Raman characterization of AB- and ABC-stacked few-layer graphene by interlayer shear modes

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1. Introduction

Monolayer graphene (1LG) has received intensive interest because of its unique properties [1–5] which provide the impetus for potential applications as electronic and photonic devices. 1LG can be stacked vertically to form N layer graphene (NLG, N > 2) with distinctive band structures. For example, 1LG is a zero-gap semimetal [2,3], whereas bilayer graphene (2LG) is a semiconductor with a tunable band gap [6]. The band structure of trilayer graphene (3LG), in fact, strongly depends on the stacking of the individual graphene sheet. Bernal (AB) and Rhombohedral (ABC) stacking orders are much common in the formation of a few-layer graphene (FLG). AB-stacked 3LG (AB-3LG) has an electrical structure of over- and under-dens are much common in the formation of a few-layer graphene (FLG). AB-stacked 3LG (AB-3LG) has an electrical structure of overlapping linear and quadratic bands [7] while that of ABC-stacked 3LG (ABC-3LG) has a cubic dispersion [8]. When an electric field is applied to 3LG, AB-3LG remains metallic at all fields while ABC-3LG behaves in a similar manner to 2LG with a tunable band gap [9]. The ABC-stacked NLG (ABC-NLG, N > 3) is predicted to have even lower kinetic energy than 1LG, 2LG and 3LG, which affords an alternative approach to promote Coulomb interaction between carriers [10]. Besides the band structure, AB-stacked NLG (AB-NLG) and ABC-NLG also exhibit different interlayer screening [11], magnetic state [12,13] and spin–orbit coupling [14]. In view of these differences, researches on NLG require a direct, practical and reliable method to characterize their stacking order at room temperature.

The intrinsic difference in symmetry between AB- and ABC-NLG brings us into the frontier of vibration spectroscopy. Although IR spectroscopy provides a mean of identifying stacking order [15], it requires the specialized instrumentation. Raman spectroscopy, on the other hand, has many advantages over IR spectroscopy and yet has been a versatile tool for studying the properties of graphene [16–18]. For example, the D mode which needs disorders for its activation is widely used to characterize the defects [19] and edges [20–22] in 1LG and FLG. The 2D mode, the second order of the D mode, affords a method to characterize the layer number (N) of AB-NLG (N = 1 ~ 4) [23]. Previous Raman characterization of AB- and ABC-stacked FLG was mainly based on the distinctive features of the 2D mode [24–26]. However, the differences in the profile of the 2D mode between AB- and ABC-NLG are much complicated and laser-energy-dependent [24,27,26]. Additionally, the 2D mode is difficult to be applied in N characterization of NLG with N > 4, and further to identify stacking order of NLG with N > 4. There is still a request for direct and applicable method to characterize the stacking order in NLG.

Interlayer vibrations, including shear (C) and layer breathing (LB) vibrational modes, have received intensive researches in FLG [18,27–33] and transitional metal dichalcogenides [34]. The frequencies of C and LB modes can not be easily observed because of their ultra-low-frequency (ULF) beyond the spectroscopy limitations until Tan et al. successfully detected the highest-frequency C modes in AB-NLG (N = 2 – 4) [28]. In fact, there are (N – 1) C modes and (N – 1) LB modes for both AB- and ABC-NLG, which we indicate as $C_{N,N-j}$ and $LB_{N,N-j}$, with $j = N – 1, N – 2, …$, 1.

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http://dx.doi.org/10.1016/j.carbon.2015.11.062
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respectively. In this notation [18,33], for a given $N$, the labels $C_{N1}$ and $L_{B1}$ are used for the highest frequency $C$ and $LB$ peaks, and the labels $C_{K_{N-1}}$ and $L_{B_{N-1}}$ are used for the lowest frequency $C$ and $LB$ peaks, respectively. The $C_{N1}$ mode is the only $C$ mode thus far observed in AB-stacked FLG at room temperature [28]. The symmetry of AB stacking and weak electron-phonon coupling (EPC) are responsible for the absence of the other C modes in the Raman spectra [28]. Recently, Lui et al. found that the $C_{31}$ mode of ABC-3LG is infrared (IR) active, while the $C_{32}$ mode is Raman (R) active [35]. They observed the $C_{32}$ mode of ABC-3LG at high temperature of about 800 K by laser heating when ABC-3LG was suspended on quartz substrate and the laser power was increased up to ~9 mW [35]. The absence of the $C_{31}$ mode of ABC-3LG is because of its Raman inactivity. Therefore, the stacking order can be revealed from the $C$ modes. Now, Si wafer covered with the SiO$_2$ layer is widely taken as a substrate to support graphene samples on which electronic devices are fabricated. The $C$ mode observation of ABC-3LG by laser heating and sample suspending is not applicable for most samples on SiO$_2$/Si substrates for the purpose of basic research and device application. Raman activities of the $C$ modes in AB-NLG have been discussed by Tan et al. [28], but those in ABC-NLG are not yet reported.

Here, we measure the ULF Raman spectra of both AB- and ABC-NLG ($N = 3, 4, 5, 6$) deposited on SiO$_2$/Si substrates at room temperature by a low laser power of 0.5 mW. We find that the $C_{N1}$ modes can only be observed in AB-NLG, but not in ABC-NLG at room temperature. The absence of $C_{N1}$ mode in ABC-NLG with odd $N$ is because of symmetry limitations, while those with even $N$ is probably attributed to small EPC. This can be utilized as a new method to distinguish the AB and ABC stacking in NLG, which will also benefit the stacking order characterization in other layered materials.

2. Experimental

AB- and ABC-NLG are produced by mechanical exfoliation and then transferred onto a Si wafer covered by 93-nm or 300-nm SiO$_2$. The layer number of graphene flakes is determined by optical contrast [36,37] and the intensity ratio between the Si peak from SiO$_2$/Si substrates and the laser power was increased up to ~9 mW [35]. The absence of the $C_{31}$ mode of ABC-3LG is because of its Raman inactivity. Therefore, the stacking order can be revealed from the $C$ modes. Now, Si wafer covered with the SiO$_2$ layer is widely taken as a substrate to support graphene samples on which electronic devices are fabricated. The $C$ mode observation of ABC-3LG by laser heating and sample suspending is not applicable for most samples on SiO$_2$/Si substrates for the purpose of basic research and device application. Raman activities of the $C$ modes in AB-NLG have been discussed by Tan et al. [28], but those in ABC-NLG are not yet reported.

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3. Results and discussions

Fig. 1(a) presents the optical image of a mechanically-exfoliated 3LG flake, whose layer number was confirmed by the measured and calculated optical contrast (Fig. 1(b)). The optical image suggests the 3LG flake is quite uniform. However, the Raman spectra measured at two spots (SA and SB) in Fig. 1(a) are significantly different. The 2D mode at SB shows an identical spectral profile to that at SB, as shown in Fig. 1(c). The 2D profile in NLG reflects its electronic structure [39]. For example, the 2D mode of 1LG is only one Lorentzian peak because Raman scattering for the 2D mode in the visible range is only one process in triple Raman resonance. However, there are two valence and conductance bands in 2LG, where the incident laser can only couple two pairs of these four bands. The two almost degenerate TO phonons in 2LG can couple all electron bands amongst them, which results in four different sub-peaks for the 2D mode [39]. The number of sub-peaks of 2D mode in NLG will significantly increase with increasing $N$ [23]. For example, there are fifteen sub-peaks in theory for AB-3LG [40]. Actually, using six sub-peaks can reproduce the profile of 2D mode in AB-3LG [23], as depicted by dash-dotted lines in Fig. 1(c) for the 2D mode at SB. AB-3LG at SB can be further verified by the position of the C mode of AB-3LG in Fig. 2, which will be discussed later. Although the optical contrast of the 3LG flake is quite uniform, the 2D mode at SA exhibits a different spectral profile from that at SB, showing a more asymmetric feature, which is identical to that of ABC-3LG [25,26]. Additionally, the $G$ mode of ABC-3LG (~1581 cm$^{-1}$) red-shifts compared with AB-3LG (~1582 cm$^{-1}$), which is attributed to the slight differences between their phonons [25]. The lateral size of the ABC-3LG in Fig. 1(a) around SA is about 4 μm, which can be easily identified from optical images. Mixed ABA and ABC stacking at different area in one graphene flake is very common. Indeed, Lui et al. have found that if the total area associated with the two different stacking orders is considered, ~85% of the area in the samples corresponds to ABA stacking, and ~15% corresponds to ABC stacking [25], which is comparable to that obtained in earlier X-ray diffraction studies of graphite [41].

Similarly, 4–6LG flake can be firstly identified by optical contrast [36,37] and the Raman mode intensity from Si substrates [38]. Most area of the 4–6LG flakes exhibits the 2D mode of AB-
stacked 4–6LG, while a few area exhibits the 2D mode of ABC-stacked 4–6LG, which is similar to the previous reported results [25, 26]. The measured Raman spectra of both AB- and ABC-NLG (N = 4, 5, 6) are shown in Fig. 2. Fig. S1 in the Supplementary information shows the fits to the 2D mode of AB-4LG and ABC-4LG. Compared with AB-4LG, the red-shifts of the G mode in ABC-4LG is ~1 cm⁻¹, but this value increases up to ~3 cm⁻¹ in ABC-5LG and ~5 cm⁻¹ in ABC-6LG. The possible reason comes from the N-dependent splitting mediated by the weak interlayer coupling [42].

The main differences between AB- and ABC-NLG in the high-frequency region are the peak position of the G mode and the profile of the 2D mode. However, in the ULF region, we can clearly observe the C modes in AB-NLG (N = 3, 4, 5, 6) while those in ABC-NLG totally disappear, as shown in Fig. 2. These observed C modes are actually the Cₙ₁ modes [28]. C₃₁ mode in AB-3LG lies at ~38 cm⁻¹, which is consistent with our previous results [28]. The C₃₁ mode increases into ~40 cm⁻¹ (C₃₀) in AB-4LG, ~42 cm⁻¹ (C₃₁) in AB-5LG, ~43 cm⁻¹ (C₃₁) in AB-6LG and finally reaches at ~44 cm⁻¹ in graphene. Besides the observed C₃₁ mode in AB-NLG, other C modes are also expected to appear in Raman spectra [28]. For example, the C₂₂ mode (~22 cm⁻¹) in AB-3LG, the C₃₄ (~17 cm⁻¹) and C₄₂ (~31 cm⁻¹) mode in AB-4LG [28]. However, except the C₃₁ mode, other C modes is too weak to be observed as a result of the symmetry limitation or a small EPC [28]. Thus, one reason for the absence of the Cₙ₁ mode in ABC-NLG probably comes from the intrinsic difference in symmetry between AB- and ABC-NLG, which makes the Cₙ₁ mode in ABC-NLG Raman-inactive. Another reason is attributed to its small EPC.

The symmetry of the crystal allows us to denote the lattice vibrations, from which we can determine each Raman (R) active vibration. For example, graphite belongs to D₆h with its C mode represented by E₂ₙ, which is R active. The symmetry of AB-NLG (N = 2, 3, 4, 5, 6) strongly depends on N, which can be divided into D₆h for even number of NLG (ENLG) and D₅h for odd number of NLG (ONLG). There are (N−1) doubly degenerate C modes in NLG. As shown in Fig. 3(c) there are two and three C modes expected in AB-3LG and AB-4LG, respectively. Because of their difference in symmetry, the denotations of C modes are significantly different. (N−1) C modes in ENLG and ONLG are represented by \( \frac{N}{2} E_g + \frac{N}{2} E_u \) and \( \frac{N}{2} E_g + \frac{N}{2} E_u \), respectively. \( E_g \) and \( E_u \) are R active. E₂ and E are IR active. According to their Raman tensors [43], only \( E_g \) and \( E_u \) can be observed under back-scattering configuration. Symmetry, frequency and normal mode displacement for each C mode of AB-3LG and AB-4LG are depicted in Fig. 3. The Cₙ₁ mode in AB-stacked ENLG (E₂), ONLG (E) and graphite (E₂ₙ) are all R active, which has been experimentally observed [28]. Accordingly, AB-NLG belongs to D₆d with their C modes represented by \( \frac{N}{2} E_g + \frac{N}{2} E_u \) for ONLG and \( \frac{N}{2} E_g + \frac{N}{2} E_u \) for ENLG. Symmetry, frequency and normal mode displacement for each C mode of AB-3LG and AB-4LG are also depicted in Fig. 3. It should be noticed that the Cₙ₁ mode in ABC-stacked ENLG (E₂) is R active, whereas that in AB-stacked ONLG (E) is IR active. It suggests that the absence of the Cₙ₁ mode in ABC-NLG (N = 3, 5, 7, ...) is the result of their intrinsic difference in symmetry between AB- and ABC-NLG. So we expect that AB- and ABC-NLG (N = 3, 5, 7, ...) can be distinguished by whether their Cₙ₁ modes are observed or not, as shown in Fig. 2 for 3LG and 5LG. The Cₙ₁ modes (E₂) in ABC-NLG (N = 6, 8, 10) are R active, thus, these C modes are expected to appear in Raman spectra as that in AB-NLG (N = 4, 6, 8, 10). However, we did not observe any C mode in ABC-4LG and ABC-6LG (Fig. 2). The possible reason comes from its small EPC, which is identical to the absence of other C modes except the Cₙ₁ modes in AB-NLG [28]. Because the electronic structure of ABC-NLG is different from that of AB-NLG, the different EPC strength for the Cₙ₁ mode compared with that in AB-NLG is expected. Thus, the EPC strength should be responsible for the absence of the Cₙ₁ modes in ABC-NLG (N = 4, 6, 8, 10), which needs further calculations. The absence of these Cₙ₁ modes in ABC-NLG (N = 3, 5, 6, 7) with other C modes either from symmetry limitations in ONLG or from EPC in ENLG, affords a direct and effective method to characterize the stacking order in NLG.

Next, we analyse the optical activities of (N − 1) doubly-degenerated C modes in ABC-NLG (N ≥ 3) based on their vibration displacements obtained from a simple linear-chain model (LCM). LCM has been applied to obtain the dependencies of the frequencies of C modes (ωC) on N in both FLG [28] and transition metal dichalcogenides [43], where only the nearest interlayer coupling is considered in layered materials. Each graphene layer in NLG can be considered as a single atom in LCM, where we do not need to account the stacking order. Thus, we can also apply LCM to ABC-NLG. By solving the dynamic matrix, we obtain a general relation between ωC(N) and N as follows: 

\[ \omega C(N) = \omega C(2) \sqrt{1 + \cos(N0/2\pi)} \]

where \( \omega C(2) = 1/\sqrt{2\pi} \sqrt{\mu/\pi} \) is the C mode frequency in 2LG, \( \mu = 7.6 \times 10^{13} \text{ g/cm}^2 \) is the mass of one graphene sheet per unit area, c is the speed of light, 12×10^{18} N/m³ is the interlayer force constant per unite area. As shown in Fig. 4(a), a pair of branches generate from (2N₀)LG where the mode frequency of one branch (denoted by C₂N₀) increases with increasing N and that of another branch (denoted by C₂N₀) decreases with increasing N. The modes of the C₂N₀ and C₂N₀ branches are actually the Cₙ₁ and Cₙ₁-1 modes, respectively [18, 33]. By solving the dynamic matrix, we also obtained the vibration displacements from which we can determine whether each mode is R active (Fig. 2(c)). The rectangle and triangle in Fig. 4 denote the R and IR active modes, respectively. The optical activity of each C mode in AB-NLG has been discussed by Tan et al. [28]. The C₂ₙ branch is either R or both R and IR active, while the C₂ branch is R only. The C₂ branch is detected in the experiment. The absence of the C₂ branch was attributed to its small EPC.

Finally, we mainly focused on the C₂ and C₂ branches in ABC-NLG. It should be noted that \( \omega C(2) \) is absent in ABC-NLG because at least three layers are required in ABC stacking order. However, we still denote the pair of branches from 2LG by C₂ and C₂ in ABC-NLG as that in AB-NLG. The C₂ branch of AB-NLG (N = 3, 4, 6) is R active, but we do not detect any C modes (Fig. 2). Liu et al. recently observed the C₂ mode (lying in C₂ branch) in ABC-3LG suspended on quartz substrate at high temperature of about 800 K by increasing the laser power up to ~9 mW [35]. The high laser power will remove the
surface adsorbates, which also allows the observation of LB modes in AB-NLG [30]. The C_{31} mode in ABC-3LG is absent in their experiments [35] even the laser power was increased up to ~9 mW. This is completely consistent with our results in Fig. 2 because the C_{31} mode is R inactive (Fig. 3(c)).

We measured the UFL Raman spectra of AB-3LG, AB-4LG and AB-5LG which are suspended on Si substrates by increasing the laser power to ~10 mW, but didn’t detect any C mode (Supplementary information, Fig. S2) because of the strong background induced by the intense laser power. The C_{32} intensity in ABC-3LG is predicted to be ~0.57 times that of the C_{31} mode in AB-3LG [35], thus, the absence of the C modes in AB-3LG suspended on SiO_{2}/Si substrates excited by a laser power of ~10 mW suggests that we cannot detect any C mode even if the suspended ABC-3LG on SiO_{2}/Si substrates is excited by a laser power of ~10 mW. Recently, Luo et al. predict that the C_{31} mode in ABC-stacked ENLG has a much smaller intensity than the C_{31} mode [44]. This is consistent with the absence of the C_{31} mode in ABC-stacked ENLG, as shown in Fig. 2. Thus, the absence of the C_{31} mode in ABC-NLG can be utilized to characterize the stacking order in FLG at room temperature.

4. Conclusion

In conclusion, we observed the highest-frequency C modes (C_{N1}) in AB-NLG (N = 3, 4, 5, 6), but not in ABC-NLG. The absence of the C_{N1} mode in ABC-3LG and ABC-5LG results from the symmetry limitations, whereas that in ABC-4LG and ABC-6LG probably comes from the weak electron-phonon coupling. AB- and ABC-NLG can be effectively characterized by whether their C_{N1} modes are observed or not at room temperature. This affords a direct and reliable method to distinguish different stacking order in FLG at room temperature. It also benefits the characterization of stacking order in other two-dimensional layered materials.

Acknowledgments

We acknowledge support from the National Natural Science Foundation of China, grants 11225421, 11434010 and 11474277.
Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2015.11.062.

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