Raman and white light spectroscopy/imaging studies of graphene

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RAMAN AND WHITE LIGHT SPECTROSCOPY/IMAGING STUDIES OF GRAPHENE

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Summary

In this thesis, the Raman/ white light spectroscopy and imaging are used to probe electronic, vibrational and optical properties of graphene samples fabricated by two common methods, micromechanical exfoliation (ME) of highly oriented pyrolytic graphite (HOPG) method or epitaxial growth method. This thesis is divided into four parts.

The first part, which covers Chapters 1-4, discusses the Raman properties of graphene including: (1) Raman scattering in graphene. We show the relationship between Raman features and electronic band structures that make it possible to experimentally probe electronic properties of graphene by Raman spectroscopy. (2) Determination of thickness of graphene. Besides white light contrast spectroscopy, we show that the Raman features, *i.e.*, the integrated intensity of G band as well as full width half maximum (FWHM) of 2D band also can be used to identify graphene layer numbers. (3) Explain the strong Raman intensity of single layer graphene (SLG) on SiO₂ (300 nm)/Si. We show that in addition to the interference due to multiple reflection of the incident laser, the interference of multiple reflection of the Raman signal inside the graphene layer must be also accounted for.

The second part (Chapter 5) discusses the effect of substrate on the electronic properties of SLG by Raman spectroscopy/imaging. Clear understanding of the substrate effect is important for the device fabrication of graphene. Therefore, the Raman studies of ME SLG on standard SiO₂ (300 nm)/Si, single crystal quartz, Si, glass, polydimethylsiloxane (PDMS) and NiFe are carried out. Our data suggest that the weak interaction (Van de Waals force) between the graphene layer and substrates are not strong enough to affect the electronic properties of graphene made by ME.

The third part, from Chapter 6-7, is stacking dependent electronic and optical property studies of bi-layer graphene (BLG). Besides BLG with Bernal stacking (AB), the twisted bi-layer graphene (TBG) samples (top layer rotates certain angle relative to the bottom layer) are successfully fabricated. Raman spectroscopy/imaging is used to probe their electronic properties. Significant blue shift of the 2D band ($\sim 14 \text{ cm}^{-1}$) of TBG compared to that of SLG is observed. This is attributed to SLG-like electronic structure of TBG but with slowing down of Fermi velocity (as much as $\sim 6.5\%$). In addition to the decoupling caused band degeneracy near the Dirac point, there are also stacking order dependent band splitting and folding in TBG sample illustrated with our first-principle calculations. We predict that the band folding effect of graphene layers may enable the G band Raman double resonance in the visible excitation range. Such prediction is confirmed experimentally with our Raman observation of the strong G band resonance in graphene layers whose resonant conditions are dependent on stacking order.

To fully understand the electronic and optical properties of TBG samples, the white light spectroscopy (excitation from 350 nm to 850 nm) is used to probe the stacking dependent optical conductivity of BLG. Our first-principle calculations show that while the optical conductivities of SLG and BLG with Bernal stacking are almost frequency independent in the visible region, TBG is frequency dependent, giving rise to an additional absorption features due to the band folding effect. Experimentally, we obtain from contrast spectroscopy the optical conductivities of BLG with different stacking geometries (different relative orientation between the two graphene layers). Some TBG samples show additional features in their conductivities which are in full agreement with our calculation results. The results obtained here are important for the future optical application of large scale graphene films which often show misoriented

stacking sequence.

The last part (Chapter 8) is the Raman study of epitaxial graphene (EG) grown on Si-SiC substrate as well as EG layer number determination by white light contrast spectrum. Raman spectroscopy is used to probe the evolution of electronic structures of EG from buffer layer to few layers. Our results reveal that the Dirac properties will not exist in buffer layer, only when next carbon layer, which is grown above this buffer layer and interacts with the buffer layer by the weak van der Waals force, has Dirac properties. In addition, all the Raman bands of EG are blue shifted relative to the graphene layers made by ME, and this observation is attributed to the compressive strain induced by the substrate. The white light contrast spectrum is used to identify layer numbers of EG. The results match quite well with the photoelectron spectroscopy (PES) measurement and make the study of layer number dependent electronic properties of EG possible.

In this thesis, I have contributed to the following parts:

- (1) Sample fabrication: (a) Fabrication graphene layers by ME method, following transfer the graphene samples to the target substrate such as SiO₂/Si, quartz, glass, etc. (b) Fabrication TBG samples with different orientation angles.
- (2) The classical electromagnetic theory and transfer matrix are used to calculate the reflection spectrum of thin film system.
- (3) The electric and magnetic field distributions among thin film system are calculated and understood.
- (4) Perform the Raman/white light spectroscopy/imaging measurements of different kinds of graphene samples, *e.g.*, ME graphene on different substrates, ME graphene with different thicknesses on SiO₂/Si substrate, TBG samples with different orientation angles. The electronic properties of ME graphene samples on different

substrate are understood. The stacking dependent electronic and optical properties of graphene layers are clearly understood.

Publications

Journal publications

1. [Y.Y. Wang](#), Z.H. Ni, Z.X. Shen, H.M. Wang and Y.H. Wu, “ Interference enhancement of Raman signal of graphene” *Applied Physics Letters*, 92 (2008) 043121 [Also selected for publication in Feb. 11, 2008 Virtual Journal of Nanoscale Science & Technology](#)
2. [Y.Y. Wang](#), Z.H. Ni, T. Yu, H. M. Wang, Y.H. Wu, W. Chen, A.T.S. Wee, and Z.X. Shen, “Raman studies of monolayer graphene: the substrate effect” *Journal of Physical Chemistry C* , 112 (2008)10637
3. [Y.Y. Wang](#), Z.H. Ni, L. Liu, Y.H. Liu, C.X. Chong, T. Yu , X.J. Wang and Z.X. Shen “Stacking dependence of optical conductivity of graphene ” *ACS Nano* , 4 (2010) 4074
4. [Y.Y. Wang](#), Z.H. Ni, H.L. Hu, Y.F. Hao, T. Yu, J. T. L.Thong and Z.X. Shen “Gold film/ graphene as a new substrate for SERS study” *Applied Physics Letters*, 97(2010) 163111
5. [Y.Y. Wang](#), Z.H. Ni, T. Yu, W. Chen, A.T.S. Wee, X.J. Wang, and Z.X. Shen “Raman spectra of buffer layer, few layers graphene on Si-SiC as well as graphene layers determination” (submitted to *Applied Physics Letters*)
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Conference papers

1. [Y. Y. Wang](#), Z. H. Ni, X. J. Wang, J. H. Zhang and Z. X. Shen "Photoluminescence investigation of nanocrystal-based transparent oxyfluoride glass ceramics" 4th International conference on Materials for Advanced Technologies (ICMAT 2007) 1 to 6 July 2007, Singapore
2. [Y. Y. Wang](#), Z. H. Ni, Z. X. Shen, H. M. Wang and Y. H. Wu, "Interference enhancement of Raman signal of graphene" 3rd MRS-S Conference on Advanced Materials, (Incorporating MRS-S and MRS-I Mumbai-Chapter Joint Indo-Singapore Meeting) 25 - 27 February 2008, IMRE, Singapore
3. Z. H. Ni, [Y. Y. Wang](#), T. Yu, Z. X. Shen, "Raman spectroscopy and imaging of graphene" ICTP conference: graphene week 2008 August 2008, Trieste, Italy
4. [Y. Y. Wang](#), Z. H. Ni, L. Liu, Y. H. Liu, C. X. Chong, T. Yu, X. J. Wang and Z. X. Shen "Stacking dependence of optical conductivity of graphene" 4th MRS-S Conference on Advanced Materials Institute of Materials Research and Engineering, 17th - 19th March 2010, IMRE, Singapore

Chapter 1

Introduction to graphene

1.1 The discovery of graphene

Graphene is a planar atomic layer of carbon with atoms arranged in hexagonal structures[1]. Since it was first successfully fabricated and studied by K. S. Novoselov *et al.* in 2004[1], graphene has become one of the hottest research topics nowadays because of its fascinating electronic and optical properties, such as the unconventional quantum Hall effect[2-6], Dirac nature of charge carriers[2-4, 7-8], the minimum conductivity[2, 9-10], quantum spin Hall effect[11], ultrahigh electron mobility[2, 12-13] as well as the universal optical conductivity[14-16]. Unusual electronic properties of graphene make it a promising candidate for fabrication of next generation electronic devices and the high transparency of graphene make it a hopeful candidate for photonic devices. Besides, graphene is also the basic building unit for graphitic allotropes, such as three-dimensional graphite, one-dimensional carbon nanotubes and zero-dimensional fullerenes individually formed by stacking, rolling and wrapping graphene layer. Therefore, a comprehensive study of graphene will allow a better understanding of other carbon allotropes.

1.2 Electronic band structure of graphene

Graphene is a two-dimensional, single layer of graphite contains carbon atoms arranged in hexagonal structures. The lattice structure of graphene is shown in Fig.1.1. The unit cell of graphene contains two carbon atoms, A and B. The unit-cell vectors of graphene $\mathbf{a}_1$ and $\mathbf{a}_2$ can be expressed as,

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3}), \quad \mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3}), \quad (1.1)$$

where $a \approx 1.42 \text{ \AA}$ is the carbon-carbon distance. The calculated reciprocal lattice vectors are given by,

$$\mathbf{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad \mathbf{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}) \quad (1.2)$$

Fig. 1.1 Honeycomb lattice structure of graphene and its Brillouin zone, adapted from Castro Neto et al.[17]. Left: The lattice structure of graphene. $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit-cell vectors of graphene with nearest-neighbor distance $a=1.42 \text{ \AA}$. Right: The Brillouin zone of graphene. High symmetry points are marked on this figure. Dirac cone structure is located at two inequivalent points K and K' since they are not connected by the unit vectors of the reciprocal lattice.

The energy bands derived from tight banding approach have the form [17]

$$E_{\pm}(k) = \pm t \sqrt{3 + f(k)} - t' f(k) \quad (1.3)$$

$$f(k) = 2 \cos(\sqrt{3} k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2} k_y a\right) \cos\left(\frac{3}{2} k_x a\right) \quad (1.4)$$

In above equation, $t \approx 2.7 \text{ eV}$ is the nearest-neighbor hopping energy and t' is the next nearest-neighbor hopping energy. The plus sign applies to π^* conduction band

and the minus sign is for the π valence band. The promising electronic properties of graphene are associated with its band structure located at the corner of the Brillouin zone: K and K' points. The coordinates of K and K' points in momentum space are respectively,

$$K = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right), \quad K' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right) \quad (1.5)$$

Expand electronic band dispersions around K (K') point, for electron momentum q (with $|q|$ is much smaller than $|K(K')|$, which is measured from K (K') point), a linearly dispersion equation is obtained which has the form:

$$E_{\pm}(q) \approx \pm v_F |q| + O\left[(q/K)^2\right] \quad (1.6)$$

Here, v_F is the Fermi velocity given by $v_F = \frac{3ta}{2}$ with a value of $\sim 1.0 \times 10^6$ m/s,

which is $\sim 1/300$ velocity of photon.

Figure 1.2 gives 3D electronic dispersion of graphene with $t = 2.7$ eV and $t' = -0.2t$. A linearly dispersion of electronic band structure located around K (K') point could be seen which is the reason of fascinating electronic properties in graphene.

Fig. 1.2 Left: 3D image of band structure of graphene. Right: The zoom in image of

band dispersion around K (K') point. A linearly dispersion of electronic band structure can be seen, adapted from Castro Neto *et al.* [17].

1.3 Electric field effect in graphene

In semiconductor industry, in order to break the limits of performance of silicon based devices, efforts have been paid to find suitable materials with extremely high carrier conductivity, thermo-dynamical stability, as well as high crystal quality.

K. S. Novoselov *et al.* fabricated graphene layers by ME of HOPG and studied their electric field effect for more than 60 graphene devices and the results are summarized below[1]. Fig. 1.3(a) shows the optical image of few layer graphene (FLG) on $\text{SiO}_2(300 \text{ nm})/\text{Si}$ substrate, while Fig. 1.3(b) and (c) give the atomic force microscope (AFM) image of FLG and SLG. Fig. 1.3(d) shows the scanning electron microscope (SEM) image of graphene based device whose schematic image is shown in Fig. 1.3(e).

Fig. 1.3 (a) Optical image of FLG on $\text{SiO}_2(300 \text{ nm})/\text{Si}$ substrate. (b) AFM image of

FLG (c) AFM image of SLG (d) SEM image of graphene based devices whose schematic image is shown in Fig. 1.3(e). Adapted from K. S. Novoselov et al.[1].

The electric field effect measurements are carried out for above graphene based devices whose layer number is no more than 3. The resistivity ρ of FLG as a function of gate voltage V_g is given in Fig. 1.4(a). As can be seen from this figure, as the gate voltage increases, the resistivity of FLG ρ shows a sharp decreasing, from $\sim K\Omega$ to $\sim 100 \Omega$. Fig. 1.4(b) gives the charge (electron or hole) conductivity $\sigma = \frac{1}{\rho}$ as a function of V_g which exhibits ambipolar field effect. However, there is a minimum conductance as can be seen from Fig. 1.4(a) and (b) even when the charge carriers tend to zero and this kind of phenomenon is due to the carriers in graphene are Dirac fermions[2, 9-10]. The electron transport in graphene is essentially governed by the Dirac's (relativistic) equation. Fig. 1.4(c) shows the Hall coefficient R_H as a function of V_g which exhibits a reversal of its sign, indicating different type of carriers in graphene devices. From field-effect and magnetoresistance measurements, the obtained carrier mobility in FLG is $\sim 10,000 \text{ cm}^2/\text{V}\cdot\text{s}$. Fig. 1.4(d) gives the temperature dependence of carrier concentration for FLG (open circle), thicker FLG (squares) as well as graphene more than 10 layers (solid circles). The overlap value of conduction band and valence band can be obtained from those measurements. As the layer number of graphene decreases, the overlap between conduction band and valence band decreases which is consistent with the theoretical prediction that SLG is a zero-gap semiconductor.

Fig. 1.4 (a) The FLG's resistivity ρ as a function of gate voltage V_g at different temperature ($T=5, 70$, and 300 K from top to bottom, individually). (b) The conductivity of FLG as a function of gate voltage at $T=70$ K. (c) Hall coefficient R_H versus V_g at $T=5$ K. (d) The temperature dependence of carrier concentration for FLG (open circle), thicker FLG (squares) and graphene sample with more than 10 layers (solid circles). Adapted from K. S. Novoselov et al.[1].

Based on above measurements, it can be seen that graphene is a good candidate for future electronic devices because of its ambipolar electric field effect, ballistic transport with sub-micrometer distances as well as the as the high charge mobility ($\sim 10,000 \text{ cm}^2/\text{V}\cdot\text{s}$ [1]), which can even reach $\sim 200,000 \text{ cm}^2/\text{V}\cdot\text{s}$ in suspended SLG[12, 18].

1.4 The Shubnikov–de Haas oscillations (SdHO) in graphene

The SdHO measurements indicate the massless fermions in SLG[1-2]. Fig. 1.5(a)

shows the fundamental SdHO frequency B_F as a function of carrier concentration n . The linear dependence of B_F on n is observed. Another phenomenon observed in SdHO measurements is that the longitudinal resistance $\rho_{xx}(B)$ exhibits maxima rather than minima at integer values of the Landau filling factor ν compared with conventional metals and this phenomenon is schematically shown in Fig. 1.5(b). In this figure, the red curve is for graphene while the blue curve is for graphite. Extrapolating these curves to the origin gives different N values for graphene ($N=1/2$) and for graphite ($N=0$), which indicates the half-filling factors of graphene in the quantum Hall effect. (Here, the longitudinal resistance $\rho_{xx}(B)$ oscillates periodically as a function of electron and hole concentrations in a constant magnetic field B , and N represents the number associated with different minima of oscillations). In addition, the cyclotron mass m_c can be measured from the temperature T dependent of amplitude of SdHO at various gate voltage and magnetic field. Fig. 1.5(c) shows the amplitude $\Delta\sigma$ of SdHO as a function of T with different carrier concentration. The obtained m_c value lies between $\sim 0.02 m_o$ and $\sim 0.07 m_o$, here, m_o is the mass of free electron. Fig. 1.5(d) gives the dependence of m_c on charge concentration n , which exhibits square root formula. The linear dependence of B_F on n and the square root dependence of m_c on n indicate that the band structure of graphene is linear dispersion as presented in Fig. 1.5(e).

Fig. 1.5 (a) The fundamental SdHO frequency B_F as a function of carrier concentration n . Positive n corresponds to electrons while negative n corresponds to holes. (b) The number associated with different minima of oscillations N as a function of SdHO frequency B_F . The red curve is for graphene and the blue curve is for graphite. (c) The amplitude $\Delta\sigma$ of SdHO as a function of T for different charge concentration n . The oscillation decays more rapidly for higher charge concentration n . (d) The square root dependence of cyclotron mass m_c on charge concentration n . (e) The band structure of SLG, a linear dispersion of electronic structure can be seen which is the reason of those fascinating electronic properties in graphene. Adapted from K. S. Novoselov et al.[2].

The unusual response of massless fermions in graphene to a magnetic field could be further revealed by the Quantum Hall Effect (QHE) measurements. Fig. 1.6 shows the Hall conductivity σ_{xy} and longitudinal resistivity ρ_{xx} as a function of carrier concentration in a fix magnetic field B . Obviously QHE plateau are visible but half-integer filling factor is obtained which is arise from the massless fermions in

graphene. Inset this figure gives the QHE measurements of BLG with Bernal stacking for comparison. The integer filling factor is obtained which is due to the parabolic dispersion of electronic band structure in BLG. The carriers in BLG with Bernal stacking no longer could be described as massless Dirac particles.

Fig. 1.6 Hall conductivity σ_{xy} and longitudinal resistivity ρ_{xx} of SLG as a function of carrier concentration at $B=14T$ and $T=4K$. Inset: the Hall conductivity σ_{xy} as a function of carrier concentration for BLG with Bernal stacking for comparison. In the quantum Hall effect, SLG exhibits half-integer filling factor while for BLG with Bernal stacking exhibits integer filling factor. Adapted from K. S. Novoselov et al.[2].

Based on above measurements, the charge carriers in graphene have zero rest mass and the transport properties are governed by Dirac's equation and those phenomena match quite well with the theoretical prediction. The experimental study of graphene is not only interesting in itself but also provides an access to the physics in quantum electrodynamics.

1.5 Universal optical conductivity in graphene

Besides the fascinating electronic properties in graphene, it also exhibits unusual optical properties, such as universal optical or AC (alternating current) conductivity ($G(\omega) = \frac{e^2}{4\hbar}$) value[14]. The universal optical conductivity also implies the optical transmittance T as well as optical reflectance R of SLG is constant under normal incident, which are individually given by,

$$T = \frac{1}{(1 + \frac{\pi\alpha}{2})^2} \quad (1.7)$$

$$R = \frac{1}{4}\pi^2\alpha^2T \quad (1.8)$$

Here, α is the fine structure constant ($\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{G}{\pi\epsilon_0 c} \approx \frac{1}{137}$)[14]. In particular,

Eg. (1.7) gives the absorption of graphene P ,

$$P = (1 - T) \approx \pi\alpha, \quad (1.9)$$

since the reflectance R from graphene is negligible ($<0.1\%$). Therefore, the fine structure constant α can be experimentally obtained from absorbance/transmittance measurements of graphene[14]. Fig. 1.7 shows the transmittance measurement of SLG. The wavelength independent $\sim 2.3\% \pm 0.1\%$ absorption is obtained from this figure.

The universal optical conductivity $G(\omega) = (1.01 \pm 0.04) \frac{e^2}{4\hbar}$ also can be obtained from this measurement which are consistent with the theoretical prediction of ideal two-dimensional Dirac fermions.

Fig. 1.7 The transmittance measurement of SLG (open circle). The red line is theoretical transmittance T for two-dimensional massless Dirac fermions while the green line is correction of transmittance after further consideration the non-linear dispersion of electronic band structure of graphene. Inset: The transmittance of white light as a function of graphene layers. For one to four layers graphene, the transmittance of graphene layers linearly decreases. Adapted from R. R. Nair *et al.*[14].

Above absorption behavior of SLG can be understood qualitatively. It is calculated by R. R. Nair *et al.*[14], for a light with electric field $\vec{\Theta}$ and frequency ω incident perpendicularly on SLG of a unit area, the incident energy flux can be expressed as

$$W_i = \frac{c}{4\pi} |\vec{\Theta}|^2 \quad (1.10)$$

The incident light will induce electronic transition from the initial state $|i\rangle$ to the final

state $|f\rangle$ in graphene satisfying energy and momentum conservation. The energy absorbed by graphene then can be calculated by

$$W_a = \eta \hbar \omega \quad (1.11)$$

Here, $\hbar \omega$ is the energy of the incident photon and η describes the number of absorption per unit time which can be calculated from Fermi's golden rule as

$$\eta = \frac{2\pi}{\hbar} |M|^2 D \quad (1.12)$$

In above equation, M describes the interaction strength between photon and Dirac fermions and D is the density of state of SLG at $\varepsilon = \frac{\hbar \omega}{2}$.

$$D\left(\frac{\hbar \omega}{2}\right) = \frac{\hbar \omega}{\pi \hbar^2 v_F^2} \quad (1.13)$$

The interaction between photon and Dirac fermions can be described by the Hamiltonian,

$$\hat{H} = v_F \vec{\sigma} \cdot \vec{p} = v_F \vec{\sigma} \cdot \left(\hat{p} - \frac{e}{c} \vec{A} \right) = \hat{H}_0 + \hat{H}_{\text{int}} \quad (1.14)$$

Here, $\hat{H}_0$ is the standard Hamiltonian for two-dimensional Dirac particles and

$$\hat{H}_{\text{int}} = -v_F \vec{\sigma} \cdot \frac{e}{c} \vec{A} = v_F \vec{\sigma} \cdot \frac{e}{i\omega} \vec{\Theta} \quad \text{describe the interaction of Dirac particles with}$$

incident electromagnetic field. Here, $\vec{A} = \frac{ic}{\omega} \vec{\Theta}$ is the vector potential and $\vec{\sigma}$ is the

standard Pauli matrix. Taking into account of valley degeneracy as well as averaging all the initial and final states involved, the obtained interaction strength of photon and

Dirac fermions M has the form:

$$|M|^2 = \left| \left\langle f \left| v_F \vec{\sigma} \cdot \frac{e}{i\omega} \vec{\Theta} \right| i \right\rangle \right|^2 = \frac{1}{8} e^2 v_F^2 \frac{|\Theta|^2}{\omega^2} \quad (1.15)$$

Substituting Eq. (1.12), Eq. (1.13) and Eq. (1.15) into Eq. (1.11), the calculated

absorption of SLG,

$$P = \frac{W_a}{W_i} = \frac{\pi \cdot e^2}{\hbar c} = \pi \alpha \quad (1.16)$$

And dynamic conductivity of SLG,

$$G = \frac{W_a}{|\Theta|^2} = \frac{e^2}{4\hbar} \quad (1.17)$$

Therefore, the universal optical conductivity of graphene arises from its carriers as Dirac fermions as well as the linear energy dispersion in graphene.

1.6 The motivation and organization of this thesis

This thesis presents Raman and white light spectroscopy and imaging studies of graphene which includes four major parts:

Motivation for Part 1(Chapter 1-4): The electronic properties of Bernal stacked graphene layers are strongly dependent on its thickness; therefore, a fast and nondestructive method to determine the thickness of graphene is necessary. Besides the white light contrast spectroscopy, we present two ways to determine the layer number of graphene: the integrated intensity of G bands as well as the FWHM of 2D band. In addition, we observe an interesting phenomenon that the Raman intensity of SLG on SiO₂ (300 nm)/Si is surprisingly high, which is almost ~ 10 times of that on Si. Therefore, we study the mechanism behind this enhancement and this study will provide guidance for enhancing Raman signals of other thin films.

Motivation for Part 2(Chapter 5): SLG is a promising candidate for device fabrication because of its ultrahigh electron mobility. The effect of substrate on electronic properties of graphene should be considered for its future use in device fabrication. Therefore, the effect of many different substrates: such as standard SiO₂

(300 nm)/Si, quartz single crystal, Si, glass, PDMS and NiFe on the electronic structure of SLG is studied by Raman spectroscopy and imaging.

Motivation for Part 3(Chapter 6-7): Large-scale growth of graphene film is one of the obstacles for further application of graphene, therefore, many chemical approaches to synthesize large-scale graphene films have been developed, such as epitaxial growth on SiC as well as using chemical vapor deposition methods growing graphene layers on metal foils. However, there is stacking disorder in those graphene layers. Therefore the study of stacking dependent electronic and optical properties of graphene will greatly help the further use of those misoriented graphene layers. We fabricate TBG sample with top layer rotates a certain known angle relative to the bottom layer and probed their electronic and optical properties by Raman and white light spectroscopy and imaging. The former can be used to excite TBG sample at particular energy and the latter provides a broader excitation range.

Motivation for Part 4(Chapter 8): It has been known that after heat treatment of semiconductor SiC at high temperature, EG can be grown on SiC substrate whose thickness is controlled by the temperature. For EG, large area, high quality fabrication can be achieved and allows for device fabrication. The understanding of electronic properties of EG will be useful for its future device application. Raman spectroscopy is used to detect the electronic properties of graphene layers grown on SiC. Up to now, an accurate, easily performed, nondestructive way to determine the layer number of graphene grown on SiC has not been obtained, and considering the successful determination of layer number by the white light contrast measurement for graphene samples on SiO₂/Si, we extend this method to determine layer numbers of graphene grown on SiC substrate.

Organization of this thesis:

In this thesis, we first briefly introduce the Raman and white light spectroscopy and imaging in Chapter 2, following we introduce experimental methods in Chapter 3. In Chapter 4, we present the Raman properties of graphene layers which including: origin of G band and 2D band, identification graphene layer numbers by Raman spectroscopy and imaging as well as origin of the strong Raman signal of SLG on SiO₂/Si substrate. We study the substrate effect on the electronic property of graphene in Chapter 5. In Chapter 6 and Chapter 7, we use Raman and white light spectroscopy and imaging to study the stacking dependent electronic and optical properties of BLG. In Chapter 8, we study the vibrational and electronic properties of EG grown on SiC by Raman spectroscopy. The white light contrast spectroscopy is used to determine the layer number of EG. Finally in this thesis gives the conclusions and future work.

Chapter 2

Theoretical background for Raman and white light spectroscopy/imaging

2.1 Raman spectroscopy/imaging

2.1.1 Scattering of light by a small particle

When the monochromatic light with frequency ν_0 is incident upon a small particle, *e.g.*, molecule whose size is much smaller than the wavelength of the incident light, it is found that some of the scattering light has the same frequency ν_0 as the incident light and this elastic scattering of incident photon phenomenon is called Rayleigh scattering. On the other hand, new frequencies $\nu_0 \pm \nu_m$ appear in the scattering light and this inelastic scattering of incident photon phenomenon is called Raman scattering after its discoverer C. V. Raman[19]. Here, ν_m is the vibrational or rotational frequency of the molecule. The $\nu_0 + \nu_m$ and $\nu_0 - \nu_m$ lines are called anti-Stokes and the Stokes lines, individually. The process of scattering of incident light by molecule is demonstrated in the Fig. 2.1.

The Raman spectroscopy is the spectroscopic technique which records the scattered light and it can provide us useful information about vibrational, rotational of molecules, even crystals. From Raman spectrum, the information about composition of material, strain/stress, crystal symmetry/orientation, quality of crystal can be obtained. After the discovery of Raman scattering, improvements in various components of Raman instruments resulted in the development of better excitation

sources to improvement of photon detection technique. Nowadays, Raman spectroscopy has been commonly used in structural chemistry, analytical chemistry, biochemical system, medical system, industry, environment and others [20].

Fig. 2.1 Schematically scattering of incident light by a small particle. Adapted from Derek A. Long[21].

2.1.2 Classical description of Raman scattering[20]

Scattered light includes light with frequency ν_0 which is the same as that of the incident light and light with frequencies $\nu_0 \pm \nu_m$. This phenomenon can be understood by the classical description of Raman scattering process. The electric field of the incident light fluctuates with time t can be expressed as:

$$E = E_0 \cos 2\pi\nu_0 t \quad (2.1)$$

Here, E_0 is the amplitude of the incident wave and ν_0 is the frequency of the incident wave. Once the incident light shines on the molecule, the induced electric dipole moment $\mathbf{P}$ in molecule is governed by

$$\mathbf{P} = \alpha E = \alpha E_0 \cos 2\pi\nu_0 t \quad (2.2)$$

Here, α is the polarizability which describes the molecule's electron cloud change by the electric field. If the molecule is vibrating with a frequency ν_m , the nuclear displacement q can be expressed as

$$q = q_0 \cos 2\pi\nu_m t \quad (2.3)$$

Here, q_0 is the amplitude of vibration. Because of small amplitude of the vibration of nuclear, the polarizability α can then be express a linear function of q ,

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q} \right)_0 q + \dots \quad (2.4)$$

Here, α_0 is the polarizaiblity when the molecule is in equilibrium position.

$\left(\frac{\partial \alpha}{\partial q} \right)_0$ is the derivative of α with respect to q at equilibrium position. Substitute Eq.

(2.3) and Eq. (2.4) onto Eq. (2.2), the electric dipole moment $\mathbf{P}$ can be expressed as

$$\begin{aligned} p &= \alpha E_0 \cos 2\pi\nu_0 t \\ &= \alpha_0 E_0 \cos 2\pi\nu_0 t + \left(\frac{\partial \alpha}{\partial q} \right)_0 q E_0 \cos 2\pi\nu_0 t \\ &= \alpha_0 E_0 \cos 2\pi\nu_0 t + \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos 2\pi\nu_m t \cdot \cos 2\pi\nu_0 t \\ &= \alpha_0 E_0 \cos 2\pi\nu_0 t + \frac{1}{2} \cdot \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 [\cos(2\pi(\nu_0 + \nu_m))t] + \frac{1}{2} \cdot \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 [\cos(2\pi(\nu_0 - \nu_m))t] \end{aligned} \quad (2.5)$$

In above equation, the first term corresponds the oscillation dipole that radiates light with frequency the same as the incident light, and the second term represents the anti-Stokes Raman scattering, the oscillating dipole emits light with frequency of $\nu_0 + \nu_m$, and the last term shows the Stokes Raman scattering with dipole emits light with frequency of $\nu_0 - \nu_m$. Based on above equation, it also can be seen that

$\left(\frac{\partial \alpha}{\partial q} \right)_0$ can not be zero if the vibration is Raman-active.

2.1.3 Selection rules for Raman spectrum[20]

Whether the vibration of molecule will be involved in the Raman scattering process are determined by the polarizability tensor of the molecule. Take a diatomic molecule for example, when the molecule is placed in an electric field induced by the incident light, the positively charge nuclei are attracted to the negative pole, while the electrons are attracted to the positive pole as demonstrated in the figure below.

Fig. 2.2 Schematic image of polarization of a diatomic molecule placed in an electric field. Adapted from John R. Ferraro et al. [20].

Therefore, there is a charge separation in molecule and a dipole moment $\mathbf{P}$ is induced in this molecule,

$$\mathbf{P} = \alpha \mathbf{E} \quad (2.6)$$

In an actual molecule, α is a matrix instead of a vector, and the relationship between dipole moment $\mathbf{P}$ and electric field $\mathbf{E}$ is governed by the following matrix,

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \quad (2.7)$$

Here, α_{ij} ($i, j = x, y, z$) is the polarizability tensor. The determination of Raman-active or not depends on the polarizability tensor. One of these components of the polarizability tensor is changed during the vibration, and then the vibration is Raman-active. While for small molecule, the polarizability ellipsoid of the molecule can be used to determine the vibration is Raman-active or not, which is three dimensional body plotted by $\frac{1}{\sqrt{\alpha_i}}$ (i represents direction). The vibration is Raman active if the size, shape or orientation of the polarizability ellipsoid changes during the vibration on the premise that the value of $\left(\frac{\partial \alpha}{\partial q}\right)_0$ can not be zero; otherwise, the vibration is Raman inactive.

2.1.4 Resonance Raman spectroscopy

The Resonance Raman scattering process occurs when the energy of incident light is close or the same with that of electronic transition of molecules or crystals. For normal Raman scattering, the electron is excited to a virtual state, while for the Resonance Raman scattering, the electron is excited to a real state instead, therefore, the intensity of resonance Raman bands can be enhanced by a factor of 10^3 to 10^5 compared with normal Raman bands[20]. The very strong signal is useful for identifying vibrations from complex system[20]. In addition, by using different excitation energy, the resonance Raman scattering can be used to enhance the intensities of particular bands, even could be used to probe electronic band structures[22-24].

Theoretically the intensity of a Raman band observed is given by [25]

$$I(\hbar\omega_l) = \frac{1}{\hbar^2} \sum_{ij} \frac{M_i H_{ij} M_j}{[(E_{ii} - \hbar\omega_l)^2 + \hbar^2 \gamma^2][(E_{ii} - \hbar\omega_l + \hbar\omega_{ph})^2 + \hbar^2 \gamma^2]} \quad (2.8)$$

Here, ω_i is the frequency of the incident light and ω_{ph} is the frequency of phonon, γ is the damping factor, E_{ii} is the electronic transition energy and H_{ij} is the electron-phonon Hamiltonian matrix element. When the energy of incident and/ or scattered photon $\hbar\omega_i / \hbar(\omega_i - \omega_{ph})$ is close to that of electronic transition energy E_{ii} , the denominator on the above equation become infinity small, therefore, enormously increase of Raman intensity can be obtained.

Fig. 2.3 illustrates Raman scattering involving virtual state as well as resonance Raman scattering involving real electronic state.

Fig. 2.3 Schematic image of IR absorption and the different light scattering process: Rayleigh scattering, Stokes Raman scattering, anti-Stokes Raman scattering, Resonance Rayleigh scattering, Resonance Stokes Raman scattering, Resonance anti-Stokes Raman scattering, individually from left to right. $\nu_{0,1,2}/\nu'_{0,1}$ are vibrational energy levels and E_1 is the electronic energy level. Adapted from John R. Ferraro et al.

[20].

2.1.5 Raman imaging

Raman imaging involves subsequent measurement of the spectra of adjacent regions of a sample. Controlled by the piezo stage, the objective region will be moved into the beam focused by a microscope after the spectrum of the previous region has been taken. The imaging of the sample is obtained until the entire region of interest has been covered. Raman images using peak intensity, peak position, or peak width generated after data analysis could provide useful information about the distribution of crystallinity, strain/stress, doping and so on. The Raman imaging has been obtained widely application in wafer inspection, semiconductors, photovoltaics (stress measurement, defect analysis), coating, thin films (chemical constitution, uniformity, thickness, surface structure), life sciences, biomedical research and so on.

2.2 White light spectroscopy/imaging

The white light spectroscopy/imaging is the easiest and most common optical microscopy technique. The white light spectrum/imaging can be used to characterize metal nanostructures[26], determine thin film thickness[27-29] as well as obtain micro-dissectioning and surface metrology[30]. In this thesis, the white light contrast spectrum is widely used in unambiguous identification of graphene layer number fabricated either by ME or by epitaxial grown on SiC, therefore, we introduce the contrast spectrum experimentally and theoretically in this section.

2.2.1 Contrast spectrum obtained experimentally

Take graphene on SiO₂/Si substrate for example, the contrast spectrum $C(\lambda)$ of

graphene can be obtained by [27-29,31]

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)}. \quad (2.9)$$

We move the graphene on SiO₂/Si substrate into the focus beam of the white light and take the reflection spectrum $R(\lambda)$; following move SiO₂/Si substrate into the focus beam of the white light and take the reflection spectrum $R_0(\lambda)$, as schematically demonstrated in the Fig. 2.4. The contrast spectrum of graphene on SiO₂/Si substrate then can be obtained from Eq. (2.9).

Fig. 2.4 Schematic image of performing contrast measurements.

2.2.2 Theoretical calculation of contrast spectrum

The calculation of reflection spectra $R_0(\lambda)$ and $R(\lambda)$ is based on Fresnel's equation. When a beam of light is incident at an interface, for example, the air/graphene or graphene/SiO₂ interface, a portion of the beam is reflected from the interface and the rest is transmitted, thus, an infinite number of optical paths are possible as schematically shown in the Fig. 2.5. Take the air/SiO₂/Si system for

example, as can be seen from Fig. 2.5, the amplitudes of the reflected waves are individually, r_{02} , $t_{02} \cdot r_{23} \cdot t'_{02} \cdot e^{-2i\phi_2}$, $t_{02} \cdot r_{23} \cdot t'_{02} \cdot (r_{23} r'_{02}) e^{-2 \cdot 2i\phi_2}$, ...

Therefore, the total reflected amplitude is governed by,

$$\begin{aligned} r &= r_{02} + t_{02} \cdot r_{23} \cdot t'_{02} \cdot e^{-2i\phi_2} + t_{02} \cdot r_{23} \cdot t'_{02} \cdot (r_{23} r'_{02}) e^{-2 \cdot 2i\phi_2} + \dots \\ &= r_{02} + \frac{r_{23} \cdot (1 - r_{02}^2) \cdot e^{-2i\phi_2}}{1 + r_{02} \cdot r_{23} \cdot e^{-2i\phi_2}} \\ &= \frac{r_{02} + r_{23} \cdot e^{-2i\phi_2}}{1 + r_{02} \cdot r_{23} \cdot e^{-2i\phi_2}} \end{aligned} \quad (2.10)$$

Here, r_{02}/t_{02} is the reflection/transmission coefficient at the air/SiO₂ interface, and r'_{02}/t'_{02} is the reflection/transmission coefficient at the SiO₂/air interface, r_{23}/t_{23} is the reflection/transmission coefficient at the SiO₂/Si interface. $\phi_2 = \frac{2\pi \cdot n_2 \cdot d_2}{\lambda}$ is the phase difference when light passes through SiO₂ layers. d_2 is the thickness of the SiO₂

layer. Under normal incident, $r_{02} = \frac{n_0 - n_2}{n_0 + n_2}$, $r_{23} = \frac{n_2 - \tilde{n}_3}{n_2 + \tilde{n}_3}$. n_0 , n_2 and $\tilde{n}_3$ are the refractive indices of air, SiO₂, and Si, respectively. The reflection spectrum from the air/ (SiO₂ on Si), $R_0(\lambda)$ can be calculated by

$$R_0(\lambda) = |r|^2 \quad (2.11)$$

For the system of air/graphene/SiO₂/Si system, the calculation of reflection spectrum $R(\lambda)$ is more complicated. We first calculate the reflection amplitude from the graphene/ (SiO₂ on Si) interface by using Eq. (2.10),

$$r' = \frac{r_{12} + r_{23} \cdot e^{-2i\phi_2}}{1 + r_{12} \cdot r_{23} \cdot e^{-2i\phi_2}} \quad (2.12)$$

Here, r' is the reflection coefficient at the graphene / (SiO₂ on Si) interface, and

$r_{12} = \frac{n_1 - n_2}{n_1 + n_2}$ is the reflection coefficient at the graphene /SiO₂ interface. n_1 is the

refractive index of graphene.

The reflection amplitude from the air/graphene/SiO₂/Si system then can be calculated by,

$$r_g' = \frac{r_{01} + r' \cdot e^{-2i\phi_1}}{1 + r_{01} \cdot r' \cdot e^{-2i\phi_1}} \quad (2.13)$$

Here, r' is calculated from Eq. (2.12). $\phi_1 = \frac{2\pi \cdot n_1 \cdot d_1}{\lambda}$ is the phase difference when light passes through graphene layer (d_1 is the thickness of the graphene layer) and

$r_{01} = \frac{n_0 - n_1}{n_0 + n_1}$ is the reflection coefficient at the air/graphene interface. The reflection

spectrum from the air/graphene/SiO₂/Si system, $R(\lambda)$ can be calculated by

$$R(\lambda) = |r_g'|^2 \quad (2.14)$$

Fig. 2.5 Multiple beam reflection and transmission from air/SiO₂/Si system and air/graphene/SiO₂/Si system.

The calculation of contrast spectrum can be obtained for graphene samples on any substrate, and this calculation method is also applicable to any other thin film

materials. Fig. 2.6 gives theoretical calculation results of contrast spectra of graphene samples with different layer numbers (1layer, 2layers, 3layers, 5layers, 7layers and 9layers) on SiO_2 (300 nm)/Si substrate under normal incident. As can be seen from this figure, there are two contrast peaks which locate around 375 nm and 600 nm. Besides, as the layer number of graphene increases, the intensity of contrast peak also increases, the one to one correspondence between intensity of contrast peak and graphene layer number, making unambiguously distinguish graphene layer number possible.

Fig. 2.6 Theoretical calculation of contrast spectra of graphene samples with different layer numbers on SiO_2 (300 nm)/Si substrate.

Chapter 3

Experimental methods

3.1 Practical ways to fabricate graphene layers

3.1.1 Micromechanical exfoliation of graphite

Graphene samples can be prepared by ME of HOPG, up to hundred μm in size can be fabricated which is large enough for laboratory research. Fig. 3.1 schematically shows the process of fabrication graphene samples. Scotch tape is needed to attach on the surface of graphite. Peel off graphene layers from graphite (repeat peeling process, until the contrast on the tape is weak). Followed by adhering the tape to the substrate using pressure by hand or tool, and gently removing off the tape. Graphene samples with different layers will then be transferred on the target substrate, *e.g.*, $\text{SiO}_2(300\text{ nm})/\text{Si}$, interacted by the weak Van de Waals force whose thickness can be identified by the white light contrast spectrum as described in Chapter 2.

Fig. 3.1 Schematic image of fabrication of graphene sample by ME of graphite. (a) Graphite is formed by stacking infinite graphene layer. (b) Attach scotch tape on the surface of graphite. (c) Peel off graphene layers from graphite using scotch tape. (d) Adhere the tape on SiO₂(300 nm)/Si substrate and gently remove off the tape. (e) Optical image of SLG, BLG and multi-layers graphene on SiO₂(300 nm)/Si substrate, different contrast here corresponding to graphene samples with different thickness.

3.1.2 Epitaxial grown on SiC substrate

It has been known that after heat treatment of semiconductor SiC at high temperature as well as in high vacuum, EG can be grown on two polar surface of SiC substrate by vacuum graphitization method [7,32]. It is believed that on different polar surface of SiC substrate, the growth mechanism is different. On the Si-terminated surface (0001), the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ (6R3) reconstruction is believed to be the precursor of the growth of graphene[33-34], which has the hexagonal structure and partially bonded to the Si atoms. Fig. 3.2 schematically shows atomic structure of this

precursor layer (also refer as buffer layer) on Si-SiC substrate. The 6R3 reconstruction is schematically shown by the diamond-shape structure drawn by blue lines. Few layers graphene are then growing upon this interface interacted by the weak Van der Waals force. The lattice mismatch between this precursor layer and graphene layers will induce the compressive stain on graphene layers which has been verified by the Raman observation that 2D/G band is blue shifted compared with graphene samples made by ME of HOPG. This kind of stain effect will release as the thickness of graphene increases[34].

Fig. 3.2 Schematic image of precursor layer on Si-SiC substrate. (a) A top view (b) A side view. The green sphere represents C atom in the precursor layer. The yellow and gray spheres represent Si and C atom from SiC. Graphene layers then are growing on above this 6R3 reconstruction structure. Adapted from Z. H. Ni et al.[34].

On the other hand, for graphene epitaxial grown on C-SiC surface $(000\bar{1})$ [33], it is believed there is no distinct interface phase exists and the interaction between graphene and the substrate is weak[33-34]. As a result, the graphene layers orient arbitrary angles relative to the substrate, and turbostatic structure of graphene layers on the C face is often observed by x-ray diffraction [35] and scanning tunneling microscope (STM)[36].

3.1.3 Epitaxial grown on transition metals

◆ (1) Epitaxial grown on Ni film

For graphene fabricated by ME of HOPG, large area fabrication is difficult and for graphene epitaxial grown on SiC substrate, ultrahigh vacuum conditions are needed. Therefore, various simple chemical methods are developed to fabricate large scale, high quality graphene layers. Recently, researchers find that graphene layers of square centimetres can be fabricated by chemical vapour deposition (CVD) method on Ni film[37-40], and the fabricated graphene layers can be transferred to any substrate. The growth mechanism is summarized in Fig. 3.3[37]. (a) A thin nickel film (~ 300 nm) is deposited on any substrate. (b) Heat the nickel layer at about 1000°C and expose the layer to a carbonaceous gas environment, *e.g.*, CH_4 . The carbon atoms are dissolving into nickel substrate. (c) Rapidly cooling the samples down to room temperature, the carbon atoms are then precipitating out of the nickel substrate. The thickness of graphene layers are controlled by the cooling rate as well as the concentration of carbon dissolved into the nickel film [37-40]. (d) Etch away the nickel film by using chloride solution (FeCl_3), then obtained free-standing graphene layers as shown in Fig. 3.3(e) are ready for transferring process to any substrate.

Fig. 3.3 CVD methods for growing large scale graphene film. Adapted from Alexander N. Obraztso[37]. (a) A thin nickel film is deposited onto a substrate. (b) Heat the Ni film at $\sim 1000^\circ\text{C}$, and exposed the film to a carbonaceous gas environment. Carbon atoms will diffuse into the film. (c) Cooling down the Ni film to room temperature, carbon atoms will then precipitate out of the Ni film. (d) Etching away the substrate. (e) The obtained free standing graphene layer is ready for transferring to any other substrate.

◆ (2) Epitaxial grown on copper foils

For graphene layers epitaxial grown on Ni foils, because of the high adsorption abilities of carbon sources in Ni foils, it is difficult to obtain thinner graphene layers. Recently, by using surface catalyzed process, centimetre scale SLG can be grown on copper (Cu) foils achieved by Rodney S. Ruoff's research group[41]. They grow graphene on copper foils at temperature up to 1000°C by CVD method using a mixture of methane and hydrogen as the source. Because of poor solubility of carbon atoms in Cu, more than 95% SLG coverage on copper surface can be obtained which is continuous across copper surface steps and grain boundaries.

Fig. 3.4 (a) SEM image of graphene on copper foil. (b) High-resolution SEM image showing graphene layers and wrinkles. Graphene film is transferred to SiO₂/Si substrate (c) and glass (d), individually. Adapted from X. S. Li et al. [41].

3.2 Confocal Raman /white light microscope

Three laser wavelengths are available for our confocal Raman microscope (457 nm, Diode Pumped Solid State Laser (DPSSL); 488 nm, Ar⁺ laser; 532 nm, DPSSL laser). Fig. 3.5 gives the schematic diagram of our WITEC CRM200 system. The laser is coupled into a single mode fiber, and then is reflected by a beamsplitter (90:10), following is focused by an objective to excite the Raman signals. Objectives with different magnification and different numerical aperture (NA) are available for our system. The laser spot size is ~ 500 nm when focused by the objective with a magnification of 100X and a NA of 0.95[26]. Both the scattered light and reflected light are collected in the backscattering configuration. This system allows to sequentially taking Raman spectrum from the interested adjacent area as the way of

obtaining Raman imaging and the movement of the sample is controlled by the piezo stage.

This system also allows for the white light microscope. The white-light source (tungsten halogen lamp, excitation range from 350 nm to 850 nm) is reflected from the color-neutral beam splitter and then focused by the objective. The reflected light is then collected by the objective. The ScanCtrl Spectroscopy Plus software from WITec GmbH is used to control the stage movement and data acquisition. The WITec Project software is used for data analysis.

Fig. 3.5 Schematic diagram of confocal Raman /white light system.

3.3 Samples used in this study

The samples used in this study are fabricated by two ways, ME of HOPG and epitaxial grown on Si-SiC substrate.

◆ (1) Micromechanical exfoliation of highly oriented pyrolytic graphite

The graphene samples with different layer numbers are prepared by ME of HOPG [1]. This kind of method makes graphene samples can be transferred to any substrates, *e.g.*, standard substrate Si wafer with ~300 nm SiO₂ capping layer, quartz single crystal, Si, glass, NiFe, PDMS and so on.

After fabricating graphene samples by ME of HOPG, the TBG samples (1+1 folded graphene) are then prepared by flushing de-ionized water across the surface of the substrate (SLG on SiO₂/Si). The area and orientation of TBG samples are then controlled by the rate and direction of the water flow[42-43]. In some cases, SLG samples are already folded after cleaving from graphite. We have fabricated several TBG samples using this method with dimensions 5 to 10 μm^2 . The orientation angle between the top layer and the bottom layer can be determined by analyzing the geometry. The crystal axis of SLG can be determined by the smooth graphene edge[44]. Once the angle α between the folded edge and the crystal axis is known, the orientation angle θ , which is the angle of the top layer rotates relative to the bottom layer, can be determined as $\theta = 2\alpha$ or $\theta = 180^\circ - 2\alpha$.

◆ (2) Epitaxial grown graphene

The epitaxial graphene samples are prepared by high temperature (~ 850 °C), high vacuum heat treatment of Si-terminated 6H-SiC (0001) sample, following annealing the sample at 1300 °C in the absence of the silicon flux[7,32,45-46]. The in-situ Low-Energy-Electron-Diffraction (LEED) and STM are used to monitor the atomic structure of graphene samples. It is believed that below the epitaxial monolayer graphene (EMG), there is a buffer layer which is covalently bonded to the SiC substrate[33,47]. The characteristic STM images of buffer layer and EMG are quite different which makes differentiate buffer layer and EMG possible[34]. The

layer thickness of EG then can be measured by monitoring the attenuation of Si 2p PES signal from bulk SiC with photon beam energy of 500 eV[45-46,48].

Chapter 4

Raman properties of graphene layers

4.1 Phonon dispersion of graphene

A clear understanding of phonon dispersion of graphene [49] is useful for us to fully understand the properties of graphene. The unit cell of graphene contains two carbon atoms A and B, as has been shown in Fig. 1.1. Therefore, there are six phonon dispersion bands. Fig. 4.1 gives the phonon dispersion branches of graphene, in which three phonon dispersion branches are optical bands (denoted as O) which describe the motion of atom A relative to atom B, while three acoustic branches (denoted as A) describe the motion of the whole unit cell (atom A and atom B together) in three-dimensional space. The phonon modes noted as L (longitudinal) or T (transverse) are distinguished according to the vibrations are along the A-B carbon-carbon directions or perpendicular to the A-B carbon-carbon directions, individually. i represents in-plane vibration while o represents out-plane vibration, here, plane is refer to the graphene plane in real space.

Fig. 4.1 Calculated phonon dispersion relation of graphene. Adapted from L. M. Malard et al. [49-50]

4.2 Raman spectrum of graphene

Graphene sample is fabricated by ME of HOPG [1] and carefully selected substrate is used for obtaining good contrast[27-28, 31]. Fig. 4.2 gives the typical Raman spectrum of SLG on SiO₂ (300 nm)/Si substrate excited by 532 nm laser line (2.33 eV). The layer number of graphene is further confirmed by the white light contrast spectroscopy as described in Chapter 2[27-28, 31]. In the detection range of 1200 cm⁻¹ to 3000 cm⁻¹, there are three major Raman features of graphene observed, including the so called G band which locates around 1580 cm⁻¹, 2D band which locates around 2680 cm⁻¹ as well as G* band which locates round at 2455 cm⁻¹. There is also a defect or disorder induced D band located around 1350 cm⁻¹ which is absent for high-quality graphene layers. The G band originates from in-plane vibration of sp² carbon atoms is a doubly degenerate (iTO and LO) phonon mode (E_{2g} symmetry) at the Brillouin zone center (Γ point)[51], while the 2D and D band originate from a double resonance (DR) Raman process involving iTO phonon along the KM direction as well as electrons along the KT direction[52-53]. The DR process determines the

dispersive of the 2D band, its band position blue shifts when the excitation laser energy increases [52]. It also can be seen from this figure, the 2D band of SLG is a single, sharp peak with FWHM of $\sim 30 \text{ cm}^{-1}$. This feature of 2D band has become a fingerprint for quick identification of SLG. The shape, width, and position of 2D band of graphene are layer number dependent which will be described latter. The G^* band is also originated from a intervalley DR process involving electrons along the KM direction as well as iTO and LA phonons along the KT direction[54]. (The G band, D band was firstly named by R. P. Vidano *et al.* in 1981[55]. 2D band was historically named as G' band because it is the second prominent peak observed in graphite samples. However, the G' band has nothing to do with the G band. Therefore, to clarity, A. C. Ferrari *et al.* prefers calls it as 2D band [56]. We use the name of 2D band in this thesis. The G^* band was named by D. L. Mafrá *et al.*[54]).

Fig. 4.2 The Raman spectrum of SLG excited by 532 nm laser line.

The G band is originated from a single resonance process as schematically shown in Fig. 4.3(a). Electron with wave vector k (measured from K (K') point) absorbs the incident photon energy and is excited to the conduction band. Following, the electron is inelastically scattered by the doubly degenerate (iTO and iLO) phonon from Γ point (with energy of $\Delta\omega_{G-ph}$), following is the recombination of electron and hole.

This scattering process is called single resonance process because either the incident light or the scattering light can match the electronic transition. The 2D band of graphene originates from DR process as schematically shown in Fig. 4.3(b). Electron with wave vector k (measured from K point) absorbs the incident photon energy and is excited to the conduction band, following inelastic scattered by a iTO phonon (phonon with momentum q and energy of $\Delta\omega_{ph}$) to a circle round K' point. After that, the electron is inelastically scattered back by the iTO phonon with reverse momentum direction $-q$, followed by the e-h recombination. Since the inelastic scattering of electron by phonon happens around inequivalent K and K' point, this kind of DR process is called an intervalley DR process. This scattering process is called DR process because two resonance conditions are satisfied: the intermediate $k+q$ state is always a real electronic state and either the initial state k or the final state k is a real state. For the 2D band of graphene, it was reported by D. M. Basko [57] that it can even be from a fully DR process: scattering of electron from the K (K') point to K' (K) point and simultaneous scattering of the hole from the K (K') point to K' (K) point. The Raman intensity of a DR process will be smaller by a factor $\sim$

$\frac{\gamma^2}{\omega_{ph}^2}$ compared with the fully double resonance process. Here, γ is the inelastic

scattering rate of electron and ω_{ph} is the energy of the iTO phonon. The 2D band is closely associated with the electronic structure of graphene located around K and K'

point, therefore, the 2D band makes the Raman spectroscopy probing the electronic properties of graphene possible.

Fig. 4.3 The single resonance process for G band and double resonance process for 2D band.

4.3 Electronic structure of bi-layer graphene and doping effect in graphene probed by Raman spectroscopy

Raman spectroscopy has been historically used to probe structural, vibrational and electronic characteristics of graphite materials, providing useful information on the defects (D band), in-plane vibration of sp^2 carbon atoms (G band) as well as the stacking orders (2D band)[53]. Raman spectroscopic studies of graphene have revealed very interesting phenomena, *e.g.*, the Raman second order (2D) band can be used as a simple and efficient way to determine the SLG[56,58], the width and position of G/2D band are used to measure the electron/hole dopants in graphene[59-60], the electronic structure of BLG with Bernal stacking can be probed by resonant Raman scattering[61], the Raman imaging obtained from the D band

intensity can be used to determine the edge chirality[44], polarized Raman spectroscopy can be used to study the anisotropic electron-phonon interaction[62], and monitoring of G/2D band position can even be used to detect amount of uniaxial strain loaded in graphene layers[63-65]. In this section, we are mainly focus on the of Raman studies of electronic properties of graphene layers which are closely related to our work. We also present the doping study of graphene which will provide guidance for our future work.

4.3.1 Electronic band structure of bi-layer graphene with Bernal stacking probed by Raman spectroscopy

The Slonczewski-Weiss-McClure (SWM) model has been used to calculate the band structure of graphite materials for long time and the band structure of BLG with Bernal stacking also can be described by SWM parameters in term of r_0, r_1, r_3, r_4 which are associated with different hopping process as indicated in the Fig. 4.4[61]. Those parameters are fundamental for understanding the electronic properties of graphite materials and which could be experimentally probed from Raman spectroscopy.

Fig. 4.4 (a) Atomic structure of BLG with Bernal stacking as well as SWM parameters in term of r_0, r_1, r_3, r_4 associated with different hopping processes are labelled in this figure. (b) First Brillouin zone of SLG, high symmetry points are marked on this figure.

Adapted from L. M. Malard et al. [61].

The 2D band of graphene is because of intervalley DR scattering process as described in Section 4.2. The observed four peaks of 2D band of BLG can be in principle attributed to the electronic band splitting effect[56]. For BLG with Bernal stacking[66], the π -electron dispersion splits into two parabolic branches near the Dirac point due to neighboring layer interaction as shown in the Fig. 4.5.

Electron in valence band (π_1, π_2) absorbs the photon energy E_L and excited to the conduction band (π_1^*, π_2^*)[61],

$$E_L = E_{\pi_i^*}(k_i) - E_{\pi_i}(k_i) \quad (4.1)$$

Where $i=1$ or 2 , k_i is the electron momentum measured from K or K' point. The electron is then scattered by a iTO phonon with phonon energy $E_p^{i,j}(k_i + k_j')$ from π_i^* band to π_j^* band,

$$E_p^{ij}(k_i + k_j') = E_{\pi_i^*}(k_i) - E_{\pi_j^*}(k_j') \quad (4.2)$$

where $i, j=1$ or 2 , since the dispersion of iTO phonon is known and the phonon energy $E_p^{i,j}(k_i + k_j')$ involved in those DR processes can be obtained by fitting the 2D band of BLG by using four peaks, individually with FWHM of 30 cm^{-1} as used for SLG. Therefore, by using different excitation energy, combining Eq. (4.1) and (4.2), the dispersion of those two conduction bands and two valence bands ($E_{\pi_i^*}(k_i)$, $E_{\pi_i}(k_i)$) could be obtained. Since the band structures of BLG with Bernal stacking are described by SWM parameters, SWM parameters can be obtained from Raman spectrum measurement of BLG using different excitation energy.

Fig. 4.5 Four allowed DR processes in BLG with Bernal stacking as labelled as P_{11} , P_{12} , P_{22} , P_{21} . Adapted from L. M. Malard et al. [61].

4.3.2 Electron/hole doping in graphene determination by Raman spectroscopy

Raman spectroscopy can be used to measure the electron/hole dopants in graphene[59-60,67-69]. The G band is related to the doubly degenerate (iTO and LO) phonon mode (E_{2g} symmetry) at the Γ point[51], while the 2D band is related to the iTO phonons near the K point[49]. Recently the electric field effect either by top gate or back gate making controllable shift the Fermi surface in graphene possible[59-60,67-69]. The Raman spectroscopy could be used to probe the interaction between those optical phonons and conduction electrons or holes. It is observed that as the doping concentration (electron or hole) increases[70]:

- (1) The width of G band will decrease because there is no longer damping of phonons with electron-hole pairs when $|E_F| > \frac{\hbar\omega_G}{2}$, determined by the Pauli principle as shown in Fig. 4.6 (a) to (c). Since the lifetime of the optical phonon increases, the

width of G band will decrease. The change of G band width can also be used to quantitatively determine the phonon electron coupling strength[59].

(2) The G band position show blue shift for both electron and hole doping because of breakdown of the adiabatic Born–Oppenheimer approximation as can be seen in Fig. 4.6(d) to (f)[59-60]. According to the time dependent perturbation energy, the G band position first decreases logarithmically and then increases when the Fermi level position moves up or down [49]. It is presented by J. Yan *et al.* that the phonon energy shift of G band $\hbar\omega_G - \hbar\omega_G^o$ (ω_G^o is ω_G at Dirac point) increase as a function of doping quantity[59]

$$\hbar\omega_G - \hbar\omega_G^o = \lambda \left\{ |E_F| + \frac{\hbar\omega_G}{4} \ln \left| \frac{2|E_F| - \hbar\omega_G}{2|E_F| + \hbar\omega_G} \right| \right\} \quad (4.3)$$

where, $|E_F|$ is the absolute value of the Fermi energy respect to the Dirac

point. $\lambda = \frac{A_{uc} D^2}{2\pi\hbar\omega_G M v_F^2}$, here, A_{uc} is the area of graphene unit cell and M is the carbon

atom mass, D is electron-phonon coupling strength and v_F is the Fermi velocity.

(3) For electron doping, the 2D band will red shift while for hole doping, the 2D band will blue shift as presented in A. Das's work[67].

Fig. 4.6 The G band width as well as G band phonon energy as a function of doping level (Fermi surface). Adapted from J. Yan *et al.* [59].

(4) The integrated intensity ratio of 2D band and G band ($\frac{I_{2D}}{I_G}$) will decrease as the doping concentration increases [69,71]. It is reported by Z.H. Ni *et al.* [71] that the intensity of 2D band can be expressed as:

$$I_{2D} = \frac{(e^2/c)^2 v^2 \omega_{in}^2}{48\pi c^2 \gamma^2} \left[\frac{9F_K^2}{M\omega_K v^2} \frac{\sqrt{27}a^2}{4} \right]^2, \quad (4.4)$$

here, v is the Fermi velocity, a is the lattice constant of graphene, M is the mass of the carbon atom, and F_K is the coupling constant. ω_{in} and ω_K are the frequencies of the incident laser and the 2D phonon around the K point, respectively. From above equation, it can be seen that I_{2D} is proportional to $\frac{1}{\gamma^2}$, where γ is the electron or hole inelastic scattering rate. As the charge impurities increase, the charge density in graphene also increases, the electron-electron/hole inelastic scattering rate γ will increase, therefore, resulting in decreasing the intensity of 2D. This charge impurity

effect on the intensity of G band can be ignored [71]. Fig. 4.7 gives the integrated intensity ratio of 2D band and G band as a function of doping concentration. From this figure, it can be seen the integrated intensity ratio of 2D and G band can be used as a quantitative way to determine doping concentration.

Fig. 4.7 The 2D band and G band integrated intensity ratio of SLG with different doping concentration. Adapted from Z. H. Ni et al.[71].

4.4 Graphene layer number determination by Raman spectroscopy/imaging

White light contrast spectrum has been successfully used to determine layer number of graphene made by ME and transfer to SiO₂/Si substrate[27-28, 31]. Besides, the layer number of graphene can also be determined by Raman spectroscopy/imaging.

4.4.1 Graphene layer number determination by the integrated intensity of the G band

The layer number of graphene can be determined by the integrated intensity of G band as a result of the G band originates from in-plane vibration of sp^2 carbon atoms[51]. Thus, the Raman intensity of G band should be proportional to the thickness of graphene/graphite samples up to the laser penetration depth which is ~ 50 nm (150 layers) under 532 nm excitation. Fig. 4.8 shows the G band Raman integrated intensity of graphene as a function of layer numbers. The thickness of graphene layers is determined by white light contrast spectra[27-28,31]. Besides the graphene layers with one, two, three, five, six, eight, and nine layers, samples *a-h* are thicker than 10 layers[27-28,31] whose thickness are ~ 5 nm to ~ 50 nm, respectively, as determined by AFM. Interestingly, it can be seen that the Raman intensity increases almost linearly until ~ 10 layers (*i.e.* ~ 3 nm) which are consistent with A. Gupta *et al.* [58] and D. Graf *et al.* [72]'s results and decreases for thicker graphite samples. Since SLG can be unambiguously distinguished by its 2D band, the G band Raman integrated intensity then can be used to identify layer number of graphene. The reason of relatively weak G band Raman intensity of graphite will be described later.

Fig. 4.8 The G band Raman integrated intensity of graphene as a function of layer numbers. The red dashed curve is a guide to eye.

We also carried out the Raman imaging study of G band integrated intensity of graphene layers. Fig. 4.9(a) gives the Raman imaging obtained from G band integrated intensity for graphene samples with 1 to 4 layers. Here, the bright color represents higher integrated intensity. It can be seen that as the layer number of graphene increases, the integrated intensity of G band also increases. The integrated intensity of the G band along the blue dashed line is given in Fig. 4.9(b). It can be clearly seen that the intensity of G band increases linearly with increasing the layer number. Therefore, besides the white light contrast spectrum, the Raman spectrum/imaging constructed by the intensity of G band also can be used for determining the thickness of graphene.

Fig. 4.9 (a) Raman imaging plotted by the integrated intensity of G band. (b) The cross section of Raman imaging, which corresponds to the dashed blue line as given in Fig.4.9 (a).

4.4.2 Graphene layer number determination by the FWHM of 2D band

As described in Section 4.2, the 2D band is because of intervalley DR Raman scattering process involving electronic states at two inequivalent points K , K' along high symmetry $K\Gamma$, $K'\Gamma$ directions and iTO phonons along the KM direction[49]. The shape, width, and position of 2D band of graphene are layer number dependent and the evolution of 2D band is closely related to band splitting of graphene layers induced by the interlayer interaction [56, 58, 72-73]. Fig. 4.10(a) gives the Raman spectra of single layer, 2 layers, 3 layers and 4layers graphene with Bernal stacking. As can be seen from Fig. 4.10(a), for SLG, the 2D band is a symmetric, sharp band with FWHM of $\sim 30 \text{ cm}^{-1}$. While for 2-layer graphene, its 2D band is broader, blue shifted, and can be decomposed into four peaks, while those of 3-layer (based on the group theory analysis, fifteen Raman peaks are involved in the 2D band for 3-layer

graphene) and 4-layer graphene are much broader and can be decomposed into more peaks.

Fig. 4.10 (a) Raman spectra of single layer, 2-layer, 3-layer and 4-layer graphene, the curve fitting results of 2D band of graphene layers are also included. (b) The FWHM of 2D band of graphene as a function of layer numbers.

It is known that the 2D band of graphene is originated from DR process. For SLG, iTO phonon with momentum q is involved in this DR process as schematically shown in Fig. 4.11(a). While for BLG with Bernal stacking, because of the strong interaction between neighboring layer, the π -electrons dispersion in the valence and conduction bands split into two parabolic branches near the Dirac point as given in the Fig. 4.11(b)[66]. iTO phonons with momentum q_1, q_2, q_3, q_4 are allowed for this DR process for BLG[56,61]. Different wave vectors here correspond to phonons with different frequencies as determined by the linearly iTO phonon dispersion curve around K point[49]. Therefore, the 2D band of BLG can be decomposed into four peaks as shown in Fig. 4.10(a). For SLG, the FWHM of 2D band is $\sim 30 \text{ cm}^{-1}$. For 2-layer graphene with Bernal stacking, $\sim 52 \text{ cm}^{-1}$ overall FWHM of 2D band is

obtained. The DR process of 3 layers graphene and 4 layers graphene are more complicated compared with those of SLG and BLG. Because of π electron interaction under Bernal stacking, the electronic bands of 3 layers and 4 layers graphene split into more complex ways as shown in Fig. 4.11 (c) and (d), respectively. Thus, iTO phonons with more different momentum are allowed for DR process for 3 layers and 4 layers graphene, resulting in increasing the width of their 2D bands. We have investigated hundreds of graphene samples and the FWHM of 2D band of graphene samples with different layer numbers are summarized in Fig. 4.10(b). It is clear that there are distinguishable ranges for 1 layer, 2 layers, 3 layers, 4 layers, and 5 layers graphene at $27.5 \pm 3.8 \text{ cm}^{-1}$, $51.7 \pm 1.7 \text{ cm}^{-1}$, $56.2 \pm 1.6 \text{ cm}^{-1}$, $63.1 \pm 1.6 \text{ cm}^{-1}$, $66.1 \pm 1.4 \text{ cm}^{-1}$, respectively. Thus, the data obtained here provide a direct standard for the determination of layer numbers of graphene.

Fig. 4.11 Electronic band dispersion and DR scattering process for SLG (a), 2 layers graphene with Bernal stacking (b). Electronic band dispersion for 3 layers graphene(c) and 4 layers graphene(d) stacking in Bernal sequence. Adapted from our published work Y. F. Hao et al. [74].

4.5 Origin of the strong Raman signal of single layer graphene on SiO₂/Si

The G band Raman intensity of graphene layers on SiO₂ (300 nm)/Si substrate as a function of layer numbers is investigated in Section 4.4.1, the G band Raman integrated intensity of SLG is comparable to that of graphite, which means the Raman

intensity of SLG is significantly enhanced. The very strong Raman signal from graphene (single and few layers) on SiO₂/Si substrate has been observed by many researchers and this makes the Raman studies of graphene available[56, 58,72]. Thus, in this section, we investigate the mechanism behind this enhancement of Raman signal of SLG on SiO₂/Si substrate.

Need to say that multi-reflection/interference effect on contrast has been well documented but the multiple reflection of Raman is not[27-28, 31]. By considering the multilayer interference of incident light as well as the interference of multi-reflection of Raman signals in graphene based on the Fresnel's equations[27-28, 31,75], the enhancement of Raman signal of SLG on SiO₂/Si substrate can be explained.

Consider the incident light from air ($n_0 = 1$) onto a graphene/SiO₂/ Si bilayer system, as shown in Fig. 4.12(a). $\tilde{n}_1 = 2.6 - 1.3i$, $n_2 = 1.46$, $\tilde{n}_3 = 4.15 - 0.044i$, are refractive indices of graphite, SiO₂, and Si at 532 nm, respectively. d_1 is the thickness of graphene which is estimated as $d_1 = N\Delta d$, and $\Delta d = 0.335\text{nm}$ [76-77], where N is the number of layers. d_2 is the thickness of SiO₂ and the Si substrate is considered as semi-infinite. When a beam of light is incident on an interface, for example, the air/graphene or graphene/SiO₂ interface, a portion of the beam is reflected and the rest is transmitted, resulting in an infinite number of transmitted/reflected beams. The G band Raman intensity of graphene layers depends on the total electric field distribution, which is a result of interference between all these transmitted beams in graphene layer.

The total amplitude of the electric field at certain depth y in graphene layer is the sum of the infinite transmitted beams, as schematically shown in Fig. 4.12 (a), whose amplitudes after considering absorption are:

$$\begin{aligned}
& t_1 e^{\beta y} \cdot e^{-i \frac{2\pi \tilde{n}_1 y}{\lambda}}, \\
& t_1 \cdot r' \cdot e^{\beta \cdot (2d_1 - y)} \cdot e^{-i \frac{2\pi \tilde{n}_1 \cdot (2d_1 - y)}{\lambda}}, \\
& -t_1 e^{\beta y} \cdot e^{-i \frac{2\pi \tilde{n}_1 y}{\lambda}} \cdot r_1 r' e^{-2i \cdot f_{i1}} \cdot e^{2\beta \cdot d_1}, \\
& -t_1 \cdot r' \cdot e^{\beta \cdot (2d_1 - y)} \cdot e^{-i \frac{2\pi \tilde{n}_1 \cdot (2d_1 - y)}{\lambda}} \cdot r_1 r' e^{-2i \cdot f_{i1}} e^{2\beta d_1}, \dots
\end{aligned} \tag{4.5}$$

where $\beta = \frac{-2\pi \cdot k_1}{\lambda}$, ($k_1 = 1.3$ is the extinction coefficient of graphite and λ is the

excitation wavelength) emerges as a measure of the absorption in the graphene layer,

$t_1 = \frac{2n_0}{n_0 + \tilde{n}_1}$ is transmission coefficients at the interface of air/graphene, $r_1 = \frac{n_0 - \tilde{n}_1}{n_0 + \tilde{n}_1}$ is the

reflection coefficient at the air/graphene interface, while $f_{i1,2} = \frac{2\pi \cdot \tilde{n}_{1,2} \cdot d_{1,2}}{\lambda}$ are the

phase differences when light passes through graphene layers and SiO₂ layers. Here,

$r' = \frac{r_2 + r_3 \cdot e^{-2i \cdot f_{i2}}}{1 + r_2 \cdot r_3 \cdot e^{-2i \cdot f_{i2}}}$ is the effective reflection coefficient of graphene/(SiO₂ on Si)

interface, where $r_2 = \frac{\tilde{n}_1 - n_2}{\tilde{n}_1 + n_2}$, $r_3 = \frac{\tilde{n}_2 - \tilde{n}_3}{\tilde{n}_2 + \tilde{n}_3}$ are individually reflection coefficient at

the interface of graphene/SiO₂ and SiO₂/Si.

Thus, the total amplitude of the electric field at the depth y is

$$t = \frac{t_1 \cdot e^{\beta \cdot y} \cdot e^{-i \frac{2\pi \tilde{n}_1 \cdot y}{\lambda}} + t_1 \cdot r' \cdot e^{\beta \cdot (2d_1 - y)} \cdot e^{-i \frac{2\pi \tilde{n}_1 \cdot (2d_1 - y)}{\lambda}}}{1 + r_1 r' \cdot e^{-2i \cdot f_{i1}} \cdot e^{2\beta \cdot d_1}} \tag{4.6}$$

In addition to the above discussion, further consideration should be applied to the interference of multi-reflection of the Raman light in graphene at the interface of graphene/air and graphene/(SiO₂ on Si), which contribute to the detected Raman signal. Fig. 4.12(b) schematically shows multi-reflection of the scattering light in

certain depth y in graphene layer. Thus, the detected signal is a result of summation of infinite transmitted light from the interface of graphene/air, which makes the amplitude multiplied by

$$r = \frac{(e^{\beta y} + r' e^{\beta(2d_1 - y)}) t_1'}{1 + r_1 r' e^{2\beta d_1} e^{-i \frac{2\pi d_1}{\lambda} \cdot 2d_1}} \quad (4.7)$$

Where $t_1' = \frac{1 - r_1^2}{t_1}$ represent the transmission coefficients at the interface of graphene/air. In the equation above interference of Raman scattering light is not considered as the phase of spontaneous Raman lights are random.

Thus, the total Raman signal as result of interference of infinite transmitted laser optical paths in graphene film followed by considering the interference of multi-reflection of Raman scattering light can be expressed as:

$$I = \int_0^{d_1} |t \cdot \gamma|^2 \Delta y \quad (4.8)$$

Fig. 4.12(c) shows the calculation results of Raman intensity of G band as a function of number of graphene/graphite layers. The black curve shows the calculation result without considering the interference of multi-reflection of Raman light in graphene, which is given by $I = \int_0^{d_1} |t|^2 \Delta y$. It can be seen that the Raman scattering intensity is strongest at ~38 layers and the intensity of bulk graphite (~1000 layers) is much stronger than that of single and bilayer graphene which is not agreed with experimental results. The red curve gives the calculated results based on Eq.(4.8) which is after considering the interference of multi-reflection of Raman light in graphene. In that case, the intensity is strongest at ~17 layers and the Raman signal of bulk graphite (~1000 layers) is weaker than that of bilayer graphene, which agrees very well with the experiment data. Thus, the consideration of the interference of

multi-reflection of scattering Raman light in graphene/graphite is necessary.

It should be noted that our calculation for Raman intensity of graphene can also be applied to other thin films and materials. This provides an effective method of enhancing weak signals, *e.g.*, as in Raman study of single molecules and individual nanowires.

Fig. 4.12 (a) Schematic laser reflection and transmission in certain depth y in graphene layers deposited on SiO_2/Si substrate. (b) Multi-reflection of the scattering Raman light (from depth y) at the interface graphene/air and graphene/ (SiO_2 on Si). The detected Raman signal is a summation of infinite transmitted light at the interface of graphene/air. (c). The calculation results of Raman intensity of G band as a function of number of layers with (red) and without (black) considering the interference of multi-reflection of Raman scattering light in graphene.

Attention is then paid to the SiO_2 layer because of it is believed to be the reason for enhancement of Raman signal of single layer graphene. Fig. 4.13 shows the

enhancement factor E as a function of $\frac{n_{\text{SiO}_2} \cdot d_2}{\lambda}$. E is a ratio of Raman intensity of single layer graphene on Si substrate with SiO_2 layer to without, which is calculated based on Eq. (4.8).

Fig. 4.13 Calculation result of enhancement factor E as a function of $\frac{n_{\text{SiO}_2} \cdot d_2}{\lambda}$

It can be seen that, the enhancement factor E value oscillates periodically with the thickness of SiO_2 and the maximum enhancement happens at $\frac{n_{\text{SiO}_2} \cdot d_2}{\lambda} \approx 1/4, 3/4$ and so on. The highest enhancement value, for example, when $\frac{n_{\text{SiO}_2} \cdot d_2}{\lambda} \approx 3/4$, ($d_2=269$ nm), can be ~ 30 . In our experiments, for SiO_2 of 300 nm, E is ~ 16 , which contributes to the high intensity of single layer graphene compared to bulk graphite. In order to verify this enhancement effect, we have also measured the G band signal of single layer graphene on quartz and SiC substrate, and their signals are $<10\%$ of that on SiO_2/Si substrate.

Based on above calculation results, it can be seen that the SiO_2 layer plays an

important role on deciding the Raman intensity of graphene. A total phase change of 2π (π at the interface of SiO_2 layer/ Si substrate plus π due to light passing through double thickness of SiO_2 layer) can be achieved by this kind of configuration. Therefore, infinite transmitted light in graphene layers have no phase change will enhance Raman signal greatly. Besides SiO_2 , Other dielectrics with lower refractive index such as PMMA ($n \sim 1.49$), CaF_2 ($n \sim 1.437$), LiF ($n \sim 1.39$), KBr ($n \sim 1.571$)[78], also can be used and semiconductors such as Ge ($n \sim 4.24$), GaSb ($n \sim 4.31$), InAs ($n \sim 4.17$) with higher refractive index can be used as the substrate[78].

Chapter 5

The substrate effect on the electronic properties of graphene

5.1 Motivation for the substrate effect study

Raman spectroscopy has been widely used to probe structural, vibrational and electronic characteristics of graphite materials. Till now, most of the Raman studies were carried out on graphene samples fabricated by ME of HOPG and transferred to Si substrate with ~ 300 nm SiO_2 layer in order to obtain the best contrast [28,31,56,72]. In addition, the Raman study of graphene on different substrates, such as indium tin oxide (ITO)[79], sapphire and glass[80] has been carried out. However, the effect of interaction between substrate and the graphene layers on the Raman features have not been sufficiently studied, and different conclusions were given by different group, *e.g.*, A. Das reports the ITO substrate can induce red shift of G band and 2D band[79], while I. Calizo reports the glass substrate can induce splitting of G band[80]. A clear understanding of the substrate effect will provide guidance for future device fabrication of graphene. Therefore, in this chapter we carry out systematical Raman study of SLG produced by ME on different substrates: standard SiO_2 (300 nm)/Si, quartz single crystal, Si, glass, NiFe and PDMS. Choosing SLG for our study is because compared with few layer graphene which are also used for the substrate effect study by I. Calizo *et al.*[80], SLG is more sensitive to the interaction between graphene layers and substrate. The comparison of the Raman features of SLG on the above-mentioned substrates and those of EMG grown on SiC substrate is carried out. For the latter there is a much stronger interaction between graphene layer

and the substrate.

Our experimental results show that the weak interaction (Van de Waals force) between graphene and substrates prepared by ME is not strong enough to affect the atomic structure as well as electronic structure of graphene layers. Only for EMG on SiC substrate, we observe a strong interaction between EMG and SiC that changes the atomic and electronic structures of EMG and consequently the Raman features of EMG.

5.2 Raman spectra of graphene samples on quartz and on SiO₂(300 nm)/Si

Fig. 5.1 (a) Optical image of graphene layers on quartz; the red circle indicates the location of SLG. (b) Raman imaging obtained by the intensity of G band. The red circle displays the position of SLG.

Fig. 5.1(a) gives the optical image of graphene layers on quartz crystal. The different contrast regions correspond to graphene layers with different thickness. The red circle indicates the location of SLG, which is further confirmed by its 2D band feature (a single sharp peak with FWHM of $\sim 30 \text{ cm}^{-1}$). Fig. 5.1(b) gives the Raman imaging obtained from the intensity of G band. As can be seen from this figure, the SLG has the lowest G band intensity (the darkest color region as marked by the red circle). As the G band intensity increases almost linearly as the layer number increases[27,72], we are able to identify the thickness of multi-layer graphene by the intensity of G band which is further confirmed by the white light contrast spectroscopy[27].

The white light contrast imaging of graphene layers on quartz substrate is given in Fig. 5.2(a). Here, the contrast value of graphene is negative due to more reflection is detected from graphene layer compared with that directly from quartz substrate. Fig. 5.2(b) shows the contrast spectra of graphene with different layer number. The contrast spectra of graphene layers show almost flat lines in the range of 450 nm to 600 nm. The contrast values for 1 layer, 2 layers, 3 layers, and 4 layers graphene are respectively, -0.068, -0.125, -0.181, and -0.247, which changes almost linearly with the number of layers.

Fig. 5.2 (a) The white light contrast imaging of graphene layers on quartz substrate. In this figure, we have reversed the scale bar in order to clearly identify graphene layer number. (b) Contrast spectra of graphene with different layer numbers on quartz substrate.

Comparison of Raman features of graphene samples on substrates: quartz substrate and SiO_2 (300 nm)/Si substrate is carried out. Fig. 5.3(a) and (b) respectively show the Raman spectra of single layer, bi-layer, three layers and four layers graphene on quartz substrates and that on the standard SiO_2 (300 nm)/Si substrate. It can be seen the Raman features of different layers of graphene present similar behaviors on those two substrates. The shape and position of 2D band change greatly from one to four layers, as shown by the curve fitting results. The 2D band of bi-layer, three and

four layers graphene can be composed into two or more bands, while SLG presents a single band [56,72]. From this figure, it can also be seen that the sharp, symmetric 2D band ($\sim 30 \text{ cm}^{-1}$) is the best indicator for SLG made by ME and this makes SLG could be easily distinguished from few layer graphene.

Fig. 5.3 The Raman spectra of single layer, bi-layer, three layers and four layers graphene on quartz (a) and on $\text{SiO}_2(300 \text{ nm})/\text{Si}$ substrate. (b) The curve fitting results of 2D band are given in (c) and (d).

5.3 Raman spectra of single layer graphene on different substrates as well as that of epitaxial monolayer graphene grown on SiC substrate

Fig. 5.4 gives the Raman spectra of SLG on different substrate: PDMS, NiFe, glass, Si, quartz and SiO₂(300 nm)/Si substrate as well as the Raman spectrum of EMG grown on SiC substrate, individually, from bottom to top. The G band and 2D band position as well as their FWHM on different substrates are summarized in Table 5.1. As can be seen from this table, the G band position ($1581 \pm 1 \text{ cm}^{-1}$) and FWHM ($15.5 \pm 1 \text{ cm}^{-1}$) as well as 2D band position ($2674 \pm 2 \text{ cm}^{-1}$) and FWHM ($29.7 \pm 2 \text{ cm}^{-1}$) are quite similar for graphene on SiO₂(300 nm)/Si, quartz, Si, glass, NiFe and PDMS substrates. The small difference in the G band position are within the range of fluctuation ($1580\text{-}1588 \text{ cm}^{-1}$) by the unintentional doping (electron or hole) reported by Casiraghi *et al.* [69] after studies more than 40 graphene samples on SiO₂/Si substrate. It is known that the 2D band of graphene is closely related to its electronic band structures due to the DR process[56]. The G band of graphene is originated from in-plane vibration of sp² carbon atoms at the Γ point[51]. Thus, the similar Raman features, *i.e.*, G band and 2D band position/FWHM observed for graphene on different substrate implies that the interaction between ME graphene layers and different substrates is not strong enough to affect the atomic and electronic structure of graphene layers. On the other hand, for graphene epitaxial grown on SiC substrate, it can be seen the intensity ratio of G band and 2D band of EMG is quite different from those of SLG made by ME. In addition, significant blue shifts of G band ($\sim 10 \text{ cm}^{-1}$) and 2D band ($\sim 39 \text{ cm}^{-1}$) of EMG are observed compared to those of graphene made by ME. There might be some covalent bonding induced carriers doping transferred from the underlying SiC to EMG[81-82]. However, it should not be the

main reason for such larger blueshift of G/2D band. It is known that the doping effect on the shift of 2D band is very weak which is $\sim 10\text{-}30\%$ compared to that of G band[59,67,83]. Therefore, the 39 cm^{-1} 2D band shift is too large to be induced by the doping effect[59-60]. Hence, this significant blueshift of Raman bands (G band and 2D band) should be related to the strain effect induced by the substrate. It is known there is an interfacial carbon layer (buffer layer) formed between EMG and SiC substrate, which has graphene like hexagonal structure. This buffer layer is covalently bonded to the SiC substrate[33,47], and such kind of bonding would change its lattice constant as well as the electronic properties. The detailed Raman feature of this buffer layer will be studied in Chapter 8. Therefore, the lattice mismatch between buffer layer and EMG may cause a compressive strain on EMG, hence shift the G band and 2D band Raman frequencies[34].

Fig. 5.4 The Raman spectra of SLG on different substrates as well as that of epitaxial monolayer graphene on SiC.

The formation of bonds between ME graphene and substrate is less possible because the formation of such band is high temperature needed[34,69,83].

Substrate	G-band Position (cm^{-1})	G-band FWHM(cm^{-1})	2D-band Position(cm^{-1})	2D-band FWHM(cm^{-1})
SiC	1591.5 ± 0.6	31.3 ± 0.6	2710.5 ± 2.6	59.0 ± 3.9
SiO ₂ /Si	1580.8 ± 0.6	14.2 ± 0.9	2676.2 ± 1.2	31.8 ± 0.4
SiO ₂ /Si ^[69]	1580-1588	6-16		
Quartz	1581.9 ± 1.0	15.6 ± 2.1	2674.6 ± 1.4	29.0 ± 1.5
Si	1580 ± 0.6	16 ± 0.5	2672 ± 1.0	28.3 ± 0.8
PDMS	1581.6 ± 0.6	15.6 ± 0.8	2673.6 ± 1.0	27 ± 0.6
Glass	1582.5 ± 0.9	16.8 ± 1.0	2672.8 ± 0.8	30.8 ± 1.1
Glass ^[80]	1580	35 (split)		
NiFe	1582.5 ± 0.6	14.9 ± 2.7	2678.6 ± 0.8	31.4 ± 2.4
GaAs ^[80]	1580	15		
Sapphire ^[80]	1575	20		
Graphite	1580.8 ± 0.6	16.0 ± 0.8	2D1: 2675.4 ± 2.9 2D2: 2720.8 ± 1.4	41.4 ± 0.4 35.6 ± 0.4

TABLE 5.1 The G band and 2D band position and their FWHM for

graphene/graphite on different substrates. Results from ref. [69] and ref. [80] are also included.

5.4 Conclusions

In summary, through our Raman studies of SLG produced by ME on different substrates: standard SiO₂ (300 nm)/Si, quartz, Si, glass, PDMS and NiFe, we conclude that the weak interaction (Van de Waals force) between graphene layers and the substrates play a negligible role in affecting the Raman features of graphene layers. Only EMG grown on SiC substrate shows strong blue shift of G/2D band which can be understood by the compressive strain effect caused by the covalent bonding between SiC substrate and epitaxial graphene, resulting in the changes of the lattice constant of graphene, and hence the Raman features. Based on our study, we show that Raman spectroscopy is a powerful tool to study the interaction between graphene layers and substrate.

Chapter 6

Electronic properties of bi-layer graphene

6.1 Electronic properties of single-layer graphene and bi-layer graphene with Bernal stacking revealed by Raman spectroscopy

The electronic properties of SLG and BLG with Bernal stacking can be probed by Raman spectroscopy and this is because the Raman bands of graphene layers, *e.g.*, 2D band, are closely related to band structures. For SLG, its 2D band is a single, sharp peak. While for BLG with Bernal stacking, its 2D band is blueshifted, broader and can be decomposed into four peaks. The Raman spectra of SLG and BLG with Bernal stacking can be found in Section 4.4.2. The observed four peaks of 2D band of BLG can in principle be attributed to the electronic band splitting effect[56]. By using Raman spectroscopy with different excitation energy, the band dispersion of SLG and BLG with Bernal stacking can also be obtained as presented in Section 4.3.1. The DR process for 2D band of graphene makes probe the electronic structure of graphene layers by Raman spectroscopy possible.

For BLG with Bernal stacking, due to the strong interlayer interaction, the electronic band near the Dirac (K) point splits into two parabolic bands. A natural question to ask would be the following: what would be the electronic structure of graphene with a stacking order different from that of Bernal stacking? This question is made more important that few-layer graphene samples grown by CVD method normally have stacking order different from Bernal stacking. In this Chapter, we study

BLG samples with known orientation angle (by folding a SLG) using Raman spectroscopy as well as theoretically. The use of such BLG allows a meaningful comparison between experiments and theoretical study.

Theoretical calculations of electronic structure of BLG with a twist between the two layers, *i.e.*, a rotational mis-orientation, are carried out. The results show that the SLG-like linear dispersion of energy bands around the Dirac point is still preserved in TBG samples with top layer rotates, individually, 21.8° , 13.2° , 9.4° and 7.3° relative to the bottom layer, but the Fermi velocity is significantly smaller[42-43]. Apart from decouple induced band degeneracy near the Dirac point, the stacking effect may even break the translational symmetry of TBG, enlarge its unit cell, reshape its Brillouin Zone. As a result the SLG-like linear dispersion range of TBG will be compressed. It is even possible that the stacking effect will result in incommensurate structures[86]. In this Chapter, we want to study the stacking dependent electronic properties of graphene layers, and this kind of study will provide guidance for future use of large scale epitaxial graphene samples which always present stacking misorientation sequence[39,85,87-88].

6.2 Monitor the slowing down of Fermi velocity in twisted bi-layer graphene by the blue shift of 2D band

We successfully fabricated bi-layer graphene samples with top layer rotated certain angle relative to the bottom layer by the methods introduced in Section 3.3. Since the Raman features of graphene layers are closely related to its band structure properties, therefore, the Raman spectroscopy/imaging is used to study the electronic properties of those TBG samples. For the works presented in this Chapter, I have

contributed to the experimental parts, for readers who are interested in more comprehensive information; please refer to our published journal articles[42-43].

In our results, obvious blue shift of 2D band ($\sim 14 \text{ cm}^{-1}$) of TBG sample with orientation angle of $\theta = 21.2^\circ$ compared with that of SLG is observed which is interpreted in terms of electronic structural change. The electronic structure of this TBG sample is similar as that of SLG but with smaller Fermi velocity. The change in Fermi velocity of TBG sample is then estimated according to the shift of 2D band. In addition to the decouple caused band degeneracy near the Dirac point, there are also stacking sequence dependent band splitting and folding effect in TBG sample as revealed with density functional theory (DFT) calculations. Abundant band splitting and folding of TBG sample make G band double resonance Raman (DRR) scattering possible whose resonance conditions are strongly depending on stacking orders.

Figure 6.1(a) gives the AFM image of SLG, BLG with Bernal stacking and TBG. Fig. 6.1(b) shows the scanning height along the blue dashed line on the AFM image. The layer distance in TBG sample is $\sim 0.38 \text{ nm}$ which is quite similar to that of BLG ($\sim 0.35 \text{ nm}$) by considering the experimental error. The smooth graphene edge, either zigzag or armchair which indicates the crystal orientation of graphene layers, is demarcated by the dashed white line[44], while the folded edge is indicated by the dashed black line. From geometry analysis, the orientation angle $\theta = 21.2^\circ$, which is the angle of top layer rotates relative to the bottom layer. Fig. 6.1(c) gives the Raman imaging plotted from the 2D band position. The boundary of TBG sample is indicated by the dashed blue line. The brighter color represents the higher vibration frequency of 2D band. Therefore, it can be seen from this figure, the TBG sample gives the higher vibration frequency of 2D band compared with that of SLG. The statistical value of 2D band position for SLG and TBG is, individually, $2673.1 \pm 0.6 \text{ cm}^{-1}$ and

$2687.1 \pm 0.5 \text{ cm}^{-1}$. About 14 cm^{-1} blue shift of 2D band is observed in this TBG sample. Fig. 6.1(d) shows the Raman imaging obtained from G band position. The uniform contrast is observed and the statistical value of G band position for SLG and TBG is $1580.7 \pm 1.6 \text{ cm}^{-1}$ and $1581.7 \pm 0.9 \text{ cm}^{-1}$, respectively, indicating no difference in G band position between SLG and TBG sample. The same G band position of TBG and SLG implies there is no doping and/or strain existing in this TBG sample[59,63], the blue shift of 2D band must be induced by other mechanism.

Fig. 6.1 (a) The AFM images of SLG, BLG with Bernal stacking, and TBG on $\text{SiO}_2(300 \text{ nm})/\text{Si}$ substrate. The scanning height along the blue dashed line on the AFM image is given in Fig. 6.1(b). (c) Raman imaging of 2D band position. (d) Raman imaging of G band position excited by a 532 nm laser line.

Figure 6.2 gives the Raman spectrum of above TBG sample, together with those of SLG and BLG with Bernal stacking for comparison under the same excitation

condition. (laser wavelength: 532 nm, the same integration time, the same focus, *et al.*) As can be seen in this figure, different from that of BLG, the 2D band of this TBG sample is quite similar as that of SLG. A single sharp peak with FWHM of $\sim 22.1 \text{ cm}^{-1}$ is observed which is even sharper than that of SLG ($\sim 27.5 \text{ cm}^{-1}$). Therefore, the electronic structure of the TBG sample should be similar to that of SLG, *i.e.*, there is no splitting of energy bands and above prediction is further confirmed by our theoretical calculation results.

The electronic structures of the TBG sample with orientation angle of 21.8° (unit cell of 28 atoms, close to 21.2° in experiments) are calculated by DFT using the local-density approximation (LDA) with the Kohn-Sham equations solved with the projected augmented wave method as implemented in the VASP code[89-90]. We have calibrated our band structure results by multiplying a parameter of 1.15 following angle-resolved photoemission spectroscopy (ARPES) and GW results[91-93], which is due to the DFT calculations will slightly underestimate the quasiparticle energy[92]. The linearly dispersion at the Dirac point is still reserved in this TBG sample which agrees very well with other group's results[84-85]. This kind of linearly dispersion has been extended to the M point, at which the band gap between conduction band and valence band is $\sim 3.18 \text{ eV}$. The blue shift of 2D band in this TBG sample is associated with the SLG-like band structure but with smaller Fermi velocity.

Fig. 6.2 The Raman spectra of BLG with Bernal stacking, SLG and TBG with orientation angle of 21.2° .

The strong blue shift ($\sim 14 \text{ cm}^{-1}$) of the 2D band of TBG sample observed in Raman spectrum (Fig.6.2) as well as in Raman imaging (Fig.6.1) is due to the SLG-like band structure of TBG sample but with slowing down of Fermi velocity. The change of Fermi velocity in TBG sample can be obtained from the blue shift of the 2D band.

Figure 6.3 schematically shows the electronic structures of TBG and SLG. The smaller value of Fermi velocity (v_F') in TBG sample is reflected in its smaller slope of energy dispersion around the Dirac point. The 2D band is originated from DR process as described in Section 4.2. As can be seen from this figure, under the same excitation energy, the phonon momentum needed for TBG sample to scatter the excited electron is larger compared to that of SLG. In this figure, q'/q represents the phonon momentum needed to scatter the excited electron for TBG/SLG sample. The iTO

phonons exhibit linearly dispersion around K point ($\frac{d\omega}{dq}$)[94] which makes phonon with higher momentum corresponding to phonon with higher vibration frequency. Therefore, by using this model, the sharpness and blue shift of 2D band of multilayer EG can be also easily understood[95], which are due to the SLG-like linear dispersion of energy band of multilayer EG but with $\sim 10\%$ slowing down of Fermi velocity [96-97] than that of SLG.

The slowing down of Fermi velocity in TBG sample could be estimated by amount of blue shift of 2D band. In the double resonance process [52], it is known that

$$\hbar v_F q \approx E_L - \hbar(\omega/2) \quad (6.1)$$

Here, E_L is the incident photon energy, v_F is the Fermi velocity, ω is the frequency of 2D band, $\hbar(\omega/2)$ is the iTO phonon energy.

Thus,

$$q dv_F + v_F dq = -1/2 \cdot d\omega. \quad (6.2)$$

Hence,

$$q \frac{dv_F}{v_F} + dq = -\frac{d\omega}{2v_F}, \quad (6.3)$$

$$\frac{dv_F}{v_F} = -(1/2 + \frac{v_F}{d\omega/dq}) \frac{1}{v_F q} d\omega, \quad (6.4)$$

Where $\frac{d\omega}{dq} = 645 \text{ cm}^{-1} \cdot \text{\AA} = 0.08 \text{ eV} \cdot \text{\AA}$ is the phonon dispersion around K point[56].

We assume it is the same as SLG as the G band position does not change for SLG and TBG.

Because $\frac{v_F}{d\omega/dq} \gg 1/2$, above equation can be written as:

$$\frac{dv_F}{v_F} = -\frac{1}{q} \frac{d\omega}{dq} d\omega = -\frac{\hbar v_F}{[E_L - \hbar(\omega/2)]} \frac{d\omega}{dq} d\omega \quad (6.5)$$

Here, $\hbar v_F = 6.5 \text{ eV} \cdot \text{\AA}$ [52], $E_L = 2.33 \text{ eV}$, $\hbar(\omega/2) = 0.166 \text{ eV}$ by taking $\omega \approx 2670 \text{ cm}^{-1}$.

Therefore,

$$\frac{dv_F}{v_F} = -\frac{37.5 \cdot d\omega}{eV} \text{ or } -\frac{0.00467 \cdot d\omega}{\text{cm}^{-1}} \quad (6.6)$$

Where $d\omega$ is the change of frequency of 2D band after fold in unit of eV or cm^{-1} ,

and $\frac{dv_F}{v_F}$ is the change of Fermi velocity in percentage. For the TBG sample with

orientation angle of 21.2° , the blue shift of 2D band is $\sim 14 \text{ cm}^{-1} \pm 0.6 \text{ cm}^{-1}$, thus, the

slowing down of Fermi velocity is about $6.5 \% \pm 0.3\%$.

Fig. 6.3 Schematic image of the electronic structures of TBG sample (black dash lines) and SLG (purple solid lines). The arrows indicate the DR process in TBG graphene (black dash lines) and SLG (red solid lines). Adapted from our published work Z. H.

Ni *et al.* [42].

We also carried out Raman imaging studies of TBG samples with different orientation angles. It is found that for TBG sample with different orientation angle, the blue shift of 2D band is different. Fig. 6.4 shows the Raman imaging of TBG samples marked as s1 to s4 with different orientation angles plotted by 2D band position. The boundaries of those TBG samples are indicated by blue dashed lines. For TBG sample s1 to s4, its 2D band is a single, sharp peak with peak width even sharper than that of SLG. The Raman spectra of those TBG samples are similar as that of TBG sample given in Fig. 6.2. The statistical results of 2D band position for TBG sample s1 to s4 and SLG are given on this figure. About 10 cm^{-1} to 13 cm^{-1} blue shift of 2D band in TBG samples can be seen, corresponding to slowing down of Fermi velocity of $\sim 4.7\%$ to 6.1% . We also observe smaller blue shift of 2D band in TBG sample which is $\sim 4\text{ cm}^{-1}$ [42]. The difference of blue shift of 2D band in TBG samples may be originated from different stacking order (top layer rotates different angle relative to the bottom layer, different translation quantity, different layer distance, *et al.*).

Fig. 6.4 Raman imaging of TBG samples with different stacking sequence plotted from 2D band position. The statistical results of 2D band position for TBG and SLG are given in this figure.

6.3 The band folding and splitting effects in twisted bi-layer graphene

In order to investigate the stacking order dependent band folding and splitting effects in TBG samples, we also carry out band structure calculations of TBG samples with other stacking sequence. Fig. 6.5(a) and (b) show the band structure of BLG with Bernal stacking as well as TBG with top layer rotates 13.2° relative to the bottom layer. The atomic structures are also included in this figure. Because of strong interlayer interaction, the band structure of BLG with Bernal stacking splits into two parabolic bands as can be seen in Fig. 6.5(a). The splitting here will have different parities induced by the exchange operation. The π band will split into π^+/π^- , while the

π^* band will split into π^{*+}/π^{*-} as shown in Fig. 6.5(a). On the other hand, the band structure of TBG with orientation angle of $\theta=13.2^\circ$ is more complicated, the electronic bands near the Dirac point still linearly disperse, similar to that of TBG with orientation angle of $\theta=21.8^\circ$. However, the shrunken Brillouin zone induced by the larger unit cell (76 atoms), compared with that of TBG with $\theta=21.8^\circ$ (unit cell: 28 atoms), shortens this linear dispersion range around the Dirac point and reduces the energy gap between conduction and valence band at M point into 2.08 eV. Apart from that, clear band splitting is shown along the $M-\Gamma$ direction induced by the interlayer interaction, where the π and π^* bands of SLG split into π_1^+ , π_1^- and π_1^{*+} , π_1^{*-} bands, while π_2^+ , π_2^- and π_2^{*+} , π_2^{*-} bands are brought by the band folding effect. Abundant bands appearing in the visible light range as well as small separation among those bands makes G phonon involved DRR process possible as schematically denoted by the blue arrow in Fig. 6.5(b).

The G band of graphene comes from a third order Raman process and the matrix element of the process can be schematically described as [71]

$$M = \sum_{S_0, S_1} \frac{\langle i | \hat{H}_{e-em} | S_0 \rangle \langle S_0 | \hat{H}_{e-ph} | S_1 \rangle \langle S_1 | \hat{H}_{e-em} | f \rangle}{(E_i - E_0 + 2i\gamma)(E_f - E_1 + 2i\gamma)} \quad (6.7)$$

here, $\langle i |$ and $| f \rangle$ are the initial and final states of the scattering process and S_0, S_1 are the intermediate states where the electron-hole is created. E_i, E_0, E_1 and E_f are the energies of these states and γ is the inelastic scattering rate. For SLG or BLG with Bernal stacking, the G band is a single resonance process. Either the incident or the scattered photon matches the electronic band transition. One term in the denominator in above equation becomes infinitely small. While for TBG sample, due to the band folding/splitting effect, both the incident photon and the scattered photon can match

the electronic band transitions. Two terms in the denominator in above equation become infinitely small, therefore, resulting in the enormously increase of G band intensity of TBG samples compared with that of SLG or BLG with Bernal stacking.

Fig. 6.5 (a) Electronic band structures of BLG with Bernal stacking (b) Electronic band structures of TBG with top layer rotates 13.2° relative to the bottom layer. The corresponding atomic structures are given at the left corner. Adapted from our published work Z. H. Ni et al. [43].

Since the DFT calculations indicate there will be abundant band folding/splitting in the visible light range and this will make G phonon involved DRR possible, the experimental confirmation of such prediction is needed and necessary. Fig. 6.6(a) shows an optical image of a folded graphene sample. Fig. 6.6(b) gives the schematic image of TBG samples which are marked as X and Y, individually. The estimated orientation angle is 0.5° for TBG sample X and that is 12.5° for TBG sample Y. Attention is then paid to the TBG sample Y which shows different behaviors under different excitation energy. Fig. 6.6(c) gives Raman spectra of TBG sample Y whose

boundary is highlighted by the dashed line under excitation of 457 nm, 488 nm, and 532 nm laser lines. Under different excitation energy, the G band Raman intensity of TBG sample Y is compared with that of SLG. Fig. 6.6(d) to (f) gives the Raman imaging of the G band integrated intensity under excitation of 457 nm, 488 nm, and 532 nm laser lines. Here, the brighter color represents the higher G band intensity. As shown in Fig. 6.6(c) to (f), the G band intensity from TBG sample Y under excitation of 457 nm laser line is ~ 15 times that of SLG. This kind of enhancement of G band intensity decreases when the excitation energy is 488 nm, the G band intensity of TBG is ~ 3 times that of SLG and further disappears under excitation of 532 nm as shown in Fig. 6.6(f), in which the G band intensity of TBG is ~ 1.5 times that of SLG. Therefore, there is a G band resonance for TBG sample Y with orientation angle of $\sim 12.5^\circ$ under excitation energy of 457 nm. Fig. 6.6(g) to (i) gives the Raman imaging of the 2D band integrated intensity under excitation of 457 nm, 488 nm, and 532 nm laser lines. Here, the brighter color represents the higher 2D band intensity. The 2D band intensity of TBG sample Y is ~ 2 times that of SLG under different excitation energy and there is no 2D band resonance phenomenon. On the other hand, for the TBG sample X, we didn't observe any G band resonance phenomenon under excitation of 457 nm, 488 nm, and 532 nm.

Fig. 6.6 (a) Optical image of SLG and TBG. (b) Schematic image of TBG sample. The estimated orientation angle is 0.5° for TBG sample X, and that is 12.5° for TBG sample Y. (c) Raman spectra of TBG sample Y under excitation of 457 nm, 488 nm, and 532 nm laser lines, individually from bottom to top. Raman imaging of SLG and TBG plotted from the G band integrated intensity under excitation of 457 nm (d), 488 nm (e) and 532 nm (f) laser lines. Raman imaging of SLG and TBG plotted from the 2D band integrated intensity under excitation of 457 nm (g), 488 nm (h) and 532 nm (i) laser lines.

Fig. 6.7(a) to (c) schematically shows the splitting/folding of conduction/valence band induced by interlayer interaction for BLG with Bernal stacking as well as that of TBG. The phonon assisted transition from band with different parity, *e.g.*, π^{*+} (π^+) to π^{*-} (π^-) is forbidden as schematically shown in Fig. 6.7(b) and in Fig. 6.5 (a)[43]. However, such constraint can be removed in twisted graphene layers where the band folding enables the transitions between electron bands with same parity possible. As

shown in Fig. 6.7(c), the scattering of phonon from $\pi_2^{*+} \rightarrow \pi_1^{*+}$ and $\pi_2^{*-} \rightarrow \pi_1^{*-}$ are allowed. In real electronic band structure, the allowed electronic transitions involved G phonons are indicated by the blue arrow as shown in Fig. 6.5(b).

Two conditions needed to be satisfied for the G phonon double resonance scattering: Condition 1: the energy difference ΔE of $\pi_2^{*+/-}$ and $\pi_1^{*+/-}$ bands should be the same as that of G phonon energy, $\Delta E = E_{ph} = 0.196$ eV. Condition 2: the energy of incident laser (E_L) matches the energy transition from valence band to conduction band ($E_L = \pi_2^{*+} - \pi_1^{-}$ or $E_L = \pi_2^{*-} - \pi_1^{+}$).

The optical transitions satisfy above resonance conditions for the visible excitations are $\pi_1^{-} \rightarrow \pi_2^{*+} \rightarrow \pi_1^{*+} \rightarrow \pi_1^{-}$ and $\pi_1^{+} \rightarrow \pi_2^{*-} \rightarrow \pi_1^{*-} \rightarrow \pi_1^{+}$ which is shown in Fig. 6.7(c), the later requires much larger excitation energy ($E_L > 3.5$ eV). Fig. 6.7(d) plots the energy difference ΔE of π_2^{*+} and π_1^{*+} bands of the 13.2° TBG (close to 12.5° in our experiments). The snowflake shape of blue cross symbols in Fig. 6.7(d) represents the energy difference ΔE equals that of G phonon energy ($\Delta E = E_{ph} = 0.196$ eV). Fig. 6.7(e) shows the 3D view of the energy difference of π_1^{-} and π_2^{*+} bands within the whole Brillouin zone. The blue crosses marked in Fig. 6.7(e) show the range where satisfy the energy difference of π_1^{-} and π_2^{*+} lying in the visible light range as well as the energy difference of π_2^{*+} and π_1^{*+} bands ΔE equaling to that of phonon energy (E_{ph}). Further consideration of effect of density of state (DOS) on resonance condition is needed and necessary. For those snowflake-shape points which satisfy the DRR process, the resonance condition is dependent on the joint density of states (JDOS). The inner-edge states are believed to have the stronger resonance because of the higher JDOS value. Based on above discussion, the estimated resonant laser energy for the 13.2° TBG will be ~ 2.73 eV (454 nm). This is very close to our experimental observations that the laser energy of G band double resonance is 457 nm.

Fig. 6.7 Schematic band folding/splitting effect in SLG (a), in BLG with Bernal stacking (b), and in TBG (c). (d) The energy difference between π_1^{*+} and π_2^{*+} bands of TBG with orientation angle 13.2° . (e) The 3D view of the energy difference of π_1^- and π_2^{*+} bands of TBG with orientation angle of 13.2° .

Similar DFT calculations have also been carried out to examine the electronic structure of TBG sample with orientation angle of 7.3° (unit cell of 244 atoms). For 7.3° TBG sample, the shrunk Brillouin Zone induce by the larger unit cell shifts the energy gap between conduction and valence band at M point to ~ 1.08 eV and this makes the DRR process occurring at much lower excitation energy, *i.e.*, 2.23 eV (556 nm), and the estimation here also matches quite well with our experiment observations (532 nm). For readers who are interested in this results, please refer to our published paper for more details[43].

6.4 Conclusions

In summary, Raman spectroscopy/imaging is used to investigate the stacking order dependent electronic property of TBG. It is believed the linear band dispersion at the Dirac point is still preserved in TBG samples but with smaller value of Fermi velocity. For different stacking order (top layer rotates different angle relative to the bottom layer, different layer distance, as well as different in-plane shift), different amount of Fermi velocity slow down is obtained from the blue shift of 2D band, which agrees well with the first-principles DFT calculation results. As predicted by the calculation results, the range of SLG-like linear dispersion in TBG sample is determined by its unit cell size. The larger unit cell with various interlayer coupling strength will shorten linear dispersion range as well as induce abundant band folding and splitting in the visible light range which will make G band DRR process possible. The experimental results indeed show the G band DRR phenomenon in TBG samples and the resonance conditions are strongly dependent on the stacking order. The stacking order dependent electronic property study of BLG is important which will provide guidance for further electronic application of large scale graphene layers grown on SiC or on transition metals which always present obviously stacking faults.

Chapter 7

Optical conductivity study of twisted bi-layer graphene

7.1 Motivation for the optical conductivity study of graphene layers

Besides the fascinating electronic properties of graphene, it also exhibit unusual optical property, *e.g.*, the extremely high transparency $\sim 97.7\%$ [14] as well as universal optical or AC conductivity ($G(\omega) = \frac{e^2}{4\hbar}$) values[14,16,98-100]. Many interesting results were obtained from recent optical conductivity studies of graphene layers. For example, the fine structure constant α ($\alpha = \frac{G(\omega)}{\pi\epsilon_0 c}$, here, ϵ_0 is the permittivity of free space and c is the speed of light) can be experimentally obtained from absorbance measurements of graphene[14,99]. Also, the energetically preferred stacking order *i.e.* Bernal stacking (ABAB) or orthorhombic stacking (AB CA) of the graphene layers can be differentiated from the calculated conductivity spectrum in the IR range[15]. In addition, the interlayer hopping rate parameter γ_1 ($\gamma_1 \approx 0.35$ eV) of BLG with Bernal stacking can also be experimentally obtained from optical conductivity measurements[101-102].

In previous chapter, we have probed the electronic properties of TBG samples by Raman spectroscopy/imaging. In this Chapter, white light spectroscopy is used to probe the optical conductivity (absorption) behaviors of TBG samples with broader excitation range which will help us comprehensively understand the electronic and optical properties of TBG samples.

We find the optical conductivities of graphene layers are strongly dependent on their stacking order. First-principle calculations show that while the optical conductivities of SLG and BLG with Bernal stacking are almost frequency independent in the visible region, the optical conductivity of TBG is frequency dependent, giving rise to additional absorption features due to band folding. Experimentally, we obtain from contrast spectra the optical conductivities profiles of BLG with different stacking geometries. Some TBG samples show additional features in their conductivity spectra in full agreement with our calculation results, while a few samples give universal conductivity values similar to that of SLG. We propose those differences in the optical conductivity spectra of TBG samples originate from the commensurate and incommensurate stacking sequence. Our results reveal that the optical conductivity measurements of graphene layers indeed provide an efficient way to select graphene films with desirable electronic and optical properties, which will provide guidance for future use of those large scale misoriented graphene films in photonic devices.

7.2 First-principle calculation of optical conductivity of twisted bi-layer graphene

The band structure calculations of SLG, BLG with Bernal stacking and TBG samples are performed using the LDA within DFT[89-90]. Here, a kinetic energy cutoff of 400 eV and k -point sampling with $0.05 \text{ \AA}^{-1}$ separation in the Brillouin zone are used. Fig. 7.1(a) gives the calculated electronic band structure of SLG. As shown in this figure, the electronic bands of SLG show the linear dispersion around the Dirac point (K point). The energy span between the conduction and valence bands at M point is $\sim 4 \text{ eV}$, after multiplying a calibration parameter of 1.15 ($4 \text{ eV} \times 1.15 = 4.6$

eV), the results match quite well with ARPES and GW results (4.6 eV)[91-93]. Fig. 7.1(b) plots the band structure of BLG with Bernal stacking, where the π -electrons dispersion in the valence and conduction bands splits into two parabolic branches near the Dirac point[66]. Due to the strong interlayer interaction, a band splitting (~ 0.35 eV) appears at the Dirac point[101]. Compared with those from BLG with Bernal stacking, the electronic band structures of TBG samples are much more complicated. Depending on the rotation angle between neighboring layers, TBG samples will be accompanied by the different unit cells and the various interlayer coupling strength, and therefore exhibit abundant electronic properties. Fig. 7.1(c) shows the band structures of TBG sample with orientation angle of 21.8° (unit cell of 28 atoms). As can be seen, the linear electronic dispersion is still presented at the Dirac point which agrees very well with other group's results [84-85]. However, the enlarged unit cell will fold its Brillouin zone, therefore shortening the linear dispersion range as well as reduce the energy span between conduction band and valence band at M point. As the band gap at the M point shifts into the visible light range, *i.e.* ~ 2.77 eV, which is ~ 3.18 eV after calibration as shown in Fig. 7.1(c), the light absorption behavior of this TBG sample will be altered accordingly.

The optical conductivities of SLG, BLG with Bernal stacking and TBG sample with a 21.8° relative rotation calculated by Kubo formula [16] are shown in Fig. 7.1(d). In the visible light range, SLG and BLG with Bernal stacking exhibit almost universal conductivity behaviors[14, 16, 100]. On the other hand, the conductivity of TBG sample is frequency dependent which has an additional peak located ~ 2.77 eV. This peak is indeed induced by the electronic transition at M point. We also calculate the electronic band structures of TBG samples with other orientation angles; top layer rotates: 13.2° , 9.4° and 7.3° , individually, relative to the bottom layer. As the

orientation angle decreases, more atoms are included in the unit cell and the energy span between conduction and valence states at M point decreases. Their band gaps at M point after calibration are 2.08 eV, 1.47 eV, and 1.08 eV for TBG samples with orientation angle of 13.2° , 9.4° and 7.3° , respectively. The electronic transition at M point of these TBG samples will induce an absorption peak in the conductivity spectrum, similar to the result shown in Fig. 7.1(d).

Fig. 7.1 (a) The band structure of SLG. (b) The band structure of BLG with Bernal stacking. (c) The band structure of TBG with orientation angle of $\theta = 21.8^\circ$ (unit cell of 28 atoms). (d) The conductivities of SLG, BLG with Bernal stacking and TBG with orientation angle of $\theta = 21.8^\circ$ calculated by the Kubo formula.

Fig. 7.2 gives the band structure and DOS of TBG sample with orientation angle of 7.3° (unit cell of 244 atoms). As can be seen, the band gap at M point of this TBG sample shifts into IR range (0.94 eV, which is 1.08 eV after calibration). Besides, the band folding and splitting appear in the visible light range that results in the additional features in the DOS spectrum correspondingly. It is known that the conductivity of graphene is proportional to JDOS which can be deduced from its DOS[103]. Therefore, the abundant peaks appearing in the DOS spectrum in the visible light range will induce enormous peaks in the conductivity spectrum. Based on above discussions, we could know that the stacking sequence (different orientation angle) will typically affect the electronic structures of TBG samples by reducing the band gap at the M point and introducing more bands in the visible light range and both of them will distinguish the optical conductivities of TBG samples from those of SLG and BLG with Bernal stacking.

Fig. 7.2 (a) The band structure of TBG with orientation angle of $\theta = 7.3^\circ$. (b) The

DOS of TBG with orientation angle of $\theta = 7.3^\circ$ (unit cell of 244 atoms).

To demonstrate the stacking dependent optical properties of graphene layers, Fig. 7.3 plots the absorption behaviours of BLG with Bernal stacking as well as that of TBG sample with orientation angle of $\theta = 21.8^\circ$. We can see that BLG with Bernal stacking shows a constant absorption of $\sim 4.6\%$ in the visible light region as a result of universal optical conductivity value[14]. In the ultraviolet light region (300 nm-380 nm), its absorption deviation from constant value is due to the electronic transition near M point. On the other hand, the TBG sample with 21.8° orientation angle has frequency-dependent absorption behaviour in the visible light range as illustrated in the right side of the figure. Beyond the absorption at the ultraviolet light range, there is an additional absorption peak in the visible light region (highlighted by a red arrow) which is induced by the electronic transition at M point of ~ 2.77 eV. Our calculation results indeed predict TBG sample will present orientation dependent additional absorption peak in the visible light range rather than the constant profile from BLG with Bernal stacking. Since that makes identifying stacking sequence of graphene layers much easy and applicable, therefore, such prediction deserves to be confirmed in careful experiments.

Fig. 7.3 Left:: Absorption of light by BLG with Bernal stacking. In the visible light range, there is a constant transmittance $\sim 95.4\%$ (absorption $\sim 4.6\%$) due to the universal value of optical conductivity. At the ultraviolet light range (300 nm-380 nm), the deviation from constant absorption is induced by the electronic transition near M point. Right: Absorption of light by the TBG sample with 21.8° orientation angle. Beyond the absorption at the ultraviolet light range, there is additional absorption peak in the visible light range (highlighted by a red arrow) which is induced by the electronic transition at M point with energy of ~ 2.77 eV.

7.3 Optical conductivity profiles of twisted bi-layer graphene obtained from their contrast spectra

TBG samples are fabricated by the methods introduced in Section 3.3. Experimentally, instead of absorption measurement, we perform the optical conductivity measurement of graphene layers which can be obtained from their contrast spectra [100]. Compared with the absorption measurement[14], the contrast

measurement could be performed on any substrate; with micron size spatial resolution [26] and no suspended sample are needed.

The contrast spectra $C(\lambda)$ can be obtained by [27-29,31]

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)}, \quad (7.1)$$

where $R_0(\lambda)$ is the reflection spectrum from the SiO₂/Si substrate and $R(\lambda)$ is the reflection spectrum from the graphene layers on SiO₂/Si substrate. The white light spot size is about 1 μm [26] focused by an objective lens with a magnification of 100X and a numerical aperture (NA) of 0.95. The detailed experimental setup could be found in Section 3.2. According to Fresnel's equation, under normal incidence, the reflection for a wavelength λ is given by,

$$R_0(\lambda) = |r_0|^2 = \left| \frac{r_{02} + r_{23} \cdot e^{-2i\phi_2}}{1 + r_{02} \cdot r_{23} \cdot e^{-2i\phi_2}} \right|^2 \quad (7.2)$$

Here, r_0 is the effective reflection coefficient of the air/(SiO₂ on Si) interface, and

$$r_{02} = \frac{n_0 - n_2}{n_0 + n_2}, \quad r_{23} = \frac{n_2 - \tilde{n}_3}{n_2 + \tilde{n}_3}$$

are the individual reflection coefficients at the air/SiO₂ and SiO₂/Si interfaces respectively. $\phi_2 = \frac{2\pi \cdot n_2 \cdot d_2}{\lambda}$ is the phase difference when light

passes through SiO₂ layers. (n_0 , n_2 and $\tilde{n}_3$ are the refractive indices of air, SiO₂, and

Si, respectively. d_2 is the thickness of the SiO₂ layer). The optical transfer properties

of graphene are governed by the matrix, $M_g = \begin{bmatrix} 1 - \beta & -\beta \\ \beta & 1 + \beta \end{bmatrix}$ [27,100], and the

reflection spectrum from graphene on SiO₂/Si, as a function of the optical conductivity of graphene, is calculated as:

$$R(\lambda) = \left| \frac{-r_0(1 - \beta) + \beta}{-r_0(-\beta) + (1 + \beta)} \right|^2 \quad (7.3)$$

Here, $\beta = \frac{c\mu_0 G(\omega)}{2}$ is 188.4 times the optical conductivity; and c and μ_0 are respectively, the speed of light and magnetic permeability in vacuum. Since the contrast spectrum $C(\lambda)$ can be obtained experimentally, the optical conductivity $G(\omega)$ could be obtained by solving Eq. (7.1), (7.2) and (7.3).

Fig. 7.4 (a) and (b) respectively show the optical and AFM images of pieces of folded graphene layers, which can be taken as TBG samples. Two different folded parts can be seen from this image whose boundaries are demarcated by yellow dashed lines. In Fig. 7.4(b), the crystal axis of SLG as well as the folded edge is indicated by white dashed lines. From the geometry analysis, the orientation angle θ is $\sim 22.6^\circ$ for the left side TBG sample and θ is $\sim 13.7^\circ$ for the right side TBG sample. Fig. 7.4(c) shows the contrast spectra of SLG, BLG with Bernal stacking, and TBG samples with $\theta = 13.7^\circ$ and 22.6° . During the experiments, we have taken contrast spectra from different areas of the TBG sample and the results are the same. For SLG, the contrast peak is located around 557 nm with the peak intensity of ~ 0.1 , while that of BLG with Bernal stacking has twice of the intensity value, which is ~ 0.2 [27]. It also can be seen from this figure that the contrast peak of TBG samples has different profiles or intensities compared with those of SLG and BLG with Bernal stacking. The optical conductivities of SLG, BLG with Bernal stacking, and TBG samples are then derived from their contrast spectra by solving Eq. (7.1), Eq. (7.2) and Eq.(7.3).

Fig. 7.4 (a) Optical image of a piece of graphene sample on SiO_2/Si substrate that contains two folded parts which can be taken as two TBG samples. The boundaries of the TBG samples are demarcated by the yellow dashed lines. The thickness of SiO_2 is $272.0 \pm 0.8 \text{ nm}$ measured by ellipsometry. (b) AFM image of the TBG samples. The crystal axis (i.e. edge of the SLG) as well as folding line is shown by the white dashed lines. The angle between an crystal axis and folding line is marked by α , and according to the geometry analysis, the orientation angle θ , which is the angle the top layer rotates relative to the bottom layer can be determined as $\theta = 2\alpha$ or $\theta = 180^\circ - 2\alpha$. The orientation angle $\theta = 22.6^\circ$ for the left side TBG sample and $\theta = 13.7^\circ$ for the right side TBG sample. (c) The contrast spectra of SLG, BLG with Bernal stacking and two TBG samples.

Figure 7.5, left column, from bottom to the top, individually shows the conductivities of SLG, BLG with Bernal stacking, and TBG samples with orientation angles $\theta = 7.5^\circ, 10.6^\circ, 12.5^\circ$, in the range of 505 nm (2.46 eV) to 705 nm (1.76 eV), while the right column gives the conductivities of TBG samples with orientation angle of $\theta = 13.7^\circ, 22.6^\circ, 53.2^\circ, 54.6^\circ$ and 55.5° [104]. Here, the normalization of the

conductivities has been carried out [105]. As shown in this figure, the conductivity of SLG is frequency independent with a value of $\sim \frac{e^2}{4\hbar}$, while that of BLG with Bernal stacking has twice of the value, *i.e.* $\sim \frac{e^2}{2\hbar}$, consistent with the theoretical predictions [102]. However, the conductivities of some TBG samples behave rather differently from those of SLG and BLG with Bernal stacking. *E.g.*, for TBG sample with $\theta = 7.5^\circ$ (close to $\theta = 7.3^\circ$ in our calculation), the conductivity is similar as that of SLG in low energy region (< 2.03 eV (610 nm)). Following the increasing photon energy (> 2.25 eV (550 nm)), its conductivity gets higher with the value $\sim 2.3 \frac{e^2}{4\hbar}$, even larger than that of BLG. The observed conductivity of this TBG sample complies with the theoretical prediction very well; whose DOS spectrum given in Fig. 7.2(b) shows the stronger absorption of the higher energy photons. While for the TBG sample with $\theta = 13.7^\circ$, there is a broad peak located around 595 nm (2.08 eV), with the height of $\sim 2.52 \frac{e^2}{4\hbar}$. Its conductivity profile also matches quite well with the theoretical result that the electronic transition at *M* point of TBG sample with $\theta = 13.2^\circ$ will induce an absorption peak at ~ 2.08 eV. Meanwhile, for TBG sample with $\theta = 54.6^\circ$, its conductivity shows a sharp increase for the wavelength shorter than 570 nm (> 2.18 eV). Those observed orientation-dependent features in the optical conductivity spectra of TBG samples are consistent with their folded electronic bands from the multiple unit cells. Moreover, the conductivities of TBG samples with $\theta = 10.6^\circ, 12.5^\circ, 22.6^\circ, 53.2^\circ$ and 55.5° , present only the frequency independent universal values ($\sim \frac{e^2}{2\hbar}$) in the detection range, similar to that of SLG. The loss of frequency dependence of the optical conductivity of these TBG samples can be understood by their

incommensurate stacking styles. For commensurate stacking of graphene layers, the Moire pattern is periodic, and there exists a unit cell to form the crystal structure[84]. While for those graphene layers with incommensurate stackings, the unit cell is infinite large, *i.e.*, there are no periodic structures. Therefore, incommensurate TBG can be viewed as two individual SLG because the interaction between the neighbouring layers has been averaged out. As a result, the incommensurate TBG will show the optical conductivity with the universal value twice that of SLG. Based on the above discussion, TBG samples with the orientation angles $\theta = 7.5^\circ$, 13.7° and 54.6° which give additional features in their spectra can be viewed as commensurate TBG samples, while TBG samples with other orientation angles $\theta = 10.6^\circ$, 12.5° , 22.6° , 53.2° and 55.5° which are similar as SLG can be view as incommensurate TBG samples.

Fig. 7.5 The conductivities of SLG, BLG with Bernal stacking, and TBG samples with rotation angle of $\theta = 7.5^\circ$, 10.6° , 12.5° , 13.7° , 22.6° , 53.2° , 54.6° and 55.5° which are obtained from the contrast spectra.

The rotation angle θ for commensurate stacked TBG samples is determined by the following equation[84]:

$$\cos(\theta) = \frac{3i^2 + 3i + 0.5}{3i^2 + 3i + 1}, i=0,1,2,3,\dots, \quad (7.4)$$

according to this equation, the rotation angle of commensurate TBG samples is exclusively given as following: $\theta=21.8^\circ, 13.2^\circ, 9.4^\circ, 7.3^\circ, 6.0^\circ, 5.1^\circ, \dots, 60^\circ - \theta$ labels the same unit cell as θ . Therefore, our experimental observation of optical conductivities of TBG samples with orientation angle of $\theta=7.5^\circ$ (close to 7.3°), 13.7° (close to 13.2°) and 54.6° (unit cell is the same as that of 5.4° , close to 5.1°) indeed close to be commensurate.

Large scale growth of graphene is one of the critical steps towards practical applications of graphene[1-4]. Many attempts have been developed to achieve fabricating large scale graphene films such as using epitaxial growth on SiC [7,32,46] as well as chemical vapor deposition on Ru[106], Ni[38-39] and Cu[41]. While the stacking order deviating from the Bernal stacking is generally observed on such large scale graphene films[39,84-85,88], the desirable frequency independent optical conductivities of those large scale graphene films can not be obtained unambiguously. However, the contrast measurements, as presented in this work, may distinguish the graphene films with different stackings that make the selective use of graphene films with particular electronic and optical properties possible.

7.4 Conclusions

In summary, first-principle calculations show that the optical conductivities of TBG samples are frequency dependent in the visible light range, contrary to the conductivities of SLG and BLG with Bernal stacking, which are frequency

independent. Experimentally, the optical conductivities of TBG samples with different orientation angles are obtained from their contrast spectra. The optical conductivities of some TBG samples indeed show additional absorption in the spectrum. Abundant electronic properties of TBG samples, *i.e.*, band folding and splitting effect make absorption behaviours of TBG samples fascinating in the visible light range. This kind of method can be applied for TBG samples on any substrates and the detection range is only determined by the white light source. The optical conductivity study of TBG samples provides guidance for further optical application of graphene in photonic devices. Combining Raman spectroscopy and white light contrast spectroscopy, the comprehensively understanding of electronic and optical properties of graphene layers are possible.

Chapter 8

Electronic structure of epitaxial graphene grown on Si-SiC

8.1 Motivation for the electronic property study of epitaxial graphene grown on Si-SiC

In previous chapters, we have studied the electronic and optical properties of SLG and BLG with different stacking sequence fabricated by ME of HOPG. However, for some applications of graphene, large-scale graphene film is needed. It has been known that after heat treatment of semiconductor SiC at high temperature (1250 °C-1450 °C), EG can be grown on SiC substrate whose thickness are controlled by the temperature[32].

Interestingly, the resent ARPES measurements show that there is a energy gap for SLG grown on Si-SiC substrate, which opens a way towards the gap engineering[81]. It is believed that during the graphitizing process, there is a buffer carbon layer formed between the graphene layer and the substrate. This carbon layer has graphene-like hexagonal atomic arrangement and some carbon atoms are covalently bonded to the SiC substrate. The buffer layer may structurally break the sublattice symmetry when another graphene layer is grown on it, therefore inducing an energy gap at the Dirac point.

In order to understand the role of this buffer layer on deciding the electronic properties of graphene grown on Si-SiC(0001), a lot of theoretical calculation of electronic structures of EG on Si-SiC are carried out based on the $(\sqrt{3} \times \sqrt{3})R30^\circ$

model[47,107] or even on a larger periodic reconstruction ($6\sqrt{3} \times 6\sqrt{3}$)R30° (6R3)[108]. It is found that there are no graphitic electronic properties in this buffer layer. Only next layer of carbon atoms grown above this buffer layer will have the Dirac properties. Later in this Chapter, we refer the layer above buffer layer as the first graphene layer.

Here, in this Chapter, the Raman spectroscopy is used to differentiate buffer layer and first graphene layer as well as to probe the electronic properties of EG. This study will provide guidance for future application of EG in electronic devices. Our results reveal that: (1) The Dirac properties will exist in first graphene layer instead of existing in buffer layer. (2) All the Raman bands of EG are blue shifted which is attributed to compressive strain effect induced by the substrate.

8.2 Electronic structures of buffer layer as well as few layers graphene probed by Raman spectroscopy

Figure 8.1 (a) and (b) respectively show the $8 \times 8 \text{ nm}^2$ STM image of the buffer layer ($V_{\text{tip}} = 2.1 \text{ V}$) and first graphene layer ($V_{\text{tip}} = 2.1 \text{ V}$) on Si-SiC substrate. The honeycombs in Fig. 8.1(a) with diameters of $20.0 \pm 2.0 \text{ \AA}$ correspond to the ($6\sqrt{3} \times 6\sqrt{3}$) R30° (6R3) reconstruction of the buffer layer[46]. In Fig. 8.1(b), on above the 6R3 honeycombs, there are some hexagonal structures as clearly revealed in Fig. 8.1(c). In Fig. 8.1(c) those red circles represent C atoms and they form the hexagonal pattern. It also can be seen that the characteristic STM images of buffer layer and first graphene layer are quite different. Therefore, STM image can be used to differentiate buffer layer and first graphene layer.

Fig. 8.1 (a) The $8 \times 8 \text{ nm}^2$ STM image of the buffer layer ($V_{tip} = 2.1 \text{ V}$). (b) The $8 \times 8 \text{ nm}^2$ STM image of first graphene layer ($V_{tip} = 2.1 \text{ V}$) on Si-SiC substrate. (c) The zoom in image of blue square area in Fig. 8.1(b).

Figure 8.2(a) schematically shows the side view of atomic configuration of buffer layer and first graphene layer on SiC substrate. Fig. 8.2 (b) gives the Raman spectra of buffer layer, first, three, five and multi layers EG on Si-SiC as well as that of SiC substrate. The number of graphene layers is determined by the white light contrast spectroscopy which will be given later. In the spectrum range (1300 cm^{-1} to 3000 cm^{-1}), graphene has two major peaks which respectively locate around $\sim 1593 \text{ cm}^{-1}$ (G band) and $\sim 2730 \text{ cm}^{-1}$ (2D band). In addition, there is a D band locating around $\sim 1367 \text{ cm}^{-1}$ which is induced by defect or disorder[53]. The G band is a doubly degenerate phonon mode (E_{2g} symmetry) at the Brillouin zone center[51], while the 2D band originates from a DR Raman process[73]. Compared the Raman spectrum of buffer layer and first graphene layer, it can be obviously seen the 2D band of buffer layer is missing. This can actually be explained by the different electronic structure of buffer layer and first graphene layer[47,107-108].

The origin of 2D band is closely related to the particular electronic structure of graphene. For isolated SLG, the electron energy dispersion around the Dirac point is

linear, and the slope of dispersion gives the value of Fermi velocity $v_F = 10^6$ m/s. In the DR process, (1) the incident photon induces the electronic transition from valence band to the conduction band at the k state, (2) electron will then be scattered by the iTO phonon with momentum vector of q , (3) the electron is then scattered back by the iTO phonon with reverse phonon momentum direction and recombined with the hole at k state. The detailed DR process can be found in Section 4.2. For buffer layer graphene, according to the theoretical calculation results[47,107-108], the electronic structure around the Dirac point is believed to show small dispersion, *i.e.*, almost a flat line along the $\Gamma - K - M$ direction. This makes the creation of electron-hole pair around the Dirac point impossible. Hence, no DR process will be preserved in buffer layer. Only first graphene layer which has the Dirac dispersion will have the 2D band[52,73]. Therefore, using Raman spectroscopy we can easily differentiate buffer layer and first graphene layer. Compared to STM, Raman spectroscopy is a non-destructive, fast way and could be much more easily performed. Another difference between buffer layer and first graphene layer is the width of the G band. The width of G band of buffer layer is much broader than that of graphene. This indicates that the structure of buffer layer is not perfect, which may be due to the interaction between buffer layer and the substrate. The covalent bonds between buffer layer and SiC create local structure on buffer layer as well as corrugate the buffer layer, therefore, resulting in the poor crystallinity of the buffer layer.

Fig. 8.2 (a) The side view of atomic configuration of buffer layer, first layer EG grown on SiC substrate. Some carbon atoms in buffer layer are bonded to the SiC substrate. First graphene layer is growing above this buffer layer interacted with the weak van der Waals force. Fig. 8.2 (b) The Raman spectra of buffer layer, first, three, five and multi layers EG on Si-SiC as well as that of SiC substrate. The curve fitting results of buffer layer graphene and first graphene layer are also included in this figure.

As can be seen from Fig. 8.2(b), when graphene layers increase from one to five, its G band intensity also increases which is consistent with our previous results as

given in Section 4.4.1[109]. It is found that the FWHM of 2D band of first graphene layer is broader ($\sim 61.3 \text{ cm}^{-1}$) compared with that of ME graphene ($\sim 30.0 \text{ cm}^{-1}$), and this is due to the poor crystallinity of EG. Comparison of Raman properties of first layer EG and three-layer EG is carried out. It is found that firstly the 2D band of first layer EG is much narrower ($\sim 61.3 \text{ cm}^{-1}$) than that of three-layer EG ($\sim 90.5 \text{ cm}^{-1}$). Secondly, the 2D band position of first layer EG ($\sim 2722.1 \text{ cm}^{-1}$) is red shift relative to that of three-layer graphene ($\sim 2739.5 \text{ cm}^{-1}$). The sharper width and the lower vibration frequency of 2D band confirm our identification of first layer graphene as what happened for MC graphene.

The 2D band of first graphene layer is located $\sim 2722.1 \text{ cm}^{-1}$ which is blue shifted compared with that of SLG ($\sim 2670.0 \text{ cm}^{-1}$) made by ME. This kind of blue shift of 2D band of first graphene layer has been explained by the compressive stress effect on graphene layers induced by the lattice mismatch between buffer layer graphene and first graphene layer. It can also be seen that for five layers EG, its 2D band position ($\sim 2731.6 \text{ cm}^{-1}$) is red shifted relative to that of three layers EG ($\sim 2739.5 \text{ cm}^{-1}$), towards the value of muliti-layer EG ($\sim 2709.4 \text{ cm}^{-1}$). The same effect is also observed for G band, for five layers EG, its G band position ($\sim 1590.6 \text{ cm}^{-1}$) is red shifted relative to that of three layers EG ($\sim 1596.5 \text{ cm}^{-1}$), towards the value of muliti-layer EG ($\sim 1584.2 \text{ cm}^{-1}$). Above phenomenon is because the substrate strain effect on EG becomes weaker, therefore the strain induced by the substrate will relax[34]. As the layer number of EG increases, the broader of 2D band of EG is observed due to the band splitting effect which is similar as that of ME graphene[74].

8.3 Graphene thickness determination by white light contrast spectrum

On the study of EG on SiC substrate, the accurate determination of graphene thickness is required. Common methods such as AFM, Transmission electron microscopy (TEM) is not possible in deciding its thickness. STM can only be used to distinguish buffer layer and first graphene layer. Although the attenuation of the Si 2p PES signal from bulk SiC could be used to monitor the thickness of graphene[45-46,48]. However, this is not an easy and efficient way. In our previous study, the white light contrast spectroscopy has been successfully used to precisely determine layer numbers of graphene on SiO₂(300 nm)/Si made by ME[27,31]. Therefore, this contrast method is extended to decide layer numbers of graphene grown on SiC substrate. It seems that the white light contrast spectroscopy is quite a simple way to determine layer number of EG on SiC substrate. Fig. 8.3(a) gives theoretical results of white light contrast spectrum of graphene on SiC. Details about theoretical calculations could be found in Chapter 2. The experimental contrasts of graphene on SiC substrate are obtained by the following calculation:

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)}, \quad (8.1)$$

where $R_0(\lambda)$ is the reflection spectrum from the SiC substrate and $R(\lambda)$ is the reflection spectrum from graphene layer (the refractive index of graphene is taken $n_g=2.6-1.3i$, and that of SiC (n_{SiC}) is obtained from Ref.110.

Fig. 8.3(a) Theoretical calculation of contrast values for one, two, three, four, five layers graphene on SiC. **(b)** Experimental contrast value of graphene with different layers on SiC.

From Fig. 8.3(a), it can be seen that the contrast value of one to five layer graphene on SiC substrate is linearly increased with a value of ~ 0.02 . Fig. 8.3(b) shows our experimental contrast results of buffer layer, first, three, and five layers graphene on SiC substrate. For first graphene layer whose thickness is further confirmed by its characteristic STM imaging, the experimental contrast value is ~ -0.02 which matches quite well with the theoretical calculation. Therefore, we deduce graphene layer with contrast value of ~ -0.06 is three layer graphene and graphene layer with contrast value of ~ -0.1 is five layers graphene. This also matches quite

well with the estimation by monitoring the attenuation of Si 2p PES signal. In Fig. 8.3(b), it can also be seen that the contrast value for buffer layer graphene is quite small which is ~ -0.0063 . The reason of this small contrast value of buffer layer may be because for this carbon layer, almost one-third of carbon atoms are covalently bonded to SiC substrate [33] and the refractive indices difference between this carbon layer and SiC substrate should be quite small. Since the contrast value of buffer layer is small, therefore, the contrast value of first graphene layer is then used as a reference to decide layer number of EG. For graphene layers exceed one, it is difficult to decide layer number by STM image or low LEED pattern[85]. White light contrast turns out to be a simpler, accurate and easier way to decide the layer number.

8.4 Conclusions

The Raman spectra of buffer layer, one, three, five layers graphene are investigated and the Raman features of buffer layer match quantitatively with the theoretical prediction of its electronic structure. The Dirac properties will not exist in the buffer layer as revealed by the Raman spectroscopy. All the Raman bands of EG, *i.e.*, G band, 2D band are blue shifted relative to that of ME graphene which is due to the strain effect induced by the substrate. White light contrast spectrum is used to decide the layer numbers of graphene grown on SiC substrate whose thickness is difficult to be determined by STM and LEED. The results obtained here make the study of layer number dependent electronic properties of EG on SiC possible.

Chapter 9

Conclusions and future work

9.1 Conclusions

In this thesis, we solved four problems:

(1) Besides white light contrast spectroscopy, layer number of graphene can also be identified by its Raman features, *i.e.*, the integrated intensity of G band as well as the FWHM of 2D band. Our study provides two fast, nondestructive ways to identify the layer number which is critical for graphene study. We also explain the origin of the strong Raman intensity of SLG on SiO₂ (300 nm)/Si. We find the multiple beam interference in graphene layer when both the incident laser and the scattering light are considered in the calculation is the reason for this enhancement phenomenon. This kind of study provides a general rule for selection substrate to enhance the Raman signal of other thin-film materials besides graphene. By carefully select substrate, the Raman signal of thin film materials can be greatly enhanced.

(2) We study the substrate effect on electronic properties of SLG by Raman spectroscopy/imaging, and we conclude that the weak interaction (Van de Waals force) between the graphene layer and substrates are not strong enough to affect the electronic properties of graphene. The clear understanding of the substrate effect is important for potential applications and device fabrication of graphene.

(3) We study the stacking dependent electronic and optical properties of graphene by using Raman/white light spectroscopy/imaging. Theoretical first-principle DFT calculations of band structure of TBG samples are carried out. Because of interlayer

interaction and enlarged unit cell, there is abundant band folding and splitting beyond the Dirac point. Experimentally, on the one hand, by using different excitation laser lines, we are able to detect the band structures of TBG sample at the particular excitation energy. On the other hand, by using white light source, we are able to monitor the absorption behaviours of TBG samples at the continuum excitation range. We conclude theoretically and experimentally that the band structures of TBG samples under different stacking orders beyond the Dirac point are abundant, due to band folding and splitting effect caused by various interlayer interaction and different unit cells. The electronic and optical property studies of TBG samples provide guidance for further application of graphene in nanoelectronic and photonic devices, because of its high electrical conductivity and high optical transparency.

(4) Finally, in this thesis, the Raman spectroscopy is also used to study the electronic properties of graphene layers epitaxial grown on SiC substrate. The evolution from buffer layer to multi-layer graphene is monitored by the Raman spectroscopy, which will provide guidance for electronic application of epitaxial graphene. The layer number of graphene is determined by white light contrast spectroscopy. The result obtained here makes study of layer number dependent electronic properties of EG possible.

9.2 Future work

(1) Graphene +Metal+Molecule or Metal+Graphene+Molecule

Recently, an interesting phenomenon was observed in graphene that when molecule (Rhodamine 6G, R6G) is attached on graphene layer, the photoluminescence from molecule under resonance excitation can be greatly quenched by resonance energy transfer between graphene and molecule[111], which makes graphene a

promising candidate in Resonance Raman Spectroscopy. However, the Raman signal from the molecule hasn't been enhanced. Therefore, we want to enhance the Raman signal from the molecule meanwhile suppress the photoluminescence from the molecule. Metal films with different thickness (gold, silver, *et al.*) will be deposited on top of graphene layers, or graphene layers will be transferred on top of metal films, following coated the substrate (graphene + metal or metal + graphene) with molecules at relative low concentration. It is aimed to investigate the resonance energy transfer between graphene layers and molecules as well as investigate the SERS effect between metal films and molecules. It has been known for a long time that the SERS effect can be used to enhance the Raman signal of molecule either because of electromagnetic theory or due to the charge transfer theory.

(2) Charge transfer between graphene and molecule (electron donor and electron acceptor)

One purpose of this study is to investigate the charge transfer between graphene and molecule by Raman spectroscopy. Two different types of molecules will be investigated: molecules worked as electron donor such as tetrathiafulvalene (TTF) and aniline and as well as molecules worked electron acceptor such as tetracyanoethylene (TCNE), tetrafluoro-tetracyanoquinodimethane (F4-TCNQ). The G band position/width, 2D band position as well as the integrated intensity ratio of 2D/G band will change upon doping concentration, which make Raman spectroscopy a powerful tool to study the charge transfer between graphene and molecule. Since the white light spectroscopy can be used to probe the optical properties of graphene layers, therefore, the absorption behaviours of graphene layers decorated by molecules will also be investigated by the contrast spectroscopy.

(3) π - π electrons interaction between graphene and molecules with delocalized π

system

Based on our previously studies, the effect of stacking order on electronic properties of graphene is significantly. Since previously study is based on interaction between graphene layers, we want to extended this study to investigate the interaction between graphene and another molecules with delocalized π electrons. The Raman/white light spectroscopy will be used to investigate the effect of π - π electrons interaction between graphene and molecule with delocalized π system such as aniline, benzene, nitrobenzene and P-aminothiophenol (PATP) on the electronic properties of graphene.

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104. The conductivity error will be amplified when the contrast value is approach to 0. For contrast value $C=0.0939\pm0.005$, the calculated conductivity error is $\sim 11.7\%$, and for contrast value $C=0.0059\pm0.005$, the calculated conductivity error is $\sim 135.4\%$, which makes the calculated conductivity unreliable at contrast value approach 0.
105. We have obtained the optical conductivity of single to four layers graphene and they are almost the same after divided by the layer numbers, and are frequency dependent. This indicates such deviation from the predicted universal optical conductivity of graphene is due to the artifact of the system, most probably the NA effect. Therefore, normalization is carried for the experimental curves, such that the conductivity of single and few layers graphene are frequency independent, following the theoretical prediction.
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