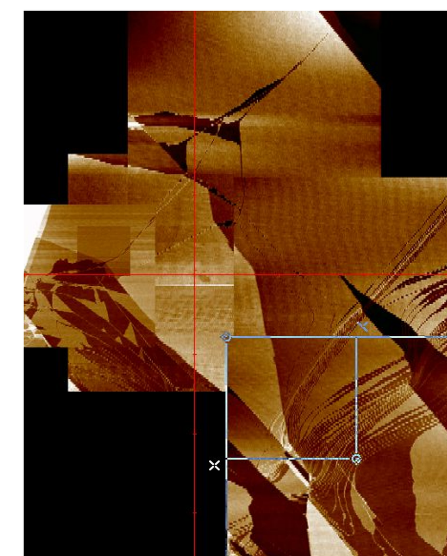

Image 3. Near Field Spectroscopy to determine stacking of trilayer graphene.

Limitations of Raman Spectroscopy

From our results, we conclude that while Raman spectroscopy can be used to determine multi-layer graphene stacking, it is severely limited in feasibility and practicality. To begin, the distinguishing power of Raman spectroscopy appears to be very low as differences between ABA* and ABC* spectra come close to the noise threshold of our measurements. In addition, due to the fine size of the laser beam (~1 μm), it is extremely difficult to precisely guide the beam. Thus, our results are further obscured by the fact that we can not be entirely certain where the sample is measured.

Assuming our technique can be significantly refined, the process of determining stacking via Raman spectroscopy is nevertheless marred by practical considerations. Graphene stacking is in-homogenous throughout a flake, and thus, multiple exposures would be required to fully characterize macroscopic stacking. This is further exacerbated by the large amount time required to setup and collect data. We therefore find that Raman spectroscopy is a plausible but not an effective technique for determining the stacking of a graphene samples in light of more precise, though more time consuming, tools such as near field.

Future Work

X-ray diffraction (XRD) is another promising tool in determine stacking registry. Like Raman spectroscopy, XRD can be used to take non-destructive measurements with minimal sample preparation and has been used in practice to determine stacking registry.[6] However, XRD will likely face similar limitations as those of Raman spectroscopy above due to its similarities with the technique.

Nevertheless, XRD is a technique worth exploring because of its potential to determine more information than stacking in a single scan: for example, crystallinity and defect concentration.[7] Future work to investigate XRD's viability as a method for characterizing graphene will be valuable.

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