Structural and electronic properties of graphene and modified graphene

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**STRUCTURAL AND ELECTRONIC PROPERTIES OF
GRAPHENE AND MODIFIED GRAPHENE**

ZHAN DA

ZHAN DA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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Summary

In this thesis, I will mainly focus on using Raman spectroscopy and imaging to probe the electronic and crystal structures of graphene that modified both chemically and physically. This thesis is divided into five parts.

The first part covers Chapter 1. It reviews the progress on modification of graphene's electronic structure, and introduces the relationship between Raman features and graphene's properties. For modification of graphene's electronic structure, I review some important and common methods, which include applying external electric and magnetic field, changing stacking status, defects, and strain.

The second part (Chapter 2) introduces the investigation of graphene edge thermal dynamics. As controlling edge chirality of graphene nanoribbon can tune its electronic structure, and thus it is of great importance to understand the thermal annealing effect on graphene edges as it is one of the inevitable processes for nano device fabrication. In my studies, the armchair edges present much better thermal stability compared to zigzag edges, while the zigzag edges are not thermal stable as revealed by the activation of Raman D band after annealing treatment. The edge atomic structure evolution under annealed at different temperature (from 200 to 500 °C) is also studied in detail by comparing the polarized Raman intensity ratio of D and G bands.

In the third part (Chapter 3), the edge dynamics of bilayer graphene is presented. Motivated by one of the most influentially reported result that the AB-stacked bulk graphite is structurally modified to many AA-stacked bilayer graphene with closed edges at both armchair and zigzag edges after anneal at extremely high temperature (2000 °C) (Phys. Rev. Lett. 102, 015501, 2009), I carried out the work for low temperature edge dynamics study. Based on the conclusions I obtained from single

layer graphene edge thermal dynamics, it is indirectly discovered by Raman image and spectroscopy that the zigzag-edge of bilayer graphene is preferred to form closed state when it anneals at low temperature. The formation of closed zigzag edges of bilayer graphene is also supported by the dramatically decreased system energy as revealed by DFT calculation. The armchair edges of bilayer graphene cannot form closed state because of geometrical incompatibility. Hence the thermal dynamic behaviour of the armchair edges of bilayer graphene can be considered as two independent armchair edges of two layers.

The fourth part (Chapter 4 and 5) introduces the Raman studies of FeCl_3 -based full intercalation few-layer graphene compounds. Both evolutions of G and 2D bands are discussed in details for identification of the modified few-layer graphene crystal structure. The electronic properties of such compound are discussed by its 2D band features. The theoretical calculation results are used to assist the explanation of its Raman features and electronic properties. Followed by the preliminary characterization, various laser energies as excitation source to probe the Raman scattering features for this compound, and the laser dependent G band intensity for graphene layers doped in different level is observed. The mechanism for the enhancement of Raman G band for some specific graphene layers is also revealed theoretically.

The fifth part (Chapter 6) introduces another kind of FeCl_3 -based trilayer graphene intercalation compounds. In this type compound, only one interlayer space of the trilayer graphene is intercalated and the other interlayer space keeps unchanged. The intercalated FeCl_3 separates the pristine trilayer graphene into two independent parts, which are single layer graphene and bilayer graphene, respectively. This kind of abnormal compound presents obvious different Raman

features compared to the full intercalation case. The electronic band structure of this new type intercalation compounds also exhibits exotic property for its opened bandgap arising from inversion symmetry breaking of the separated bilayer graphene.

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Chapter 1

Introduction to graphene and its Raman characterizations

1.1 The electronic properties of graphene

In 2004, Novoselov and Geim using a very simple method isolated single layer graphene from its precursor bulk graphite. These two scientists shared the Nobel Prize (physics) in 2010 for their great contribution on opening the study of graphene. Graphene is one of the most promising materials for future applications in nanoelectronics because of the quantum confinement effect for graphene's 2D lattice structure and the consequent electronic properties,^{1, 2} such as anomalous quantum Hall effect,^{3, 4} fine structure constant defined optical absorption,⁵ and Klein tunnelling *et al.*^{6, 7} The special carbon-based sp²-hybridized lattice structure confined in one atomic thickness gives rise to mass-less Dirac-fermion-like charge carrier behaviour with extremely high Fermi velocity.^{3, 4, 8} Hence graphene is also a very attractive material for high frequency circuit applications as the charge carriers in graphene can move and respond much faster and travel longer than in normal semiconductors, i.e. extremely high charge carrier mobility (ideally can reach $2 \times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).^{9, 10} Despite the fact that graphene can be used in applications based on its physical and chemical properties, such as its high surface to volume ratio¹¹⁻¹⁴, the most desirable application of graphene is utilizing its intriguing electronic properties serving for next generation nanoelectronic devices.^{3, 4, 15-17} Thus the controllable tuning of electronic properties of graphene based on modifying its electronic structure becomes highly important.

Graphene is a carbon layer that consists of a honeycomb lattice structure with the nearest carbon-carbon distance of 1.42 Å. The unit cell of graphene contains 2

equivalent atoms (A and B as shown in Figure 1.1a). This crystal structure results in the touching between bonding (π) and anti-bonding (π^*) orbitals at each energy valleys K and K' when considering hopping only occurs between the nearest neighbor atomic sites.^{1, 18} The π electrons of low-energy bands around K and K' can be described by the Dirac-like Hamiltonian:^{8, 17}

$$H_{K'} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} \quad (1.1)$$

$$H_K = -\hbar v_F \begin{pmatrix} 0 & k_x + ik_y \\ k_x - ik_y & 0 \end{pmatrix} \quad (1.2)$$

The sign '+' and '-' for both equivalent valleys Hamiltonian resembles the spinor functions in quantum electrodynamics, and it can be considered as an extra degree of freedom which is 'pseudospins'. It results in a linearly dispersive electronic band structure at low-energy regime around K and K' (Figure 1.1b), and the energy can be expressed by $E = \pm \hbar v_F k$, which indicates the low-energy carriers in graphene is zero-mass and its speed is independent of energy. The carriers' speed, called as Fermi velocity, is as high as 10^6 m/s ($\sim 1/300$ c , where c is velocity of light), and thus the electrical transport properties of graphene are remarkable ascribed to such photon-like relativistic Dirac fermions. Particularly, the gapless graphene displays ambipolar electric field effect with ballistic property presenting room temperature mobility > 20000 $\text{cm}^2/\text{V}\cdot\text{s}$ as observed experimentally.^{3, 4, 19, 20} Furthermore, graphene can be both negatively/positively doped with electrons/holes concentration up to $\sim 10^{13}$ cm^{-2} .

The electronic behavior of graphene is also dependent on its stacking sequence. For bilayer graphene (BLG), the most energetically favourable one is stacked by the AB sequence. The AB-stacked BLG consists of four atoms in a unit cell,

labelled A_1 , B_1 , A_2 and B_2 (Figure 1.1c), where each subscript numerical index represents the different layers. Considering both the nearest neighbour hopping in-plane (from A_1 to B_1 and A_2 to B_2) and out-of-plane (from A_2 to B_1), the Hamiltonians for these bands can be expressed by equation (3) and (4):²¹

$$H_k = -\frac{\hbar^2}{2m} \begin{pmatrix} 0 & (k_x - ik_y)^2 \\ (k_x + ik_y)^2 & 0 \end{pmatrix} \quad (1.3)$$

$$H_{k'} = -\frac{\hbar^2}{2m} \begin{pmatrix} 0 & (k_x + ik_y)^2 \\ (k_x - ik_y)^2 & 0 \end{pmatrix} \quad (1.4)$$

Figure 1.1 Crystal structures of graphene single layer (a) and AB-stacked bilayer (c). The unit cell of single layer graphene and bilayer graphene consist of 2 and 4 atoms in each unit cell, respectively. The hopping between nearest neighbor atom sites A and B resulting the linear dispersive electronic band structure (b). The interlayer coupling for bilayer graphene cannot be ignored as the hopping between A_1 and B_2 affected the electronic band structure and resulting two parabolic electronic bands (d).

Different from the single layer graphene (SLG) which only presents one linear electronic band at low-energy regime, two groups of parabolic bands present (Figure 1.1d) due to the interlayer coupling effect. Therefore, the electronic band structure of these parabolic bands can be modified by tuning the electronic coupling between layers. For example, breaking the unit-cell symmetry chemically or electrically, as well as rotating one layer respective to the other, can intentionally modify the corresponding electronic band structure.

1.2 Modification of electronic structures of graphene

1.2.1 The effects of electric and magnetic fields

The Fermi level of pristine graphene is coincident with its Dirac point, and thus that can be intentionally tuned to shift up and down continuously by doping electrons or holes, respectively. In fact, the conductivity of graphene also increases with the doping of electrons or holes. One simple way to achieve doping electrons and holes is by applying a gate voltage to graphene, in which the ambipolar electric field effect can be observed (Figure 1.2a).³ When the Fermi level goes from the valence band (region A in Figure 1.2a) to the conduction band (region B in Figure 1.2a), it must cross the neutrality point (the boundary between A and B) at which the carrier density of states is zero as indicated by the inset schematic energy spectrum images of Figure 1.2a. The conductivity of graphene decreases with less charge carrier when the Fermi level gets closer to charge neutrality point (Dirac point). One interesting phenomenon should be noticed is that the conductivity of graphene cannot approach zero, even as the Fermi level overlap with this Dirac point. The theoretical explanation of this remained non-zero

minimum conductivity of graphene is still in debate.^{1, 2} Furthermore, the carrier density n_s and mobility μ of graphene can be quantitatively characterized by Hall measurement.^{3, 4, 15, 19, 22} The evolutions of n_s and μ with the gate voltage for graphene are shown in Figure 1.2b. It can be seen that the charge carrier density increases linearly with the absolute value of gate voltage (note that the positive and negative gate voltages correspond to electron and hole doping, respectively), and the mobility increases dramatically when the shifted Fermi level approaches the charge neutrality point.

Figure 1.2 (a) The conductivity of graphene as a function of gate voltage measured at 10 K. The blue (A) and red (B) regions represent the hole- and electron-doped graphene. The insets show the electronic spectra of positively (left), neutrally (middle) and negatively (right) doped graphene at around the Dirac point. (b) Charge carrier density n_s (open circles) and mobility μ (solid circles) of graphene as a function of gate voltage. Adapted from K. S. Novosolve et al.³ and Y. B. Zhang et al.⁴.

With the extremely high-mobility and the 2-D structure, the exciting room-temperature quantum hall effect (QHE) is possibly observed by redistribution of density of states (DOS) quantized under the external magnetic field perpendicular

to the graphene plane.^{3, 4, 23} The Landau level DOS and corresponding quantum hall conductance is shown in Figure 1.3a. In this figure, the pronounced QHE plateaus are clearly resolved, indicating the DOS redistributed quantization in energy scale.^{3, 4} It is worth noting that there is no zero conductivity plateaus through the whole quantum regime as the Hall conductivity can be expressed as $\sigma_{xy} = (N + 1/2) 4e^2/h$ (red curve in Figure 1.3a), where N is the Landau level index, e is the electron charge, and h is Planck constant. Such “half-integer” QHE behavior for graphene can be understood based on the massless Dirac fermions in graphene.⁴ The energy quantization of the graphene electronic structure in a magnetic field B is described by $E_N = \pm v_F \sqrt{2e\hbar BN}$, where $\pm$ refers to electrons and holes, B is external magnetic field.^{24, 25} It is worth noting that graphene is the only material that can present room temperature QHE at a very high magnetic field (Figure 1.3b).²⁶ Most recently, it is reported that the quantum number of QHE can also exist in form of fraction called the ‘fractional QHE’ (FQHE) as observed from high-mobility graphene.²⁷⁻²⁹ Such FQHE is very robust, appearing at low temperatures (e.g., 1.2 K) in a magnetic field as low as 2 T and a temperature persisting up to 20 K in a field of 12 T.²⁷

On the other hand, the interlayer coupling induced by AB-stacked BLG can also affect the redistributed quantum hall states as the Fermions in such system is not massless anymore. The undoped AB-stacked BLG behaves integer QHE which can be expressed by $\sigma_{xy} = M4e^2/h$, where M is integer and $M \neq 0$, and the missed plateau for $M=0$ is indicated by the red arrow (Figure 1.3c). It also means that the BLG is metallic at the neutrality point.²⁵ For the doped BLG, as the green curve in Figure 1.3c, the redistributed quantum DOS are further affected not only by the shifted neutrality point, but also by the appearance of the missed plateau $M = 0$.³⁰

Actually, this is the only case in which the ‘standard QHE’ is observed in graphene. All the plateaux present indicate that the doping induced electric field breaks the inversion symmetry of the two layers and the consequent bandgap opening leads to the phase change from metallic to semiconducting.³⁰ The doped BLG can be considered as a massive-Fermion semiconductor system, and thus the standard QHE can be observed in doped BLG.

Figure 1.3 (a) Hall conductivity σ_{xy} (red curve) and longitudinal resistivity ρ_{xx} (green curve) of single layer graphene as a function of doped charge concentration at $B=14 \text{ T}$ (perpendicular to the graphene surface) and $T=4 \text{ K}$. (b) The schematic redistributed quantized DOS of the single layer graphene. (c) Hall conductivity σ_{xy} (red curve) and longitudinal resistivity ρ_{xx} (blue curve) of single layer graphene as a function of gate voltage measured at 45 T magnetic field and room temperature. The inset is schematic DOS shows similar shape as that of (b). (d) Anomalous QHE for massive Dirac fermions in BLG at zero-doping (red curve); the neutrality point shifted negatively and the $M=0$ plateau state is recovered for BLG after doping, indicating that an energy gap is opened by the electric field effect induced inversion symmetry breaking (green curve). Adapted from K. S. Novosolve et al.³, A. K. Geim et al.²⁰, and K. S. Novosolve et al.²⁶.

Figure 1.4 (a) Schematic graph showing that the AB-stacked BLG is dual gated both on top and bottom with electrical displacement of D_t and D_b , respectively. (b) The resistance of BLG as a function of top gate voltage V_t at various fixed bottom gate voltage V_b . (c) schematic electronic band structure of the BLG with open bandgap upon the displacement fields, and Δ is the shifted Fermi level E_F due to the charge doping. (d) Infrared absorption spectra at charge neutral point for different applied average displacement fields. (e) Absorption difference of BLG between electron-doped and charge neutral states at different average displacement fields. Adapted from Y. B. Zhang *et al.*³¹.

Since the breaking of inversion symmetry of BLG was theoretically predicted for opening bandgap,³²⁻³⁴ scientists have paid great effort trying to experimentally investigate the research topic.^{30, 35} The discussed doped BLG with opened gap revealed by the presentation of standard QHE²⁸ and by transport property³² are still not the direct evidences. Later on, some research groups respectively reported the direct observation with infrared micro spectroscopy that the bandgap can be open and even tuned in a wide range by applying a perpendicular electric field to the

AB-stacked BLG.^{31, 36-38} As shown in Figure 1.4a, two independent tunable electrical gates applied to the AB-stacked BLG. The top and bottom electrical displacement fields D_t and D_b arise from two independent electrical gating at top (V_t) and bottom (V_b) of BLG sample, respectively. The values of D_b and D_t can be expressed as $D_b = +\epsilon_b(V_b - V_b^0)/d_b$ and $D_t = -\epsilon_t(V_t - V_t^0)/d_t$, where the ϵ and d are the dielectric constant and thickness of dielectric layer and V^0 is the effective offset voltage due to initial environmental molecules induced natural doping (i.e. O_2).^{38, 39} The net carrier doping of the sample is determined by $\delta D = D_b - D_t$, which is also proportional to the Fermi level shift. Meanwhile, the inversion symmetry of bernal-stacked bilayer graphene is broke by the average of the two electrical displacement fields, which is $\bar{D} = (D_b + D_t)/2$. The resistance as function of V_t shows a lot of peak resistance when V_b is fixed (Figure 1.4b),³¹ each of these resistance peak is actually the neutrality point approached at $\delta D = 0$. Although each resistance peak satisfies $\delta D = 0$ (or $D_b = D_t$) at various V_t and V_b , it is clearly seen that the peak resistance differs from each other arising from different $\bar{D}$ induced bandgaps. The minimum (black curve) and maximum (red curve) peak resistances correspond to the minimum and maximum $\bar{D}$ and mean that the lowest and largest bandgap have been approached, respectively. It can be roughly considered that $\bar{D} = D_b = D_t \approx 0$ gives rise to the minimum peak resistance point, and $\bar{D} = D_b = D_t \gg 0$ gives rise to the maximum peak resistance point. The opened bandgap for the high electrical displacement applied BLG has also been directly observed using infrared absorption spectroscopy as denoted by transition I (Figure 1.4c).³¹ The electrical gate dependent absorption peak below 300 meV is obviously seen in Figure 1.4d.³¹ The absorption peak position is observed for BLG

at high electrical displacement ($\bar{D} \geq 1.4 \text{ V} \cdot \text{nm}^{-1}$),³¹ corresponding to the opened bandgap from gapless BLG ($\bar{D} = 0 \text{ V} \cdot \text{nm}^{-1}$).³¹ The directly observed bandgap determined by the absorption peak is found to be tunable widely from 150 meV to 250 meV with $\bar{D} = 1.4 \text{ V} \cdot \text{nm}^{-1}$ to $3.0 \text{ V} \cdot \text{nm}^{-1}$ (Figure 1.4d).³¹ For the small bandgap corresponding to $\bar{D} < 1.2 \text{ V} \cdot \text{nm}^{-1}$, the direct bandgap transition I is too weak to be detected. However, for the small bandgap induced by low $\bar{D}$, absorption difference between electron-doped ($\delta D > 0 \text{ V} \cdot \text{nm}^{-1}$) and charge-neutral ($\delta D = 0 \text{ V} \cdot \text{nm}^{-1}$) BLG at ~ 400 meV can be resolved and the peak position varies with $\bar{D}$. This absorption difference between electron-doped and charge-neutral BLG is due to transition channel IV (shown in Figure 1.4c).³¹ Because the lower conduction band moves up and the upper conduction band keeps unchanged with the increasing of $\bar{D}$, and hence this absorption peak tends to shift to lower energy region (Figure 1.3e).³¹ The experimental observed transition channel I at high $\bar{D}$ and the transition channel IV at low $\bar{D}$ are also confirmed by theoretical calculation results.³¹

As elucidated, the magnetic field can change the DOS distribution from conscious to quantized states. On the other hand, using electrical gating method, I can intentionally tailor graphene electronic band structure and its Fermi level. By applying both magnetic and electric fields, the capability in controlling the electronic properties of graphene may be enhanced further.

1.2.2 The effects of tuning the stacking geometry

Naturally, graphite with the AB stacking sequence in c-axis is the most energetically favorable structure. The AB-stacked BLG has gapless band structure with the parabolic bands behaving as massive Dirac quasi-particles instead of

massless Dirac Fermions present by SLG. The AB-stacked BLG has been studied intensively owing to its tunable bandgap as elucidated in the previous section. Actually, in addition to AB-stacked BLG that normally prepared by mechanical exfoliation, the misoriented (or twisted) stacking is easily formed by epitaxial growth on SiC or CVD methods; furthermore, the electronic band structure of such twisted BLG differs a lot from that of AB-stacked BLG, and it depends only on the twisted angle between two graphene layers. More interestingly, it would typically possess SLG-like linear band dispersion around K point, which is different with that of AB-stacked BLG.⁴⁰ . In this section, I will discuss the relation between stacking geometry of graphene and its electronic properties.

The first scheme was proposed by Hass *et al.*⁴⁰ that multilayer graphene grown epitaxially on SiC (0001) surface displayed a high degree of rotation angle θ between the adjacent layers. The bilayer structures with the relative rotation ($\theta=30^\circ \pm 2.204^\circ$) observed in experiment exhibited a remarkable electronic decoupling (Figure 1.5a) and their *ab initio* calculations showed that this faulted stacking indeed preserves the Dirac cone and Fermi velocity characteristic as similar to that of SLG. This statement was then bolstered when Latil *et al.* demonstrated that the linear dispersion of SLG was also preserved in another rotation case ($\theta=38.21^\circ$) using *ab initio* calculations.⁴¹ Almost simultaneously, employing tight-binding method, dos Santos *et al.*⁴² found that twisted BLG still possesses massless Dirac fermions, but with a renormalization of the Fermi velocity especially for small rotation angles with respect to SLG. Later on, the experimental results provided some positive evidence further.⁴³ On the other hand, Shallcross *et al.* preformed a systematic study of the electronic behaviors for various rotation angles ($\theta = 30^\circ \pm 2.20^\circ$, $30^\circ \pm 8.21^\circ$, $30^\circ \pm 12.10^\circ$, and $30^\circ \pm 20.57^\circ$) between adjacent layers and

deduced from *ab initio* calculations that the Fermi velocity is unchanged in twisted bilayers compared to its value in SLG.^{44, 45} Subsequent Raman studies also plunged into the debate for twisted bilayer graphene.⁴⁶⁻⁵⁰ Ni *et al.*⁴⁷ found a blueshifted single 2D peak and concluded that the energy shift was a signature of a reduced Fermi velocity as predicted by dos Santos *et al.*⁴² while Poncharal *et al.*⁴⁹ stucked to their statement: only a modification of the phonon dispersion rather than slowing down of Fermi velocity.

Figure 1.5 (a) Upper: LEED image acquired from 4H-SiC (000-1) with ~10 graphene layers, showing only graphene spots and diffuse arcs. Below: X-ray azimuthal scans of the diffuse graphite arc. (b) Tight-binding band structures for rotation angles of $\theta = 21.79^\circ, 9.43^\circ, 2.65^\circ, 1.47^\circ$. For comparison in each panel the band structure of SLG is shown green lines. (c) Velocity ratio v_{bi} / v_{mono} for a commensurate (n, m) bilayer cell versus rotation angle θ . Circles indicate *ab initio* calculations while crosses indicate TB calculations. Adapted from J. Hass *et al.*⁴⁰, S. Shallcross *et al.*⁵¹, and G. T. De Laissardiere *et al.*⁵².

In fact, the rotation angle θ is the unique parameter that dictates the electronic structure and the above contrary assertions are derived from various rotation angles. The theoretical breakthroughs have been achieved respectively by de Laissardiere *et al.*⁵² and Shallcross *et al.*⁵¹ through exploring a wide range of rotation angles. Figure 1.5c shows the Fermi velocity of rotated bilayer, compared to that of SLG, for rotation angles θ varying between 0° and 60° .⁴²

Clearly, three regimes as a function of the rotation angle θ can be found in Figure 1.5b and c. For large θ ($15^\circ < \theta < 30^\circ$) the Fermi velocity is unchanged and identical to that of SLG. For the intermediate values of θ ($3^\circ < \theta < 15^\circ$), a velocity renormalization exists that is in agreement with the prediction of dos Santos *et al.*⁴² But for the small θ ($\theta < 3^\circ$), the flat bands occur and the velocity reduces remarkably to zero. In this regime, the carriers mainly localized in registry with the Moiré pattern and lead to a Van Hove singularity (VHS) in the density of states, suggesting that the perturbative theory of Lopez dos Santos *et al.* becomes not applicable.⁴² The observation of VHS in twisted graphene layers has also been proved by STM studies.⁵³

From an experimental viewpoint, most recently, Luican *et al.*⁵⁴ shed light on the relationship between stacking rotations and electronic properties by combining STM topography with Landau level spectroscopy. Convincingly, they confirmed the previous theoretical analysis: For large θ ($\theta > 20^\circ$), the electronic behaviors of the twisted layers were indistinguishable from SLG; for small angles ($\theta < 3^\circ$), the excitations were massless Dirac fermions but with a reduced Fermi velocity in agreement with theoretical predictions quantitatively;⁴² for the smallest angle ($\theta = 1.16^\circ$), the Fermi velocity suppression picture broke down and VHSs became

dominant in the band spectrum. Therefore, the previous contrary assertions deserve a reasonable explanation according to above discussions.

It is worth noting that we have to make some sort of compromise as the rotation angles have been chosen artificially for commensurated alignments between adjacent layers.^{44, 55} On the other hand, for small rotation angles, the continuum models are expected to be more accurate and the moiré Bloch bands can be evaluated at arbitrary twist angles, not only at commensurate values.⁵⁶⁻⁵⁹ Furthermore, the many-body effects become more important as the Fermi velocity is reduced,^{51, 56} especially for the low-energy band structure and it may dramatically change the nature of the small angle electronic structure.⁵¹

Given that twisted bilayers exhibit the drastic behaviors varying with its orientation, one can expect a new controllable way for possible device applications, such as ultra-sensitive strain gauges, pressure sensors or ultra-thin capacitors.⁵⁶ For smaller rotation angles, as the spatial distribution of carriers is strongly modified by Moiré patterns, it may have the properties of specific absorption and selective reorganization of atoms or clusters.⁵² Additionally, VHS peaks in the DOS near the Fermi energy often lead to superconductivity.⁵³ The next step is to afford particular insights into small rotation angle limits, and also improve the experimental control of rotation angles.⁵⁶

1.2.3 The effects of defects

Although the ideal graphene shows outstanding electronic properties, such a perfect 2-D material without any defects does never exist. It is well known that the electronic structure of graphene and its transport properties would be influenced by the existence of defects even for rather small concentration.^{27-29, 60} Defects can also

be intentionally introduced into graphene by many methods, such as irradiation by electrons⁶¹⁻⁶⁴/ions⁶⁵⁻⁶⁸ beam, hydrogenation⁶⁹⁻⁷² and oxidation^{11, 34, 73}. The former methods by electrons/ions irradiation normally create intrinsic defects, such as point defects and one-dimensional defects; the latter two methods generating covalent bonds between carbon atoms and hydrogen or oxygenated functional groups will give rise to the mixture of sp^2 and sp^3 hybridized carbons.

Figure 1.6 (a) The schematic formation process of the Stone-Wales defects. By rotation of a pair of bonded carbon atoms (red atoms) in plane, and finally form the SW defects with 90° rotation. The band structures of SLG (b), BLG (c) and TLG (d) with SW defects randomly distributed on each graphene layers. Adapted from L. Li et al.⁷⁴ and X. Y. Peng et al.⁷⁵.

1.2.3.1 Intrinsic defects

It is worth noting that the presence of defects in graphene is not always playing a negative role despite the fact that they are scattering centers for electron waves which decreases the carrier mobility and sheet conductance. For example, lacking a bandgap has limited graphene for the application in nanoelectronics, while some types of defects, such as Stone-Wales (SW) defects,^{74, 76} can induce bandgap in graphene up to 0.3 eV.^{75, 77, 78} SW defects have the lowest formation energy compared to any other intrinsic defects in graphene. It can be obtained by rotating a pair of bonded carbon atoms by 90° with bonds rearrangement to form 5-7-7-5 ring cluster as shown in Figure 1.6a.⁷⁴ As shown in Figure 1.6b-d, for SLG, BLG and TLG with randomly distributed Stone-Wales defects, each of them present a bandgap because Stone-Wales defects can break the local lattice symmetry, and the bandgap shows a decrease trend with the increasing of layers.⁷⁵ Furthermore, it is worth noting that the dispersion of the bands at low energy regime has not been distorted and the bandgap opening is the only effect. This is in contrary to the electric field effect as I discussed in chapter 1.1. For that case, the modified band structure of BLG opens a bandgap by external electric field, but the parabolic bands dispersion is distorted and the carrier mobility is reduced consequently; that would largely degenerate the transport performance of graphene. Therefore, the defect-mediated bandgap opening may be another engineering route for the future application of graphene in field effect transistors. Furthermore, by controlling the types of defects, such as single vacancy, the prominent localized states near Fermi level can be formed that results in magnetic moments.⁶⁸ Moreover, the extended line defects across grain boundary of two graphene domains can also induce localized states near Fermi level, and the metallic-wire behaviour of such extended one-dimensional carbon defects (non-hexagonal rings) could probably replace

copper to serve as the interconnects for the fabrication of all-carbon nanoelectronic devices.^{79, 80}

1.2.3.2 Extrinsic defects

Besides the modification of electronic band structure by intrinsic defects, the covalently bonded extrinsic defects in graphene can also change its electronic band structure. The extrinsic defects can be introduced by hydrogenation of graphene, of which the planar sp^2 networks converted to the distorted sp^3 structure as carbon atoms react with hydrogen despite the fact that graphite is one of the most chemically inert materials.^{70, 81-83} The conducting π bands would be gradually removed and a bandgap started to be opened with the increasing of the concentration of sp^3 hybridized carbons. When all the carbons are hydrogenated, it can be called as graphane, a new graphene-based material possessing a bandgap of 3.5 eV at Γ point.⁸⁴ Furthermore, it is theoretically predicted that the B-doped graphane would present superconducting state with extremely high transition temperature of ~ 90 K, which exceeds the boiling temperature of liquid nitrogen.⁸⁵

On the other hand, oxygenation of graphene to form graphene oxide (GO) by chemically attaching functional groups on its surfaces and edges can also adjust effectively its electronic structure. The electronic properties of GO as well as its practical applications have been studied in number of papers.^{11, 12, 34, 86-91} However, there are only few studies on electronic band structure of GO because its crystal structure is still a mystery,⁹²⁻⁹⁵ and more importantly GO is a chemical compounds that consists of many functional groups with non-fixed chemical ratio. Here I would review the electronic properties of GO very briefly. GO can be considered as graphene-based chemical compounds with mixed sp^2 -carbon and sp^3 -carbon.

The π - π conjugation of GO is destroyed and thus it does not present metallic behavior anymore, of which the conductivity is about 6-8 orders lower than that of pristine graphene.^{34, 86, 87} GO can be reduced both thermally and chemically, in which a large amount of functional groups can be removed; the conductivity of such reduced graphene oxide is about 4-6 orders higher than its precursor GO due to the recovery of sp^2 networks.^{11, 34, 87, 88, 90}

1.2.4. The effects of strain

Silicon is the most traditional semiconductor material that dominated microelectronics market for more than half century. In recent years, it has been discovered that the strain effect can tune its electronic band structure and enhance its electronic performance because of the higher electron mobility. Similarly, strain effect can also modify the graphene's electronic band structure and thus change its properties accordingly. To date, the strain effect on graphene has been studied intensively both theoretically and experimentally in recent years.⁹⁶⁻¹⁰⁷ In this chapter, I will briefly discuss the strain effects on modifying graphene's electronic band structure.

As graphene is 2-D material, from the geometric point of view, symmetrical strain (graphene's hexagonal symmetry keeps unchanged) and asymmetrical strain (graphene's hexagonal symmetry deformed) in plane are generally considered. The Brillouin zone would be deformed accordingly by strain as the unit cell changed in real space. The symmetrical tensile strain uniformly compresses the unit cell of graphene, resulting that the electronic bands get close to the Fermi level, and consequently, modifies the bands dispersion more smooth with respect to the momentum space. The trend of symmetrical compress strain effect is opposite to

that of tensile strain. On the other hand, the small and moderate uniaxial strain can change the electronic band structure of graphene because it distorts the lattice. However, it can only shift the Dirac point but still showing the gapless band structure,^{96, 97} unless the strain along very specific direction and the deformation exceeds 20%, the bandgap can be opened.⁹⁸ Uniaxial strain on graphene can be quantitatively detected by Raman for its G band shift and splitting,^{104, 106} because Raman is very sensitive to small tensile strain ($\sim 0.1\%$) of graphene due to the phonon softening effect. However, the experimental reports on enormous strain on graphene are limited despite the fact that it can change the electronic and magnetic properties prominently.^{99, 107} This probably because that it is very difficult to approach enormous strain on graphene while keep it stable.¹⁰⁸

Recently, it is theoretically predicted that strain with triangular symmetry can induce energy gaps in graphene because of self-generated extremely high pseudo-magnetic field.⁹⁹ Followed by that, Levy N. *et al.* experimentally proved this conception by observing the QHE states using STM tip scanning across triangular nanobubbles with enormous strain,¹⁰⁷ which means that an extremely high pseudo-magnetic field (higher than 300 Tesla) can be self-generated because of enormous strain, and consequently, it is able to form Landau level with the quantized DOS and energy gaps at low temperature.¹⁰⁷

1.3 Raman studies of graphene

1.3.1 Introduction to Raman scattering

When the light incident to the matter (atoms or molecules), a large portion of the photons would scatter with the same energy as that of the incident photons, which is the so called Rayleigh scattering, but a very few portion of them would be

scattered inelastically with exchanging energy between the incident photons and matters. The energy difference between the incident and the inelastic scattered light is equal to the electronic, vibrational and rotational energy-levels of the matter. It was firstly discovered by S. C. V. Raman, and thus also called as Raman scattering.¹⁰⁹

There are two types of Raman scattering, Stokes and anti-Stokes scattering, which are respectively corresponding to the emission and absorption of phonons when the photons interact with matter. Therefore, the energy of the Stokes scattered photon is lower compared to the incident photon, and the energy of the anti-Stokes scattered photon is larger than that of the incident photon. If the incident photons are monochromatic light (such as laser) with frequency ν , and the vibrational or rotational frequency of the molecule is ν' , thus the Stokes and anti-Stokes scattering photon frequency are $\nu - \nu'$ and $\nu + \nu'$, respectively. For clearly understanding of these scattering, Rayleigh, Stokes and anti-Stokes scattering processes are schematically shown in Figure 1.7.

Normally the Raman scattering arises from the exchange of molecular vibrational or rotational energy with incident light, therefore, the vibrational and rotational frequency of the specific molecule can be indirectly measured by comparing the difference between energies of incident and scattered photons, which is the so called Raman spectroscopy. The Raman spectrum is a powerful scientific tool that can be carried out in normal ambient-air environment, and thus it can let us know the information rapidly about the material's chemical composition, strain (stress), and crystal quality. With the development of Raman instrument, Raman spectroscopy has been widely used in chemistry, physics, materials, biochemical sciences, industry, environment.¹¹⁰

Figure 1.7 The schematic scattering processes of incident monochromatic light by small particle.

1.3.2 The molecular Raman spectroscopy based on its vibrational modes¹¹¹

The electronic, vibrational and rotational transitions are possibly involved in Raman scattering, and the vibrational Raman scattering based on condensed matters is of great importance in both fundamental scientific studies and practical applications. In this sub-chapter, I will introduce the molecular vibrational modes based Raman scattering.

When monochromatic radiation falls on the molecular sample and is not absorbed by it, the oscillating electric field E of the radiated electro-magnetic wave induces in the molecule an electric dipole μ which is related to E by the polarizability as described in formula 1.5:

$$\mu = \alpha E \quad (1.5)$$

Where the α is the polarizability, and it is a measure of the degree to which the electrons in the molecule can be displaced relative to the nuclei. The polarizability α is a tensor property, and it can be expressed in the form of a matrix as shown in formula 1.6.

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \quad (1.6)$$

Where the diagonal elements α_{xx} , α_{yy} , α_{zz} , are the values of α along x , y and z axes of the molecule, and the matrix is symmetrical in the sense that obeys the following relations:

$$\alpha_{xy} = \alpha_{yx} \quad (1.7)$$

$$\alpha_{xz} = \alpha_{zx} \quad (1.8)$$

$$\alpha_{yz} = \alpha_{zy} \quad (1.9)$$

Figure 1.8 The polarizability ellipsoid

Each of these can be assigned to one of the symmetry species of the point group to which the molecule belongs. These assignments are indicated in the right-hand

column of each character table. In general, the polarizability of a molecule is an anisotropic property, which means that, at equal distances from the centre of the molecule, α may have different magnitudes when measured in different directions. A surface drawn so that the distance from the origin to a point on the surface has a length a $\alpha^{1/2}$, where α is the polarizability in that direction which forms an ellipsoid as shown in Figure 1.8. Generally, this has elliptical cross-sections in the xy and yz planes, and the lengths of the axes in the three directions are unequal. From viewpoint of the classic treatment by Taylor series expansion, the variation of α with molecular vibration is expressed as:

$$\begin{aligned}\alpha &= \alpha_0 + \left(\frac{\partial \alpha_0}{\partial q} \right)_0 q + \dots \\ &= \alpha_0 + \left(\frac{\partial \alpha_0}{\partial q} \right)_0 q_0 \sin 2\pi \tilde{\nu}_{vib} t \\ &= \alpha_0 + \alpha_1 q_0 \sin 2\pi \tilde{\nu}_{vib} t\end{aligned}\tag{1.10}$$

Where the α_0 is the average polarizability during vibration, q is nuclear displacement, and q_0 is the amplitude of vibration, $\left(\frac{\partial \alpha_0}{\partial q} \right)_0 = \alpha_1$ can be considered as the change of polarizability due to vibration, and $\tilde{\nu}_{vib}$ is the vibration frequency.

Meanwhile, the magnitude E of the vector can be expressed as :

$$E = A \sin 2\pi \tilde{\nu} t\tag{1.11}$$

Where A and $\tilde{\nu}$ are the amplitude and frequency of the monochromatic radiation, respectively. The magnitude of the polarizability varies during vibrational motion leading to a vibrational Raman effect, and the variation can be visualized because the increase and decrease of the bond length give rise to the polarizability ellipsoid expanding and contracting (Fig. 1.8).

Substitute the formulas 1.10 and 1.11 into 1.5, we can get the following equation:

$$\mu = \alpha_0 A \sin 2\pi \tilde{\nu} t - \frac{1}{2} \alpha_1 A \cos 2\pi(\tilde{\nu} + \tilde{\nu}_{vib})t + \frac{1}{2} \alpha_1 A \cos 2\pi(\tilde{\nu} - \tilde{\nu}_{vib})t \quad (1.12)$$

The first term corresponds to Rayleigh scattering of which the scattered radiation has the same frequency as that of the incident light ν . The second and third terms correspond to anti-stokes and stokes Raman scattering which changed the frequency with respect to the incident radiation. It is worth to note that normally the vibration frequency ($\tilde{\nu}_{vib}$) is much smaller than that of the monochromatic radiation ($\tilde{\nu}$). Hence the changed frequency by Raman scattering ($\tilde{\nu} + \tilde{\nu}_{vib}$ and $\tilde{\nu} - \tilde{\nu}_{vib}$) only shows a little bit difference compared to the incident radiation $\tilde{\nu}$.

1.3.3 The properties of graphene probed by Raman spectroscopy

Compared to most of the powerful scientific tools (TEM, STM) which normally need high vacuum, Raman measurement can be carried out in ambient-air condition. Graphene with its hexagonal atomic structure belongs to D_{6h} point group. It has two prominent Raman active bands with intense peaks, G and 2D bands (red curve in Figure 1.9), the former one corresponds to the E_{2G} vibrational mode at Γ point in Brillouin zone and the later one corresponds to the second order A_{1g} breathing mode at around K point in Brillouin zone. It is very interesting that the first order A_{1g} breathing mode (D band) is silent for perfect crystalline graphene but its second order mode (2D band) has a very strong peak. But the D band becomes Raman activated and the intensity of 2D band becomes weaker with introducing defects in graphene (blue curve in Figure 1.9). Normally, the features of D, G and 2D bands can be used to study graphene's properties, such as edge

chirality, strain, defects and doping. In this section, I will briefly introduce the application of Raman spectroscopy for studying various properties of graphene.

Figure 1.9 Raman spectra for pristine (red) and defected (blue) graphene excited by 514 nm laser. Adapted from Z. H. Ni et al.⁷².

1.3.3.1 Raman for probing defects of graphene

Figure 1.10 Double resonance scattering process for the activation of D band (a) and 2D band (b), and triple resonance scattering process for activation of 2D band (c).

Both the D band and 2D band are arising from the double resonant Raman scattering as shown schematically in Figure 1.10. For the activation of D band (Figure 1.10a), as graphene has gapless bandgap and the conduction and valence bands touch each other at the K point, there will be a specific point that allows laser resonantly excite electrons from valence band to conduction band ($A_1 \rightarrow B_1$), and the D phonon with momentum k can scatter this electron to the other energy

valley around K' point with exchanging both energy and momentum ($B_1 \rightarrow C_1$), then the electron scattered by defect elastically by exchanging momentum $-\mathbf{k}$ but without exchanging energy ($C_1 \rightarrow D_1$), and finally the recombination of electron and hole ($D_1 \rightarrow A_1$) by emission a photon. This Raman process can let us measure the energy difference between incident and scattered light which equals to the energy of single D phonon. Thus it is easily understood that the defects must be involved for the activation of D band. Different from the case of D band of which the step $C_1 \rightarrow D_1$ is driven by defect scattering, the case of 2D band double resonant Raman scattering process at step $C_2 \rightarrow D_2$ (Figure 1.10b) is fulfilled by another D phonon that participates to scatter the electron from energy valley K' back to K. In addition to the electrons involved double resonance for activation of 2D band, it is worth noting that the Raman scattering process involving both electrons and holes can also activate the 2D band. As shown in Figure 1.10c, an incident photon firstly excites an electron from valence band to conduction band ($A_3 \rightarrow B_3$) and meanwhile, a hole is created at A_3 . The created hole at A_3 can be occupied by an electron that is scattered by a D phonon with momentum $-\mathbf{k}$ from energy valley K' (D_3) to K (A_3), and simultaneously, a hole is created at D_3 . On the other hand, another D phonon with momentum $\mathbf{k}$ can scatter the excited electron from B_3 to C_3 . Finally, the electron at conduction band C_3 recombines with hole at D_3 by emission a scattering photon. The later schematic Raman process shown in Figure 1.10c is called the triple resonance process, and it is the dominant process for the 2D band in graphene. Hence the measured Raman shift equals to ~ 2 times energy of D phonon, and this band can be always activated if the good crystalline quality of graphene can be preserved.

The defects can be introduced by many methods, such as ions bombardment, hydrogenation and oxidation. For the defected graphene, the crystal domain size can be quantitatively calculated by the value of intensity ratio of D and G bands (I_D/I_G) because the I_D/I_G is related to the crystalline domain size of graphene.¹¹² Therefore, we can rapidly know the crystalline quality of graphene by comparing the I_D/I_G .

1.3.3.2 Raman for identifying graphene thickness

Figure 1.11 (a) Evolution of the Raman 2D band with the number of graphene layers using 514 nm laser. (b) Evolution of the Raman 2D band with the number of graphene layers using 633 nm laser. Adapted from A. C. Ferrari et al..¹¹³

When discuss the topic of the thickness for the 2-D material, we intuitively will think about using atomic force microscopy (AFM), but actually for graphene thickness identification, Raman can give us a more accurate thickness identification result compared to that of AFM. Figure 1.11 is a typical thickness dependent Raman spectra. As I introduced before that the Raman 2D band is

arising from the double resonance, thus the measured D phonon is sensitive to the evolution of electronic band structure around K point. The obvious difference in electronic structure between SLG and few-layer graphene gives rise to the difference in Raman 2D band features.

1.3.3.3 Raman for identifying edge chirality of graphene

Graphene is one atomic thick carbon forms in honeycomb structure. Its crystal edge is normally terminated by two types, the so called zigzag and armchair edges which are schematically shown in Figure 1.12b. It can be seen that for a perfect crystalline graphene, the orientation along zigzag and armchair directions forms an angle of $(2n+1) \times 30^\circ$, where n is integer. Therefore, if the adjacent graphene edges form an angle of 30° or 150° , then we can say that these two edges possess different chirality, such as shown in Figure 1.12a. To identify these two edges, HRTEM and STM are two available methods but they are still very challenge as the C-C bond is only 1.4 Å and Carbon is a very light chemical element. Nevertheless, Raman provides us a very flexible way to identify the graphene edge chirality. Because I have introduced that the activation of D band needs defects. Despite the fact that both the zigzag and armchair edges can be considered as defects, but the D band can be observed by armchair edge only and it keeps silent at zigzag edge. This is because of that the involvement of defects for activation of D band needs another important necessary condition, which is the momentum conservation.¹⁶⁴ For this interesting topic, I will discuss it in detail in chapter 2.

Figure 1.12 (a) A typical optical image of multi-layer graphene shows that the adjacent edges of graphene sheets are 60 and 150, respectively. (b) Illustration of the relationship between angles and the chiralities of the adjacent edges. Adapted from Y. M. You et al.,¹¹⁴

1.3.3.4 Raman for probing strain in graphene

Because the phonon is arising from the lattice vibration, thus the lattice constant variation can change the phonon frequency. For graphene, both the peak positions of G and 2D bands are strain dependent, and particularly that the 2D band is more sensitive. Ni *et al.* using the polyethylene terephthalate (PET) as substrate to support graphene, in which the whole system is available for approaching tensile strain easily. The analyzed 2D frequencies of both single- and three- layer graphene decreases dramatically with the applied uniaxial strain even at less than 0.2%. The three-layer graphene shows a slower drop compared to the single layer as shown in Figure 1.13.

Figure 1.13 The 2D band frequency of single- and three- layer graphene as function of uniaxial strain. Adapted from Z. H. Ni *et al.*¹⁰⁴

1.3.3.5 Raman for analyzing electron and hole doped graphene

As we know that the Fermi level crosses the Dirac point for pristine graphene and thus doping either electrons or holes can shift the Fermi level continuously to conduction and valence bands, respectively. Das *et al.* did a very systematic analysis on the evolution of both G and 2D bands of single layer graphene with respect to the doping from electrons side to holes side, the doping is approached by applying a top gate voltage (V_{TG}) to graphene.¹¹⁵

Figure 1.14 (a) Raman spectra of graphene at values of V_{TG} between -2.2 V and + 4.0V. (b) The G peak position (top panel) and FWHM (bottom panel) as a function of electron and hole doping. The solid lines are predicted based on non-adiabatic trends.¹¹⁶ (c) The 2D peak position as a function of doping. The solid line is DFT calculation result. Adapted from A. Das et al..¹¹⁵

From Figure 1.14a, it can be seen that no matter the doping is hole or electron type, the position of G band shows same blueshift trend and the full width of maximum (FWHM) of G band becomes relatively sharp. The stiffening effect of G band for doped graphene is due to the non-adiabatic removal of the Kohn anomaly from the Γ point.¹¹⁶ The blockage of phonon decay channel into electron-hole pairs gives rise to the sharpening effect of G band due to the Pauli exclusion principle. The peak position of 2D band shows different trend compared to that of G band. The position of 2D band for hole doped graphene shifts to higher frequency but it does not show prominent change for electron doping at low level, and it finally shifts to lower frequency when the doping level reaches $2.5 \times 10^{13} \text{ cm}^{-2}$ or even

higher.¹¹⁵ Therefore, by measuring both G and 2D positions, it can let us know the shifted Fermi level with respect to the neutral Dirac point.

1.4 The motivation and organization of this thesis

This thesis presents Raman studies of both crystal and electronic structures of modified graphene which includes two major parts:

Motivation for part 1 (Chapter 1): Graphene attracted tremendous interests in the past few years mainly owing to its outstanding electronic properties. Furthermore, the flexible tuning of its electronic structure for various purpose applications is also one unique advantage for this 2-D material. Therefore, I briefly summarize the current methods for tuning graphene's electronic structure in the first part. Followed by that, as this thesis is focusing on Raman studies of the crystal and electronic structures modified graphene, thus I also briefly introduce the mechanism for Raman scattering and the application of Raman for characterizing different kind of properties of graphene.

Motivation for part 2 (Chapter 2-3): The edge dynamics of graphene is a very important research topic because the electronic structure of graphene nanoribbon can be flexibly tuned by controlling its edge chirality. From the viewpoint of application, annealing is one of the inevitable process for fabricating graphene-based nano device, thus the thermal effect on graphene edges becomes very important. At this background, the thermal dynamics for single layer graphene edge is studied based on polarized Raman spectroscopy in Chapter 2. The detailed analysis reveals the atomic structure evolution at edges under annealing condition. Followed by that, I will present in Chapter 3 for the edge dynamics of few-layer graphene based on polarized Raman spectroscopy investigation. One of the most

exciting discoveries is that the zigzag edge of AB-stacked bilayer graphene prefers to form closed structure when it is annealed at low-temperature. The closed-edge bilayer graphene shows exotic electronic properties as revealed by theoretical calculation.

Motivation for part 3 (Chapter 4-6): Graphite intercalation compounds have been studied for many years in last century. However, the few-layer graphene intercalation compounds have not been reported until 2009.¹¹⁷ Actually, the insertion of extra molecules or atoms (intercalant) into graphene interlayer space and the intercalants can electronically interact with the adjacent graphene layers. Another function of the intercalant is to decouple the adjacent graphene-graphene electronically. Hence the newly formed superlattice structure performs different electronic properties compared to the pristine graphene. In Chapter 4, I mainly introduce the FeCl_3 -based few-layer graphene intercalation compound (FLGIC) and its Raman features. The modified electronic structure of FLGIC is also calculated based on the proposed superlattice crystal structure. In Chapter 5, an interesting phenomenon that the laser energy dependent Raman G band intensity for graphene layers at different position (outer or inner layer) in FLGIC has been studied, and it concludes that the electronic structure coupling between graphene and FeCl_3 layer would give rise to extra channel for enhancing resonant Raman scattering. In Chapter 6, the asymmetric intercalated trilayer graphene has been investigated by Raman spectroscopy, and the electronic structure of this kind of new graphene-based form present a bandgap opened electronic structure due to the inversion symmetry breaking. It is very important for the realization of such air-ambient stable and bandgap opened graphene form as it may benefit graphene-based field-effect-transistor applications in near future.

Organization of this thesis: In this thesis, I will introduce the current methods for modifying graphene's electronic structure in Chapter 1, and the Raman studies on graphene's properties will be introduced in this chapter. Then the low-temperature graphene edge dynamics for single layer and bilayer cases will be respectively discussed in Chapter 2 and 3. Followed by that, I will introduce one kind of modified graphene crystal structure in Chapter 4: Few-layer graphene intercalation compounds. The Raman features of such new graphene form are systematically studied, and the corresponding electronic structure is given for assisting the explanation of Raman results. The laser energy dependent Raman G band intensity for different type of graphene will be discussed in Chapter 5. In Chapter 6, the asymmetrically intercalated trilayer graphene with bandgap opened electronic structure will be present. Finally in this thesis, the conclusions will be summarized and some related future works will be proposed.

Chapter 2

Thermal dynamics of single layer graphene edges

2.1 The importance of graphene edges

Figure 2.1 Schematic illustration of crystal structure of graphene edges: (a) zigzag edge; (b) armchair edge; The insets of (a) and (b) show the schematic of intervalley electron scattering in double resonance process, where zigzag/armchair segments cannot/can fulfill the scattering condition.

As a real material, graphene is not infinitely large, and it is typically terminated by two types of edges, which are zigzag and armchair. With the reducing size, graphene transforms from 2-D to 1-D, and its edge effect becomes pronounced to modify its electronic band structure (such as opening bandgap and forming localized state) and consequently the transport properties.⁶⁴ Therefore, graphene ribbons characterized with edges, so called graphene nanoribbons (GNRs), have been intensively and extensively studied,^{114, 118-127} both experimentally and

theoretically. The crystal structures of the zigzag edges (Z-edges) and armchair edges (A-edges) are shown in Figure 2.1a and b. The pioneer works on this topic are based on theoretical calculations. The atomic structure of graphene armchair and zigzag edged GNRs (denoted as AGNR and ZGNR, respectively) are schematically shown in Figure 2.2a and b. The electronic band structure of the zigzag and armchair terminated GNRs was firstly reported theoretically using the tight-binding method.¹²⁸ It is predicted that, independent of the ribbon width, ZGNR always presents metallic behavior with zero bandgap, while the AGNR would present semiconducting behavior except when $N = 3p - 1$, where N denotes the ribbon width by number of atoms (Figure 2.2a) and p is an integer.¹²⁸ In 2006, Son *et al.* calculated the electronic band structure of both ZGNR and AGNR using first principle theory, and found that AGNR should always be semiconducting with a finite bandgap inversely proportional to the ribbon width, in spite of the fact that there is an energy gap difference for $N = 3p$, $3p + 1$ and $3p + 2$ cases.¹¹⁸ Compared to the results calculated by tight binding method,¹²⁸ one more important discovery by using first principle theory is that ZGNR also possesses a finite bandgap when considering the spin effect.¹¹⁸ The summarized bandgap for GNR based on different calculation methods are shown in Figure 2.2c and d.¹¹⁸ However, the different calculated electronic band structures are strongly depending on the calculation techniques (Figure 2.2e), so that the experimental examination of such results are highly demanded.

Experimentally, Kim's and Dai's groups respectively fabricated the GNRs by physical and chemical approaches. Interestingly, all the GNRs they reported are showing semiconducting properties with observed bandgap inversely proportional to the ribbon width.^{129, 130} As both the works did not resolve the graphene edges in

Figure 2.2 The schematic atomic network of an armchair ribbon ($N=10$) (a) and a zigzag ribbon ($N=5$) (b). The bandgaps of AGNRs as a function of width w_a at three typical N_a obtained from calculations of tight binding (c) and first principles theory (d). (e) The schematic chart showing that the bandgap opening is dependent on the calculation technique, the 'YES' and 'NO' represent bandgap opening and gapless band structure, the LDA is shorten for local-density approximation. Adapted from Nakada et al. (a and b)¹²⁸ and Son et al. (c and d)¹¹⁸.

atomic scale, it is not able to determine the edge types of the tested GNRs. On the other hand, both zigzag and armchair edge atoms are not sp^2 saturated and hence they are relatively not stable compared to the center region carbons.⁶⁴ So neither nanolithography nor chemical exfoliation can obtain the graphene edges with pure chirality. Instead, the edges of GNRs should be mixed by both zigzag and armchair segments. Later, using STM to resolve the atomic scale of graphene edges, Ritter and Lyding experimentally demonstrated that zigzag segments predominated GNRs also exhibit a finite energy gap, but it significantly decreases with increasing of the concentration of zigzag segments,¹³¹ the relatively narrow GNR (2.3 nm) with concentration of 95% zigzag segments exhibits an energy gap of 0.14 eV which is much smaller compared to the wider GNR (2.9 nm) consisting of only 15% zigzag segments.¹³¹

Therefore, tailoring the electrical/electronic properties of GNRs by modifying its edge chirality or shape, for example by thermal annealing, would be a very interesting research topic. Furthermore, graphene edges are preferred sites for functionalization and chemical decoration,¹²¹ while thermal annealing is commonly used for sample cleaning^{130, 132, 133} as well as in semiconductor manufacturing process.^{4, 22, 129-132, 134-136} Therefore, a good understanding of the thermal stability and dynamics of graphene edges is important for guiding future graphene-based nanoelectronics processing and chemical decoration. Recently, Girit *et al.* probed the edge stability and dynamics by using high resolution TEM.⁶⁴ However, the energy of electron beam used in TEM is very large and the temperature induced might be very high. Therefore, the *in situ* TEM study of graphene edge dynamics is actually the study of stability of graphene edges against

electron collision or irradiation, and it is difficult to control the experimental conditions, *i.e.* effective temperature induced by irradiation.

Raman spectroscopy is one of the most commonly used methods for characterization of graphene-based materials because of the advantages of simple, non-destructive and high-throughput. It is also proved as one of the most effective methods for identifying types of graphene edges.¹¹⁴ The Raman D mode (Breathing mode A_{1g}) is inactive for perfect Z-edges, because the exchanged momentum by scattering from the Z-edges (d_z) cannot connect the adjacent Dirac cones K and K' (Inset of Figure 2.1a), hence does not fulfill the double resonance process.^{21, 137, 138, 164} On the other hand, the exchanged momentum from A-edges can satisfy the intervalley scattering process between K and adjacent K' (Inset of Figure 2.1b); hence its D band is Raman active. Furthermore, the perfect A-edges gives rise to the polarization dependence of the D peak intensity as $I(D) \propto \cos^2\theta$, where θ is the angle between incident laser polarization and the edge direction throughout this paper.

Motivated by the aforementioned background, I present Raman spectroscopy investigation of the thermal stability and dynamics of graphene edges in this chapter. It is found that graphene edges (both armchair and zigzag) are not stable and undergo modifications even at temperature as low as 200°C. Based on polarized Raman results, I provide possible structural models on how graphene edges change during annealing. The zigzag edges rearrange and form armchair segments that are $\pm 30^\circ$ relative to the edge direction, while armchair edges are dominated by armchair segments even at annealing temperature as high as 500°C. The modifications of edge structures by thermal annealing (zigzag segments

rearrange in form of armchair segments) provide a flexible way to control the electronic properties of graphene and graphene nanostructures.

2.2 Experimental

Graphene flakes were prepared by micromechanical cleavage on silicon wafer covered by 300 nm SiO₂, and single layer graphene were confirmed by Raman^{113, 139} and optical contrast spectra.¹⁴⁰⁻¹⁴³ The Raman spectra were carried out with a WITEC CRM200 Raman system, with 532 nm excitation and 100× objective (Numerical Aperture, NA=0.95). The laser power at sample is below 1 mW to avoid possible laser heating induced sample damage.¹⁴⁴⁻¹⁴⁶ Raman images with a spatial resolution of ~400 nm are realized with a piezo stage (step size 100 nm) and the integration time at each position is one second. The polarization-dependent Raman spectra at edges were obtained by changing the angle of incident polarization with a half wave plate. The exact position of graphene edge is determined by Raman line scan (step size 100 nm) across the edge to make sure the maximum intensity of D peak is approached.¹²⁴ Samples with angle of 30° and 150° between adjacent edges were selected so that for each sample, one edge is A-edges (strong D peak) and the other is Z-edges (weak D peak). Four different graphene flakes were annealed in vacuum (5×10^{-5} mbar) for 15 minutes at 200°C (sample b), 300°C (sample a), 400°C (sample c), and 500°C (sample d), respectively.

2.3 The edge thermal dynamics investigated by Raman spectroscopy and image

Figure 2.3a is the optical image of a single layer graphene flake (sample a) with angle between adjacent edges of 150° . Figure 2.3b and 2.3c are Raman images of intensities of G and D peaks of this sample. It can be seen clearly from Figure 2.3c that for the pristine graphene, edge a_1 presents a strong D peak while edge a_2 shows only a very weak D peak. To avoid the Raman intensity dependence on the relative angle between the edge and laser polarization direction, the incident laser is polarized (shown in Figure 2.3b) along the direction perpendicular to the bisector. Therefore, it can be confirmed that edge a_1 is A-edge while edge a_2 is Z-edge.¹¹⁴ Then the sample is annealed in vacuum (5×10^{-5} mbar) in order to

Figure 2.3 (a) Optical image of single layer graphene (sample a), the dashed red lines show the angle between two adjacent edges is 150° . (b) Raman image of G peak intensity of graphene (sample a) before annealing. The arrows indicate the incident laser polarization. (c) and (d) are Raman images of D peak intensity of graphene (sample a) before and after annealing at 300°C , respectively. (e) Raman spectra of pristine and annealed edges (a_1 and a_2).

study the thermal stability of graphene edges. Figure 2.3d presents Raman image of D peak intensity of the same sample after annealed at 300°C for 15 minutes. It can be clearly seen that the D peak intensity of edge a_2 becomes comparable to that of edge a_1 . This suggests that there is a significant change for the Z-edges (edge a_2) after thermal treatment, where the edge atoms may undergo rearrangement to satisfy double resonance and hence activate the Raman D peak. Raman spectra collected from the edges (Figure 2.2e) also demonstrate the obvious increase of the D peak intensity of Z-edge a_2 after annealing. In the meanwhile, the Raman spectra from the center region of graphene flake do not show any D peak (not shown). For comparison of the temperature effect, the Raman images the other three samples which were annealed at 200, 400 and 500°C (sample b, c and d) show similar changes, with a significant increase of D peak intensity of Z-edges after annealing

Figure 2.4 (a) Optical image of single layer graphene (sample b), the dashed red lines show the angle between two adjacent edges is 150°. (b) Raman image of G peak intensity of graphene (sample b) before annealing. The arrows indicate the incident laser polarization. (c) and (d) are Raman images of D peak intensity of graphene (sample b) before and after annealed at 200°C, respectively. (e) Raman spectra of pristine and annealed edges (b_1 and b_2).

Figure 2.5 (a) Optical image of single layer graphene (sample c), the dashed red lines show the angle between two adjacent edges is 30°. (b) Raman image of G peak intensity of graphene (sample c) before annealing. The arrows indicate the incident laser polarization. (c) and (d) are Raman images of D peak intensity of graphene (sample c) before and after annealed at 400°C, respectively. (e) Raman spectra of pristine and annealed edges (c₁ and c₂).

Figure 2.6 (a) Optical image of single layer graphene (sample d), the dashed red lines show the angle between two adjacent edges is 150°. (b) Raman image of G peak intensity of graphene (sample d) before annealing. The arrows indicate the incident laser polarization. (c) and (d) are Raman images of D peak intensity of graphene (sample d) before and after annealed at 500°C, respectively. (e) Raman spectra of pristine and annealed edges (d₁ and d₂).

as shown in Figure 2.4 – 2.6. However, the intensity of D peak after 200°C annealing is relatively small, which suggests that 200°C is the critical temperature where Z-edges start to change/rearrange. The experimental results suggest that graphene edges (A-edges to be discussed later) are not stable even at temperature as low as ~200°C. Such annealing temperature (or even higher temperature) is commonly used for graphene cleaning as well as process in device fabrications.^{4, 22, 129-132, 134-136} Furthermore, I should point out that vacuum annealing can naturally induce p-doping on graphene.^{39, 147} This would definitely give rise to the stiffening (blueshift) and sharpening effect on G peak as shown in Figure 2.3e, due to the non-adiabatic removal of the Kohn anomaly at Γ point.^{115, 148} For the 2D peak of annealed sample, the significantly decrease of intensity compared to that of pristine graphene is observed (not shown), which is in agreement with the previously reported result elsewhere,¹⁴⁹ and this is also because of that doping gives rise to the increase in electron-electron collision and inelastic scattering, and thus strongly decreases the 2D peak intensity.^{150, 151}

As aforementioned, Z-edges do not fulfill double resonance condition and hence do not present D peak. The appearance of small D peak in pristine Z-edges (<5% of the intensity of G peak as shown later in Figure 2.9a) is attributed to small amount of armchair segments and short range defects.^{114, 124} For the significant increase of D peak intensity of annealed Z-edges, two possible edge modifications are proposed: (1) carbon atoms of Z-edges reconstructed to form armchair segments $\pm 30^\circ$ respect to the edge direction (A-30°), as shown in Figure 2.7b and 2.8a; (2) short-range defects formed, *i.e.* the edge structures with coherence length less than the electron wavelength 0.6 nm (for electron excited by 532 nm laser)¹²⁴

cannot be considered as proper edges, instead they can be considered as point defects. The possible formation of C-O bonds at graphene edges during annealing can also be considered as short-range/point defects.¹⁵² Note that the 5-7-7-5 and 5-8-5 defects are excluded in the samples as these defects normally formed at much higher temperature.^{123, 153} Besides the two proposed edge segments, some of the zigzag segments may remain unchanged (Z-0°), while some may rearrange as zigzag segments at $\pm 60^\circ$ respect to the original zigzag direction (Z-60°) during the annealing process, although these two components are D peak inactive. The structure of ideal pristine Z-edges and rearranged structure of annealed Z-edges are shown in Figure 2.7a and b, respectively.

Figure 2.7 Schematic illustration for the edges rearrangement. (a) Ideal zigzag edge (Z-edge). (b) Annealed Z-edges contain unchanged zigzag segments (Z-0°), rearranged armchair segments at $\pm 30^\circ$ (A-30°) and zigzag segments at $\pm 60^\circ$ (Z-60°), as well as point defects (short-range defects). (c) Ideal armchair edge (A-edge). (d) Annealed A-edges contain unchanged armchair segments (A-0°), rearranged zigzag segments at $\pm 30^\circ$ (Z-30°) and armchair segments at $\pm 60^\circ$ (A-60°), as well as point defects (short-range defects). Blue atoms denote the zigzag

segments, red atoms denote the armchair segments, and green atoms denote the point defects (short-range defects).

2.4 The edge components characterized by polarized Raman spectroscopy

In order to estimate the portions of each type of edge segments in annealed edges, polarized Raman studies were carried out. As different types of edge structures scatter electrons in different directions, the D peak induced by them have different polarization dependence, *i.e.* the dependence of D peak intensity of ideal A-edges on incident laser polarization can be expressed as $I_D \propto \cos^2\theta$. On the other hand, for short-range/point defects, the D peak intensity does not have any polarization dependence.^{124, 125} Therefore, the polarization studies of graphene edges can be used as a useful way to estimate the amount of each type of edge segments. For annealed Z-edge, both rearranged A-30° edges and point defects are D peak activated, while only A-30° defects present incident laser polarization dependence. The detailed structure of rearranged A-30° defects is shown in Figure 2.8a, and the dependence of D peak intensity of A-30° edges on incident laser polarization can be expressed as:

$$I_D \propto \frac{1}{2} [\cos^2(\theta - 30^\circ) + \cos^2(\theta + 30^\circ)] \quad (2.1)$$

Figure 2.8 (a) Schematic of rearranged A-30° segments with respect to the original Z-edges direction. The inset shows that electrons scattered from such edges can fulfill the double resonance condition. (b) The normalized D peak intensity as function of the incident laser polarization for ideal A-edges (black curve) and rearranged A-30° segments (red curve) as well as point defects (green curve).

For comparison, the polarization dependence of D peak intensity for ideal A-edges (i.e. $\cos^2\theta$), A-30° edges ($\frac{1}{2}[\cos^2(\theta-30)+\cos^2(\theta+30)]$), and point defects are drawn in Figure 2.8b. It is obvious that the D peak from A-30° edge has weaker polarization dependence compared with that from an ideal A-edge, while that from point defects does not show any polarization dependence. If we assume that in annealed Z-edges, the A-30° edges and point defects weight f_1 and f_2 , respectively; while unchanged zigzag segments Z-0° and those rearranged Z-60° weight f_3 and f_4 . Thus $f_1 + f_2 + f_3 + f_4 = 1$, and the polarization dependence of D peak intensity can then be expressed by:

$$\frac{f_1}{2}[\cos^2(\theta-30)+\cos^2(\theta+30)]+f_2 \quad (2a)$$

$$\text{or } \frac{1}{4}f_1 + f_2 + \frac{1}{2}f_1 \cos^2 \theta \quad (2b)$$

Figure 2.9 Polarization dependence of I_D/I_G , θ is the angle between laser polarization and edge direction. (a) and (f) are pristine Z-edges and A-edges, respectively. (b), (c), (d) and (e) are annealed Z-edges at 200°C, 300°C, 400°C and 500°C, respectively; (g), (h), (i) and (j) are annealed A-edges at 200°C, 300°C, 400°C and 500°C, respectively. All the polar graphs are with same scale bar, which is from 0 to 0.5.

Figure 2.9a-e show the experimentally obtained I_D/I_G as function of θ for pristine Z-edges and Z-edges annealed at 200°C, 300°C, 400°C and 500°C, respectively (In this chapter, the intensity ratio of I_D/I_G is used instead of absolute values of D peak intensity in order to minimize measurement error). The D peak of pristine Z-edges (Figure 2.9a) is very weak but non-zero as edges are not perfect in real case. For 200°C annealed Z-edges (Figure 2.9b), the I_D/I_G becomes obviously larger than that of pristine Z-edges. The polarization dependence of I_D/I_G presents similar shape as that expected from ideal A-30° edges (the red curves in Figure 2.7b and 2.8b). Thus it can be concluded that a small portion of zigzag segments in Z-edges start to modify and form A-30° segments at the annealing temperature of

200°C. For Z-edges annealed at higher temperature (300°C or above), the D peak intensity grows much stronger and is comparable to that of annealed A-edges (as shown in Figure 2.9c-e). This suggests that the values of f_3 and f_4 are very small compared with $f_1 + f_2$ (or else, the appearance of zigzag segments would certainly reduce the intensity of D peak), and could be ignored. Fitting the data in Figure 2.9b-e with formula (2), we can roughly obtain the values of f_1/f_2 , which are ~80, ~14.5, ~6.6 and ~4.9 for Z-edges annealed at 200°C, 300°C, 400°C and 500°C, respectively. The portion of armchair components (A-30°) on Z-edges annealed at different temperatures is shown by the red triangles in Figure 2.10b. (The D peak intensity of 200°C annealed Z-edges is only ~35% of that of pristine A-edges, taking into account the shape of A-30°, the portion of armchair segments (A-30°) for 200°C annealed sample is estimated to be ~54%.) It can be seen that, the portion of A-30° segments increases dramatically at ~200°C (~54%) and reaches maximum at ~300°C (~93%). At higher temperature (400 and 500°C), A-30° segments still dominate in the annealed Z-edges (87% and 83% respectively), but the portion of short-range point defects slightly increases.

Different from Z-edge, the D peak intensities of A-edges do not have obvious change after annealing at different temperatures except that the polarization dependence of D peak intensity becomes much weaker after annealing. The intensity ratio of I_D/I_G of different A-edges and Z-edges with laser polarization at 90° and 0° relative to edges are shown in Figure 2.10a. It can be seen that the ratio between maximum I_D/I_G ($\theta=0^\circ$) and minimum I_D/I_G ($\theta=90^\circ$) of pristine A-edges is ~7 before annealing, while after annealed at 200, 300, 400 and 500°C, this ratio decreased to ~3.5, ~3.0, ~2.3 and ~2.3, respectively. These results clearly indicate that A-edges are also not stable and undergo modifications during annealing. The

schematic crystal structures of pristine and annealed A-edges are shown in Figure 2.7c and 2.7d. For A-edge, we assume the armchair segments remain unchanged (A-0°) weights f_5 ; those rearranged armchair segment at $\pm 60^\circ$ (A-60°) and zigzag segments at $\pm 30^\circ$ (Z-30°) weight f_6 and f_7 , respectively; the point defects weights f_8 . Therefore, $f_5 + f_6 + f_7 + f_8 = 1$. Giving the factor that $(I_D/I_G)_{\theta=0^\circ} / (I_D/I_G)_{\theta=90^\circ}$ of annealed A-edges kept almost unchanged from pristine A-edges (Figure 2.10a), it would be reasonable to claim that Z-30° segments (f_7) are negligible (or else, the appearance of zigzag segments would certainly reduce the intensity of D peak). The polarization dependence of D peak intensity can then be written as:

$$f_5 \cos^2 \theta + \frac{f_6}{2} [\cos^2(\theta - 60) + \cos^2(\theta + 60)] + f_8 \quad (2.3a)$$

$$\text{or } \frac{1}{2} (2f_5 - f_6) \cos^2 \theta + \frac{3}{4} f_6 + f_8 \quad (2.3b)$$

Figure 2.9f shows the I_D/I_G as function of laser polarization for pristine A-edge. As can be seen, for pristine A-edge, I_D/I_G almost follows $\cos^2 \theta$ polarization dependence, and the value of $(I_D/I_G)_{\theta=0^\circ} / (I_D/I_G)_{\theta=90^\circ}$ is very large, this suggests that A-0° segments (f_5) dominate in A-edges. Fit the data in Figure 2.9f and data from other three pristine samples with formula (3), it can be obtained that the portion of A-0° (f_5) segments is around ~83% for pristine A-edges, and the remaining ~17% could mostly be A-60° segments as portion of point defects are very small at low temperature according to the results of annealed Z-edges. After annealing, the polarization dependence of I_D/I_G becomes much weaker, as shown in Figure 2.9g to j. The portion values of A-0° obtained from fitting as a function of annealing temperature is shown in Figure 2.10b. It is clearly seen that the portion of A-0° becomes less with higher temperature annealing, but still values ~57% even after 500°C anneal. The rest edge components consist of A-60° and point defects, and

we are not able to extract their exact portions based on formula (2.3) only. However, the ratio between A-60° and point defects can be roughly estimated from the results of annealed Z-edges, which are ~80, ~14.5, ~6.6 and ~4.9 for edges annealed at 200°C, 300°C, 400°C and 500°C, respectively. With such estimation, the portion of A-0°, A-60°, and point defects of annealed A-edges can be calculated respectively. Here, we mainly concern the armchair segments (A-0°+A-60°) for annealed A-edges, which are shown by blue stars in Figure 2.9b. It can be seen that, the armchair segments (A-0°+A-60°) dominate on annealed A-edges at different temperatures, with a slight drop at high temperature (300-500°C) due to the appearance of point defects.

Based on above discussion, we could conclude that armchair segments are more stable compared to zigzag segments during thermal treatment, *i.e.* zigzag would change and form armchair at high temperature. This agrees well with the theoretical calculation that armchair have lower energy compared to zigzag.¹²² However, this result is different from the stability of graphene edges under electron beam irradiation, where the zigzag edge is relatively more stable than armchair.⁶⁴ This is possibly due to the very different experimental conditions for the two experiments. There was also an argument that the “zigzag” segments observed in that experiment are actually “reconstructed zigzag” (5-7 defects).¹²³ Meanwhile, I notice that graphene center region (Carbon atoms in form of intact sp² hybridization) is very stable as the D-peak keeps inactive even I annealed graphene at 700°C (5×10⁻⁵ mbar).

It is theoretically predicted that A-edges GNRs are semiconducting with energy gap inversely proportional to the width,¹⁵⁴ and it is also experimentally demonstrated that the higher concentration of zigzag segments would significantly

reduce the energy gap of GNRs.¹³¹ Thus, the modifications of edge structures by thermal annealing (zigzag segments rearrange in form of armchair segments) provide a flexible way to control the electronic structure (such as energy gap) of graphene and graphene nanostructures.

Figure 2.10 (a) I_D/I_G of A-edges (both pristine and annealed) and Z-edges (annealed) as a function of annealing temperature. (b) Edge components evolution as a function of annealing temperature for Z-edges (red triangles for A-30°) and A-edges (black squares for A-0°; black circles for A-60° and blue stars for A-0°+A-60°), respectively.

2.5 Conclusions

In summary, it is experimentally confirmed by polarized Raman spectroscopy that different from center region of graphene, the graphene edges are not thermally stable even at low annealing temperature, *i.e.* 200°C. The zigzag edges rearrange and form armchair segments that are $\pm 30^\circ$ relative to the edge direction, while armchair edges are dominated by armchair segments even at the annealing temperature as high as 500°C. These results could be very useful in guiding future application or modification of graphene's properties based on its edges. It also provides valuable information for the device fabrication of graphene-based

nanoelectronics, in which the energy gap of graphene nanostructures could be effectively controlled by tuning the concentration of each edge segments (zigzag and armchair) with thermal annealing.

Chapter 3

Edge dynamics of AB-stacked few-layer graphene

3.1 Significance of the edge dynamics for AB-stacked bilayer graphene edges

In Chapter 2, the importance in both fundamental and practical sciences of graphene edges are introduced. The most key factor for graphene, the electronic and transport properties, are showing strong dependence on its edge structures,⁶⁴ and therefore the graphene nanoribbons (GNRs), have been intensively studied^{114, 118-127} since its experimental isolation. As the crucial step for fabricating graphene into future nanoelectronics,¹⁵⁵⁻¹⁵⁷ understanding the thermal dynamics of its edges has been the major focus among those studies. For single layer graphene, the zigzag edge (Z-edge) is thermally unstable and it can be easily modified to form armchair segments along $\pm 30^\circ$ with respect to the original edge direction.¹⁵⁵ For bilayer graphene (BLG), Liu *et al.* observed by HRTEM¹⁵⁶ that BLGs would transform to AA-stacked style with closed edges after extremely high temperature annealing (2000 °C). Meanwhile, using NEXFAS¹⁵⁷, Joly *et al.* indirectly observed the loop formation of the edges of few-layer graphene (FLG) after high temperature annealing (1500-2000 °C). The closed edges bilayer graphene (CEBG) is a recent discovered novel form of graphene structures,^{153, 156} whose regulated edge states may critically change the overall electronic behaviours. If stacked properly with the AB style, the bilayer graphene with closed zigzag edges may even present amazing electronic properties of bandgap opening and charge

separation (it will be introduced later). Experimentally, the CEBG has been confirmed recently with HRTEM observations after extremely high temperature annealing (2000 °C).^{153, 156} From the application point of view, the low temperature closing of the graphene edges would be much more feasible for large-scale graphene-based electronic devices fabrication. AB stacking (Figure 3.1a,b) is the native stacking style of graphene layers¹⁵⁸ and low temperature processing of graphene is also much more practically desirable, thus the further investigation on low temperature thermal dynamic behaviors of AB-stacked BLG edges would be timely and meaningful towards the complete understanding of BLG edge dynamics. One interesting phenomenon but few reports notice the rule is that for AB-stacked BLG under low temperature which impeded layer gliding, geometry incompatibility limit armchair edges (A-edges) form closing edges with perfect sp^2 hybridized C-C bonds (Figure 3.1d,f), and allow only zigzag edges (Z-edges) form closed edge loop (Figure 3.1c,e). Therefore, AB-stacked CEBG with Z-edges could be possibly formed under low temperature. In this chapter, I will scientifically demonstrate my recent work that the zigzag edges of AB-stacked bilayer graphene will form curved close structure naturally at low annealing temperature (< 500 °C) based on Raman observation and first principles analysis. Of great importance, such findings may illuminate a simple and easy way to engineer graphene electronics.

Figure 3.1 Schematic atomic structure for AB-stacked bilayer graphene (BLG), x -axis is along zigzag direction; y axis is along armchair direction; z -axis is perpendicular to the basal plane. (a), Top view. (b), Cross-section view along x -axis for open-edge BLG. (c), Cross-section view along x -axis for closed-edges BLG. (d), Cross-section view along y -axis for BLG. (e), Cross-section view along y axis shows that the closed structure formed along zigzag edges is geometrically compatible. (f), Cross-section view along x axis shows that the A-edges cannot form closed structure because of geometrically compatible.

3.2 Experimental

Graphene samples were prepared by conventional micromechanical cleavage method on silicon wafer covered by 300 nm SiO₂. The layer number from 1L to 3L of graphene flakes was confirmed by Raman and contrast spectra.^{139, 142, 143}

The Raman spectra were carried out with a WITEC CRM200 Raman system, with excitation laser wavelength of 532 nm and 100× objective (Numerical Aperture, NA=0.95). The laser power at sample is below 1 mW to avoid possible laser heating induced sample damage.¹⁴⁶ Raman images with a spatial resolution of ~600 nm are realized with a piezo stage (step size 100 nm) and the integration time at each position is one second. Samples with straight edges and angle of 150° between adjacent edges were selected so that for each sample, one edge is A-edges (strong D peak) and the other is Z-edges (weak D peak). Each single Raman spectrum of graphene edges is determined by Raman line scan (step size 50 nm) across the edge to make sure the maximum intensity of D peak is approached. The annealing process for each graphene sample keeps at the same condition: annealing at 500 °C for 15 minutes and the vacuum level is 5×10^{-5} mbar.

The energy barriers of edge closing of bilayer graphene, modeled as Fig. 2, have been studied with nudged elastic band method. First principles total energy calculations of Density Functional Theory (DFT) are performed within Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation. The projected augmented wave method as implemented in the VASP code¹⁵⁹⁻¹⁶¹ is employed to solve the Kohn-Sham equations. A kinetic energy cutoff of 400 eV and the k-points sampling of $24 \times 1 \times 1$ are used for simulating CEBGs. All model structures are optimized with the vacuum separation set to be more than 10 Å, and the total energy converges to 1 meV.

In this chapter, the Density Functional Theory (DFT) calculation is used to predict that the AB-stacked CEBG can be formed easily because of the favourable energy. Polarized Raman spectroscopy and Raman images were carried out to investigate the thermal dynamics of AB-stacked FLG edges, and the experimental results provide clear evidence that the AB-stacked CEBG can be formed at very low temperature (<500 °C).

3.3 The theoretical model for the AB-stacked CEBG formation

The formation of AB-stacked CEBG can be understood by DFT calculation results. Figure 3.2 shows the evolution of system energy for AB-stacked BLG from its initial open edge to the final relaxed state with closed Z-edges through a dynamic process. In this simulation study, we did not observe any energy barrier from the initial open edge state to closed edge state, instead, the system energy undergoes more than 2 eV drop when the atoms on the top and bottom Z-edges firstly bonded. Afterward, the system energy further decreases slightly (Figure 3.2g) by structure relaxing (Figure 3.2b-f). Therefore, it is clear that the AB-stacked CEBG is dynamically and energetically favorable. Furthermore, it is also reported that the open and sharp Z-edges of AB-stacked BLG can be transformed to CEBG rapidly according to the quantum molecular dynamics simulation results.¹⁶²

Figure 3.2 Modeling of the closed Z-edges of BLG formation from the initial open edges configuration. a and b, Edge structure evolution from open edges to closed edges; c-f, The energy relaxation dynamics of closed edges by curvature smoothing. g, The system energy evolution versus the modeled structure configurations as shown in a-f.

To confirm this theoretical prediction, I carried out systematic experimental studies based on Raman spectroscopy. Raman spectroscopy is a non-destructive, fast and effective tool for investigating graphene-based material²¹, not only for

Figure 3.3 Raman images for SLG, BLG and TLG. **a-c**, G peak intensity for pristine SLG, BLG and TLG, respectively; **d-f**, D peak intensity for pristine SLG, BLG and TLG; **g-i**, D peak intensity for annealed SLG, BLG and TLG. The polarizations of the incident laser are all horizontal and the scale bar for each image is $1\mu\text{m}$.

detecting defects, doping and intercalation^{104, 151, 163, 164} but also for identifying edge structures:^{114, 124, 126, 155, 164} the D band is inactive for Z-edge but it is activated for A-edge, and its intensity is strongly dependent on incident laser polarization. Figure 3.3a-c show the integrated G peak Raman images of graphene flakes with layer number of 1 (SLG), 2 (BLG) and 3 (Trilayer graphene, TLG), respectively (both BLG and TLG have AB stacking sequence). Each graphene sample consists of two sharp edges with angle of 150° , meaning that two edges must have different chiralities. Figure 3.3d-f show Raman images of D peak intensity for pristine graphene samples of SLG, BLG, and TLG, respectively. A prominent D peak observed along the left edge (edge A₁, B₁, and C₁) of each sample indicates an A-

edge, while the absence of obvious D peak for the right edge for each sample (edge A₂, B₂, and

Figure 3.4 Raman spectra for SLG, BLG and TLG. Pristine (a) and annealed (b) Z-edges; Pristine (c) and annealed (d) A-edges.

C₂) indicates a Z-edge.^{114, 124, 126, 165} Raman images of the D peak intensity of the same samples after 500 °C annealing are shown in Figure 3.3g-i. It is noticed that

there is no obvious change in the D peak intensity for annealed A-edges (left edges) of each sample as they still show prominent D peak. Furthermore, Figure 3.4c,d respectively show the Raman spectra for pristine and annealed graphene A-edges, and there is no obvious difference in the I_D/I_G intensity ratio between pristine and annealed A-edges for SLG, BLG and TLG. The results of Raman images and spectra indicate that thermal dynamic behavior for few-layer graphene (BLG and TLG) A-edges is similar to that of SLG¹⁵⁵, and I will show detailed analysis of the annealed A-edges by polarized Raman results later.

On the other hand, for Z-edges, SLG and TLG respectively show strong D peak after annealing, while the D peak of BLG almost keeps Raman inactive after annealing. Raman spectra for pristine and annealed Z-edges are respectively shown in Figure 3.4a,b. It is clearly seen that only Z-edges of SLG and TLG show prominent D peak after annealing while the BLG still shows absence of the D peak similar to that of precursor pristine sample. I have examined more than 20 Z-edges and all SLGs and TLGs show obvious activated D peak after annealing while the BLGs do not. The behavior of SLG can be easily understood as thermal dynamics of Z-edges of SLG has been discussed in last Chapter.¹⁵⁵ It has been revealed that Z-edges of SLG are not thermally stable and can be easily transformed to armchair segments at $\pm 30^\circ$ with respect to the original edge direction after annealing, and thus it present strong D peak¹⁵⁵. However, the behavior of BLG after annealing is very different. One reasonable explanation for BLG Z-edges is that the low temperature annealing leads the carbon atoms of top and bottom edges bond to each other to form intact sp^2 hybridized smooth loop configuration, which follows the simulation results (Figure 3.2). As there is no open edges, it is reasonable to expect the D band remains absent when the loop is smooth enough.¹⁶⁶

Figure 3.5 Polarization dependence of I_D/I_G for SLG, BLG and TLG. θ is the angle between laser polarization and edge direction. a-c, Pristine A-edges for SLG, BLG and TLG, respectively. d-f, Annealed A-edges for SLG, BLG and TLG, respectively. g-i, Annealed Z-edges for SLG, BLG and TLG, respectively. The scale bar for the polar graphs is 0-0.5 for SLG, 0-0.35 for BLG and 0-0.2 for TLG.

Because D peak intensity is strongly dependent on laser polarization for armchair segments, I carried out polarized Raman study to further analyze the

thermal dynamic behavior of A-edges and Z-edges in detail. Figure 3.5 shows the experimentally obtained I_D/I_G as function of θ for pristine and annealed edges (SLG, BLG and TLG). θ is the angle between incident laser polarization and edge direction; for each θ , line scan was used to determine the exact edge position by observing maximum D peak intensity I_D . The fitted curves for A-edges and Z-edges are based on the formulas described in Ref. [175] throughout this paper. For annealed Z-edges, BLG only shows very weak I_D/I_G even when the incident laser polarization is parallel to the edge direction; while TLG not only shows obvious activated D peak similar to that of SLG, but the polarization dependent tendency is also very similar. For SLG, a large portion of the Z-edge is easily modified in form of armchair segments at $\pm 30^\circ$ after 500 °C annealing, and hence I_D/I_G shows some extent polarization dependence.¹⁵⁵ Based on above results, I conclude that for TLG, although two of the adjacent open Z-edges may form closed structure, the D peak must be activated because at least one lonely Z-edge of TLG should follow similar structure modification as that of SLG upon annealing.¹⁵⁵

For A-edges, the pristine SLG, BLG and TLG present obvious polarization dependent intensity ratio of I_D/I_G (Figure 3.5a-c). After annealing, the polarization dependent intensity ratio of I_D/I_G becomes slightly weaker (Figure 3.5d-f). For SLG, the weaker polarization dependence of A-edge is explained as the edge structure modification (*i.e.* Some portion transforms to armchair segments at $\pm 60^\circ$ with respect to the original edge direction and hence weaken the total polarization dependence).¹⁵⁵ The similar dependent tendency of polarized intensity ratio of I_D/I_G for TLG and BLG to that of SLG indicates that the A-edges of TLG and BLG have similar thermal dynamic behavior as that of SLG. In other words, the A-edges of TLG and BLG can be respectively considered as three and two independent

individual A-edges when they are undergone thermal treatment. This is reasonable because unlike Z-edges which can form closed structure upon annealing, the adjacent A-edges of AB-stacked FLG cannot form perfect sp^2 hybridized closed structure due to geometrical incompatibility as aforementioned (Figure 3.1c,d).

3.4 Discussion for the edge dynamics of AB-stacked BLG from low-T to high-T

Liu *et al.* recently reported that AB-stacked graphite transformed to AA-stacked BLGs with both A-edges and Z-edges closed after extremely high temperature annealing (2000 °C).¹⁵⁶ Here, I propose a thermal dynamic model to elucidate the structure evolution for AB-stacked BLG edges (both Z-edges and A-edges) according to the low temperature experimental results and high temperature results elsewhere.¹⁵⁶ When AB-stacked BLG annealed at low temperature, Z-edges start to form closed structure because such edge structure is geometrically compatible and energetically favourable (Figure 3.1a,b and Figure 3.2), while the A-edges keep open because of geometrical incompatibility for the formation of closed structure (Figure 3.1c,d). When the temperature increases, the thermal vibrating amplitude of carbon atoms becomes much larger (Figure 3.1a,b). When the annealing temperature is high enough (*i.e.* ~2000 °C), the top and bottom graphene layers have very high opportunity to transform to AA stacking sequence which requires a shift of the graphene layer by a C-C bond length along the x-axis (Figure 3.1d). In that case, atoms on the A-edges can bond each other to form interconnected configuration similar to Z-edges.¹⁶⁷ This thermal dynamic model for the edge structure evolution explains the results that AB-stacked graphite transforms to AA-stacked BLGs with both closed Z-edges and A-edges.¹⁵⁶

Figure 3.6 The schematic edge dynamics of AB-stacked bilayer graphene anneal at temperature from low to extremely high. (a) The pristine open-edge of AB stacking bilayer graphene, (b) The zigzag edges transform to closed edges when anneal at low temperature, (c) With temperature continuously increase, the top and bottom layers start to slide with respect to each other and the closed zigzag edges can be consider as hinges. (d) When the sliding makes the stacking style to AA, then armchair edges can form closed structure and hence lowering the energy of the whole system.

3.5 The electronic structure of closed-edge bilayer graphene

The discovery of the edge dynamics shows us that the AB-stacked bilayer graphene edges can transform to closed state along zigzag direction. Actually, the formation of closed edges not only changes crystal structure of graphene, but also modifies its electronic band structure.

Figure 3.7 The crystal structure of AB-stacked CEBG which forms at zigzag edges. The red and green balls represent pseudospin up and down, respectively.

As we know that the equivalence of the two unit-cell atoms of graphene leads the bonding (π) and anti-bonding (π^*) orbitals touching each other at opposite Brillouin zone corners of K and K' (Figure 1.10), and also gives an extra degree of freedom (i.e. pseudospin) to its low-energy (LE) quasi-particles. In the basis of pseudospins, the LE π electrons have been formally described by the Dirac-like Hamiltonian as:

$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \vec{\sigma} \cdot \vec{k} \quad (3.1)$$

Where v_F , $\vec{\sigma}$ and $\vec{k}$ are Fermi velocity, Pauli vector and the wave vector away from the K/K' point, respectively. The corresponding eigenstates show clearly the chiral nature of the LE quasi-particles, which is similar to the spinor wave function in quantum electrodynamics, as.

$$\Psi_{s,\vec{k}}(\vec{r}) = \begin{pmatrix} 1 \\ s\bar{k}e^{i\theta_{\vec{k}}} \end{pmatrix} \quad (3.2)$$

Here, $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ are Bloch sums of π orbitals on two sublattices, $s = \pm 1$ is the

band index and $\theta_{\vec{k}}$ is the polar angle of the wave vector $\vec{k}$. These zero-mass low-

energy carriers, pseudospin states, which behave as relativistic Dirac fermions are responsible for the remarkable electrical transport properties of graphene. While the magnitude of the bandgap has been found to equal the on-site energy difference of the unit-cell atoms, in order to open the π - π^* bandgap of graphene, its sublattice equivalence has to be broken as most of current graphene bandgap opening techniques. For the CEBG, the electronic coupling between the bottom and top graphene layers is not only limited by the interlayer electron hopping, but also the pseudospin interaction is switched on when these two layers bonded at edges (Figure 3.7). It is worth to note that the pseudospin interaction effect is only observed for AB-stacked CEBG. To explain this, I need to start from introducing the sublattice of graphene. The sublattice of graphene has two distinct sublattices which are denoted as A and B, respectively. For clear identification of the top and bottom graphene layers, I use A' and B' to denote the bottom layers as shown in Figure 3.8c and d (Actually, A and A' belong to the same sublattice, and B and B' belong to the other same sublattice). For AB-stacked CEBG, we can see the geometry that the sublattice A at the top layer couples to the A' in the bottom (Figure 3.8c), and thus the pseudospin repulsion in this system would be prominent which gives rise to the effect that opens its bandgap (Figure 3.8a). But for AA-stacked CEBG, there is no pseudospin repulsion between the top and bottom layers because the coupled sublattices between these two layers possess opposite chirality (Figure 3.8d), and thus the zero-bandgap keeps.

Figure 3.8 Calculated electronic band structures of AB-stacked (a) and AA-stacked (b) CEBG. Insets are zoom-in of the bandgap regions around Dirac points. Schematic pseudospin interactions in AB-stacked (c) and AA-stacked (d) CEBG.

For AB-stacked bilayer graphene, breaking the sublattice equivalence can open its bandgap. In CEBG, I present another novel mechanism, namely pseudospin interaction that drives for opening bandgap. Thus it opens a new route for graphene's bandgap engineering.

3.6 Conclusions

In conclusion, I revealed by DFT calculations and systematic Raman investigations that the AB-stacked open Z-edges of BLG can transform to closed sp^2 hybridized structure easily even at very low annealing temperature because such structure is geometrically compatible and energetically favorable, and the closed edges is thermally stable. In contrast to thermal dynamic behavior of Z-edges, A-edges of AB-stacked BLG cannot form closed sp^2 hybridized structure

due to geometrical incompatibility, and thus the A-edges for BLG behaves as two independent SLGs. The formation of closed Z-edges for AB-stacked BLG by low temperature treatment matches the semiconductor manufacturing process, thus this finding may benefit graphene-based nanoelectronics as closed edges of AB-stacked BLG is predicted to present exotic electronic properties, such as pseudospin repulsion induced bandgap opening and charge separation.¹⁶⁸

Chapter 4

FeCl₃-based full intercalated few-layer graphene

4.1 Graphite intercalation compounds

Graphite intercalation compounds (GICs) are complex materials formed by insertion of atomic or molecular layers of different chemical species between graphite interlayer space.^[169] The interlayer distance of graphite is dramatically increased due to presence of intercalants, which would strongly affect the electronic coupling between graphene layers, hence changes its properties. Moreover, due to the wide variation of intercalants, different physical properties can be achieved for GIC, such as electrical, thermal and magnetic properties.^[169-171]

The GIC occurs in highly anisotropic layered structures where the intra-planar binding forces are much larger than that of inter-planar. For GIC, the graphene layers play a function as host material is of particular physical interest due to their relatively high degree of structural ordering.

The guest intercalant molecule species can be flexibly selected, thus the intercalation can modify graphite's many physical properties in a wide range. Intercalation with different chemical species and concentrations provides controllable tuning the electrical, thermal, magnetic properties of graphite.

4.1.1 Preparation of graphite intercalation compounds

The intercalants can be divided into two groups, donor and acceptor types. The donor and acceptor type intercalants can respectively dope electrons and holes to

the adjacent graphene layers. To date, the most reported donor type guest intercalant species in GIC are alkali metals, alkali earth metals; and halogens and some transition-metal-based chlorides and fluorides are the acceptor type intercalants.

The preparation of the GIC normally needs to use two-zone vapour transport method. As schematically shown in Figure 4.1, the guest intercalant specie and graphite are separated at two regions in a sealed vessel. Then put the vessel into a furnace to heat it, and control the temperature at intercalant region (T_i) higher than its melting point while keeping the graphite side (T_g) at a higher temperature than T_i . The intercalation concentration (stage number) of the final synthesized products can be controlled by controlling both the reaction time and temperature difference $T_g - T_i$.

Figure 4.1 Schematic diagram of the two-zone vapor transport method, where T_g and T_i are the temperature of the graphite and intercalant, respectively.

4.1.2 The identification of stage number of graphite intercalation compounds

The graphite-based host material intercalation can be formed in different chemical ratios even for the same guest intercalant material, which is called the staging phenomenon. As shown in Figure 4.2, the stage number is defined by the number of graphene layers that separate the adjacent intercalant layers.

Figure 4.2 Schematic diagram for the potassium-based GIC with different stages.

Adapted from M. S. Dresselhaus and G. D. Dresselhaus.¹⁷²

There are two typical ways that can let us easily know the ‘stage number’ of the synthesized product. One is X-ray diffraction and the other is using Raman spectroscopy.

The repeat distance (I_c) of the a GIC with stage number ‘ n ’ can be expressed as:

$$I_c = (n-1)c_0 + d_s \quad (4.1)$$

Where $c_0 = 3.35 \text{ Å}$, is the distance between adjacent graphite layers and d_s is the distance separating two graphite layers between which an intercalate layer is sandwiched.¹²⁰ Therefore, I_c is dependent on the stage number n , and thus the n can be concluded by analyzing (00 l) diffractograms.

By using Raman spectroscopy to analyze the stage number of GIC for acceptor type (transition metal chloride, halogens), the mechanism is to compare the G band

Figure 4.3 Schematic diagram of stage 5 acceptor type GIC. The bound layers and inner layers are indicated by green and black solid lines, respectively, and the intercalant is indicated by dotted line. The intensity ratio of Raman G bands of I_{Gb}/I_{Gi} is expected to be $\sim 2/3$.

intensity for three different type graphene layers. For stage 1 case in which the intercalant fully intercalated into every interlayer space of graphite, the graphene layers are doped by hole heavily, as I introduced in Chapter 1 that the G band position is sensitive to the doping level, and thus a very large shift from ~ 1580 to $\sim 1625 \text{ cm}^{-1}$ can be observed. For stage 2 case, as the graphene layers only be flanked by one side of intercalant, thus the doping level is lower compared to the stage 1 case, a $\sim 32 \text{ cm}^{-1}$ shift for the G band can be observed in this case. For stage number 'n' larger than 2, in one repeat superlattice along the out-of-plane direction, there are 2 graphene layers (bound layers) doped as same as in stage 2 case and while the rest n-2 graphene layers are not affected by intercalant as they are inner layers. The bound layers would contribute the G band intensity at position around

$\sim 1612\text{ cm}^{-1}$ (G_b), while the inner layers would contribute the G band intensity at position as similar to the pristine graphene which is at $\sim 1583\text{ cm}^{-1}$ (G_i). Hence the intensity ratio of I_{Gb}/I_{Gi} can be used to determine the stage number. Figure 4.3 is a schematic stage 5 GIC, and the I_{Gb}/I_{Gi} is expected to be $\sim 2/3$.

4.1.3 The electronic properties of graphite intercalation compounds

Among all the modified physical properties, electronic property is of greatest importance. Graphite is normally considered as semimetal with high conductivity but not as good as that of the traditional metals. However, the intercalation of the guest molecules or atoms into the interlayer space would give rise to the conductivity enhancement effect. This is mainly because the guest-host coupling modifies the electronic band structure of graphene and consequently the electronic transport properties are changed. No matter the intercalation is acceptor or donor type, at least one order enhancement in conductivity will be observed for the stage 1 GIC, particularly that the intercalation of AsF_5 can let the whole system possess the electrical conductivity even higher than that of copper.¹⁷³

Another important outstanding electronic property for GIC is superconducting. So far, the superconductors based on single chemical elements are mainly observed for the transition metals. For both alkali metals and alkali earth metals, there is no superconducting phase. Graphite is also a non-superconductor material, but the reconstructed superlattice by intercalation of alkali metals or alkali earth metals can present superconducting phase, particularly the calcium-based graphite intercalation compound presents a transition temperature higher than 10 K.^[170, 171]

[illegible]

Figure 4.4 Periodic table of the superconductor elements. The black color denoted elements are superconductor metals. The red color denoted elements can be superconducting when forming GIC.

Other than the alkali and alkali earth metals, Yb-based GIC also present superconducting state with transition temperature around 6 K.^[170, 171] For clear comparison, the periodic table of superconductor elements is given in Figure 4.4.

4.2 Motivation for studying few-layer graphene intercalation compounds

Graphene has been recognized by scientists experimentally for more than 8 years. Therefore, there are a lot of research progresses have been achieved: (1) The most important and fundamental is that the scientists have already found a lot of ways to fabricate graphene.^[19, 34, 174-176] such as mechanical cleavage of graphite, epitaxial from SiC, separate graphite oxide, chemical vapour deposition. (2) The exotic electronic, thermal and mechanical properties have been discovered;^{[3, 4, 19,}

^{144, 177-179]} (3) graphene-based prototype devices have been successfully fabricated and some of them have been applied in industry.^[12, 14] However, it is worth to note that many of the unique properties are mainly presented by single layer graphene (SLG) owing to its linear dispersive electronic band structure. Modification of few-layer graphene (FLG) to make it behave as SLG is much desired. Actually, scientists have discovered that through rotating the layer stacking status, the FLG can indeed present SLG-like properties and this part is also introduced in Chapter 1.2.2 of this thesis. Intercalation is one promising way that can also make FLG behaves like SLG electronically because the intercalants separate the adjacent graphene layers. Before I carried out the experiment on FeCl₃-based FLG intercalation compound (FLGIC), Jung *et al.* reported their results on Br₂ and I₂ intercalated FLG, however, the FLG is not fully intercalated in terms of the Raman spectra and the structural model.^[117] In this chapter, I will introduce the fully intercalated FeCl₃-FLGIC (Without additional instruction, I use FLGIC instead of FeCl₃-FLGIC throughout the whole thesis). The preparation and Raman-based characterization of FLGIC are all discussed. For more clearly understanding the electronic properties of such kind of novel material, first principle calculations are also carried out to assist the analysis for the experimental results.

4.3 Experimental

Pristine graphene sheets were deposited on silicon wafer covered by 300 nm thick SiO₂ by using the conventional tape-based mechanical cleavage method. The thickness of graphene (1 layer (1L) to 4 layers (4L)) was confirmed by both Raman spectroscopy and contrast spectra.^[142, 143] The two-zone vapour transport method was used to fabricate FeCl₃-FLGIC. The chemical reaction took place inside a

normal glass tube. The graphene samples and anhydrous FeCl_3 powder (~ 0.03 gram) were separated by ~ 6 cm in the tube as shown in Figure 4.5. The glass tube was pumped to 10^{-2} torr and sealed at this vacuum state. In this experiment, two-zone method was processed using only single furnace instead of traditional two-furnace technique. The temperature distribution in the furnace was firstly measured precisely by a thermocouple before experiment. The reaction vessel was put inside the proper position in furnace to guarantee the two-zone temperatures are what I want (graphite powder side is ~ 360 °C and anhydrous FeCl_3 powder side is ~ 310 °C). The heating rate is not a very important factor, and it is set as 10 °C /min in this experiment, and the vessel was kept for 10 hours after the furnace reaches the setting temperatures. Finally the furnace was cooled to room temperature with a rate of ~ 10 °C /min.

Figure 4.5 Schematic diagram of the two-zone transport method for FLGIC preparation.

For comparison, I also fabricated some hole doped graphene by using the simple vacuum annealing method.^[87, 152] Firstly, graphene sample was put into a vacuum chamber equipped in a THMS 600 Linkam thermal stage. Once the vacuum of ~ 0.5 Pa was achieved by a mechanical pump, the temperature of the chamber was

started to increase to 500 °C with a rate of 20 °C/min. Then the temperature dwelled for 30 min at 500 °C, and finally the temperature decreased to room temperature with a rate of 20 °C. Once the vacuum broke, the graphene would be suddenly doped by O₂ from air-ambient.^[87, 152]

The final products were characterized by using both Raman spectroscopy and image, which were recorded by WITEC CRM200 system with spectral resolution of $\sim 1 \text{ cm}^{-1}$. A 532 nm (2.33 eV) laser is used as the excitation source and the laser power at sample is below 0.5 mW for avoiding heating effect. The objective lens with magnification of 100 $\times$ and a numerical aperture of 0.95 was used. For Raman mapping scanning, the sample is moved with step size of 250 nm by a piezo-stage and Raman spectrum is recorded at every point in the scanned area.

The structure model of FeCl₃-based stage 1 FLGIC is based on the previous reported results by M. S. Dresselhaus *et al.*^[172, 180, 181], and this structure is simulated with the density functional theoretical (DFT) calculation. A super-cell is constructed with lattice constants $a = 12.12 \text{ \AA}$ and $c = 9.37 \text{ \AA}$, where the layered FeCl₃ with 2 $\times$ 2 periods is taken as commensurate with the 5 $\times$ 5 unit cells of graphene (Figure 4.6). Then the DFT calculations based on the generalized gradient approximation (PBE-GGA)^[182] are performed by using the plane-wave basis VASP code.^[183] The projector augmented wave (PAW) method is also used to describe the electron-ion interactions. A kinetic energy cutoff of 400 eV and k-points sampling with separation of π in the Brillouin zone are also used. The modelled structure is then optimized by a conjugate gradient algorithm with a force convergence criterion of 0.01 eV/ $\text{\AA}$.

Figure 4.6 Schematic crystal structures of FLGIC. a) 2L-FLGIC. b) 3L-FLGIC. c) 4L-FLGIC. The model is constructed based on $\text{FeCl}_3\text{-GIC}$.^[169, 181, 184] The graphene layers flanked on one/both side(s) by FeCl_3 layer(s) are denoted as yellow/orange. Cl atoms and Fe atoms are denoted as green and blue, respectively.

4.4 Raman G Peak Features investigation for the Full intercalation structure of FLGIC

As aforementioned that the stage number is a key factor for GIC, where the definition of stage means the number of graphene layers sandwiched between the adjacent intercalated layers.^[185] Previously for bulk GIC, scientists used Raman spectroscopy to identify the intercalation stage of GIC based on its features of G band. The G band is E_{2g} mode of graphite representative of the in plane vibration. The frequency of G band of GIC is known to be affected by three main effects: charge transfer, intercalate-coupling effect and variation of lattice constant,^[186, 187]

And it is very sensitive to the degree of charge transfer.^[186, 188] For FeCl₃-GIC, both the G band's position and shape can differ under different intercalation conditions. For example, the position of singlet G peak can blue shift from 1580 cm⁻¹ (pristine graphite) to ~1612 cm⁻¹ for stage 2 GIC, representing graphene layer flanked on only one side by FeCl₃; or it can be blue shifted to ~1626 cm⁻¹ for stage 1 GIC, representing each graphene layer is flanked by FeCl₃ on both sides.^[180, 189] Furthermore, singlet G peak would be split into doublet structure for higher stage (stage>2) or mixed stages GIC.^[180, 189] The information of both position and intensity ratio of each component of doublet peaks can be used to identify the exact situation.

For the traditional two-zone method fabricated FLGIC (see Experimental Section), the Raman spectra for graphenes (1 layer (1L) to 4 layers (4L)) after intercalation are present in Figure 4.7. Because there is no interlayer space for SLG, thus it is not possible to be intercalated. The doping induced stiffening and sharpening of the G peak for SLG is still observed as this phenomenon is quite normal for SLG after vacuum annealing and exposure to air (blue shifts from 1581 to 1604 cm⁻¹).^[87, 152]

Now let us consider 2L graphene. Its G peak position is located ~1580 cm⁻¹ before intercalation, and it blue shifts to ~1612 cm⁻¹ (G₁) after intercalation. This is similar to the previous reported stage 2 bulk GIC's G peak position.^[174, 184] Because the shift of G peak position is extremely hug (~32 cm⁻¹), thus the substrate or interface charge density doping can be excluded as they normally only introduce a shift of less than 10 cm⁻¹ for graphene.^[139, 190] The similar Raman spectra for 2L-FLGIC and stage 2 GIC is ascribed to their similarity in structures. For 2L-FLGIC, both graphene layers are respectively flanked on one side by FeCl₃

layer (Figure 4.2a), which is as same as the structure of stage 2 GIC. Hence, it is reasonable that the G peak of 2L-FLGIC still presents one singlet peak even it is intercalated, and its position is very close to that of bulk-based stage 2 GIC.

Figure 4.7 The Raman Spectra of 1L doped graphene and 2L- to 4L- FLGIC shown in range of G and 2D bands. All the spectra were measured under same experimental conditions. The 2L-FLGIC presents a singlet G peak (G_1) at $\sim 1612 \text{ cm}^{-1}$, while 3L- and 4L- FLGIC show doublet G peaks (G_1 and G_2 peaks locate at $\sim 1612 \text{ cm}^{-1}$ and $\sim 1623 \text{ cm}^{-1}$, respectively) with different intensity ratio. The G_1 and G_2 peaks are fitted with dashed red and blue curves, respectively. Each spectrum shows single Lorentzian 2D peak and the intensity increases with the number of layers.

For 3L and 4L graphene after intercalated by FeCl_3 fully, both of them present doublet G band. One of the peaks locates at $\sim 1612 \text{ cm}^{-1}$ (G_1) and the other peak

locates at $\sim 1623\text{ cm}^{-1}$ (G_2). Figure 4.6b and c show the schematic structures of 3L- and 4L-FLGIC, the top and bottom graphene layers (carbon atoms in yellow) are flanked on one side by FeCl_3 layer, and they contribute to the G_1 peak similar as in 2L-FLGIC, and thus the peak intensity of G_1 without showing any layer dependence (2L to 4L) is reasonable as each of them just possesses two outer graphene layers (Figure 4.7). On the other hand, the inner graphene layer(s) (carbon atoms in orange) is(are) flanked on both sides by FeCl_3 layers, which is very similar to the case of stage 1 bulk-based GIC,^[174, 184] and they contribute to the more blue shifted G_2 peak at $\sim 1623\text{ cm}^{-1}$. The integrated intensity ratio of I_{G1}/I_{G2} is in the range of 1.2-1.8 and 0.4-0.8 for 3L-FLGIC and 4L-FLGIC, respectively. In fact, according to the schematic crystal structure illustrated in Figure 4.6b and c, the intensity ratio for 3L-FLGIC and 4L-FLGIC should be closed to 2 and 1, respectively. This conflict for the measured values and the theoretical values is not easy to be understood at beginning, but finally it is found that the difference is induced by the resonant contribution from FeCl_3 electronic band. I will introduce it later in Chapter 5.

4.5 Strong Charge Transfer Chemical Doping

The E_{2g} phonons stiffening (blue shift of G_1 and G_2 peaks) for graphene layer in FLGIC is mainly because of charge transfer induced doping effect.^[117] For FeCl_3 molecule, the Fe^{3+} is surrounded by Cl^- , thus the electro-negativity value (x) difference between Cl^- and Fe determines the charge transfer direction between FeCl_3 and C in FLGIC. The charge would be transferred from FeCl_3 to graphite if $x_{\text{Cl}^-} < x_{\text{C}}$, and the charge would be transferred from graphite to FeCl_3 if $x_{\text{Cl}^-} > x_{\text{C}}$. The electron-negativity x is expressed by:

$$x = \frac{3.59 \times 10^3 z^*}{r^2} + 0.744 \quad (4.1)$$

In Formula 4.1, z^* is the effective nuclear charge, r is the covalent radius. Thus by solving Formula 4.1, it is found that the values of $x_{\text{cl-}}$ and x_{C} are 2.72 and 2.55, respectively. Therefore, each graphene layer is positively doped in FLGIC as FeCl_3 is more electron-negative compared to pristine graphene.^[187] The strong charge transfer effect gives rise to the downshift of Fermi surface of graphene, and consequently it causes stiffening effect for G band due to the nonadiabatic removal of the Kohn anomaly at Γ point.^[70, 115, 148] The even larger blue shift of the G_2 peak compared with the G_1 peak is because that the inner graphene layers are affected on both sides by the FeCl_3 layers (G_2) while the outer layers are only affected by one side (G_1). Besides the obvious observation for the stiffening effect of E_{2g} phonons, the much smaller linewidths of G_1 ($\sim 7 \text{ cm}^{-1}$) and G_2 ($\sim 6 \text{ cm}^{-1}$) peaks compared to that of pristine graphene ($\sim 15 \text{ cm}^{-1}$) are also observed, which is due to the blockage of phonon decay from electron-hole pairs when the Fermi level shifts away from the Dirac point.^[115]

The evolution of G peak position from 1L to 4L for FLGIC is shown in Figure 4.8. For comparison, the doped FLG and pristine FLG are also shown. It can be seen in Figure 4.8 that the G peak position for pristine graphene is independent of number of layers and keeps fixed at $\sim 1580 \text{ cm}^{-1}$. For doped 1L graphene, it shifts from $\sim 1580 \text{ cm}^{-1}$ to $\sim 1605 \text{ cm}^{-1}$. The amount of blue shift shows an overall decreasing trend with the increasing of graphene layer number from 2L to 4L. On the other hand, the phenomena are totally different for FLGIC. The G peak blue shifts to 1612 cm^{-1} for 2L-FLGIC, and it splits into two peaks (G_1 and G_2) when the number of graphene layers increases to 3 and more. The G_1 peak intensity is

Figure 4.8 Evolution of the G peak position from 1L to 4L for FLGIC (green and blue), doped FLG (red) and pristine FLG (black). The SLG has similar spectrum as doped SLG even after intercalation process (purple). The intensity of G peak is represented by different radius of the solid circles.

almost fixed as a constant in my experiments, while the G₂ peak intensity becomes stronger with increasing the graphene layer number. The relative intensities of the peaks are also represented by the size of the solid circles in Figure 4.8. The trend of G band intensity evolution from 2L- to 4L-FLGIC shows that the G₂ peak will gradually dominate the doublet G band with the increase of the number of graphene layers, and finally it should present single peak as that of stage 1 bulk-based GIC case ($\sim 1626 \text{ cm}^{-1}$).^[174, 184] This is because that the top and bottom layers' contribution for the G₁ peak can be ignored when the number of inner layers is far greater than 2.

4.6 Raman 2D band for probing the electronic band Structure of FLGIC

Figure 4.9 FWHM of the 2D band of doped FLG (red circles), pristine FLG (black squares), and FLGIC (green triangles), where doping instead of intercalation for 1L case.

I already introduced in Chapter 1 that the 2D band has fingerprint feature for identifying number of layers of pristine graphene, because the 2D band arises from double resonance and thus it is dependent on the graphene's electronic band structure around K point at the Brillouin zone.^[191] The 2D band of fully intercalated FLGIC samples shown in Figure 4.7 presents essential difference from that of pristine FLG in the following three aspects. (1) Only one single Lorentzian peak can be well fitted for all FLGIC samples (2L- to 4L- FLGIC) as shown in Figure 4.7. This is similar to both of SLG^[113] and mis-oriented bilayer graphene.^[47] Normally, the 2D peak of pristine 2L graphene are fitted by four Lorentzian peaks

and those of other FLG are fitted by many Lorentzian peaks.^[113, 191] (2) The 2D peak linewidth is much sharper for FLGIC compared to that of pristine FLG, as shown in Figure 4.9. While for pristine and doped graphene, the linewidth broadens dramatically when the thickness increases from 1L to few layers. However, the 2D linewidths are much sharper for FLGIC compared to that of FLG and they only show slight broadening with the increase of number of layers. (3) The integrated intensity of 2D peak for the pristine FLG does not show obvious change with the increase of number of graphene layers.^[113] However, 2D peak intensity increases with number of layers for FLGIC, (In Fig. 4.7, all the spectra were measured under same condition).

These differences for the 2D peak features between FLGIC and FLG are mainly because of two reasons: (1) The interlayer space between adjacent graphenes is enlarged from ~ 3.4 Å (pristine) to ~ 9.4 Å (FLGIC) after intercalation.^[180, 181, 189] Hence, the adjacent graphene layers can only interact with each other electronically through the intercalant layer, which results in much weaker coupling. The decoupling effect leads the properties of FLGIC very similar to that of SLG, as indicated by the sharp SLG-like 2D peaks. (2) Graphene and FeCl_3 are structurally incommensurate because the lattice constant of FeCl_3 and graphene are 6.06 Å and 2.46 Å,^[172, 180, 181] respectively. Therefore, the coupling between graphene and FeCl_3 is relatively weak. As a result, the fully intercalated FeCl_3 -FLGIC can be viewed as few quasi-individual graphene layers superimposed together with very weak coupling effect through the intercalant layers. The electronic properties of FLGIC behaves like SLG with single and linear dispersion near Dirac point, resulting in single Lorentzian 2D peak with peak intensity increasing with number of layers.

4.7 Electronic Band Structure by First Principle Calculations

Figure 4.10 Electronic band structures of SLG (red dashed line) and FeCl_3 -based stage 1 GIC (blue solid line). The horizontal bands of GIC originate from the d orbital of iron. Except for those bands, the band structure of GIC and SLG are very similar. An obvious difference is that the Dirac point of SLG locates exactly at Fermi surface while that of GIC locates at ~ 1 eV, suggesting that GIC is strongly hole doped.

The band structure of FeCl_3 -based stage 1 GIC (blue solid curve) and SLG (red dashed curve) are calculated and shown in Figure 4.10. It can be seen that the GIC possesses a series of horizontal bands in the range of 0 and 1.5 eV, which originate

mostly from the d orbitals of iron. Actually, the band structure of GIC is very similar to that of SLG around K point except that for those horizontal bands. The band of GIC is also presenting a single and linear dispersion band near the Dirac point. This is in agreement with the Raman spectra of FLGIC which only show single and sharp 2D peak. With considering the on-site Coulomb interaction of Fe^{3+} ions, the spin-dependent DFT calculation (LSDA+U) is used to confirm the role of FeCl_3 insertion in FLG. While bringing little disturbance to the band of SLG, the main effect of the inserted FeCl_3 layers on SLG is charge transfer effect and the consequent shifting Fermi level. The Fermi level of FLGIC shifts about ~ 1.0 eV below the Dirac point, which indicates that the FLGIC is heavily doped by holes. This effect of hole doping induced by charge transfer from graphene to FeCl_3 can well explain the significant blueshift of G peak for FLGIC. Particularly for the G_2 peak locates at $\sim 1623 \text{ cm}^{-1}$, and it can be converted to the 0.8-0.9 eV shift of Fermi level from the extrapolated gate controlled doping result.^[115] Therefore, the experimental value matches the calculated value of 1.0 eV quite well.

4.8 Homogenous Intercalation of FeCl_3 on FLGIC

The optical image of pristine graphene samples with different thickness are shown in Figure 4.11a. The 1L and 2L graphene were identified by Raman and contrast spectra before intercalation, and the light contrast also can let us know that they are 1L and 2L. Raman images of the G peak and 2D peak intensity after intercalation are shown in Figure 4.11b and c, respectively. It can be seen that the intensities of both G and 2D peaks of 2L-FLGIC are much stronger than those of 1L graphene. However, it is also noticed that the linewidth of 2D peak does not

Figure 4.11 Raman images of 2L-FLGIC and 1L-graphene. a) Optical image of graphene samples before intercalation. b) Raman image of the G peak intensity after intercalation. c) Raman image of the 2D peak intensity after intercalation. d) Raman image of the 2D peak FWHM (linewidth) after intercalation. The intensities of G and 2D peaks of 2L-FLGIC are much stronger than those of 1L graphene, while no noticeable difference in the 2D linewidth between 2L-FLGIC and 1L-graphene. The 2D linewidth of 2L-FLGIC region is uniform at ~ 35 cm^{-1} . The scale bar is $2\ \mu\text{m}$ for all images.

show any noticeable difference between 1L graphene and 2L-FLGIC (Figure 4.11d). All the observed phenomena are in consistent with the results shown in Figure 4.2 and 4.5. The uniform 2D linewidth across the whole 2L-FLGIC region indicates the homogenous intercalation by FeCl_3 . Furthermore, the FeCl_3 -based

FLGIC samples show very good ambient stability and the G and 2D Raman peaks remain unchanged for more than 3 years. This result is very similar to the bulk based FeCl_3 -GIC.^[192] The FLGIC remain good crystalline quality as there is no obvious D peak.

For other intercalants, Br_2 - and I_2 - based FLGIC has been reported by Jung *et al.*^[117] Compared to their results, FeCl_3 is relatively easier to be fully intercalated. This is not surprising as the Br_2 -based GIC are normally formed in type of stage 2.^[193] Furthermore, the observed complete quenching effect of 2D band in Br_2 -FLGIC might be due to the commensurate structure between Br_2 and graphene layers, resulting in stronger interaction and modification of the electronic structure of graphene.^[83, 117] On the other hand, FeCl_3 is incommensurate with graphene and hence the interaction between FeCl_3 and graphene is minimum. The main effect of FeCl_3 intercalation is to: 1. Introduce strong charge transfer doping. 2. Increase the effective distance between the graphene layers and thus the electronic structure of FeCl_3 -based FLGIC becomes similar to that of SLG. Such effects could be further demonstrated by electrical transport measurements, where a significant shift of neutral point (Dirac point) as well as characteristics of SLG (i.e. Berry's phase π)¹⁹⁴ should be present on FLGIC. Therefore, the electrical transport properties of FLGIC are presumably very interesting and deserved for further studies. The different effects of FLGIC using different intercalants suggest FLGIC offers a promising method to achieve desirable properties for FLG samples for both fundamental research and future applications.

4.9 Conclusions

In summary, air ambient stable FeCl_3 -FLGIC samples with homogenous concentration of intercalant have been successfully prepared. My results show that FLG samples are much easier to be fully intercalated compared with bulk graphite, which normally takes ~ 6 days in high concentration Cl_2 atmosphere.^[195] Raman spectroscopy and imaging confirm that FeCl_3 is fully intercalated into FLG, while simultaneously introduces strong charge transfer chemical doping. FLGIC show single and sharp 2D peak, similar to that of single layer graphene, indicating the loss of electronic coupling between adjacent graphene layers. The observed phenomena agree very well with first principle calculations. FLGIC are quite promising materials not only because of the modification of the graphene electronic structure, but also the possible modification of electrical, thermal, and magnetic properties with choice of different intercalants, particularly the Ca-FLGIC, which is expected to show superconductivity.^[196]

Chapter 5

Electronic bands coupling for extra resonant excitation quantum channels in FeCl₃-intercalated few-layer graphene

5.1 Background introduction

Ever since the inelastic light scattering phenomenon observed by Raman,¹⁹⁷ it has been taken as a vibrational fingerprint for characterizing various properties of materials, and so does for graphene.^{70, 113, 115, 142} However, it is noticed that the observations of Raman inelastic process of graphene initially start from the intrinsic electronic excitation of the material itself by incident photons, and the extra resonant excitation quantum channels from extrinsic electrons have not been reported to date. My studies reveal that intercalation of FeCl₃ in graphene layers not just only dope graphene strongly and shift its Fermi level, but also induce strong electronic bands coupling between graphene and intercalants (FeCl₃) as revealed by first principle calculations. This strong electronic coupling can provide extra resonant excitation quantum channels for enhancing Raman scattering in graphene.

Pristine graphene is considered to be neutral as the Fermi level is located exactly at the Dirac point, but it can be electron or hole doped by both chemical and electrical ways,^{6, 22, 31, 39, 115, 198, 199} and such doping can shift the Fermi level above or below the Dirac point. Recently, Basko suggested that the matrix element for the Raman G band of graphene increases when the Fermi level is close to the $E_{ex}/2$ (E_{ex} is the excitation photon energy) according to calculation result.²⁰⁰ Kalbac *et al.* experimentally discovered that the electrical top gating induced heavy

hole doping of graphene present enhanced Raman G peak signal when the shifted Fermi energy ($|E_F|$) approaches $E_{ex}/2$.²⁰¹ Chen *et al.* explained in detail that the transition pathways can be partially blocked when the shifted $2|E_F|$ approaches the energy states with $E_{ex} - E_G/2$ (E_G is the energy of G phonon) which are the region of quantum phase transition of Raman pathway amplitude, and such blocking eliminated the destructive interference and thus enhancing Raman G peak signal; the G peak intensity would decrease dramatically if the shifted $2|E_F|$ became greater than $E_{ex} - E_G/2$ because more in-phase pathways are blocked.²⁰² In addition to top gating method, intercalation of $FeCl_3$ to few-layer graphene (FLG) to form few-layer intercalation compounds (FLGIC) can also introduce strong hole doping effect because the insertion of such acceptor-type intercalants expand the layer distance and make each graphene layer behave as independent single layer graphene (SLG) with tremendous downshifted Fermi level (0.6 – 0.9 eV).^{147, 203, 204} Furthermore, the intercalated $FeCl_3$ can couple to adjacent graphene at some extent and thus present different electronic, optical and magnetic properties compared to the electrical gated graphene.^{147, 203, 204} In this chapter, it is revealed by enhanced Raman scattering and first principle calculation that different from electrical gating which only induce doping to graphene and block transition quantum pathways when $2|E_F|$ approaches $E_{ex} - E_G/2$, $FeCl_3$ intercalated FLG can provide extra quantum channels and enhance Raman scattering because of strong electronic bands coupling between $FeCl_3$ and graphene.

5.2 Experimental

Fabrication of pristine SLG, FLG and FLGIC: Graphene samples were prepared by conventional micromechanical cleavage method on silicon wafer covered by

300 nm SiO₂. The layer number from 1L to 3L of graphene flakes were confirmed by Raman^{113, 143} and contrast spectra.¹⁴² Then the FLGIC were prepared by the conventional two-zone vapor transport method, and the recipe is as same as the one introduced in Chapter 4.¹⁴⁷

Raman Spectroscopy Measurement: Raman spectra were recorded by Renishaw system with four different excitation lasers (1.58, 1.96, 2.33 and 3.81 eV) and spectral resolution of $\sim 1 \text{ cm}^{-1}$ for laser energy of 1.58, 1.96 and 2.33 eV, and $\sim 3 \text{ cm}^{-1}$ for laser energy of 3.81 eV. To avoid laser heating effect, I strictly controlled the laser power less than 0.5 mW for each measurement.

Electronic Band Structure and Charge Distribution Calculation: The structure of stage 1 FeCl₃-GIC is modeled by M. S. Dresselhaus *et al.*,^{172, 180, 181} and it is simulated with the density functional theoretical (DFT) calculation as same as introduced in Chapter 4.¹⁴⁷ The calculations were performed based on the Perdew-Burke-Ernzerhof form generalized gradient approximation (PBE-GGA) with projector augmented wave (PAW) method. A kinetic energy cutoff of 400 eV and k-points sampling with $0.01 \text{ \AA}^{-1}$ separation in the Brillouin zone were used in order to obtain the exact distribution of charge in the coupling region between graphene layer and FeCl₃. The distribution of transferred charges was calculated by the charge difference as given by formula (2):

$$\Delta CH(r) = CH_{\text{FeCl}_3\text{-GIC}}(r) - CH_g(r) - CH_{\text{FeCl}_3}(r) \quad (2)$$

Where $CH_{\text{FeCl}_3\text{-GIC}}(r)$, $CH_g(r)$ and $CH_{\text{FeCl}_3}(r)$ are the real-space electronic charge distribution of FeCl₃-GIC system, free graphene and free FeCl₃ layer, respectively.

5.3 Laser dependent Raman G band intensity

I selected pristine SLG, full intercalated 2LGIC and 3LGIC for detailed analysis of their Raman spectra features. The schematic atomic structure of

Figure 5.1 Normalized Raman spectra (baseline removed) for SLG, 2LGIC and 3LGIC excited by various photon energies. a-d, Excitation photon energy of 1.58, 1.96, 2.33 and 3.81 eV, respectively. A strong enhancement of G_1 is observed by excitation photon energy of 1.58 eV; while enhanced G_2 peak can be observed by excitation photon energy of 1.96 and 2.33 eV.

FLGICs can be seen in Figure 4.4. It is obvious that the interlayer space between adjacent graphene layers is dramatically increased by the insertion of FeCl_3 molecules. Therefore, the adjacent graphene layers decoupled each other; meanwhile, the charge transfer induced hole-doping effect for each layer of

graphene is very strong because FeCl_3 is typical acceptor-type intercalant¹⁸⁷. Therefore, the full intercalated FLGIC can be roughly viewed as individual graphene layers superimposed together and strongly hole doped.^{147, 204, 205}

Raman spectra for FLGIC with various excitation laser energies are shown in Figure 5.1. There are some similarities for the evolution of G band from SLG to 3LGIC excited by four different laser energies: 1) For SLG, the position of G_0 is $\sim 1581 \text{ cm}^{-1}$, while for intercalated 2LGIC, the position of G band dramatically blueshifts to $\sim 1612 \text{ cm}^{-1}$ (G_1); 2) it splits into two peaks for 3L-FLGIC, which locate at $\sim 1612 \text{ cm}^{-1}$ (G_1) and $\sim 1623 \text{ cm}^{-1}$ (G_2), respectively. This because the inner and outer graphene layers are suffered different degree of doping effect due to the different quantity of adjacent FeCl_3 molecules (Fig. 4.6). Obviously, the inner graphen layer is doped heavier than the outer graphene layers because it is affected by FeCl_3 in both sides, and thus it gives rise to larger blueshift (G_2 for inner layer and G_1 for out layer); 3) The intensity of G_1 almost keeps constant from 2LGIC to 3LGIC when excited by same laser beam as both of them consist of 2 outer layers. Based on the shifted Raman G band position,¹¹⁵ it is estimated that the concentration of carrier charges (holes) for outer and inner layer graphene are respectively $\sim 3 \times 10^{13}$ and $4.5 \times 10^{13} \text{ cm}^{-2}$, which correspond to ~ 0.65 and 0.85 eV downshift of Fermi level from the Dirac point. Meanwhile, there are obvious differences in Figure 5.1, where the relative intensity of G_1 , G_2 , and G_0 differs a lot at different excitation energy. For example, the intensity ratio of G_1/G_0 is ~ 10 at excitation energy of 1.58 eV , while for other excitations ($1.96, 2.33, 3.81 \text{ eV}$), it is only ~ 2 . For 3LGIC, The ratio of G_1/G_2 is ~ 15 for 1.58 eV excitation, and it is ~ 1 , 1 and 2 for $1.96, 2.33$ and 3.81 eV excitations, respectively. This is due to the different resonant conditions for G_1 and G_2 peak and will be discussed in detail.

Figure 5.2 Normalized Raman G peak intensity for simulated electrical doped graphene and FLGIC as a function of incident laser energy. The solid curves are G peak intensity of electrical doped graphene at high level (red and blue) simulated based on conclusions of electrical gating induced Fermi level shifted graphene reported elsewhere.²⁰² The red circles and blue squares represent the normalized intensity of G^*_1 and G_2 , respectively. All the points follow the simulated curves very well except that G^*_1 excited by 1.58 eV photon, and G_2 respectively excited by 1.96 and 2.33 eV photons present obvious stronger enhancement effect compare to the simulated curves. The blue triangles curves represent the corresponding DOS of $\text{FeCl}_3\text{-GIC}$ (the case of G_2) at valence band which resonant with the incident photon energy.

The intensity ratio of G^*_1/G_0 and G_2/G_0 under different excitation energy is shown in Figure 5.2 (red circles and blue squares for G^*_1/G_0 and G_2/G_0). For fairly comparing the G band intensity induced by outer layer and inner layer graphene, the intensity of G_1 for 2LGIC and 3LGIC should be weighted by a factor of 1/2

(labeled as G^*_1) as they have two identical layers at bottom and top (Figure 4.2). As we can see, there is an extremely large intensity ratio of G^*_1/G_0 (~ 5.5) under 1.58 eV excitation, indicating the obvious enhancement. Recent experiments observed that the G peak intensity can enhance as high as ~ 4 times when shifted $2|E_F|$ equals to $E_{ex} - E_G/2$. This is explained by the theory that some of the quantum pathways are blocked and the destructive interference effect is decreased²⁰². The simulated G peak intensity as function of excitation photon energy for graphene samples hole doped by 0.65 and 0.85 eV are respectively plotted by the red and blue curves in Figure 5.2 (The simulation is based on Basko's paper reported elsewhere.⁷⁵). Here, I only consider the shifted Fermi level (0.65 eV for G_1 and 0.85 eV for G_2) but ignore the change of band structure for these two simulated curves. As we can see, for G_1 , the experiment and theory matches quite well, except for the deviation for the point at 1.58 eV (stronger intensity than theoretical prediction); for G_2 , such deviation becomes more obvious. Both the points for 1.96 eV and 2.33 eV show much stronger enhancement compared to theory curve. According to the theory of quantum pathway blocking, the enhancement effect of G peak becomes significant (≥ 2) only at a very narrow region that the $2|E_F|$ approaches $E_{ex} - E_G/2$ in less than 0.1 eV. However, G^*_1 enhances more than 5 times when excited by 1.58 eV photons despite the $2|E_F|_1$ and $E_{ex} - E_G/2$ differs ~ 0.2 eV; When excited by 2.33 eV photons, G_2 still shows obvious enhancement even the $2|E_F|_2$ and $E_{ex} - E_G/2$ differs ~ 0.5 eV. Therefore, other effects should be considered for $FeCl_3$ intercalation induced chemically doped graphene other than the theory of quantum pathway blocking.

5.4 Theoretical explanation and discussion

For FeCl_3 -based graphite intercalation compound (FeCl_3 -GIC), the adjacent graphene layers decouple each other and behave as SLG presenting downshifted Fermi level and linear dispersive electronic bands near K point, but the band structure still shows obvious difference: The electronic bands keep linear dispersion only at the energy around the Dirac point, and it is deviated from linear at the energy region 0.7 eV lower than Dirac point and couples to the electronic bands of FeCl_3 (along K- Γ and K-M as shown by flat blue bands in Fig. 5.3a). This is mainly because of that in FeCl_3 intercalated FLG, FeCl_3 plays a role as electron sea in this intercalation configuration (as can be seen in Fig. 5.4a), moreover, the flat electronic bands of FeCl_3 near the Fermi level dominate the whole system (Fig. 5.3a) and hence the Fermi level of outer and inner layer graphene are both determined by FeCl_3 and they share the same Fermi Level (as shown in Fig. 5.3c,d). Furthermore, from the plotted charge distribution of FeCl_3 intercalated bilayer graphene (Fig. 5.4), it is clearly that there is strong charge coupling between graphene and FeCl_3 . Such charge coupling would effectively affect the electron density of states (DOS) as shown in Figure 5.3b, where DOS of FeCl_3 -GIC keeps high value from 0 to -0.4 eV (0.85-1.25 eV below the Dirac point). It is hybridized DOS of graphene and FeCl_3 , and it is mainly contributed by FeCl_3 as compare to the DOS of pristine SLG (red curve). I also notice such FeCl_3 intercalated FLG is not the special chemical doping case to present high DOS at Fermi level, recently, it is theoretically demonstrated that B-doped graphane have

Figure 5.3 Coupled electronic bands between graphene and FeCl_3 at around Fermi level provide extra resonant excitation channels for enhancing Raman scattering. *a*, The electronic band structure of FeCl_3 -GIC. The electronic bands of FeCl_3 -GIC keep linear dispersion around Dirac point (red lines), but it deviated from linear dispersion and coupled strongly with electronic bands of FeCl_3 (flat blue lines) at energy close to Fermi level (black dotted line). *b*, The DOS of SLG (red curve) and FeCl_3 -GIC (black curve) at around Dirac points, respectively. *c, d*, The schematic graphs show that the Fermi level of outer layer and inner layer degenerate at same energy because of FeCl_3 , which determines Fermi level of the strong chemically doped graphene. The two wide blue lines represent the strongly coupled electronic bands between graphene and FeCl_3 and hence provide extra resonant excitation channels for enhancing Raman scattering.

large DOS at around Fermi level and the electron-phonon coupling (EPC) dramatically enhanced, resulting high temperature superconductor.⁸⁵ The enhanced DOS may play an important role to provide excitable electrons and hence extra quantum channels for graphene to enhance its one-phonon involved resonant Raman scattering as demonstrated in Figure 5.3c,d.

The G peak intensity is given by the formula (1):⁷⁵

$$I_G \propto \frac{2\pi\lambda_T}{3} \left(\frac{e^2}{c} \right)^2 \left(\frac{E_{ex}a}{c} \right)^2 f \left(\frac{E_{ex}}{t_0} \right) \quad (1)$$

Figure 5.4 The charge density distribution of FeCl₃-2LGIC. *a*, The calculated charge density difference in 2LGIC. Obviously, the embedded FeCl₃ layer dominates the total charges of the whole configuration, most charges accumulated at around Cl atoms. *b*, Valence charge density distribution of 2LGIC, the isosurface level set to 0.04. Obviously, the electrons of Cl from FeCl₃ couple with graphene strongly.

Where λ_F is the EPC near Γ point in k-space, e is the charge of electron, a is the length of C-C bond, c is the speed of light, t_0 is the nearest-neighbor coupling matrix element, and $f(E_{ex}/t_0)$ is a dimensionless function that only dependent on E_{ex}/t_0 . Therefore, the G peak intensity is considered to be proportional to λ_F . Because it is known that the EPC is normally proportional to the density of states (DOS) at Fermi level, thus the increase of DOS at range of 0.85-1.25 eV below Dirac point for FeCl₃-GIC would strongly affect the intensity of resonant G peak. Blue triangles curve in Figure 5.2 quantitatively show the effect of DOS in the intensity of G peak as a function of excitation photon energy, which can fulfill the resonant process to excite electrons from valence band to corresponding conduction band. The DOS curve keeps high value at resonant excitation photon energy ranged from 1.7 to 2.5 eV, but it drops to much low value for higher photon energy (3.81 eV included). This explains that despite the excitation energy 1.58 and 2.33 eV are respectively far away from $2|E_F|_1 + E_G/2$ and $2|E_F|_2 + E_G/2$, the obvious enhanced Raman G peaks still can be observed. My results provide evidence that there is strong electron coupling between graphene and FeCl₃ intercalants, and thus provide excitable electron and extra quantum channels for graphene to enhance its one-phonon involved resonant Raman scattering

This new discovery explains the additional mechanism for Raman enhancement when E_{ex} approaches $2|E_F| + E_G/2$. Here, I should point out that the intensity relationship between G_1 and G_0 is usually used to define the stage number 'n' (for $n \geq 2$) for GIC: stage number = $2(G_0+G_1)/G_1$ (ref. ⁷). Therefore, this formula is obviously failed to rule the stage number if using excitation photon energy of 1.58 eV as G_1 is obviously enhanced (Fig. 5.1a and Fig. 5.2). But anyhow, this formula

is still valid if excitation laser energy far away from $2|E_F|_1 + E_G/2$ (i.e. 1.96, 2.33 and 3.81 eV) (Fig. 5.2).

5.5 Conclusions

In conclusion, enhanced Raman scattering in inner and outer graphene layers of FeCl_3 -intercalated FLG is observed by selective resonant excitation photon energy. Different from the electrical gating that only induce carrier doping to graphene, the FeCl_3 -intercalated FLG shows strong electronic bands coupling between graphene and FeCl_3 at around Fermi level, which provide extra resonant excitation quantum channels for enhancing Raman scattering. The observation of strong coupling of electronic bands between graphene and FeCl_3 can also guide to understand the electronic properties of hybridized nanoscaled materials. Furthermore, and most importantly, the strong coupling of electrons at around Fermi level may leads some even more interesting physical phenomenon, such as charge density wave, which is a key factor for investigating superconductor.

Chapter 6

Asymmetrical intercalation of FeCl₃ in trilayer graphene

6.1 Background Introduction

Graphene is novel two dimensional material considered as a potential candidate for ultrahigh-speed nanoelectronics owing to its exotic electronic properties, such as room-temperature quantum Hall effect,^{3, 4} Berry phase and Klein tunneling.^{6, 7} However, lack of bandgap greatly limits its application in field-effect-transistor for logic device applications, and thus the modification of graphene structures for opening its bandgap is indeed a crucial step towards the practical applications in graphene-based nanoelectronics. To date, many methods have been theoretically predicted to open bandgap for graphene,^{70, 75, 78, 109} and only two of them are the main methods that have been experimentally proved for approaching bandgap opening of graphene, one is modifying graphene to form nanoribbons,^{118, 205} and the other is applying an electrical gate voltage perpendicular to AB-stacked bilayer graphene (BLG) to break the inversion symmetry of the two equivalent layers.^{31, 35, 191, 206} The disadvantages of the former method are owing to its complicated semiconductor processes for cutting graphene into the nanoribbon shape, as well as inducing defects, which lower the mobility significantly;⁷² For the later method, in order to open a bandgap of ~0.2 eV, high effective electric field such as ~3 V/nm need to be applied to break the inversion symmetry between top and bottom layers, but it is worth noting that such high electric field cannot be easily obtained except

using specific polymer-based top gating, which is not suitable for practical applications.³¹

Figure 6.1 The schematic crystal structure evolution from pristine AB-stacked trilayer graphene (a) to the FeCl₃ asymmetrically intercalated trilayer graphene (out-of-plane) (b). The charge transfer effect forms a quasi-electric-field perpendicular to the BLG.

Most recently, Yang *et al.* demonstrated theoretically that an obvious bandgap can be opened effectively if FeCl₃ adsorbed by AB-stacked BLG.²⁰⁷ I also notice that such modeled adsorption of FeCl₃ on graphene surface is unstable at ambient-air and thus it cannot be used for practical applications.^{204, 208} Motivated by this inversion symmetry breaking induced bandgap opening, I will present a novel graphene structure that the FeCl₃ molecules intercalate into only one interlayer space of the AB-stacked trilayer graphene (TLG) to separate it into two independent graphene systems, one is a single layer graphene (SLG) and the other is bilayer graphene (BLG) (Figure 6.1b). The separated BLG suffers from nonhomogeneous hole doping effect for its top and bottom layers as they are different in distance with respect to the electron-negative intercalant FeCl₃, and the activation of antisymmetric vibration phonon mode G^- as observed by Raman spectroscopy and image indicates that the inversion symmetry of these two layers

is breaking. The First principle theory calculated that such inversion symmetry broken BLG present a prominent opened bandgap. Furthermore, this novel graphene-based crystal structure is expected to be very stable in ambient-air as both sides of FeCl_3 layer are protected by graphene. Therefore, realizing the ambient-air stable and bandgap opened graphene-based configuration is a potential way towards future nanoelectronics based on graphene field-effect-transistors.

6.2 Experimental

AB-stacked TLG samples were deposited on silicon wafer coated with a 300 nm SiO_2 using conventional micromechanical cleavage method. The layer number of graphene flakes were confirmed by both Raman^{113, 143} and contrast spectra,¹⁴² respectively. It is noticed that the recently reported FeCl_3 -based full intercalated few-layer graphene are all fabricated using two-zone methods with long reaction time (more than 6 hours).^{147, 204, 208} To fabricate the aforementioned out-of-plane asymmetrical intercalated trilayer graphene (AITG), I also used conventional two-zone vapour transport method,¹⁴⁷ but controlled the reaction time of only ~1 hour which is much shorter than the previously reported recipes,^{147, 204, 208} and I will show the details of identification of such AITG by both Raman spectroscopy and AFM image later. The density functional theory calculations were performed using Vienna *ab initio* Simulation Package (VASP).^{47, 183} Exchange-correlation interactions were described by the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form.²⁰⁹ For all systems, a kinetic cutoff energy of 400 eV is used. The Brillouin-zone integration was performed within Monkhorst-Pack scheme using a $(4 \times 4 \times 1)$ mesh. All model structures are optimized with the vacuum separation set to be more than 10 Å.

6.3 Identification of AITG structure by using Raman spectroscopy

Because of the high throughput and nondestructive, Raman spectroscopy became a powerful tool to characterize graphene-based materials, including identifying number of layers, doping, defects, strain and edges,^{39, 66, 104, 113-115, 126, 147, 198, 199, 210-212}

Figure 6.2 The optical images of the trilayer graphene sample before (a) and after (b) intercalation process. (c) Raman spectra for the pristine trilayer graphene (black), region A (red), region B (green), and one nonhomogeneously doped BLG (blue).

Figure 6.3 The white light contrast spectra (300 - 800 nm) for SLG, BLG and TLG on the Si substrate with coated 300 nm SiO₂. The maximum contrast at ~570 nm increases linearly with the graphene thickness.

particularly that the thickness and superlattice sequence along z-direction can be identified accurately.^{113, 142, 147, 208} The optical image of a pristine graphene sample is shown in Figure 6.2a. The optical contrast is uniform across the whole area of the sample, and the Raman spectrum (Black curve in Figure 6.2c) and optical contrast spectra (Figure 6.3) of this sample indicate that it is TLG.^{113, 142} After the TLG physically reacted with FeCl₃ using the aforementioned modified recipe, it still present very uniform optical contrast as shown in Figure 6.2b. But meanwhile, it is noticed that two regions present different Raman features and the corresponding Raman spectra are shown in Figure 6.2c. For the regions at the left side of the white dashed lines of the TLG sample (region A), the Raman G band consists of only one single Lorentzian peak, and the peak position blueshifts to ~1584 cm⁻¹ indicating that it is lightly charge doped TLG as compared to pristine

graphene of which the G band position normally located at $\sim 1580\text{ cm}^{-1}$. I can conclude that the slight blueshift of G band for region A is not because of intercalation effect due to the very low doping level, but owing to surface molecular doping as such effect is normally observed for graphene samples which annealed in vacuum and then exposure to air.^{38,39} For region B , the green curve of Raman spectrum presents two Lorentzian fitted G peaks respectively located at $\sim 1590\text{ cm}^{-1}$ (G^-) and $\sim 1610\text{ cm}^{-1}$ (G^+) as shown in Figure 6.2c. For the previously reported full intercalated few-layer graphene, the blueshifted G band at positions of ~ 1612 and $\sim 1625\text{ cm}^{-1}$ are the signs for the graphene layers respectively flanked on one and two sides by FeCl_3 , respectively,^{204,212} thus the region B should not be the full intercalated TLG due to the non-observed $\sim 1625\text{ cm}^{-1}$ Raman peak. It is clearly seen that the intensity of the high-frequency peak G^+ is much stronger than that of the low-frequency peak G^- , giving the intensity ratio of $I_{G^+}/I_{G^-} \approx 5$. Furthermore, different from fully intercalated TLG of which the 2D band consists of only one single Lorentzian peak,¹⁴⁷ the 2D band of the modified TLG from region B consists of two obvious separated peaks with different intensity, located at ~ 2696 and $\sim 2730\text{ cm}^{-1}$, respectively. Both the abnormal curve shapes of G and 2D bands of region B are different from that of lightly doped TLG or fully intercalated few-layer graphene,^{142,147} but similar to the nonhomogeneously (out-of-plane) doped BLG as shown by blue curve in Figure 6.2c, which is similar to the Raman features reported elsewhere^{38,199}. Thus the splitting of G and 2D bands for region B is possibly the expected AITG structure as shown in Figure 6.1b, of which the new obtained crystal forms C-C- FeCl_3 -C sequenced out-of-plane from bottom to up. Compared to the pristine AB-stacked TLG shown in Figure 6.1a, the schematic crystal structure of FeCl_3 -AITG shown in Figure 6.1b consists of two

independent graphene systems that are separated by FeCl_3 , one is single layer graphene (SLG) locating above the FeCl_3 and the other is AB-stacked BLG locating below the FeCl_3 (Figure 6.1b). The two layers of AB-stacked BLG are hole doped in different level apparently because of the different distance with respect to the FeCl_3 , then the inversion symmetry breaking of the AB-stacked BLG gives rise to the transformation of its representative point group from D_{3d} to C_{3v} , which causes the activation of G^- band because the silent anti-symmetric vibration mode E_u at Γ point for D_{3d} group belongs to degenerated E representation for C_{3v} group. It is worth noting that the G^+ band is always active as it arises from the symmetric vibration phonon mode E_g at the Γ point of Brillouin zone. Thus the observation of two components of the G band is due to the mixing of the symmetric E_g and anti-symmetric E_u modes. The much stronger intensity of I_{G^+} compared to that of I_{G^-} is another evidence to show that the AB-stacked BLG is symmetry inversion breaking.¹⁹⁹ For the SLG standing above FeCl_3 (Figure 6.1b), it can be considered as an quasi-independent SLG suffering from strong hole-doping effect,¹⁴⁷ and another function of this graphene layer is protecting FeCl_3 from being deliquesced.

6.3 The uniform AITG characterized by Raman images

The Raman images (Figure 6.4a,b) demonstrate a clear identification of regions *A* and *B*. The G_0/G^- band (the G_0 band denotes the E_{2g} vibration mode in non-intercalated TLG) with integrated wavenumber from 1560 to 1595 cm^{-1} reflected by region *A* presents obvious intensity, but the G^+ band is absence in this region; contrarily, region *B* shows very strong intensity of G^+ band, but very weak for G^- band. Meanwhile, none of the regions present G_2 band which stands for the G band

position blueshifted to $>1620\text{ cm}^{-1}$ for graphene layers which flanked on both sides of FeCl_3 (Figure 6.4c),¹⁴⁷ indicating that there is no graphene layer flanked by two sides of FeCl_3 for both regions *A* and *B*. Therefore, based on the information of Raman images, it is concluded that there is no intercalation for region *A*, while region *B* is the AITG as I expected. The height profile of transition region from *A* to *B* can be clearly seen by AFM image as shown in Figure 6.4d, the thickness of region *B* is about 0.61 nm thicker than that of region *A*. From previous theoretical works, the distance between adjacent graphene layers is expanded from 0.34 to 0.94 nm (0.60 nm) after insertion of FeCl_3 ,¹⁸⁴ thus the AFM image further confirmed that region *B* is AITG as the experimental data is in agreement with the value reported theoretically and experimentally.^{169, 174}

Figure 6.4 The Raman images for the trilayer graphene sample after reacted with FeCl_3 : (a) The G_0/G^- band intensity with the integrated wavenumbers from 1560 to 1595 cm^{-1} . (b) The G^+ band intensity with the integrated wavenumbers from 1595 to 1615 cm^{-1} . (c) The G_2 band intensity with the integrated wavenumbers from 1615 to 1635 cm^{-1} . (d) The AFM image of the white square region labeled in Raman images, and the cross section height profile of the white line is demonstrated as well.

6.4 The electronic band structure of AITG

Because the AB-stacked BLG, flanked by one side of FeCl_3 is inversion symmetry breaking, thus it should present essential different electronic properties compared to that of pristine BLG, particularly that the bandgap may be opened. To further examine the difference of electronic structure between AITG and its precursor TLG, their electronic band structures have been calculated using First principles theory. As shown in Figure 6.5a, the electronic coupling effects between adjacent layers give rise to the formation of four-fold degenerate zero-energy level for pristine TLG. The intercalated FeCl_3 in region *B* separates SLG and BLG leading to the band structures modified. As shown in Figure 6.5b, the electronic bands denoted by red curves present linear dispersive behavior due to the separated SLG, and the Fermi level is downshifted ~ 0.58 eV with respect to the Dirac point. For the separated BLG below the FeCl_3 layer, it consists of two pairs of electronic bands: (π_1, π_1^*) and (π_2, π_2^*) . For pristine BLG, the electronic bands π_1 and π_1^* at low-energy regime touch each other at Dirac point,^{21, 213} but these two bands do not touch each other at Dirac point anymore for the BLG in AITG, and they separated away from each other at around Dirac point (Figure 6.5b). It is clearly

seen that the separated electronic bands, π_1 and π_1^* , present an energy gap $\Delta E_k \approx 0.20$ eV at Dirac point, but it should be noticed that the opened bandgap $E_g \approx 0.13$ eV is smaller than the energy gap ΔE_k as shown in Figure 6.5b. The observation of the opened bandgap E_g and energy gap ΔE_k for the BLG is in agreement with the recent calculated results.²⁰⁷

It is worth noting that to date, a lot of experimental works based on doping graphene chemically have been reported, but only a few dopants have been proved for achieving strong doping effect, such as $> 3 \times 10^{13} \text{ cm}^{-2}$, and the other dopants

Figure 6.5 The electronic band structure around Dirac point of the graphene sample: (a) The pristine trilayer graphene stacked in ABA geometry does not possess a bandgap. (b) The electronic bands of AITG can be divided into three

independent parts: 1) the linear dispersive bands arise from the independent SLG (red); 2) the bandgap opened BLG (blue), the bandgap ($E_g = 0.13$ eV) and energy gap ($\Delta E_k = 0.20$ eV) are clearly observed; 3) the FeCl_3 bands (grey).

Figure 6.6 The optical image of another TLG sample. Raman image of the 2D band width for the TLG sample after reacted with FeCl_3 (the integrated wavenumbers are from 1595 to 1615 cm^{-1}). (c) The Raman spectra for the two distinct colored regions shown in Raman image indicate they are fully intercalated TLG and AITG, respectively.

which adsorbed on graphene surface only present low-level doping due to the weak charge transfer effect, particularly for the commonly used organic compounds,

such as triazine, An-CH₃, TCNQ, and TPA.^{38, 108, 198} Notwithstanding the adsorption of triazine gives rise to relatively low-doping level for BLG, the bandgap as high as ~111 meV was still observed and the current on/off ratio is enhanced at least one-order compared to the pristine graphene sample.³⁸ Therefore, the realization of such FeCl₃-AITG structure is crucial for graphene bandgap engineering, particularly that the actual bandgap of the separated BLG should be even larger than the calculated result (~0.13 eV) as the bandgap value obtained by First principle method is normally considered as smaller than the real case.⁴⁶ Furthermore, the theoretically modeled BLG that adsorbed by FeCl₃ on its surface is not ambient-air stable possibly because FeCl₃ is a very active compound that can deliquesce easily by reacting with small amount of H₂O in air ambient,^{204, 207, 208} but the experimentally fabricated FeCl₃-AITG structure shows very good environmental stability as I have not found any obvious changes up to now since the sample was prepared two years ago. Furthermore, it is worth to note that as shown in Figure 6.6, more than 2/3 area of a very large TLG sample (~50 × 15 μm) has been transformed to AITG structure by repeating the same preparation recipe as I introduced in this chapter, and thus the recipe with less reaction time is indeed an effective method for preparing AITG structure.

6.5 Conclusions

In conclusion, the ambient-air stable FeCl₃-based AITG structure has been prepared by using the traditional two-zone method with less reaction time. The AITG's out-of-plane C-C-FeCl₃-C structure is confirmed by both Raman spectra and AFM images. Raman spectroscopy shows that compared to the pristine graphene, the *G* band of AITG split into two peaks with different intensity ($G^+ \gg$

G^-), which is as same as that of asymmetric doping induced inversion symmetry broken BLG; and the 0.6 nm height difference between non-intercalate TLG and AITG is in agreement with the previous theoretical prediction value. The giant blueshift of the high frequency G^+ peak indicates that the BLG in AITG is heavily doped, and the First principle study shows that a 0.13 eV bandgap is opened for the separated BLG. The naturally bandgap opened and ambient-air stable AITG structure opens a new route for graphene gap-engineering and it is essentially crucial for graphene-based field-effect-transistor applications in near future.

Chapter 7

Conclusions and future work

7.1 Conclusions

In this thesis, two ways for modifying graphene's crystal and electronic structures are proposed and characterized by Raman spectroscopy systematically.

(1) Thermal dynamics of two chirality edges of single layer graphene are investigated by polarized Raman spectroscopy. The result shows that the zigzag edges can be transformed to armchair segments after annealing treatment, while armchair edges present relatively thermal stable behaviour. Because the electronic band structure of graphene nanoribbon is dependent on its concentration of edge chirality segments, thus the understanding of thermal stability of these two edges can provide us a flexible way to control its electronic band structure via annealing. Therefore, it is very important for guiding fabrication of graphene nanoribbon device.

For the AB-stacked bilayer graphene edges, the transformation from open-edge to closed-edge along zigzag direction is concluded by Raman image and spectroscopy results. The formation of closed edges for AB-stacked bilayer graphene switches on the pseudospin interaction effect which gives rise to the opening of bandgap. Therefore, opening bandgap of graphene arising from this novel physics mechanism extends both graphene-based fundamental researches and practical applications.

(2) For FeCl_3 -based few-layer graphene intercalation compounds, two type cases are discussed:

a) The full intercalated few-layer graphene possesses the electronic band structure as similar as that of single layer graphene at around Dirac point, which disperses linearly. The 2D band presents a single and sharp Lorentzian peak which is different from the Bernal stacking few-layer graphene. G band features, such as shifted wavenumbers and relative intensity can be used to identify the modified crystal structure in real space. Compared to graphite-based intercalation compound which is normally mixed in various stages (experimentally), the few-layer graphene intercalation compounds possess very clear crystal model and its physical parameters can be measured exactly. Therefore, the successful fabrication of few-layer graphene intercalation compounds can let us study this kind of material in much more details.

Furthermore, it is discovered that the relative G band intensity for outer and inner layers are dependent on excitation laser energy: The intensity for inner layers get enhanced when excited by 1.96 and 2.33 eV lasers; and the intensity for outer layers get enhanced when excited by 1.58 eV laser. The enhancement of the G band indicates that the electronic structure coupling between FeCl_3 layer and its adjacent graphene layer provides extra channel for resonant Raman process.

b) Another very interesting intercalation status is identified by using both Raman spectroscopy and image: the asymmetrical intercalated trilayer graphene (AITG), where one interlayer space is intercalated by FeCl_3 and the other interlayer space keeps as same as original. Two functions are played by the intercalated layer of FeCl_3 . It separates single layer and AB-stacked bilayer graphene to make them behaves as independent system, and meanwhile the strong

hole doping effect to the AB-stacked bilayer graphene can break the inversion symmetry and thus opens its bandgap. This kind of special intercalation compound is potential for future graphene-based field-effect-transistor fabrication.

7.2 Future work

(1) Despite the fact that graphite intercalation compounds have been investigated for more than 40 years, scientists still do not know how the intercalation process happens and which edges of few-layer graphene (or graphite) are relatively preferred to be inserted. As I introduced that the zigzag edges of AB-stacked bilayer graphene can form closed state at annealing condition, thus the armchair edges may be the open-gate for intercalants insertion. This topic would be interesting and deserves for further investigation from both theoretical and experimental ways. Simply speaking, for the former, the molecular dynamics can be simulated, and for the later, the experiments can be divided into two steps: the closed-edge of zigzag edges of bilayer graphene can be firstly obtained by annealing, and then the preliminary identification can be obtained by checking if this kind of bilayer graphene can be intercalated.

(2) The electronic properties of few-layer graphene intercalation compounds deserve for detailed studies. For the full intercalation case, it is expected to present similar electronic properties as that of single layer graphene except that it is more conductive due to strong chemical doping effect. For the asymmetrical intercalation of trilayer graphene, the bandgap opened bilayer graphene separated by FeCl_3 can be measured by IR absorption spectroscopy which can provide the

direct evidence for the opened bandgap. The electrical gate dependent conductivity of such new compound in asymmetrical geometry can also assist the investigation.

(3) In addition to FeCl_3 , many molecules can be intercalated into graphene interlayer space. As the inserted chloride can electronically interact with graphene to modify the whole system's electronic band structure, thus other kind of chlorides, such as BiCl_3 - and SbCl_5 -based intercalants, deserve for further studies. Furthermore, intercalation of alkali and alkali earth metals can lead to superconducting state, thus for few-layer graphene case, these metal elements also deserve to be selected as intercalant for studies.

(4) I studied graphene edge dynamics by using polarized Raman spectroscopy and theoretical calculation. Actually, the direct evidence to show the atomic-dynamics at graphene edges is very desirable. To date, HRTEM and STM are two main scientific tools which can provide atomic-scale resolution for carbon-based materials, thus these two tools can be used for studying this topic, particularly that the HRTEM can be used to realize the in-situ temperature dependent study.

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