Deformation Micromechanics of Graphene Nanocomposites

A thesis submitted to
The University of Manchester
for the degree of
Doctor of Philosophy
in the
Faculty of Engineering and Physical Sciences

2012

Lei Gong

School of Materials
CONTENTS

ABSTRACT ........................................................................................................................................... 6

LIST OF SYMBOLS .............................................................................................................................. 7

LIST OF ABBREVIATIONS .................................................................................................................... 11

LIST OF TABLES .................................................................................................................................. 13

LIST OF FIGURES ............................................................................................................................... 14

DECLARATION ...................................................................................................................................... 25

COPYRIGHT STATEMENT ..................................................................................................................... 26

ACKNOWLEDGEMENTS ....................................................................................................................... 27

CHAPTER 1  INTRODUCTION .............................................................................................................. 28

1.1 GRAPHENE ..................................................................................................................................... 29

1.1.1 Preparation ................................................................................................................................ 29

1.1.2 Characterisation .......................................................................................................................... 32

1.1.3 Mechanical properties ................................................................................................................. 34

1.2 GRAPHENE OXIDE ...................................................................................................................... 38

1.2.1 Preparation ................................................................................................................................ 38

1.2.2 Characterisation .......................................................................................................................... 41

1.2.3 Mechanical properties ................................................................................................................. 44

1.3 BULK NANOCOMPOSITES ......................................................................................................... 46

1.3.1 Preparation ................................................................................................................................ 47

1.3.2 Micromechanics of reinforcement .............................................................................................. 48

1.3.3 Mechanical properties ................................................................................................................. 51

CHAPTER 2  RAMAN SPECTROSCOPY ................................................................................................. 80

2.1 INTRODUCTION ............................................................................................................................ 80

2.2 CLASSICAL THEORY OF RAMAN EFFECT .................................................................................... 80

2.3 QUANTUM THEORY OF THE RAMAN EFFECT ............................................................................. 82
2.4 RAMAN SPECTROSCOPY OF GRAPHENE ........................................... 84
  2.4.1 D band ...................................................................................... 85
  2.4.2 G band ...................................................................................... 89
  2.4.3 2D band .................................................................................... 92
    2.4.3.1 Double Resonance process of the 2D band ......................... 93
    2.4.3.2 2D band dispersive behaviour ............................................ 95
    2.4.3.3 The dependence of 2D band on the number of layers .......... 97
    2.4.3.4 Strain-induced shifts of the 2D band ................................. 100
    2.4.3.5 2D band splitting under uniaxial strain ............................. 102

CHAPTER 3 EXPERIMENTAL .............................................................. 110
  3.1 MATERIALS PREPARATION ......................................................... 110
    3.1.1 Graphene on SiO$_2$/Si wafers ............................................... 110
    3.1.2 Graphene/PMMA composite .................................................. 111
    3.1.3 Graphene/SU-8 composite ...................................................... 111
  3.2 OPTICAL MICROSCOPY (OM) .................................................... 112
  3.3 SCANNING ELECTRON MICROSCOPY (SEM) .............................. 113
  3.4 RAMAN SPECTROSCOPY ............................................................ 113
    3.4.1 Raman spectrometer ............................................................... 113
    3.4.2 Raman data analysis ............................................................... 114
    3.4.3 Deformation analysis .............................................................. 116

CHAPTER 4 CHARACTERISATION OF GRAPHENE USING RAMAN
  SPECTROSCOPY .............................................................................. 119
  4.1 INTRODUCTION ........................................................................... 119
  4.2 MONOLAYER GRAPHENE ............................................................. 119
  4.3 BILAYER GRAPHENE .................................................................. 122
  4.4 TRILAYER GRAPHENE .................................................................. 126
  4.5 FEW LAYER GRAPHENE .............................................................. 130
  4.6 HIGHLY ORIENTED PYROLYTIC GRAPHITE (HOPG) ............... 133
  4.7 DEPENDENCE OF THE 2D BAND POSITION ON THE NUMBER OF LAYERS .... 136
## 4.8 CONCLUSIONS

### CHAPTER 5  INTERFACIAL STRESS TRANSFER IN A GRAPHENE MONOLAYER NANOCOMPOSITE

- **5.1 INTRODUCTION**  
- **5.2 MATERIALS AND METHODS**  
- **5.3 RESULTS AND DISCUSSION**
  - 5.3.1 Strain mapping
  - 5.3.2 Theoretical analysis
  - 5.3.3 Implications
- **5.4 CONCLUSIONS**

### CHAPTER 6  STRAIN MAPPING IN A GRAPHENE MONOLAYER NANOCOMPOSITE

- **6.1 INTRODUCTION**  
- **6.2 MATERIALS AND METHODS**  
- **6.3 RESULTS AND DISCUSSION**
  - 6.3.1 Strain calibration
  - 6.3.2 Strain mapping
  - 6.3.3 High strain deformation
  - 6.3.4 Interfacial shear stress
- **6.4 CONCLUSIONS**

### CHAPTER 7  OPTIMIZING THE REINFORCEMENT OF POLYMER-BASED NANOCOMPOSITES BY GRAPHENE

- **7.1 INTRODUCTION**  
- **7.2 MATERIALS AND METHODS**  
- **7.3 RESULTS AND DISCUSSION**
  - 7.3.1 Graphene deformation
  - 7.3.2 Theoretical analysis
  - 7.3.3 Variation of strain across the flake
CHAPTER 8   POLARISED RAMAN STUDY OF GRAPHENE

DEFORMATION ................................................................. 201

8.1 INTRODUCTION ......................................................... 201
8.2 MATERIALS AND METHODS ........................................... 202
8.3 DETERMINATION OF GRAPHENE CRYSTALLOGRAPHIC ORIENTATION ...... 202
8.4 2D BAND SPLITTING ...................................................... 207
8.5 RAMAN SHIFT RATE DEPENDENCE UPON POLARISATION ..................... 214
   8.5.1 2D band shift rate dependence upon polarisation direction .......... 214
   8.5.2 G band shift rate dependence upon polarisation ....................... 216
8.6 2D BAND STRAIN MAPPING ............................................. 218
8.7 CONCLUSIONS ............................................................. 220

CHAPTER 9   CONCLUSIONS AND FUTURE WORK ............................... 224

9.1 CONCLUSIONS ............................................................. 224
   9.1.1 Monolayer graphene reinforced nanocomposites ....................... 224
   9.1.2 Bilayer, trilayer and few-layer graphene reinforced nanocomposite
   ...................................................................................... 226
   9.1.3 Polarisation dependence of Raman band .................................. 226
9.2 FUTURE WORK .............................................................. 227
   9.2.1 Inner-layer stress transfer in the tri- and few-layer graphene .......... 227
   9.2.2 Defect monitoring in graphene nanocomposite .......................... 229
   9.2.3 Graphene oxide and functionalised graphene sheet reinforced
       nanocomposites .................................................................. 230

World Count: 53366
Abstract

Graphene nanocomposites have been successfully prepared in this study in the form of a sandwich structure of PMMA/graphene/SU-8. It has been proved that Raman spectroscopy is a powerful technique in the characterisation of the structure and deformation of graphene.

The 2D band of the monolayer graphene has been used in the investigation of stress transfer in the graphene reinforced nanocomposites. It has been demonstrated that the 2D band moves towards low frequency linearly under tensile stress, which is shown to be significant method of monitoring the strain in graphene in a deformed specimen. The Raman spectroscopy behaviour under deformation validates that the monolayer graphene acts as a reinforcing role in nanocomposites although it is only one atom thick.

A systematic investigation of the deformation of bilayer, trilayer and few-layer graphene has been undertaken with a view to determine the optimum number of layers for the reinforcement of nanocomposites. It has been demonstrated that monolayer graphene is not necessarily the optimum material to use for reinforcement in graphene-based polymer nanocomposites and bilayer graphene will be equally as good as monolayer graphene. There is therefore a balance to be struck in the design of graphene-based nanocomposites between the ability to achieve higher loadings of reinforcement and the reduction in effective Young’s modulus of the reinforcement, as the number of layers in the graphene is increased.

Both the G and 2D bands have been found to undergo splitting under high strain levels or asymmetric band broadening in lower strain deformation. The G band polarisation property has been utilized to determine the crystallographic orientation of monolayer graphene by measuring the intensity ratio of $G/G^+$ bands. Analogously, the 2D band also undergoes strain-induced splitting where the $2D^-$ band has higher Raman shift rate than that of the $2D^+$ band.
List of Symbols

%         percent
∞         infinity
&         and
°C        degree Celsius
$A_0$      combined area of the annulus between the layers and the centre of the nanotube
$A_1$      cross-sectional area of the outermost shell
$A_T$      total area of the MWNT excluding the annulus and central hole
$C$        constant of integration
$D$        constant of integration
$d_a$      wavevectors of armchair edges
$d_z$      wavevectors of zigzag edges
$\varepsilon$  strain
$\varepsilon_m$  matrix strain
$\varepsilon_{ll}$  graphene strain at longitudinal direction
$\varepsilon_{tt}$  graphene strain at transverse direction
$E$        Young’s modulus
$E_1$      molecular energy levels before the impinging
$E_2$      molecular energy levels after the impinging
$E_c$      Young’s modulus of the composites
$E_{cb}$   energy of conductive band
$E_{ef}$   electric field strength
$E_{eff}$  effective graphene Young’s modulus
$E_g$      Young’s modulus of the graphene flake
$E_i$      photon energy of the incident laser
$E_{Laser}$  laser energy
$E_m$      Young’s modulus of the matrix
$E_o$      vibration amplitude
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p$</td>
<td>Young’s modulus of the particles</td>
</tr>
<tr>
<td>$E_q$</td>
<td>phonon energy</td>
</tr>
<tr>
<td>$E_s$</td>
<td>scattered photons energy</td>
</tr>
<tr>
<td>$E_{vb}$</td>
<td>energy of valence band</td>
</tr>
<tr>
<td>$E_p^{11}, E_p^{22}, E_p^{12}, E_p^{21}$</td>
<td>phonon energy of related DR process</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>shear strain</td>
</tr>
<tr>
<td>$G_m$</td>
<td>shear modulus of the matrix</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>$I$</td>
<td>intensity</td>
</tr>
<tr>
<td>$k$</td>
<td>wave vector</td>
</tr>
<tr>
<td>$k_1, k_2, k'_1, k'_2$</td>
<td>reciprocal space vectors</td>
</tr>
<tr>
<td>$k_i$</td>
<td>parameter of the efficiency of stress transfer</td>
</tr>
<tr>
<td>$l$</td>
<td>length</td>
</tr>
<tr>
<td>$l_c$</td>
<td>critical length</td>
</tr>
<tr>
<td>$n$</td>
<td>effective measure of the interfacial stress transfer efficiency</td>
</tr>
<tr>
<td>$n_l$</td>
<td>number of layers</td>
</tr>
<tr>
<td>$o$</td>
<td>degree</td>
</tr>
<tr>
<td>$p$</td>
<td>peak position</td>
</tr>
<tr>
<td>$P$</td>
<td>electric dipole moment</td>
</tr>
<tr>
<td>$P_{11}, P_{22}, P_{12}$ and $P_{21}$</td>
<td>DR processes</td>
</tr>
<tr>
<td>$q$</td>
<td>wavevector of phonon</td>
</tr>
<tr>
<td>$q$</td>
<td>momentum</td>
</tr>
<tr>
<td>$RS_0$</td>
<td>strain gauge resistance without loading</td>
</tr>
<tr>
<td>$RS_i$</td>
<td>strain gauge resistance with loading</td>
</tr>
<tr>
<td>$s$</td>
<td>aspect ratio of the graphene</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>axial stress parallel to the flake axis</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>graphene flake stress</td>
</tr>
<tr>
<td>$S_{gf}$</td>
<td>strain gauge factor</td>
</tr>
<tr>
<td>$t$</td>
<td>thickness of graphene</td>
</tr>
</tbody>
</table>
List of Symbols

\( T \)  
thickness of the polymer layers

\( \tau \)  
shear stress

\( t_o \)  
time

\( u \)  
displacement of the matrix

\( u_g \)  
displacement of graphene

\( V_g \)  
volume fractions of the graphene

\( v_i \)  
frequent of the incident photons

\( V_m \)  
volume fraction of matrix

\( v_o \)  
electric field frequency

\( V_p \)  
volume fraction of particles

\( v_s \)  
frequency of the scattered photons

\( v_{vib} \)  
vibrational frequency

\( \omega_{2D} \)  
Raman wavenumber of 2D band

\( \omega_o^- \)  
frequency of G' band

\( \omega_o^+ \)  
frequency of G^+ band

\( W_p \)  
full width at half maximum of the peak

\( \xi \)  
parameter of measure of reinforcement geometry

\( \alpha \)  
molecular polarisability

\( \alpha_o \)  
equilibrium polarisability

\( \beta \)  
shear deformation potential coefficient

\( \gamma \)  
Grüneisen parameter

\( \Delta v \)  
frequency discrepancy between incident photons and scattered photons

\( \eta \)  
parameter, the ratio of the Young’s modulus of the filler to that of the matrix

\( \theta \)  
angle

\( \theta_i \)  
incident light polarisation with respect to the strain axis

\( \theta_o \)  
cattered laser polarisation with respect to the strain axis

\( \kappa \)  
charge rate of polarisability
List of Symbols

\( \lambda \) wave length

\( \nu \) Poisson’s ratio

\( \pi_1 \) upper valence band

\( \pi_2 \) lower valence band

\( \pi^* \) lower conduction band

\( \pi^*_z \) upper conduction band

\( \varphi_s \) an arbitrary angle between the strain axis and the graphene crystallographic axis (zigzag axis)

\( \omega_0 \) G band Raman frequency at zero strain

\( I_p \) peak intensity

\( I_{G^-} \) Raman intensity of G\(^-\) band

\( I_{G^+} \) Raman intensity of G\(^+\) band

\( I_{2D^-}^{Z} \) Raman arbitrary intensity for 2D\(^-\) band at the zigzag orientation

\( I_{2D^+}^{Z} \) Raman arbitrary intensity for 2D\(^+\) band at the zigzag orientation

\( I_{2D^-}^{A} \) Raman arbitrary intensity for 2D\(^-\) band at the zigzag orientation

\( I_{2D^+}^{A} \) Raman arbitrary intensity for 2D\(^+\) band at the zigzag orientation

\( I_{2D^-} \) Raman arbitrary intensity for 2D\(^-\) band

\( I_{2D^+} \) Raman arbitrary intensity for 2D\(^+\) band
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>aGO</td>
<td>As-produced graphene oxide</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>bwGO</td>
<td>Base-washed graphene oxide</td>
</tr>
<tr>
<td>C</td>
<td>Carbon atom</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>DR</td>
<td>Double resonance</td>
</tr>
<tr>
<td>eV</td>
<td>Electronvolt</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>G⁻</td>
<td>Lower wavenumber component of G band</td>
</tr>
<tr>
<td>G⁺</td>
<td>Higher wavenumber component of G band</td>
</tr>
<tr>
<td>GNP</td>
<td>Graphite nanoplatelets</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>GPa</td>
<td>GigaPascal</td>
</tr>
<tr>
<td>H</td>
<td>Hygrogen atom</td>
</tr>
<tr>
<td>H₂</td>
<td>Hygrogen</td>
</tr>
<tr>
<td>HeNe</td>
<td>Helium–neon</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>iTO</td>
<td>in-plane transverse optical</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>kg</td>
<td>Kilogram</td>
</tr>
<tr>
<td>LO</td>
<td>Longitudinal optical</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>MPa</td>
<td>MegaPascal</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen atom</td>
</tr>
<tr>
<td>OD</td>
<td>Oxidative debris</td>
</tr>
<tr>
<td>OM</td>
<td>Optical microscopy</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>S</td>
<td>Siemens</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>SU-8</td>
<td>Photoresist</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TPa</td>
<td>TeraPascal</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
List of Tables

Table 3.1 Polarised configurations with the various arrangements of the two half $\lambda$ plates and the polariser. ................................................................. 114

Table 4.1 Various 2D band positions for the different number of graphene layers with different lasers and different substrates.................................. 137

Table 7.1 Measured 2D Raman band shift rates (with standard deviations) for the uncoated and coated graphene nanocomposite specimens described in Figure 7.5 & 7.6 (laser excitation 785 nm). All bands were fitted to a single Lorentzian peak and the number of flakes on which the measurements were made is indicated.................................................................. 184

Table 8.1 Summary of $d\omega/d\varepsilon$ (cm$^{-1}$/% strain). ................................. 203
List of Figures

Figure 1.1 A molecular model of a single layer of graphene. .......................... 28
Figure 1.2 Optical micrograph of a graphene monolayer (indicated by an arrow) prepared by mechanical cleavage and deposited on a polymer substrate. • 30
Figure 1.3 Raman spectra of graphene showing the difference in spectra between monolayer, bilayer and multilayer samples. ........................................ 33
Figure 1.4 Measure and calculated stress-strain curve for the deformation of a graphene monolayer. ................................................................. 35
Figure 1.5 Shift of the Raman 2D band with strain for a graphene monolayer. • 37
Figure 1.6 Thermogravimetric analysis in air of as-produced graphene oxide (aGO, top) and the two components after base-washing; the black precipitate (bwGO, middle), and the remaining water soluble fraction (OD, bottom). 39
Figure 1.7 TEM image of a single GO sheet on a lacy carbon support; a double fold is visible in the top right corner. (b) Selected-area diffraction pattern of the centre of the region shown in (a), the diffraction spots are labelled with Miller-Bravais indices. (c) Intensity profile through the diffraction spots labelled in (b). ......................................................... 42
Figure 1.8 (a) C 1s XPS spectra of aGO and bwGO. (b) Raman spectra of aGO and bwGO obtained using a 633 nm laser excitation. ......................... 42
Figure 1.9 The structure of graphene oxide produced by Hummers’ method and the modification to the structure produced base washing. ............. 44
Figure 1.10 Mechanical properties of nanocomposites consisting of reduced graphene oxide in PVA at various loadings (volume %). (a) Stress-strain curves. (b) Tensile strength and elongation at break versus graphene loadings. .......................................................................................... 51
Figure 1.11 Stress–strain curves for nanocomposites consisting of solvent-exfoliated graphene in a polyurethane matrix with different loadings of graphene (weight %). ....................................................... 53
15

Figure 1.12 Predicted and measured variation of $E_c/E_m$ with the volume fraction, $V_p$, of graphene-based filler particles for (a) rigid polymers and (b) elastomers. ................................................................. 55

Figure 2.1 Schematic diagram of Rayleigh, Stokes-Raman and anti-Stokes Raman scattering. ............................................................................................................. 82

Figure 2.2 Raman spectra for bulk graphite and monolayer graphene at 514 nm. (a) shows the G band ($1580 \text{ cm}^{-1}$) and 2D band ($2700 \text{ cm}^{-1}$) features and were measured on the SiO$_2$/Si substrate. (b) The D band structure for graphite and monolayer. ................................................................................................. 84

Figure 2.3 Schematic process for the Double Resonance for (a) D band and (b) D’ band of graphene. ............................................................................................................. 85

Figure 2.4 Polar plots for the D band scattering intensity versus polarisation angle $\theta$. The incident and scattered light were parallel to each other. (b) Dependence of the D band intensity on the polarisation direction of the incident and scattered light. ................................................................. 86

Figure 2.5 (a) Schematic illustration of the typical atomic structure of the graphene edges. (b) First Brillouin zone of Graphene, showing that the inter-valley Double Resonance scattering of the armchair edges satisfies the conservation of momentum but that of the zigzag edges does not. .................................................. 87

Figure 2.6 Raman D bands (edge excitation) for various numbers of layers of graphene. ............................................................................................................. 88

Figure 2.7 Schematic diagrams for Raman active $E_{2g}$ mode: (a) LO phonon mode, (b) iTO phonon mode and (c) illustrates the first-order G band process. ................................................................. 89

Figure 2.8 (a) G band Raman spectra under various applied uniaxial strain showing the splitting phenomenon. (b) The $G^+$ and $G^-$ subbands positions are plotted as a function of applied uniaxial strain. .................................................. 89

Figure 2.9 (a) Polar plot of the fitted $G^+$ and $G^-$ subbands as a function of the angle among the incident light, scattered light and the strain axis angle to the zigzag direction of zigzag. (b) Schematic diagrams for the angles between strain
axes, incident light and scattered light in the same panel. The $x$ axis is parallel to the zigzag direction of graphene. ....................................................... 91

Figure 2.10 Raman spectra of bilayer graphene with 514.5 nm and 633 nm laser respectively. Both the spectra are fitted with four Lorentzian peaks. ...... 93

Figure 2.11 Schematic diagram for the inter-valley DR process of monolayer graphene. ........................................................................... 94

Figure 2.12 Schematic diagram shows the electron dispersion of bilayer graphene near the Dirac K and K’ points. The four DR processes are indicated which corresponds with the four sub-peaks. ............................................ 94

Figure 2.13 (a) Raman spectra of 2D band and G* of a monolayer graphene for various laser excitation energies. (b) The 2D band position dependence of laser energy. The circles correspond to the graphene and the squares correspond to turbostratic graphite. .................................................. 96

Figure 2.14 The position of four components of the bilayer graphene 2D band as a function of the laser energy. .................................................. 96

Figure 2.15 The real space top-view for bilayer graphene crystal lattices with (a) AB stacking and (b) non-AB stacking. ........................................... 97

Figure 2.16 The 2D Raman band obtained using a 2.41 eV laser energy for (a) monolayer, (b) bilayer, (c) trilayer, (d) four-layer and (e) HOPG [10] and (f) the statistical data of FWHM with respect to the different thickness graphene. ................................................................. 97

Figure 2.17 2D Raman bands of mono-, bi-, tri-, five-, and six-Bernal stacked layers (blue) and when folded (red). (b) Raman spectroscopy for CVD grown bilayer graphene, few layer graphene and graphite. ......................... 99

Figure 2.18 (a) The 2D band of monolayer graphene unstrained, at 0.78% strain and with strain released. (b) The 2D band position as a function of applied strain for monolayer and trilayer graphene. .............................. 100

Figure 2.19 Plot of the 2D band position of monolayer graphene as a function of tensile and compression strain. ............................................. 101
Figure 2.20 The 2D band features of monolayer under uniaxial tensile strain. The left and right panels were obtained with the incident light parallel and perpendicular to the strain axis, respectively. ........................................ 102

Figure 2.21 (a) Inner and outer DR processes. Reciprocal lattice diagram of monolayer graphene for (b) unstrained, (c) armchair-direction strained and (d) zigzag-direction strained. ........................................ 103

Figure 3.1 Schematic diagrams for preparation of mechanically-cleavage graphene. .................................................................................................................. 110

Figure 3.2 Schematic diagrams for the preparation of graphene on a SiO$_2$/Si Wafer. .................................................................................................................. 111

Figure 3.3 Structures for Graphene/PMMA composites. ..................................... 111

Figure 3.4 Chemical structures for cross-linked SU-8. ...................................... 112

Figure 3.5 Structure for Graphene/SU-8 composite. ........................................... 112

Figure 3.6 Schematic diagram for Renishaw Raman spectrometer. ................. 113

Figure 3.7 An example of a monolayer 2D band with a single Lorentzian peak fit. .................................................................................................................. 115

Figure 3.8 Four-point bending test sample. ...................................................... 116

Figure 3.9 Raman four-point bending rig and diagram of test process. .............. 116

Figure 4.1 Raman spectra for the monolayer graphene on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser. ....................................................... 121

Figure 4.2 The 2D band position of monolayer graphene as a function of laser excitation energy on different substrates. ........................................ 122

Figure 4.3 Raman spectra for the bilayer graphene on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser. ....................................................... 124

Figure 4.4 The 2D band position of the bilayer graphene as a function of laser excitation energy on different substrates. ........................................ 125
Figure 4.5 An example for four Lorentzian components fit (green solid lines) to the 2D band with 633 nm laser for bilayer graphene on the SiO$_2$/Si substrate. ................................................................. 125

Figure 4.6 Raman spectra for the trilayer graphene on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser. ................................................................. 127

Figure 4.7 The 2D band position of the trilayer graphene as a function of laser excitation energy on different substrates. ........................................... 128

Figure 4.8 Examples for (a) six Lorentzian components (green solid lines) and (b) four Lorentzian components fit (green solid lines) to the 2D band with the 633 nm laser for the trilayer graphene on the PMMA substrate. .......... 129

Figure 4.9 Raman spectra for the few layer graphene on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser. ................................................................. 132

Figure 4.10 The 2D band position of the few layer graphene as a function of laser excitation energy on different substrates. ........................................... 133

Figure 4.11 An example for two Lorentzian components fit (green solid lines) to the 2D band with the 633 nm laser for the few layer graphene on the SiO$_2$/Si substrate. ................................................................. 133

Figure 4.12 Raman spectra for the HOPG on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser. ................................................................. 135

Figure 4.13 The 2D band position of HOPG as a function of the excitation energy on different substrates. ................................................................. 136

Figure 4.14 An example for two Lorentzian component fit (green solid lines) to the 2D band at 633 nm laser for HOPG on SiO$_2$/Si substrate. .......... 136

Figure 4.15 The 2D band position dependence to the number of the graphene layers. ................................................................. 137
Figure 5.1 Single monolayer graphene composite. (a) Optical micrograph showing the monolayer graphene flake investigated. (b) Schematic diagram (not to scale) of a section through the composite. .................................. 142

Figure 5.2 Shifts of the Raman 2D band during loading and unloading of the monolayer graphene composite. (a) Change in the position of the 2D band with deformation. (b) Shift of the band peak position as a function of strain. (The blue circles indicate where the loading was halted to map the strain across the flake). .............................................................. 143

Figure 5.3 Distribution of strain in the graphene in the direction of the tensile axis (x) across a single monolayer at 0.4% strain. (a) Variation of axial fibre strain with position across the monolayer in the x-direction (The curve fitted to the data is Equation (5.15)). (b) Variation of graphene strain in the direction of the tensile axis (x) across a single monolayer at 0.6% matrix strain. (The solid lines are fitted to the data to guide the eye. The dashed curve is the shear-lag fit to the data in Figure 5.3(a) at 0.4% strain.) .................................. 145

Figure 5.4 Deformation patterns for a discontinuous flake in a polymer matrix. .................................................. 146

Figure 5.5 Balance of stresses acting on an element of length, dx, of the flake of thickness, t, in the composite. .................................................. 146

Figure 5.6 Model of a flake within a resin used in shear-lag theory. The shear stress, τ, acts at a radius ρ from the flake centre. ......................... 147

Figure 5.7 (a) Distribution of strain in the graphene in direction of the tensile axis across a single monolayer at 0.4% strain. The curves are fits of Equation (5.13) using different values of parameter ns. (b) Variation of interfacial shear stress with position determined from Equation (5.14) for the values of ns used in (a). .................................................. 151

Figure 5.8 Distribution of strain in the graphene in direction of the tensile axis across a single monolayer at 0.4% strain showing the variation of fibre strain with position across the monolayer in the vertical direction. The curves were calculated from Equation (5.13) using different values of ns. .......... 152
Figure 6.1 Optical micrograph of the graphene monolayer before deformation. (The faint straight lines in the background are from scratches on the PMMA beam.) ................................................................. 159

Figure 6.2 Position of the 2D Raman band in the uncoated graphene as a function of strain on the beam corresponding increasing FWHM. ...................... 160

Figure 6.3 Contour maps of strain over the graphene flake at 0% and 0.4% strain in the uncoated and coated states. ................................................. 161

Figure 6.4 Variation of the strain in the graphene along the monolayer both undeformed (0%) and at a strain of 0.4%. (a) Specimen uncoated and (b) following coating the with a SU-8 film. (The arrow indicates the point on the monolayer at which the calibration measurements were undertaken).···· 162

Figure 6.5 Position of the 2D Raman band in the coated graphene as a function of strain on the beam during reloading to 0.8% and unloading. ............... 163

Figure 6.6 Contour maps of strain over the coated graphene flake in the relaxed states and at 0.8% and 0.6% strain. .............................................. 164

Figure 6.7 Variation of graphene strain along the middle of the monolayer relaxed and reloaded to 0.6%. (The open triangles are the data points at 0.6% strain for the first loading in Figure 6.4(b).)............................................. 165

Figure 6.8 Variation of strain along the middle of the monolayer relaxed and reloaded to 0.8%. ................................................................. 166

Figure 6.9 Schematic diagrams of the deformation of the graphene monolayer in the model composite. (a) Specimen before deformation, (b) graphene monolayer undergoing fragmentation and (c) cracking of both the PMMA and SU8 polymer coating. (Diagrams not to scale)......................... 167

Figure 6.10 Optical micrograph of the specimen after deformation showing the formation of cracks in the coating that developed during loading. (The tensile axis is horizontal.) ...................................................... 168

Figure 6.11 SEM micrograph showing cracking on the surface of the polymer-coated specimen following deformation to 0.8%. (The straining direction is horizontal.) ...................................................... 168
Figure 7.1 Shift with strain of 2D Raman band of the graphene fitted to a single peak during deformation upon the PMMA beam (laser excitation 633 nm). (a) A graphene monolayer deformed before and after coating with SU-8. (b) A graphene bilayer deformed before and after coating with SU-8. (Schematic diagrams of the deformation of the uncoated (above) and coated (below) graphene are also included.)

Figure 7.2 Details of the 2D Raman band for the bilayer graphene both before and after deformation to 0.4% strain when it is either uncoated or coated. The fit of the band to four sub-bands is shown in each case in green and the fitted curve is shown in red (laser excitation 785 nm).

Figure 7.3 Graphene flake on a PMMA beam showing monolayer, bilayer and trilayer regions. (a) Optical micrograph (the fine straight lines are scratches on the surface of the beam). (b) Schematic diagram of the flake highlighting the different areas (the rectangle shows the area of the flake over which the strain was mapped). (c-f) Raman spectra of the 2D band part of the spectrum for the monolayer, bilayer (fitted to 4 peaks), trilayer regions (fitted to 6 peaks) and a few layer graphene flake, elsewhere on the beam (laser excitation 633 nm).

Figure 7.4 (a) Shift with strain of the four components of the 2D Raman band of the bilayer graphene shown on the specimen in the Figure 7.3 along with the shift of the 2D band in an adjacent monolayer region on the same flake (laser excitation 633 nm). (b) Shifts with strain of the 2D band for adjacent monolayer, bilayer and trilayers regions on the specimen in Figure 7.3, along with the shift with strain for the 2D band of a few layer flake on the same specimen (all 2D bands were force fitted to a single Lorentzian peak).

Figure 7.5 Three sets of data for the shift of the 2D Raman band with strain for uncoated monolayer graphene flakes (laser excitation 785 nm).

Figure 7.6 Representative shifts with strain of the 2D Raman bands band for different graphene flakes regions. (a) Uncoated condition. (b) Coated condition. Data were obtained from different flakes without and with an
SU-8 coating. All 2D bands were force fitted to a single Lorentzian peak and the laser excitation was 785 nm. ................................................................. 183

Figure 7.7 Derived values of $E_{\text{eff}}/E_g$ as a function of the numbers of layers, $n_l$, in the graphene. The theoretical lines are given using Equation (7.2) for the uncoated samples and Equation (7.3) for the coated ones. (The error bars for $E_{\text{eff}}/E_g$ represent one standard deviation). ........................................ 188

Figure 7.8 Maps of strain in the graphene bilayer regions of the flake shown in Figure 7.3, determined from the shift of the $2D_{1A}$ component of the 2D Raman band, for different levels of matrix strain in the direction indicated by the arrow (laser excitation 633 nm). The black dots indicate where measurements were taken and the individual rows of data analyzed later are marked. The monolayer and trilayer regions in the flake have been masked out for clarity. ................................................................. 190

Figure 7.9 Variation of strain in the graphene bilayer with position along row 2 (indicated in Figure 7.8), at different levels of matrix strain, $\varepsilon_m$, showing the development of a matrix crack (see schematic diagram). ......................... 191

Figure 7.10 (a) Variation of strain in the monolayer and bilayer regions of graphene with position along row 13 (indicated in Figure 7.8) at an applied strain of 0.6%. The theoretical curve is a fit to the data points using Equation (5.15) derived from shear lag theory with $n_s = 10$. (b) Correlation of measured strains in adjacent regions of the monolayer and bilayer graphene in rows 11-13 (Figure 7.8) at 0.6% applied strain. (The schematic diagram shows the variation of the number of graphene layers across the row). . . 193

Figure 7.11 Schematic diagram of the microstructure of graphene-based nanocomposites based upon either monolayer or trilayer reinforcements. The interlayer spacing of the graphene is 0.34 nm and the effective thickness of the polymer coils is assumed to be to be around 2 nm. ......................... 194

Figure 7.12 (a) Effective graphene Young’s modulus, $E_{\text{eff}}$, and maximum graphene volume fraction for different indicated polymer layer thicknesses, as a function of the number of layers, $n_l$, in the graphene flakes. (b) The
maximum nanocomposite modulus predicted for different indicated polymer layer thicknesses as a function of the number of layers, \(n_l\), in the graphene flakes. .............................................................................................................. 195

Figure 8.1 The Raman G band peaks under various uniaxial strains. (a) Tensile loading. (b) Tensile unloading. ......................................................... 204

Figure 8.2 An example for Two Lorentzian peaks fit (green solid lines) to the Raman G band. The black dots are the original data and the red solid line is the sum of the fitting peaks. ................................................................. 204

Figure 8.3 Plots of the \(G^-\) and \(G^+\) bands as a function of applied uniaxial strain. (a) Loading plots. (b) Unloading plots. ........................................ 205

Figure 8.4 Schematic diagram of angles between strain axis, graphene zigzag direction and laser polarisation. ............................... 206

Figure 8.5 The Raman 2D band features for a monolayer graphene with various strains. (a)Tensile loading. (b) Tensile Unloading. ....................... 207

Figure 8.6 Plots of the \(2D^-\) and \(2D^+\) bands as a function of applied tensile strain. (a) Tensile loading. (b) Tensile unloading. ......................... 208

Figure 8.7 Schematic diagrams for reciprocal lattice of the graphene Brillouin zone. (a) Unstrained. (b) Under strain with a 12.5\(^{\circ}\) orientation angle. .... 209

Figure 8.8 The arbitrary intensities of the 2D band at 0\%, and the \(2D^-\) and \(2D^+\) bands at 0.7\% applied strain......................................................... 210

Figure 8.9 Arbitrary intensities of (a) the \(2D^-\) and (b) \(2D^+\) peaks as a function of angle of incident light with respect to the strain axis. Solid lines were curve-fits using Equation (8.12) and (8.13). .......................... 212

Figure 8.10 Intensity ratio of (a) \(2D^+\) to \(2D^-\) and (b) \(2D^-\) to \(2D^+\) peaks as a function of \(\theta_i\). ................................................................................. 213

Figure 8.11 Monolayer graphene Raman 2D band shift rate as a function of \(\theta_i\). (a) Single Lorentzian peak fit. (b) Two Lorentzian peaks fit. ......... 214

Figure 8.12 The monolayer graphene Raman 2D band line shapes for different incident laser polarisation at the 0.7\% applied strain. The black curve is the
original data collected from the graphene, the red curve presents its single-peak curve fitting and the blue curves are the two-peak fittings.

Figure 8.13 Monolayer graphene Raman G band shift rate as a function of $\theta_i$. (a) Two Lorentzian peaks fit. (b) Single Lorentzian peak fit.

Figure 8.14 Optical micrograph of the monolayer graphene. (The red dot square is the selected mapping area).

Figure 8.15 Contour strain maps at 0.5% applied strain of a selected monolayer area. (a) Single peak fit. (b) The 2D$^-$ band. (c) The 2D$^+$ band.

Figure 8.16 Contour strain maps at 0.7% applied strain of a selected monolayer area. (a) Single peak fit. (b) The 2D$^-$. (c) The 2D$^+$ band.

Figure 9.1 The Raman 2D bands for (a) the monolayer and (b) bilayer graphene under various applied strains.

Figure 9.2 (a) The Raman 2D band for the trilayer graphene under various applied strains. (b) The trilayer FWHMs as a function of the applied strain.
Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Any part of the thesis that has already been published in a scientific Journal is indicated in the footnote at the start of the relevant chapter.
Copyright Statement

i. The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

ii. Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

iii. The ownership of certain Copyright, patents, designs, trade marks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and commercialization of this thesis, the Copyright and any Intellectual Property and/ or Reproductions described in it may take place is available in the University IP Policy (see http://www.campus.manchester.ac.uk/medialibrary/policies/intellectual-property.pdf), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.manchester.ac.uk/library/aboutus/regulations) and in The University’s policy on presentation of Theses.
Acknowledgements

First, the author would like to express his gratitude and appreciation to Professor Robert J. Young for the enthusiastic supervision and encouragement throughout this project.

Second, the author would also like to thank Professor Ian Kinloch for the guidance and discussions during this project.

The author would also like to thanks Professor Kostya Novoselov of the School of Physics & Astronomy for the supplying samples.

The author would also like to give thanks to the staff at the Materials Science Centre, especially Mr Andrew Zadoroshnyj for his assistance and advice in Raman spectroscopy.

The author would also like to thanks Dr. Yat-Tarng Shyng, Dr. Libo Deng, and Dr. Shuang Cui for their guidance and suggestions through different stages of this project. Special thanks are due to everyone in Raman group for their help and friendship.

Finally, the author would like to give his special appreciation to his parents for their understanding, encouragements and constant support. Without their supporting and efforts, I would not have a chance to study in the UK.
Chapter 1 Introduction*

The study of graphene is one of the most exciting topics in materials science and condensed matter physics [1] and graphene has good prospects for applications in a number of different fields [2-3]. There has been a rapid rise of interest in the study of the structure and properties of graphene following the first report in 2004 of the preparation and isolation of single graphene layers in Manchester [4]. It had previously been thought that the isolation of single-layer graphene would not be possible since such 2D crystals would be unstable thermodynamically [5] and/or might roll up into scrolls if prepared as single atomic layers [6]. A large number of studies since 2004 have shown that this is certainly not the case. There was excitement about graphene initially because of its electronic properties, with its charge carriers exhibiting very high intrinsic mobility, having zero effective mass and being able to travel distances of microns at room temperature without being scattered [1, 7]. The majority of the original research upon graphene had concentrated upon electronic properties, aimed at applications such as using graphene in electronic devices [8-9].

Figure 1.1 A molecular model of a single layer of graphene. (Courtesy of F. Ding, Hong Kong Polytechnic University).

* This chapter is based upon a paper of “The mechanics of graphene nanocomposites: A review”, published in Composites Science and Technology 72(12) 2012, DOI: 10.1016/j.compscitech.2012.05.005.
Graphene is the basic building block of all graphitic forms of carbon. It consists of a single atomic layer of $sp^2$ hybridized carbon atoms arranged in a honeycomb structure as shown in Figure 1.1. Research upon the material has now broadened considerably as it was soon realised that graphene might have other interesting and exciting physical properties such as high levels of stiffness and strength, and thermal conductivity, combined with an impermeability to gases. One obvious application of graphene is in the field of nanocomposites [10-12] and researchers working upon other forms of nanocomposites, such as those reinforced by nanotubes or nanoclays, have now refocused their efforts towards graphene nanocomposites. Additionally there was pre-existing expertise in the exfoliation of graphite (e.g. expanded graphite) and in the preparation of graphene oxide (originally termed “graphite oxide”). It will be shown how graphene oxide is relevant to the study of graphene, in that it can be modified chemically to produce a material that is closely related to graphene.

### 1.1 Graphene

#### 1.1.1 Preparation

There has already been considerable effort put into the development of ways of preparing high-quality graphene in large quantities for both research purposes and with a view to possible applications [13]. Since it was first isolated in 2004 two general approaches have been employed to prepare the material. One is to take graphite and break it down into graphene by techniques such as a mechanical cleavage or exfoliation (sometimes termed “top-down”). The other method is to synthesize graphene using techniques such as chemical vapour deposition (CVD) (often known as “bottom-up”).

Expanded graphite was developed more than 100 years as a filler for the polymer resins that were being developed at the same time and investigated extensively over the intervening period [14-15]. More recently there have been developments in the preparation of thinner forms of graphite, known as graphite nanoplatelets (GNPs) [16].
They can be produced by a number of techniques that include the exposure of acid-intercalated graphite to microwave radiation, ball-milling and ultrasonication. The addition of GNPs to polymers has been found to lead to substantial improvements in mechanical and electrical properties at lower loadings than are needed with expanded graphite [17-18]. The definition of GNPs covers all types of graphitic material from 100 nm thick platelets down to single layer graphene [16]. It is, however, the availability of single- or few-layer graphene that has caused the most excitement in recent times.

![Figure 1.2 Optical micrograph of a graphene monolayer (indicated by an arrow) prepared by mechanical cleavage and deposited on a polymer substrate. (Specimen kindly provided by Prof. Kostya Novoselov of the University of Manchester, Department of Physics and Astronomy)](image)

The simplest way of preparing small samples of single- or few-layer graphene is by the mechanical cleavage (i.e. the repeated peeling of graphene layers with adhesive tape) from either highly-oriented pyrolytic graphite or good-quality natural graphite [4]. Figure 1.2 shows an optical micrograph of a sample of monolayer graphene prepared by mechanical cleavage and then deposited upon a polymer substrate. Typically, this method produces a mixture of one-, two- and few-layer graphene flakes that have dimensions of the order of tens of microns.

The rapid rise of interest in graphene for use in applications that require high volumes of material, such as in composites, led to people investigating methods of undertaking large-scale exfoliation [19-31]. One of the first successful methods was the exfoliation
and dispersion of graphite in organic solvents such as \(N\)-methylpyrrolidone [21, 23-24]. This method yields about 1% of graphene monolayer material along with bi-layer and few layer graphene. The material produced by this method is relatively free of defects and is not oxidised but the lateral dimensions of the graphene layers are typically no more than a few microns. Coleman and coworkers [20, 25] demonstrated that it was also possible to disperse and exfoliate graphite to give graphene suspensions in water-surfactant solutions and then showed that this approach could be extended to other inorganic layered compounds such as molybdenum disulphide, \(\text{MoS}_2\) [26-27]. They went on to show that the process could be improved to give dispersions with higher concentrations of graphene by using longer ultrasonication times [19] or better controlled centrifugation [29]. Other improvements have been achieved by refining the exfoliation process such as increasing the mean lateral size of the graphene flakes [30] or by obtaining graphene dispersions in low boiling point solvents [31] that facilitates better deposition of individual graphene flakes on substrates.

As well as producing graphene by exfoliation of graphite there are a number of way in which it can be grown directly using “bottom-up” methods. In the surface science literature there are a number of reports, that date back more than 40 years, claiming the preparation and observation of thin graphitic layers on metallic substrates, and Wintterlin and Bocquet [32] have recently reviewed the literature upon the formation of graphene on metal surfaces. In addition, soon after the reports of the preparation of single graphene layers by mechanical cleavage, it was demonstrated that ultrathin epitaxial graphite films consisting of few layer graphene could be produced by thermal deposition on the (0001) surface of 6H-SiC [33].

An important breakthrough has been the use of CVD to grow graphene films with macroscopic dimensions on the surfaces of metals such as nickel [34] or copper [35] using methane/\(\text{H}_2\) mixtures. Thick graphite crystals, rather than graphene, usually form on foils in the case of nickel and this problem has been overcome by depositing
thin Ni layers of less than 300 nm on SiO$_2$/Si substrates [34]. In the case of copper, growth takes place upon Cu foils via a surface-catalyzed process and thin metal films do not have to be employed [35-37]. For both metals, it was found that the graphene films could be transferred to other substrates [38]. This process has now been scaled-up to a roll-to-roll production process in which the graphene is grown by CVD on copper-coated rolls. It can then be transferred to a thin polymer film backed with an adhesive layer to produce transparent conducting films [37, 39]. It has been found that such films have a low electrical sheet resistance and optical transmittance of the order of 97.4%. They are found to be predominantly covered with a monolayer graphene film but also have some bilayer and few layer islands.

Graphene nanoribbons can be produced by the unzipping of multi-walled carbon nanotubes. This can be done by an oxidative treatment in solution [40-41] or by an Ar plasma etching method upon nanotubes partially-embedded in a polymer substrate [42]. The approach has been extended recently to use small clusters of metals such Co or Ni as nanoscalpels that cut open nanotubes to create graphitic nanoribbons [43]. This is in fact a development of the use of these metal nanoparticles to undertake the controlled nanocutting of graphene [44-45]. The technique is capable of cutting graphene into pieces with well-defined shapes that can be used in a variety of applications including the fabrication of graphene devices.

1.1.2 Characterisation

A single atomic layer of graphene absorbs 2.3 ± 0.1 % of white light and its absorption is virtually independent of wavelength [46]. This means that it can be observed in an optical microscope at relatively low magnification, as shown in Figure 1.2. In fact, it is possible to distinguish between flakes of graphene with different numbers of atomic layers relatively easily in a transmission optical microscope [47]. Atomic force microscopy (AFM) was one of the first methods used to characterized graphene and it is still employed widely. Novoselov et al. [4] noted in their original study of graphene that AFM indicated that some of their graphene layers were only
0.4 nm thick. This is a signature of single-layer graphene since the interlayer spacing in graphite is around 0.335 nm and AFM is now used routinely for estimating the number of layers present in few-layer graphene samples [13]. X-ray diffraction is another technique that can be used to characterize few-layer graphenes. This is because graphite has a sharp 002 Bragg reflection at $2\theta \sim 26^\circ$ (using Cu Kα radiation of wavelength 0.154 nm). This becomes broadened as the number of layers decreases and it is possible to use the Scherrer formula to estimate the number of layers contributing to the 002 reflection for few-layer graphene from this peak broadening [13].

![Raman Spectra Graphene](image)

Figure 1.3 Raman spectra of graphene showing the difference in spectra between monolayer, bilayer and multilayer samples. [48]

Raman spectroscopy is a particularly useful technique to characterize graphene monolayers, bilayers and trilayers since, quite remarkably, Raman spectra can even be obtained from a single layer of carbon atoms. This is because the material undergoes very strong resonance Raman scattering [49]. Moreover, graphene samples with different numbers of layers show significant differences in their Raman spectra as can be seen in Figure 1.3. In the case of single layer graphene, the $G'$ (or 2D) Raman band is twice the intensity of the $G$ band whereas in the two-layer material the $G$ band is stronger than the 2D band. In addition, the 2D band is shifted to higher wavenumber
in the two-layer graphene and has a different shape, consisting of 4 separate bands due to the resonance effects in the electronic structure of the 2-layer material [49]. In fact it is possible to use Raman spectroscopy to distinguish between two separate single layers overlapping and a graphene bilayer in which the original Bernal crystallographic stacking is retained [50]. As the number of layers is increased the 2D band moves to higher wavenumber and becomes broader and more asymmetric in shape for more than around 5 layers very similar to the 2D band of graphite. It should also be noted that in the Raman spectra shown in Figure 1.3 the D band, which is normally found in different forms of graphitic carbon due the presence of defects, is not present indicating that the mechanically-exfoliated graphene used to obtain the spectra in Figure 1.3 has a very high degree of perfection [49]. More prominent D bands are found in samples of imperfect or damaged graphene such as some CVD material or in the vicinity of edges of small exfoliated fragments.

The atomic structure of graphene can be observed directly using transmission electron microscopy (TEM) [51-59]. It is found that both an image of the graphene lattice and well-defined electron diffraction patterns can be obtained from suspended graphene sheets in the TEM [52]. The sheets, however, are not exactly flat but have static ripples out of plane on a scale of the order of 1 nm [55]. It was also found that there was no tendency for the graphene sheets to scroll or fold in contradiction to one of the preconceptions of its behaviour [6]. Moreover, it was found that a sliver of graphene could extend nearly 10 μm from the edge of a metal TEM grid without any external support. This was taken as an indication that the graphene monolayers have a very high level of stiffness [53].

1.1.3 Mechanical properties

Lee et al. [60] undertook the direct determination of the mechanical properties of monolayer graphene through the nanoindentation of graphene membranes, suspended over holes of 1.0 - 1.5 μm in diameter on a silicon substrate, in an atomic force microscope (AFM). They isolated the monolayers through the use of optical
microscopy and identified them with Raman spectroscopy. They determined the variation of force with indentation depth and derived stress-strain curves with non-linear stress-strain behaviour by assuming that the graphene behaved mechanically as a 2D membrane of thickness 0.335 nm. The geometric centre of the graphene membrane was chosen manually for indentation test and their accuracy of positioning of the centre was estimated to be within 50 nm considering the thermal drift. The breaking stress is determined from the breaking force distribution. It was found that failure of the graphene took place by the bursting of the single molecular layer membrane at large displacements with failure initiating at the indentation point. The stress-strain curve for the graphene derived from the analysis of the indentation experiments is shown in Figure 1.4. It can be seen that the stress-strain curve becomes non-linear with increasing strain and that fracture occurs at a strain of well over 20%.

![Stress vs Strain Graph](image)

**Figure 1.4** Measured [60] and calculated [61] stress-strain curve for the deformation of a graphene monolayer.

Using density functional theory, Liu, Ming and Li [61] had earlier undertaken an *ab initio* calculation of the stress-strain curve of a graphene single layer. This is also plotted in Figure 1.4 and it can be seen that there is extremely good agreement between the theoretical analysis and the experimentally-derived curve. The value of Young’s modulus determined from the indentation experiment [60] is $1000 \pm 100$
GPa and this compares very well with the theoretical estimate [61] of 1050 GPa. It is also similar to the value of 1020 GPa determined many years ago for the Young’s modulus of bulk graphite [62]. In addition, the strength of the graphene monolayer was determined experimentally to be up to 130 ± 10 GPa. This is the order of $E/8$, where $E$ is the Young’s modulus, and so is close to the theoretically-predicted value of the strength of a defect-free material [63]. The theoretical failure stress can also be determined from the maximum stress in the calculated stress-strain curve in Figure 1.4. Liu, Ming and Li [61] found that the behaviour of the graphene at high-strains should differ slightly depending upon the crystallographic direction in which the graphene is deformed. They predicted the strength to be in the range 107 - 121 GPa, which is again in very good agreement with the range of values measured experimentally.

It was explained earlier that Raman spectroscopy is an extremely useful technique for the identification and characterization of different forms of graphene, and it is also a very good way of following the molecular deformation of graphene through observing stress-induced Raman band shifts. A number of high-performance materials, such as high-modulus polymer fibres [64], carbon fibres [65], and carbon nanotubes [66], also display stress-induced Raman band shifts and the experience gained from the study of these materials can be used in the study of graphene. In general, it is found that the rate of band shift per unit strain of such high-performance materials scales with their Young’s moduli [64]. For example, when carbon fibres are deformed in tension the G and 2D band positions shift approximately linearly with strain to lower wavenumber [65, 67]. It was found by Cooper, Young and Halsall [68] that the rate of shift for the 2D band per unit strain increased with increasing carbon fibre modulus. They were able to show that there was a linear dependence of the shift rate upon modulus, implying that there is a universal dependence of band shift upon stress for the 2D band in graphitic forms of carbon of -5 cm$^{-1}$/GPa [67]. Since both carbon nanotubes and graphene have well-defined 2D bands, then the Young’s modulus of these materials can also be estimated if it is assumed that the universal calibration for
carbon fibres can be used for the same band in all forms of carbon. Recently Frank et al. [68] have undertaken a similar study of the shift of the Raman G band for carbon fibres and were able to determine a universal calibration factor for use with the G-band of graphene.

Large stress-induced shifts of both the G and 2D Raman bands are found when graphene is subjected to deformation [48, 68-80] showing that significant bond stretching and lattice distortion takes place when the graphene is deformed. The ability of using Raman spectroscopy to probe the mechanical properties of graphene has recently been reviewed by Ferralis [81]. The simplest way of deforming the material is to deposit exfoliated graphene on a substrate which is then stretched or flexed in a Raman spectrometer. The behaviour is shown in Figure 1.5 for the deformation of a graphene monolayer on a beam of poly(methyl methacrylate) [82]. There is a large shift in the position of the 2D band with strain and the slope of the line is of the order of -60 ± 5 cm⁻¹/% strain. This slope corresponds to a Young’s modulus for a graphene monolayer of 1200 ± 100 GPa using the universal calibration of -5 cm⁻¹/GPa for carbon fibres [68]. This is similar to the values for monolayer graphene both measured directly [60] and calculated theoretically [52].

![Figure 1.5 Shift of the Raman 2D band with strain for a graphene monolayer. [82]](image-url)
Detailed analysis of the behaviour of the G and 2D bands during deformation shows that they can broaden and split, as well as shift position [71-72, 77, 79]. In fact, it is possible to use the splitting to determine the orientation of the graphene crystal lattice relative to the direction of straining. The shift rate is slightly different in different directions in the plane of the crystal but in many applications, such as strain measurement in graphene, the simple universal calibration can be employed [68].

1.2 Graphene Oxide

1.2.1 Preparation

Long before the recent upsurge of interest in graphene-based materials, considerable expertise had been developed in the preparation of graphite oxide which is made up of individual graphene oxide sheets. Over 150 years ago, in an attempt to determine the “atomic weight” of graphite, Brodie [83] first reported the preparation of graphite oxide, though the oxidation of graphite using potassium chlorate and fuming nitric acid. The graphite oxide produced was found to be highly-oxidised with a C/O/H ratio of around 2.2/1/0.8 [83] which is typical of material made by these chemical routes. The Brodie method was modified by Staudenmaier [84] and then refined by Hummers and Offeman [85] who found they could treat the graphite quicker and more safely by employing a water-free mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate. Ruoff and co-workers [86-88] have reviewed and summarized the current state-of-the-art in the preparation of graphite oxide.

The interlayer spacing of the graphene oxide sheets in graphite oxide is between 0.6 nm and 1.0 nm depending upon the relative humidity [86]. Its structure is similar to that of graphite which is made up of stacks of more closely-spaced graphene sheets, but an important difference is that graphite oxide can be readily exfoliated by sonication to produce colloidal suspensions of graphene oxide sheets using a range of different solvents [86-87]. The ability to scale up production to produce material in large quantities for applications such as in composites has led to the present upsurge
of interest in graphene oxide. The material that is produced directly from graphite oxide is, however, not particularly useful in that it is unstable thermally and a poor conductor of electricity.

![Graph showing Thermogravimetric analysis in air of as-produced graphene oxide (aGO, top) and the two components after base-washing; the black precipitate (bwGO, middle), and the remaining water soluble fraction (OD, bottom).](image)

The properties of graphene oxide can be improved greatly through reduction, either chemically or thermally, although it has not yet been found to be possible to reduce the material fully back to graphene. The use of hydrazine is one of the most popular methods of chemically-reducing graphene oxide [89-90] and sodium borohydride has also been employed [91]. This can lead to a significant reduction, by many orders of magnitude, in the electrical resistance of material made from chemically-reduced graphene oxide but the C/O ratio is still not much better than 6/1 [88]. Another method that has been used to reduce graphene oxide is thermal treatment and it is interesting to note that Brodie [83] found, in his original study, that heating of his graphite oxide led to a loss of mass and a significant increase in the C/O ratio. Upon heating, graphite oxide undergoes a significant mass loss above about 200 °C and,
unless it is in an inert atmosphere, a further loss of mass above 600 °C due to the burning of the carbon [92]. In contrast, there is no mass loss for the graphite powder until it is heated to over 700 °C. The pressure of CO₂ that is produced during the thermal reduction of graphite oxide also aids exfoliation by forcing the sheets apart, leading to the production of a high proportion of single graphene oxide monolayers [93-94]. Reasonable levels of electrical conduction are obtained for compacted sheets of the thermally-reduced material [87] and it is possible to employ CVD to heal some of the defects in reduced graphene oxide and so improve its conductivity significantly [95].

A recent study [96] has shown that graphene oxide, as produced by the Hummers method, is composed of functionalized graphene sheets decorated by strongly-bound oxidative debris, which acts as a surfactant to stabilize aqueous graphene oxide suspensions. This is similar to the way in which polycyclic aromatic acids are found to stabilize aqueous suspensions of oxidized multi-walled carbon nanotubes [97]. If a suspension of the as-produced graphene oxide (aGO) is treated with an aqueous solution of NaOH, a black aggregate separates out (base-washed, bwGO) that cannot be resuspended in water. When the supernatant liquid is reprotonated and dried a white powder is obtained which contains oxidative debris (OD). Thermogravimetric analysis (TGA) curves of the aGO, bwGO and OD are shown in Figure 1.6 [96]. The aGO shows an initial mass loss due to absorbed water, a mass loss at around 200 °C which had previously been explained to be due to the decomposition of functional groups, and a mass loss at around 600 °C attributable to sublimation or burning of the damaged graphitic regions [98]. In contrast, the TGA of bwGO shows a significantly-reduced mass loss at around 200 °C and complete mass loss at around 600 °C. Also a significant low-temperature mass loss at around 200 °C is seen for the OD but none at around 600 °C suggesting there are no graphitic regions in this fraction. Moreover, measurements [96] on 0.5 - 1 µm thick films indicated the bwGO is conducting, with a conductivity of order $10^0 - 10^1$ S m⁻¹ which is roughly five orders of magnitude more conducting than aGO, and only an order of magnitude less
than values reported for graphene oxide reduced by chemical or low-temperature thermal treatments [86].

1.2.2 Characterisation

There is considerable interest in the characterization of graphene oxide particularly in view of the desire to reduce it back to graphene and also in exploiting its potential as a template to undergo chemical reactions that could be used to produce functional groups to control interfaces in composites. The structures of both graphite oxide and graphene oxide have therefore been analysed in detail by employing a large number of experimental techniques.

Solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy was employed several years ago to probe the chemical structure of graphite oxide and hence also that for graphene oxide. The structure proposed using this technique [99-100] became the most well-known and widely-accepted model. It was suggested that graphene oxide sheets consist of aromatic ‘islands’ of variable size that have not been oxidised and are separated by a combination of aliphatic 6-membered rings containing, C–OH groups, epoxide groups and double bonds.

Using wide-angle X-ray diffraction, the sharp (002) Bragg reflection of graphite at $2\theta \sim 26^\circ$ is found to disappear during its transformation to graphite oxide and a new peak at $2\theta \sim 14^\circ$ appears that corresponds to a layer spacing of around 0.7 nm [94]. Following heat treatment, this new peak disappears as the material is exfoliated into single sheets of graphene oxide [94]. AFM one of the most direct methods of quantifying the degree of exfoliation to graphene oxide and minimum sheet thicknesses of 1 nm and 1.1 nm have been measured for materials produced by chemical [90] and thermal [94] exfoliation respectively. These values are higher than the layer spacing found by X-ray diffraction, but the determination of sheet thickness
for graphene oxide is complicated by issues such as adsorbed moisture or solvents, and the wrinkled sheets [10].

Figure 1.7 (a) TEM image of a single GO sheet on a lacey carbon support; a double fold is visible in the top right corner. (b) Selected-area diffraction pattern of the centre of the region shown in (a), the diffraction spots are labelled with Miller-Bravais indices. (c) Intensity profile through the diffraction spots labelled in (b). [92]

Figure 1.8 (a) C 1s XPS spectra of aGO and bwGO. (b) Raman spectra of aGO and bwGO obtained using a 633 nm laser excitation. [92]

High-resolution TEM has also been used to study the structure of both graphene oxide [90, 101-102]. The structure of graphene oxide is remarkably similar to that of graphene at low magnification and the electron diffraction patterns are virtually identical (Figure 1.7). This means that the sheets of graphene oxide are not completely amorphous, and that the structure has both short- and long-range order and there is also no order in the oxygen-containing functional groups [92]. In the case of
reduced graphene oxide [103], it is found that the structure consists of graphene islands of between 3 nm and 6 nm in size, surrounded by holes and defect clusters forming quasi-amorphous $sp^2$ bonded areas. This again was consistent with the generally-accepted structural model for the sheets of reduced graphene oxide.

X-ray photoelectron spectroscopy (XPS) is one of the most widely used techniques to assess the chemical nature of graphene oxide. The C$_{1s}$ XPS spectrum shows four different components in graphene oxide; the ring C and evidence for C–O, carbonyl C=O and carboxylate O–C=O bonds [87, 89]. These four components are still present when the material is reduced chemically or thermally but the intensity of the oxygen functionalities is greatly reduced. The C 1s XPS spectra of as-produced (aGO) and based-washed graphene oxide (bwGO) are given in Figure 1.8(a) [96]. The peak at around 284.5 eV is due to C bonded to C, whilst the higher binding energy components that are greatly reduced in the bwGO, are due primarily to C bonded to O. The XPS analysis enables the C/O ratio to be calculated which is 2/1 for the aGO and 4/1 for the bwGO. The degree of oxidative functionality is clearly reduced in the bwGO compared to the aGO, but still remains significant.

The Raman spectrum of graphene oxide is quite different from that of graphene [92, 96] as can be seen from Figure 1.8(b). The G band is considerably broadened in graphene oxide and there is also a strong D band that is not present in exfoliated graphene. The appearance of the D band is a clear indication of the presence of $sp^3$ bonding in the graphene oxide although other features of the spectrum indicate defects in the structure [104]. The relative intensities of the G and D bands can be used to follow structural changes that occur during the reduction of graphene oxide [89, 104]. Figure 1.8(b) shows Raman spectra in this region for aGO and bwGO using a 633 nm laser excitation [96]. The aGO material shows broad D and G peaks, with a ratio of integrated peak intensities of D/G = 1.9. The bwGO shows an almost identical response with D/G = 1.9. In contrast Raman spectra from the oxidative debris show no evidence of D or G peaks [96]. Together with the XPS and TEM results, this
confirms that the bwGO consists of oxidatively functionalized graphene-like sheets, similar to those envisaged in the original model [99-100], and suggests that the sheets themselves are not altered significantly by the base wash process.

Figure 1.9 The structure of graphene oxide produced by Hummers’ method and the modification to the structure produced base washing. [92]

The latest model proposed for the structure of graphene oxide is summarized in Figure 1.9 [96]. Graphene oxide produced using the Hummers method [85] is found to be a stable complex of oxidative debris adhering strongly to functionalized graphene-like sheets. Under basic conditions the oxidative debris is stripped from the graphene-like sheets. The base-washed graphene oxide is electrically conducting and cannot easily be resuspended in water.

1.2.3 Mechanical properties

The mechanical properties of graphene oxide are inferior to those of graphene due to the disruption of the structure through oxidation and the presence of $sp^3$ rather than $sp^2$ bonding. Dikin et al. [105] first investigated the mechanical properties of micron thick samples of graphene oxide paper and found it to have a stiffness of up to 40 GPa but a strength of only 120 MPa. Subsequent studies [88, 106-107] upon graphene oxide paper have not produced material with significantly better mechanical properties. The elastic deformation of monolayers of chemically-reduced graphene
oxide was investigated by Gomez-Navarro, Burghard and Kern [107], using a similar AFM indentation technique on a suspended film of material to that used previously for exfoliated graphene [60]. They suspended single layers of graphene oxide up to 1 \( \mu \text{m}^2 \) in size over a trench in a SiO\(_2\)/Si wafer and monitored force-displacement curves as the AFM tip was pushed into the graphene oxide film. Although there was considerable scatter in their data, they determined a Young’s modulus of 250 ± 150 GPa. In addition they noted that graphene oxide sheets consisting of 3 or more layers appeared to have a Young’s modulus an order of magnitude lower. Suk et al. [108] undertook a similar study of the AFM indentation graphene oxide that had not been reduced and measured a Young’s modulus of 208 ± 23 GPa when an effective thickness of the graphene of 0.7 nm was used.

A theoretical study to compare the stress-strain behavior of graphene and graphene oxide containing both epoxide and hydroxyl groups was undertaken by Paci, Belytschko, and Schatz [109]. They again predicted a modulus in excess of 1000 GPa for pristine graphene. Its structural modification, however, leads to the graphene oxide being predicted to have a modulus of only 750 GPa, for a sheet of graphene oxide of the same thickness as a graphene monolayer (\( \sim 0.34 \text{ nm} \)). The effective thickness of the graphene oxide is, in reality, at least twice this value and this leads to a predicted modulus of less than 400 GPa and so closer to the measured values [107-108]. In the theoretical paper [109] the effect of the oxidation of graphene upon its mechanical properties was calculated. Changes in chemical bonding due to oxidation were found to halve the strength compared to pure graphene (again assuming the same sheet thickness). The presence of holes, due to missing carbon atoms, was found to drop the strength even further. It was concluded that it may be the presence of these holes that limits the strength of graphene oxide.

Gao et al. [110] have recently undertaken a study of the mechanical properties of graphene oxide paper and also followed its deformation using Raman spectroscopy. In particular they shows that they were able to tailor the adhesion between the interfaces
in the paper and so improve the mechanical properties by introducing small molecules, such as glutaraldehyde and water molecules, into the gallery regions. The Young’s modulus of the graphene oxide paper was found to increase by a factor of 3 following this chemical treatment. Gao et al. [110] were also able to follow molecular deformation in the graphene oxide sheet from shifts of the Raman G band. They found that there was a significant increase in the rate of band shift per unit strain, again by a factor of about 3, following the chemical treatment. The rate of shift of the G’ component of the band for the treated material was found to be about \(-15 \text{ cm}^{-1}/\%\) strain which can be compared to \(-32 \text{ cm}^{-1}/\%\) strain for the same band in exfoliated graphene [72].

1.3 Bulk Nanocomposites

There are a number of reasons for developing graphene-based composites. The first and most obvious reason is that addition of a filler with such impressive mechanical properties would be expected to lead to a significant improvement in the mechanical properties of the host polymer matrix. It is also found, however, that changes to the mechanical properties are also accompanied by modification of functional properties such as electrical conductivity, thermal conductivity and barrier behaviour. This presentation will be concerned principally with mechanical properties but a brief discussion of the effect of graphene upon the functional properties of a polymer matrix is also included.

The preparation and properties of bulk graphene composites has been recently reviewed in detail by a number of researchers [10-11, 111-112]. The vast majority of work in this area has been undertaken using graphene oxide, often in the reduced form, although some research has also been undertaken upon composites containing graphite nanoplatelets (GNP). It is often difficult to tell the form of graphene that has been used just from the title of a paper, since the word “graphene” is often used to describe work upon graphene oxide, and careful reading of the original papers is often
necessary to determine exactly the type of graphene that was employed. It will be shown that the number of reports of research undertaken on bulk composites based upon fully-exfoliated graphene is currently limited.

Graphene oxide has many attractions over graphene since it is readily obtainable in large quantities, much easier to exfoliate and disperse in a polymer matrix, and has built-in functional groups available for bonding to form a strong interface with a polymer matrix. The individual nanoplatelets of graphene oxide are, however, often wrinkled and it was shown earlier that graphene oxide has significantly inferior mechanical properties to graphene. Graphene nanoplatelets have also been employed but are often poorly exfoliated and so do not lead to very high levels of reinforcement. In the following discussion care will be taken to distinguish between works upon the different forms of graphene.

1.3.1 Preparation

Obtaining a good distribution of the nano-reinforcement is one of the greatest challenges in the preparation of polymer-based nanocomposites [113] since it will be demonstrated that the properties of the nanocomposites can be compromised by a poor dispersion. Experience has shown that carbon nanotubes have a tendency to form bundles that can be difficult to break down and so much of the effort in the area of nanotube-based composites has focussed upon developing methods of obtaining good distributions of nanotubes using techniques such as chemical functionalization of the nanotubes [114]. In the case of graphene or graphene oxide, however, the formation of bundles is not an issue although there can still be a tendency for incomplete exfoliation to be obtained and restacking to occur.

Graphene oxide has one major advantages for processing in that it can be exfoliated in water and so nanocomposites can readily be prepared with the use of water-soluble polymers such as poly(vinyl alcohol) [115] and poly(ethylene oxide) [116]. Nanocomposites can also be prepared using solution-based methods with
non-water-soluble polymers such as poly(methyl methacrylate) [117] and polyurethanes [118] by modifying the graphene oxide chemically.

An attractive method of preparing graphene-based composites is in situ polymerisation of the polymer matrix although solvents are often employed to reduce the viscosity of the dispersions. For example, intercalative polymerisation of methyl methacrylate [119] and epoxy resins [120-121] has been achieved with graphene oxide to produce nanocomposites with enhanced properties. In situ polymerization has been employed to successfully produce polyethylene- [122] and polypropylene-matrix graphene oxide nanocomposites [123].

Melt blending offers a simple way of dispersing nanoparticles in a polymer matrix and it has been used to disperse thermally-reduced graphene oxide in a number of polymers that include polycarbonate [124] and poly(ethylene- 2,6-naphthalate) [125]. It has also been employed to disperse expanded graphite into a biodegradable polylatide [126]. Reasonable levels of dispersion can be obtained in these systems but the addition of the nanoparticles increases the viscosity of the polymer melt significantly and clearly makes processing more difficult. Solid-state shear dispersion, using a modified twin-screw extruder, has been employed as a simple method to produce nanocomposites of unmodified, as-received graphite dispersed in polypropylene [127]. Significant property improvements were reported although it was found by X-ray diffraction and electron microscopy that the composites contained graphite nanoplatelets ranging from a few to 10 nm thick and so containing up to 30 graphene layers, rather than individual graphene platelets.

1.3.2 Micromechanics of reinforcement

The reinforcement of polymers by rigid particles and the effect of particulate reinforcement upon the mechanical properties have been discussed in detail by Young and Lovell [128]. The Young’s modulus of particulate-reinforced polymers can be predicted relatively easily, although in practice only upper and lower bounds can be
determined rather than single values. To determine the Young’s modulus it is necessary to undertake the analysis in two distinct situations where the particles and matrix (and hence the nanocomposite) are subjected to either uniform strain or uniform stress.

For a particulate composite, in the case of uniform strain, it is found that the Young’s modulus $E_c$ of the composites is given by the rule of mixtures as

$$E_c = V_p E_p + V_m E_m$$

(1.1)

Or

$$\frac{E_c}{E_m} = V_p \frac{E_p}{E_m} + V_m$$

(1.2)

where $E_p$ is the Young’s modulus of the particles, $E_m$ is the Young’s modulus of the matrix and $V_p$ and $V_m$ are the volume fraction of particles and matrix respectively, within the composite (where $V_p + V_m = 1$).

The other situation that must be considered is the case of uniform stress where the Young’s modulus of the composite is given by

$$\frac{1}{E_c} = \frac{V_p}{E_p} + \frac{V_m}{E_m}$$

(1.3)

and this can be rearranged to give

$$\frac{E_c}{E_m} = \frac{E_p}{V_m E_p + V_p E_m}$$

(1.4)

It is found that these equations give very large differences in the prediction of the Young’s modulus of particulate composites, especially in cases where $E_p \gg E_m$, and they are normally taken as upper and lower bounds of the properties. There is normally a distribution of stress in the reinforcement in which case that the particles are subjected to neither uniform stress nor uniform strain. The Young’s modulus normally lies between the two predictions that can be considered to be upper (uniform strain) and lower (uniform stress) bounds of composite Young’s modulus.
Having such widely-separated bounds of modulus prediction has given rise to significant uncertainty about properties and over the years there have been a number of attempts to produce more appropriate predictions of the Young’s modulus of particulate reinforced composites, without having such widely-separated bounds [129-132]. Halpin and Tsai developed an approach based upon the self-consistent micromechanics method of Hill that enabled them to predict the elastic behaviour of a composite for a variety of both fibre and particulate geometries. This approach was employed by Halpin and Thomas [132] to predict the behaviour of ribbon-shaped reinforcements which is clearly relevant to graphene-based composites. Their theory predicts that in the case of an aligned reinforcement, the ratio of the Young’s modulus of the composite to that of the matrix is

\[
\frac{E_c}{E_m} = \frac{1 + \xi \eta V_p}{1 - \eta V_p} \tag{1.5}
\]

where the parameter, \( \eta \), is given by

\[
\eta = \frac{E_p}{E_m} - 1 + \frac{E_p}{E_m} \xi \tag{1.6}
\]

In this equation, the parameter \( \xi \) is a measure of reinforcement geometry that depends upon the loading conditions and it is a parameter that is essentially controlled by the aspect ratio of the reinforcement. The limiting values of \( \xi \) are \( \xi = 0 \) and \( \xi = \infty \) and for the prediction of the longitudinal modulus of reinforcement by a ribbon of length \( l \) and thickness \( t \), the value of \( \xi \) can be taken as \( 2l/t \) [129]. Equation (1.5) tends to the lower, uniform stress, bound (Equation 1.4) as \( \xi \to 0 \) and to the upper, uniform strain, bound (Equation 1.2) as the aspect ratio of the reinforcement increases and \( \xi \to \infty \). A number of other approaches have been employed to model the reinforcement by nanoparticles [130-131] but the Halpin-Tsai approach for aligned reinforcement [129], that produces relatively-simple equations, has been employed widely for the analysis of graphene-based nanocomposites. It will be used next in the assessment of the measured levels of reinforcement reported for graphene-based nanocomposites.
1.3.3 Mechanical properties

Figure 1.10 Mechanical properties of nanocomposites consisting of reduced graphene oxide in PVA at various loadings (volume %). (a) Stress-strain curves. (b) Tensile strength and elongation at break versus graphene loadings. [133]

The simplest way of assessing the reinforcement of polymers upon the addition of graphene is through stress-strain curves as shown in Figure 1.10 which shows results upon poly(vinyl alcohol) reinforced with reduced graphene oxide [133]. It can be seen that there is a large effect upon the stress-strain curve with a loading of only 0.3% by volume of reduced graphene oxide but the addition 10× more material (up to 3.0%) leads to a less spectacular effect upon properties. Both the Young’s modulus and tensile strength of the polymer are found to increase with the loading of reduced
graphene oxide but the elongation at break decreases. This behaviour is typical of many graphene/polymer systems of which there are a number of reports in the literature. For example, Song et al. investigated the stress-strain behaviour of polypropylene reinforced with reduced graphene oxide [134]. Again a significant improvement was found for a loading of only 0.1% by weight of reduced graphene oxide but the elongation at break then decreased with further loading and the tensile strength and Young’s modulus peaked at a loading of around 0.5-1.0% by weight of reduced graphene oxide. These two reports [133-134] are typical of many in the literature where the formulations are produced by weighing materials and so data are often given in terms of weight fraction. Most theories, however, are formulated in terms of filler volume fraction and so data are often converted into volume fractions. Since most polymers have a density of around 1000 kg/m$^3$ and graphene-based fillers have a density of about 2000 kg/m$^3$, for a given loading, the volume fraction will be approximately half the weight fraction. Hence the addition of 2% of filler by weight will give rise to a volume fraction of 1%.

The two reports [133-134] are also similar in that they refer to “graphene” in the title but careful reading reveals that they used reduced graphene oxide which was shown earlier to be quite different from graphene, with a different structure and mechanical properties. Coleman and coworkers [135] investigated the reinforcement of a polyurethane by pristine graphene (characterized by Raman spectroscopy) produced by solvent exfoliation and therefore not reduced graphene oxide. Figure 1.11 shows a series of stress-strain curves for different loadings of the graphene by weight. It can be seen that there is a large increase in the slope of the stress-strain curve (the Young’s modulus increases by a factor of around $10^2$ for their highest loadings) and the strain to failure decreases with graphene loading. They also found that for a given loading of graphene, the reinforcement effect decreased as the graphene flake size decreased [135]. Another aspect of their work is that they were looking at the reinforcement of flexible polyurethane with a Young’s modulus of only around 10
MPa. It will be shown that much higher levels of reinforcement are generally found with low-modulus polymers than with more rigid matrix materials.

![Stress–strain curves for nanocomposites consisting of solvent-exfoliated graphene in a polyurethane matrix with different loadings of graphene (weight %).](image)

Figure 1.11 Stress–strain curves for nanocomposites consisting of solvent-exfoliated graphene in a polyurethane matrix with different loadings of graphene (weight %). [135]

Direct evidence of stress transfer to a graphene-based reinforcement has recently been demonstrated by Gao et al. [110] who followed the deformation of graphene oxide paper with and without impregnation by glutaraldehyde. The monitored the deformation of the graphene oxide sheets from stress-induced shifts of the Raman G band. They found that during deformation of the graphene oxide paper, the G component of the band shifted by around -4.2 cm\(^{-1}\)/% strain but that this increase considerably up to -14.6 cm\(^{-1}\)/% strain upon treatment with glutaraldehyde which appears to greatly improve the interlayer adhesion. They then compared this behaviour with the shift rate with strain of -31.7 cm\(^{-1}\)/% strain for the Raman G band of monolayer graphene found by Mohiuddin et al. [72] and deduced that the stress transfer efficiency increased from \(\sim 0.13\) in the as-received graphene oxide paper to \(\sim 0.46\) in the glutaraldehyde-treated paper. They also reported an increase in the
macroscopic Young’s modulus of the graphene oxide paper from around 10 GPa to 30 GPa upon treatment with glutaraldehyde and went on to use the Raman bands shift data to model the mechanical properties of the paper, using the simple rule of mixtures. They showed that when they took into account the volume fraction of graphene oxide in the paper (∼0.3 in the as-received paper to ∼0.23 in the treated material), the stress transfer efficiency factors (∼0.13 for the as-received paper and ∼0.26 for the treated material) and the effective modulus of the graphene oxide (which they took as 400 GPa [107]), they were able to derive Young’s modulus values similar to the measured ones for both materials as long as they included a factor of the order of 0.6-0.8 to account for misalignment of the sheets (which they were unable to measure directly). It was explained earlier that the Young’s modulus of graphene oxide is probably lower than 400 GPa and so it may be possible to model the behaviour without the need to invoke sheet misalignment. It was shown earlier that stress transfer from a polymer matrix to graphene reinforcement can be demonstrated in model nanocomposites but it is clear that this approach of Gao et al. [110] points the way forward in allowing us to also correlate the bulk mechanical properties of graphene-based nanocomposites with stress-induced bands shifts, and hence deformation, of the reinforcement.

The classical way of assessing the level of reinforcement imparted upon a polymer matrix by a filler is to plot the ratio of the Young’s modulus of the composites to that of the matrix, $E_c/E_m$ against the volume fraction of filler particles, $V_p$ as shown in Figure 1.12. It can be seen that the upper and lower bounds given by Equation (1.2) and Equation (1.4) for uniform strain and uniform stress respectively are widely-spaced. Equation (1.5) gives the expected behaviour for a ribbon-shaped reinforcement but the form of this relationship depends upon both the aspect ratio $\xi$ and the ratio of the Young’s modulus of the filler to that of the matrix, $E_p/E_m$ through the parameter, $\eta$ (Equation 1.6). It is necessary therefore to make different plots for families of materials with different ratios of $E_p/E_m$ and values of $\xi$ in order to compare the behaviour of different systems.
Figure 1.12 Predicted and measured variation of $E_c/E_m$ with the volume fraction, $V_p$, of graphene-based filler particles for (a) rigid polymers and (b) elastomers.

The majority of the published research upon the mechanical properties of graphene-reinforced polymers is concerned with the reinforcement of either rigid polymers (both glassy and semi-crystalline) for which $E_p/E_m \sim 10^3$, taking the
Young’s modulus of graphene as around 1 TPa or elastomers for which \( E_p/E_m \sim 10^6 \), since most elastomers have a Young’s modulus of the order of 1 MPa. General plots for the two types of matrix materials with a series of lines for different values of \( \xi \) can therefore be produced. The values of \( E_p/E_m \) determined experimentally as a function of \( V_p \) for nanocomposites with either rigid [117, 119, 121, 124-125, 133-134, 136-149] or elastomeric [144, 146, 150-153] matrices are also given on these plots. Since some of the literature data were presented in terms of the weight fraction of filler, it has been necessary to convert this to volume fraction using the density of the filler and matrix. Where only weight fraction data are given in the original publication, a filler density of 2280 kg/m\(^3\) has been assumed for the data in Figure 1.12. This is by no means a complete review of the published data but it serves to give a general picture of the behaviour. There are also reports of the reinforcement of polyurethanes using functionalized graphene sheets [154-156]. These data are not included in the plots in Figure 1.12 as the Young’s modulus values of the polyurethane matrices tend to lie between those of rigid and elastomeric polymers.

It is instructive to examine the relationship between the experimental data and theoretical predictions. It would be expected that the parameter \( \xi (= 2l/t) \) would be of the order of at least 1000 in the case of fully-exfoliated graphene or graphene oxide and that if the particles were providing good reinforcement, the experimental data should therefore lie above the line for \( \xi = 1000 \). It can be seen that in the case of the rigid reinforcement (Figure 1.12 (a)) the data generally lie close to the line for \( \xi = 1000 \) only at very low volume fractions (< 0.1%) and then fall away in the range 1000 <\( \xi \) < 100 for volume fractions up to around 0.5%. Above volume fractions of 1% the data points lie in the region in for which 100 <\( \xi \) < 10. In the case of the fewer data available for elastomeric matrices it can be seen in Figure 1.12 (b) that the data are all in the range 1000 <\( \xi \) < 100. It appears therefore that, except at very low volume fractions, the level of reinforcement measured experimentally is less than what would be expected from the theoretical Young’s modulus value for graphene. There are a number of possible reasons why this might be the case:
1) Equation (1.5) and (1.6) are only strictly valid for aligned platelets and the predicted values of \( \frac{E_p}{E_m} \) will be lower in the case of randomly-oriented platelets [121, 157-158]. The waviness of the reinforcing flakes that is found particularly in the case of thermally-reduced graphite oxide and this will contribute to the further reduction of modulus [121, 143].

2) Most of the data in Figure 1.12 are for composites reinforced with graphene oxide rather than pristine graphene and it was shown earlier that defects and holes in the material will reduce the Young’s modulus of the reinforcement to around 250 GPa [107-108].

3) In many cases the length of the flakes is relatively short and reinforcing material is not completely exfoliated [125]. This will have the effect of making the appropriate value of \( \xi \) significantly less than 1000.

4) The dispersion of the reinforcement may be poor, particularly at higher volume fractions, leading to clustering. This is a similar problem to that encountered with nanotubes [113]. There may also be a tendency of the graphene platelets to re-aggregate.

5) The interface between the platelets and the matrix may not be particularly strong and this will lead to poor stress transfer. There may be some advantage of using graphene oxide, despite its lower Young’s modulus, since the presence of the functional groups on the surface of may help to provide a stronger interface with a polymer matrix than in the case of pristine graphene or graphite nanoplatelets. It has also been shown that an improvement in Young’s modulus of the nanocomposites can be obtained through the use of coupling agents [159].

Although the levels of reinforcement achieved so far in graphene-based composites have generally been disappointing more impressive mechanical are now being reported [118, 135] as a better understanding of the mechanisms of reinforcement [48,
82, 160] is being gained. It is clear, however, that there is considerable scope to overcome some of the issues listed above and produce nanocomposites with even better mechanical properties.

### 1.3.4 Functional properties

As well as having interesting and exciting mechanical properties the possibility of using graphene composites in functional applications is receiving rapidly increasing interest. For example, polymers can be made to be electrically conductive by the addition of graphene in a similar way to the addition of other nanofillers [161] such as carbon black [162-163] and carbon nanotubes [113, 164]. The conductivity of the polymer matrix may be increased by many orders of magnitude. The presence of such fillers can lead to percolation pathways through which the electrical charge can pass and this will occur if there is a good distribution of the material. It is possible, in fact, to use the conductivity of the nanocomposite to monitor the quality of the filler distribution. It has been demonstrated that it is possible to make a number of different polymers electrically conductive by the addition of graphite nanoplatelets [17-18] and different forms of graphene [118-119, 125, 127, 130-131, 143, 165-167]. An important factor that needs to be taken into account is the percolation threshold which is the amount of filler needed to render the polymer conductive and it depends strongly upon the shape and distribution of the individual filler particles. The percolation threshold has been found to be of the order of 0.1% by volume of chemically-reduced graphene oxide in polystyrene [89] and this is approaching the best values obtained for carbon nanotubes [164]. The thresholds for percolation of graphene in a number of different polymers in term of volume fraction of graphene have been reviewed by both Kim, Abdala and Macosko [10] and Potts et al. [112] it is found that they vary from 0.1% to more 2% depending upon the matrix polymer, form of graphene and processing methods employed. There is also considerable interest in making conductive polymer films as indium tin oxide replacement for touch-sensitive
screens using thin layers of graphene oxide where the conductivity is high enough to be useful but the film still has some transparency [168-169].

It is found that the addition of graphene to polymers can have a significant effect upon their thermal properties. Pristine graphene platelets have been found to have a very high thermal conductivity of around 3000 W/m K [170-171] compared with polymers such as epoxy resin that have a conductivity of only the order of 0.2 W/m K. The thermal conductivity of the graphene decreases, however, as the number of graphene layers is increased from 2 to 4 [172]. It has been found that the addition of graphene nanoplatelets to polymers can improve the thermal conductivity of the polymer [173] by a factor of over 3000% if particles with high aspect ratios (~200) are employed [174]. This enhancement is found to be superior to that found with nanotubes [175] although a synergistic effect has been reported with a mixture of single-walled nanotubes and graphene nanoplatelets out-performing composites made using the pure nanofillers [176]. Although significant increases in thermal conductivity can be achieved, it is not so spectacular as the increase in electrical conductivity that can be obtained, since there is less scope to do so as the thermal conductivity of the graphene is only 4 orders of magnitude higher than that of the polymer matrix, compared with a difference of more than 10 order of magnitude in the case of electrical conductivity.

Polymers generally have high thermal expansion coefficients and the addition of aligned graphene nanoplatelets to polypropylene has been shown to reduce the thermal expansion coefficient in two directions rather than one in the case of aligned fibres [177]. A similar reduction in the thermal expansion coefficient of an epoxy resin is obtained with the use of graphene oxide [120]. It is also found that the addition of graphene-based nanofillers to a polymer can increase thermal stability [178-179]. This effect has been attributed to the suppression of the mobility of polymer segments at the filler-polymer interface [178]. Even the addition graphene oxide, which is known to be thermally unstable (Figure 1.6), has been found to improve thermal stability in some cases [111, 151]. It has also been suggested [10]
that graphene-based polymer nanocomposites may have good flame-retardant properties based upon experience with nanotube-based nanocomposites [180].

Finally, when it was found that a monolayer graphene membrane is completely impermeable to common gases including helium [181] it was anticipated that graphene-based polymer nanocomposites should have good gas barrier properties. Kalaitzidou, Fukushima and Drzal [177] showed that the incorporation of appropriately-aligned graphite nanoplatelets into polypropylene increased the oxygen barrier of the material more efficiently than when other nanofiller particles were employed. The gas permeation data for a series of different polymer nanocomposites has been reviewed and summarised by Kim et al. [10]. Levels of reduction of the diffusion rate for a variety of common gases for loadings of around 1.5-2.2% graphite oxide or reduced graphite oxide in a number of different polymers are found to be in the range 30-90% [118, 125, 127, 143].
References


48. Gong L., Kinloch I.A., Young R.J., Riaz I., Jalil R., Novoselov K.S., 
Interfacial stress transfer in a graphene monolayer nanocomposite. Advanced 

49. Ferrari A.C., Meyer J.C., Scardaci V., Casiraghi C., Lazzeri M., Mauri F., 
Piscanec S., Jiang D., Novoselov K.S., Roth S., Geim A.K., Raman spectrum 
97(18):187401.

50. Poncharal P., Ayari A., Michel T., Sauvajol J.L., Raman spectra of 

51. Meyer J.C., Kisielowski C., Erni R., Rossell M.D., Crommie M.F., Zettl A., 
Direct imaging of lattice atoms and topological defects in graphene 

52. Meyer J.C., Geim A.K., Katsnelson M.I., Novoselov K.S., Booth T.J., Roth S., 

53. Booth T.J., Blake P., Nair R.R., Jiang D., Hill E.W., Bangert U., Bleloch A., 
Gass M., Novoselov K.S., Katsnelson M.I., Geim A.K., Macroscopic 
8(8):2442-2446.

3(11):676-681.

55. Bangert U., Gass M.H., Bleloch A.L., Nair R.R., Geim A.K., Manifestation of 
ripples in free-standing graphene in lattice images obtained in an 
aberration-corrected scanning transmission electron microscope. Physica 

56. Bangert U., Gass M.H., Bleloch A.L., Nair R.R., Eccles J., Nanotopography of 
206(9):2115-2119.


Chapter 1 Introduction


Chapter 1 Introduction


Chapter 2  Raman Spectroscopy

2.1 Introduction

Raman spectroscopy is a powerful technique for the investigation of structural and dynamic information on molecular level, particularly in carbon materials. It is based upon the Raman scattering which was first discovered by the Indian physicist Sir C. V. Raman in 1928 [1]. He found a phenomenon that, when a light impinges upon a transparent medium scattering occurs at different frequencies. These different light frequencies are termed as the “Raman scattering” and due to the interactions between the incident light and the molecules inducing interaction with the electron cloud and the bonds of that molecule. However, Raman scattering became a technique widely used in physical and chemical analysis only when high power lasers were introduced in the 1960s [2-3].

Raman spectroscopy has been proved to be an excellent non-destructive tool for the characterisation of carbon based materials such as diamond, fullerenes and carbon nanotubes. Recently it has been employed in the identification and characterisation of graphene. It has been demonstrated to measure and probe the intrinsic and mechanical properties of small carbon allotropes and their composites under different deformation conditions. In this chapter, the basic theory of Raman scattering and the characteristic Raman features of graphene are presented.

2.2 Classical theory of Raman Effect

In the classical theory of Raman effect, generally, the incident light could be regarded as an oscillating electric field. When a molecule is placed in such an electric field, the positive charged nucleus is attracted towards to the negative pole of the electric field while the electrons move to the opposite way. Therefore, as a result of this movement,
the molecular bond is distorted and further induces a distortion of the electron distribution [4]. The electric dipole moment, \( P \), is dependent on the magnitude of the electric field, \( E_{\text{ef}} \), and the molecular polarisability, \( \alpha \), which is defined as the distortion of the polarised molecule relating with the structure and composition of the material,

\[
P = \alpha E_{\text{ef}}
\]  
(2.1)

The electric field strength is fluctuating sinusoidally with time \( (t_o) \) with a frequency \( (v_o) \), and can be expressed by:

\[
E_{\text{ef}} = E_o \sin(2\pi v_o t_o)
\]  
(2.2)

where \( E_o \) is the vibration amplitude. Replacing \( E \) in Equation (2.1) with Equation (2.2), the dipole moment can be given by:

\[
P = \alpha E_o \sin(2\pi v_o t_o)
\]  
(2.3)

Furthermore, the molecule has internal motions such as vibration and rotation. Therefore the polarisability can be changed periodically. The relationship between intrinsic polarisability of a molecule, \( \alpha \), and a vibrational frequency, \( v_{\text{vib}} \), can be expressed as [5]:

\[
\alpha = \alpha_o + \kappa \sin(2\pi v_{\text{vib}} t_o)
\]  
(2.4)

where \( \alpha_o \) is the equilibrium polarisability and \( \kappa \) is the charge rate of polarisability corresponding with the internal vibration. Substituting Equation (2.4) into Equation (2.3) gives:

\[
P = \alpha_o E_o \sin(2\pi v_o t_o) + \frac{1}{2} \kappa E_o \left[ \cos(2\pi (v_o - v_{\text{vib}}) t_o) - \cos(2\pi (v_o + v_{\text{vib}}) t_o) \right]
\]  
(2.5)

As can be seen from the above equation, there are three components \( v_o \), \( v_o - v_{\text{vib}} \) and \( v + v_{\text{vib}} \) that constitute to the fluctuation of the electric dipole. The first term in Equation (2.5), predicts that a dipole will be induced at the same frequency as the excitation laser, which is Rayleigh scattering. The second term indicates that the photon will be scattered at a frequency of \( (v_o - v_{\text{vib}}) \) and \( (v_o + v_{\text{vib}}) \), which respectively corresponds to anti-Stokes and Stokes scattering. According to the second term, it is
clear that the change of polarisability with respect to the nuclear displacement is required in Raman scattering.

### 2.3 Quantum theory of the Raman Effect

The Raman effect can also be understood using quantum theory, which can elucidate the unexplained aspects of the classic theory such as Rayleigh and Raman resonance. Generally, Raman scattering is due to the interactions between the electrons of the molecules and the light, where the light can be recognized as a steam of photons when the incident beam irradiates a sample. As a result, the interaction between the electrons in the molecule and the incident photons causes both the elastic and inelastic scattering. Here, the collision with no energy change of between photon and molecule is termed to be elastic scattering. On the other hand, the inelastic scattering refers to the molecular energy change during the collision [6-7].

![Figure 2.1 Schematic diagram of Rayleigh, Stokes-Raman and anti-Stokes Raman scattering. [8]](image)

The incident light can be considered as a beam of photons, while focusing on a molecule or atoms, interacts and distorts the cloud of electrons around the nuclei. The photon energy of the incident laser, $E_i$, can be expressed by:

$$E_i = h\nu_i$$  \hspace{1cm} (2.6)

where $h$ is the Planck’s constant and $\nu_i$ is the frequent of the incident photons. According to the conservation-of-energy principle:
\[ E_i + E_s = E_1 + E_2 \]  \hspace{1cm} (2.7)

where \( E_s \) is the scattered photons energy, and \( E_1 \) and \( E_2 \) are the molecular energy levels before and after the impinging respectively. Rearranging Equation (2.6) and Equation (2.7) gives:

\[ \hbar v_s + E_i = \hbar v_s + E_2 \]  \hspace{1cm} (2.8)

where \( v_s \) is the frequency of the scattered photons. Therefore, the frequency discrepancy between incident photons and scattered photons, \( \Delta v \), can be obtained as follow:

\[ \Delta v = v_i - v_s = \frac{E_2 - E_1}{\hbar} \]  \hspace{1cm} (2.9)

\( \Delta v \) depends on the value of \( E_1 \) and \( E_2 \). Thus it could be zero, positive and negative which correspond to the Rayleigh, Raman Stokes and Raman anti-Stokes scattering, respectively. Figure 2.1 shows these Raman scattering processes in the form of electronic transitions. A molecule is excited by the incident photon from the ground state to a virtual state. The molecule then relaxes and correspondingly emits a photon. The emitted photon returns to a certain vibrational state. Therefore, the variance between the original state and the final vibrational state leads to a shift in the emitted photon’s frequency away from the excitation frequency. In the case where the molecular energy of the new state is higher than the initial state, and then the emitted photon will be shifted to a lower frequency, which is called the Stokes shift or Stokes scattering. If the molecular energy of the final vibrational state is lower than the initial state, then the emitted photon will be shifted to a higher frequency, which is called the anti-Stokes shift or anti-Stokes scattering. A large amount of scattering process is Rayleigh scattering in which the molecule final vibrational state equal to the original state. It is intuitive to understand that Rayleigh scattering is an elastic scattering process and can be contrasted to the Stokes scattering and anti-Stokes scattering which are inelastic scattering processes undergoing the energy shift between the initial and final state. Generally, it should be noted that the intensity of anti-Stokes scattering is lower than that of Stokes scattering since the Boltzmann distribution
theory means that an electron at ambient temperature is more likely to be in a low energy state.

2.4 Raman spectroscopy of Graphene

Raman spectroscopy has been employed to characterise the structure and deformation of graphene [9]. Furthermore, it is a reliable technique to distinguish between monolayer, bilayer and trilayer graphene from multilayer graphene and graphite. Graphene monolayers have characteristic spectra in which the 2D band can be fitted with a single peak, whereas the 2D band in bilayers is made up of 4 components, which is a consequence of the difference between the electronic structures of the two types of materials. In comparison, trilayer graphene has a broader 2D band which consists of 15 peaks [10]. However, these peaks mostly overlap with each other. Hence, in order to simplify the analysis, the 2D band of the trilayer graphene is generally fitted by six Lorentzian peaks. Figure 2.2 shows the typical Raman spectra from an isolated monolayer graphene and graphite obtained using a 514 nm laser.

![Raman spectra for bulk graphite and monolayer graphene at 514 nm. (a) shows the G band (1580 cm$^{-1}$) and 2D band (2700 cm$^{-1}$) features and were measured on the SiO$_2$/Si substrate. (b) The D band structure for graphite and monolayer. [9]](image)
2.4.1 D band

The D band is the result of the disorder or defect-induced double-resonance processes widely involved in graphite and carbon nanotubes. It is associated with the second-order process, involving one iTO phonon and one defect, which is observed at around 1360 cm\(^{-1}\) [9-11]. Normally \(sp^2\) carbons have high symmetry, and any breaking of the symmetry can be observed sensitively by Raman spectroscopy through the appearance of a D band [12-14]. Therefore, the intensity of the D band is proportional to the amount of disorder in the sample, and the ratio of \(I(D)\) and \(I(G)\) has been employed to quantify disorder [10, 15]. It should however be noted that monolayer graphene is a perfect crystal that no defects exist in the centre of the flake. So it is hard to see any D band in the graphene Raman spectrum but the disorder band can still be found around the boundary of the graphene crystal as shown in Figure 2.2(b).

The activation mechanism of the D band is identified by double resonance [9, 16-17] which illustrates that the iTO phonon is strongly dispersive with an excitation energy according to the Kohn Anomaly at \(K\) (Dirac point) [18]. Three steps for the Double Resonance (DR) process of the D band: (i) a laser induced excitation of an electron/hole pair; (ii) electron-defect scattering with an exchanged momentum; (iii) electron/hole recombination. The DR condition is satisfied if the energy is conserved in all these transitions [16].

Figure 2.3 Schematic process for the Double Resonance for (a) D band and (b) D’ band of graphene. [10, 17]
Figure 2.3(a) shows the double resonance schematic process for the D band of the graphene. The intensity of the D band is strongly dependent on the sample quality. Mechanically-cleaved graphene has a perfect crystal structure so that it is rare to detect defects anywhere in the flake except at the edges. The D band is dispersive so that the Raman frequency changes with the excitation laser energy with a slope of $53 \text{ cm}^{-1} \text{eV}^{-1}$ [19]. The D band gives rise to the D’ peak beside the G band (1620 cm$^{-1}$). The D’ band also has a weak dispersive behaviour with the slope about $10 \text{ cm}^{-1} \text{eV}^{-1}$ [19].

The mechanism of dispersive behaviour of D’ band is analogous to the D band that can be understood as the double resonance Raman scattering [16, 20]. In the other words, the D band corresponds with the so-called “inter-valley” DR process while the D’ band is “intra-valley” as shown in Figure 2.3(b) [10-11, 21]. Both these DR processes refer to the movement of phonons near the $\Gamma$ and K (or K’) points in the Brillouin zone. In the case of Inter-valley DR process, the photoexcited electron scatters between states in inequivalent carrier pocket where the intra-valley DR process is between electronic states within the same carrier pocket [10, 22-23].

![Figure 2.3(a)](image1)

![Figure 2.3(b)](image2)

Figure 2.4 Polar plots for the D band scattering intensity versus polarisation angle $\theta$. The incident and scattered light were parallel to each other [21]. (b) Dependence of the D band intensity on the polarisation direction of the incident and scattered light [24].
Figure 2.5 (a) Schematic illustration of the typical atomic structure of the graphene edges. (b) First Brillouin zone of Graphene, showing that the inter-valley Double Resonance scattering of the armchair edges satisfies the conservation of momentum but that of the zigzag edges does not. [10, 19]

Recently, several groups [21-22, 24] have reported that the D band intensity is dependent of the polarisation of the incident laser beam and the edge direction (zigzag and armchair). It has been reported that the intensity of D band is proportional to $\cos^4\theta$, where $\theta$ is the angle between the incident polarisation and the average edge direction. Figure 2.4(a) illustrates in polar plots of Raman scattering intensity against the angle $\theta$ of the incident light relative to the nearby edge. The dotted line, fitted by a $\cos^4\theta$ function, sketches out that the D band scattering is the result of a product of two $\cos^2\theta$ factors, one for photon absorption and the other for photon emission [21]. Figure 2.4(b) shows the dependence of the D band intensity on the polarisation direction of the incident and scattered light. The configuration VV means the incident light and scattered light are parallel to each other, and VH means the incident light and scattered light perpendicular with each other. The armchair edges structure exhibits a distinct D band while the zigzag edges have no D band. Figure 2.5(a) shows the structure of a graphene edge and (b) illustrates the inter-valley double resonance processes for armchair and zigzag edges respectively. As has been mentioned above, the existence of a D band should satisfy the double resonance condition that the phonon vector $\mathbf{q}$ is scattered from K to K’ in the Brillouin zone, consequently, in order to conserve momentum, a phonon with wavevector $-\mathbf{q}$ scatters out when the
electron transfers back from K’ to K. As shown in Figure 2.5(a), $d_a$ and $d_z$ stand for the wavevectors of armchair and zigzag edges, which are perpendicular to their edge lines. It can be seen that the armchair vector ($d_a$) is responsible for the inter-valley double resonance process between the K and K’ points. On the other hand, however, the zigzag vector ($d_z$) cannot go back to K point due to it does not have enough momentum. As a result, only the armchair edges not zigzag edges gives rise to the D band in the graphene Raman spectra. Moreover, the D’ band is expected to be independent of the edge structure since it is due to the intra-valley double resonance process that the vector connects the same K point which satisfies the momentum conservation for both armchair and zigzag edges [24].

![Figure 2.6 Raman D bands (edge excitation) for various numbers of layers of graphene. [21]](image)

In addition, the D band profile also depends on the number of layers of the graphene. As can been clearly seen from Figure 2.6, monolayer graphene exhibits a narrow and symmetry peak which can be fit by one Lorentzian peak with the FHWM of 14 cm$^{-1}$. In comparison, the bilayer graphene gives a more complex structure D band and Gupta et al. fitted this band to four Lorentzian components [21], which is quite similar in the case of the 2D band in bilayer graphene and will be discussed in the subsequent
parts [9]. As the thickness increases, the D band lineshape changed dramatically for very thin graphene flakes (less than three layers). Nevertheless, in the case of graphene flakes with more than five layers, it is difficult to distinguish the D band profile in counting the number of layers. With the increase of thickness, the appearance of the D band for graphene approaches that of the graphite.

### 2.4.2 G band

![Figure 2.7 Schematic diagrams for Raman active $E_{2g}$ mode: (a) LO phonon mode, (b) iTO phonon mode [25] and (c) illustrates the first-order G band process.](image)

The G band originates from the doubly degenerate Raman active optical mode ($E_{2g}$ symmetry) at the Brillouin zone centre which is located at around 1580 cm$^{-1}$ [10, 14].

![Figure 2.8 (a) G band Raman spectra under various applied uniaxial strain showing the splitting phenomenon. (b) The $G^+$ and $G^-$ subbands positions are plotted as a function of applied uniaxial strain [26].](image)
It exists in $sp^2$ carbon system in which the carbon atoms move or vibrate in the graphene plane as shown in Figure 2.7. Two phonons, the optical in-plane transverse phonon (iTO) and the longitudinal optical phonon (LO), are responsible for the G band. Both the iTO and LO phonons have the same frequency at the Brillouin zone centre. The G band is a first order Raman scattering process in graphene.

Generally, the iTO and LO phonon frequencies are mixed with each other. However, under applied strain, these two phonon frequencies split into two bands and the gap of splitting increases with rising strain [10, 15]. The applied strain makes the bond lengths and the angle between C-C bonds become distorted. The symmetry of the hexagonal lattice is thus broken. Such a symmetry-breaking process causes the splitting of the G band into clearly G$^-$ and G$^+$ sub-bands as shown in Figure 2.8 (a) which correspond to the LO and iTO phonon frequencies [26-27]. The wavenumber of these two subbands decreases with the applied tensile strain increases as shown in Figure 2.8 (b) [26].

The frequencies $\omega_{G^+}$ and $\omega_{G^-}$ for the G$^+$ and G$^-$ subbands are given by [26]

$$\omega_{G^+} = -\omega_0 \gamma (\varepsilon_{ll} + \varepsilon_{tt}) + \frac{1}{2} \beta \omega_b (\varepsilon_{ll} - \varepsilon_{tt})$$  \hspace{1cm} (2.10)

$$\omega_{G^-} = -\omega_0 \gamma (\varepsilon_{ll} + \varepsilon_{tt}) - \frac{1}{2} \beta \omega_b (\varepsilon_{ll} - \varepsilon_{tt})$$  \hspace{1cm} (2.11)

where $\omega_0$ is the G band Raman frequency at zero strain, $\gamma$ is the Grüneisen parameter for the doubly degenerate in-plane Raman active $E_{2g}$ phonon, $\varepsilon_{ll}$ and $\varepsilon_{tt}$ are the graphene strains at longitudinal and transverse direction [28], $\beta$ is the shear deformation potential coefficient [29-30]. In the case of uniaxial strain, $\varepsilon_{ll}$ and $\varepsilon_{tt}$ are related by the Poisson’s ratio $\nu$ that $\varepsilon_{ll}=\varepsilon$ and $\varepsilon_{tt}=-\nu \varepsilon$. Therefore, Equation (2.10) and (2.11) are rearranged to become:

$$\omega_{G^+} = -\omega_0 \gamma (1-\nu) \varepsilon + \frac{1}{2} \beta \omega_b (1+\nu) \varepsilon$$  \hspace{1cm} (2.12)

$$\omega_{G^-} = -\omega_0 \gamma (1-\nu) \varepsilon - \frac{1}{2} \beta \omega_b (1+\nu) \varepsilon$$  \hspace{1cm} (2.13)

It should be noted that in the case of free standing graphene, the Poisson’s ratio is the graphene in-plane Poisson’s ratio. However, in the case of graphene deformation on
certain substrates, the strain is transferred from the matrix to the graphene, so that the matrix Poisson’s ratio can be used.

The experimental Raman G band splitting and the shift rates for $G^+$ and $G^-$ sub-bands, can be used to predict the orientation of free standing graphene under uniaxial strain from the measured parameters and the graphene in-plane Poisson’s ratio $\sim 0.13$ [31]:

$$\gamma = -\frac{\omega_{G^+} + \omega_{G^-}}{2\omega_0(1-\nu)e}$$

$$\beta = -\frac{\omega_{G^+} - \omega_{G^-}}{2\omega_0(1+\nu)e}$$

Figure 2.9 (a) Polar plot of the fitted $G^+$ and $G^-$ subbands as a function of the angle among the incident light, scattered light and the strain axis angle to the zigzag direction of graphene. (b) Schematic diagrams for the angles between strain axes, incident light and scattered light in the same panel. The $x$ axis is parallel to the zigzag direction of graphene [26].

One of the other significant applications of the shift and splitting behaviour of the G band is to evaluate the crystallographic orientation of the graphene [26-27]. Mohiuddin et al. [26] measured the splitting of G band with an analyser for the scattered light parallel to the strain direction and rotated the incident polarisation light around $360^\circ$, as shown in Figure 2.9 (a). The black and red solid lines are the fitted lines to $I_{G^-} \propto \sin^2(\theta + 34^\circ)$ and $I_{G^+} \propto \cos^2(\theta + 34^\circ)$. 

91
The valuation of the intensity of $G^+$ and $G^-$ bands were determined by [26-27]:

$$I_{G^+} \propto \cos^2(\theta_i + \theta_o + 3\phi)$$  \hspace{1cm} (2.16)

$$I_{G^-} \propto \sin^2(\theta_i + \theta_o + 3\phi)$$  \hspace{1cm} (2.17)

where $\theta_i$ and $\theta_o$ are the incident light and scattered light relative to the strain axis, and $\phi$ denotes the graphene crystal orientation (based on the zigzag direction) to the strain direction. It can be seen that the polarisation of the Raman scattering light is determined by the angle between the strain axis and the graphene crystal axis. Therefore, the investigation on the polarisation dependence of the Raman spectrum gives an effective approach to evaluate the orientation of the graphene flake.

### 2.4.3 2D band

The 2D band is the second order two-phonon process generally located at around 2680 cm$^{-1}$ using a 2.41 eV excited laser. As can be seen from Figure 2.2 (a), the bulk graphite has a two-component 2D peak which are defined as 2D$_1$ and 2D$_2$ or (2D$^+$ and 2D$^-$) [32-33]. The intensity of graphite 2D band is roughly half that of the G band. However, the 2D band in a monolayer graphene is approximately 2 to 4 times more intense than that of the G band. This difference in graphene has been attributed to a triple resonance mechanism by Malard et al.[10]. It should be noted that the 2D band lineshape, position and linewidth shift as the number of the graphene flakes changes [9]. Historically, the 2D band was also named the G’ band [32], the G’ band however is nothing to do with the G band and is essentially an overtone of the D band. Since the frequency is approximately twice the D band, it has been named as 2D band [9].

As discussed in Section 2.4.1, both the D and 2D bands are second-order Raman scattering processes where the D band is due to one-elastic and one-inelastic scattering processes while the 2D band consists of two inelastic scattering processes. In the case of Bernal stacked bilayer graphene, the 2D band has a much broader structure that consists of four components as shown in Figure 2.10. These four components are named as 2D$_{1B}$, 2D$_{1A}$, 2D$_{2A}$ and 2D$_{2B}$, two of which, 2D$_{1A}$ and 2D$_{2A}$, have higher intensity than the other two [9].
2.4.3.1 Double Resonance process of the 2D band

The band structure in graphene has no energy gap so that the valence band and conduction band are linear dispersion near the Fermi level. When a photon is incident on a monolayer graphene, an electron from the valence band is excited to the conduction band vertically with the wave vector \( k \) satisfying the laser energy, \( E_{\text{Laser}} \),

\[
E_{\text{Laser}} = E_{\text{cb}}(k) - E_{\text{vb}}(k)
\]  

(2.18)

where \( E_{\text{cb}} \) and \( E_{\text{vb}} \) are the energy of conductive band and valence band. The electron on the conductive band is then scattered by emitting a phonon with an exchanged momentum \( q \) to a state at \( k+q \). In the third step, the electron is scattered back to \( k \) state with an emitted phonon \(-q\). Finally the electron is recombined with a hole at the valence band. So that it is clearly that the phonon process will be resonant when there is a phonon in the vibrational structure of graphene with a wave vector \( q \) and phonon energy \( E_q \) inducing the phonon with momentum \( q \) connecting two conduction electronic states at the K and K’ points in the Brillouin Zone [9-10, 15, 19] as shown in Figure 2.11.
For bilayer graphene, the special electronic structure consists of two conduction and valence bands as shown in Figure 2.12. The upper and lower valence band are labelled as $\pi_1$ and $\pi_2$ whereas the upper and lower conduction band are labelled $\pi^*$ and $\pi^*_1$.

Figure 2.11 Schematic diagram for the inter-valley DR process of monolayer graphene. [10]

Figure 2.12 Schematic diagram shows the electron dispersion of bilayer graphene near the Dirac K and K’ points. The four DR processes are indicated which correspond with the four sub-peaks. [34]

In process $P_{11}$ shown in Figure 2.12 (a), an electron with a wave vector $k_1$ is resonantly excited from the valence $\pi_1$ to the conduction band $\pi^*$ by the absorption of a phonon with the energy $E_{\text{Laser}}$. The electron is then scattered to the $k'_1$ state by
emitting a phonon with the momentum $q_{11}$ and energy $E_{p11}$. Afterwards, the electron is scattered back to the state $k_1$ by emitting a second phonon and it is recombined with a hole exciting a phonon with the energy $E_3 = E_1 - 2E_{p11}$. The phonon wave vector was measured from the Dirac $K$ point along the $KM$ direction so that $q_{11} = k_1 + k'_1$. Similarly, Figure 2.12 (b), (c) and (d) illustrate the DR process of $P_{22}$, $P_{12}$ and $P_{21}$, respectively. The energies of the associated phonon are $E_{p22}^{22}$, $E_{p12}^{12}$ and $E_{p21}^{21}$, and the phonons are $q_{22} = k_2 + k'_2$, $q_{12} = k_1 + k'_2$ and $q_{21} = k_2 + k'_1$, respectively [34]. Since the 2D band DR Raman scattering involves two phonons of the iTO branch [19, 35] and the energy of iTO phonon along KM direction increases with increasing the wave vector $q$, the highest frequency component $2D_{2B}$ is associated with the $P_{11}$ process which has the largest wave vector $q_{11}$. Clearly, the $P_{22}$ process is associated with the smallest phonon wave vector $q_{22}$ resulting in the lowest frequency component $2D_{1B}$. The two dominant intensity components $2D_{1A}$ and $2D_{2A}$ are associated with the $P_{21}$ and $P_{12}$ processes.

2.4.3.2 2D band dispersive behaviour

In order to satisfy the DR condition, it is expected that the change of laser energy will also cause the wave vector $q$ and the phonon energy $E_q$ to change. Figure 2.13(a) shows the Raman spectra for the 2D bands with different laser excitation energies. There is another called $G^*$ band, but due to its weak intensity, it will not be discussed further. Figure 2.13(b) shows the 2D and $G^*$ bands frequencies as a function of the laser energy for monolayer graphene and graphite. The DR 2D band of the monolayer exhibits a highly dispersive behaviour with the slope of 88 cm$^{-1}$/eV.
Figure 2.13 (a) Raman spectra of 2D band and G* of a monolayer graphene for various laser excitation energies. (b) The 2D band position dependence of laser energy. The circles correspond to the graphene and the squares correspond to turbostratic graphite [36].

In the case of bilayer graphene, the profile of the 2D band was shown in Figure 2.10. Figure 2.14 shows the laser energy dependence of the positions of the four peaks that comprise the 2D band for bilayer graphene.

Figure 2.14 The position of four components of the bilayer graphene 2D band as a function of the laser energy. [34]
2.4.3.3 The dependence of 2D band on the number of layers

Since the 2D band of graphene behaves dispersively, it can be employed to identify the number of layer of graphene. It should be noted that, this method is only valid when the graphene has an AB stacking order. Figure 2.15 shows the two types of bilayer graphene lattices for AB stacking and non-AB stacking structure [37]. AB stacking, also termed Bernal stacking, the hexagonal networks of individual graphene layers in the direction of perpendicular to the plane are stacked such that the vacant centres of the hexagons on one layer have carbon atoms on the hexagonal corner sites on the two adjacent graphene layers.

![Figure 2.15 The real space top-view for bilayer graphene crystal lattices with (a) AB stacking and (b) non-AB stacking. [37]](image)

Figure 2.16 The 2D Raman band obtained using a 2.41 eV laser energy for (a) monolayer, (b) bilayer, (c) trilayer, (d) four-layer and (e) HOPG [10] and (f) the statistical data of FWHM with respect to the different thickness graphene. [37]
Basically, the number of layers can be "counted" from the line shape and position of the 2D band. Figure 2.16(a)-(d) show the 2D peaks for different numbers of graphene and (e) is the typical HOPG 2D band. The 2D band for monolayer graphene gives a single Lorentzian peak that is located at around 2680 cm\(^{-1}\), and the distinct feature is that the 2D band has a much higher intensity than that of the G band. In terms of bilayer graphene, the 2D band becomes complex and has a broader peak. This broad peak can be fitted theoretically with four Lorentzian peaks as described in Section 2.4.3.1. Turning to the trilayer graphene, in the structure of lattice, there are six carbon atoms in the unit cell. Considering the DR process, Malard \textit{et al.} [38] have modelled the possibility that 15 different electron transitions occurs between the three layers. However, the transition energies among these fifteen processes are close to each other making it hard to distinguish the peaks one by one in a trilayer graphene 2D peak. Most of the subbands are overlapped, and in order to explicitly expound the feature of the trilayer, the 2D peak is generally fitted to six Lorentzian peaks with the FWHM of approximately 24 cm\(^{-1}\) as shown in Figure 2.16(c). The situation becomes more complex when the number of layers is more than 3. For example, four-layer graphene exhibits a much broader 2D band. The corresponding transitions of electron-hole pairs and phonon scattering processes accordingly increase with an increasing number of layers. Therefore, more resonance processes contribute to the 2D band of four-layer graphene and give rise to an even broader peak. With further increase of the number of layers, the electronic structure reveals stepwise variations and eventually approaches the appearance of graphite [39-41]. The graphite 2D band feature illustrated in Figure 2.16(e) is simply separated into a two-peak structure. For graphene with more than four layers, Raman spectroscopy is difficult to use to identify the exact thickness due to the appearance of the 2D band approaching that of graphite.

It is interesting that the FWHM of the 2D band for the various number of graphene layers differs as shown in Figure 2.16(f). Hao \textit{et al.}, [37] statistically analysed the width of the 2D band with different number layers that mono-, bi-, tri-,four-, and
five-layer graphene range the FWHM to be around 27.5 cm\(^{-1}\), 52 cm\(^{-1}\), 52.6 cm\(^{-1}\), 63.1 cm\(^{-1}\) and 66.1 cm\(^{-1}\), respectively. Moreover, the FWHM range for individual thicknesses of graphene do not superimpose and can be distinguished clearly from the plot in Figure 2.16(f). Consequently, the FWHM of 2D band provides another reliable approach to identify the number of graphene layers.

![Figure 2.17](image)

Figure 2.17 2D Raman bands of mono-, bi-, tri-, five-, and six-Bernal stacked layers (blue) and when folded (red) [42]. (b) Raman spectroscopy for CVD grown bilayer graphene, few layer graphene and graphite [43].

On the other hand, for non-AB stacked graphene, it has been observed that the electronic properties are different to AB stacking graphene [44]. It has been known for decades that the 2D band is very sensitive to the stacking order [45-46]. Thirty years ago, Nemanich and Solin observed that the 2D band shape change from one peak to two peaks from polycrystalline graphite and crystalline graphite, respectively [33, 47]. They attributed this phenomenon to the stacking order. Figure 2.17 (a) shows
the 2D band Raman features for graphene with different number of layers both unfolded and folded over on a substrate. The folded graphene does not change the band shape significantly particular in monolayer and bilayer but the 2D band shifts to higher frequency. Furthermore, CVD grown graphene shows a similar phenomenon as the folding graphene owing to the stacking of the layers is often not being AB Bernal stacked [43, 48]. Therefore, the using of 2D band to identify the thickness is restricted to the AB Bernal stacked graphene only.

2.4.3.4 Strain-induced shifts of the 2D band

Several methods have been adopted to apply strain to the graphene. One is to deposit graphene on a substrate which can be chemical functionalised [49] and piezo positioners treated [50]. Second method is to use the difference of thermal expansion coefficients of the substrate and graphene to induce strain by thermal processes [51-52]. A third common method is to couple the graphene onto a flexible substrate such as PDMS [27, 53], PMMA [26, 54] and PET [55] and to stretch or bend directly. Rouxinol et al. developed a method that fixed a free stranding multilayer with metal contacting on both sides to apply an electric field on the metal electrodes to induce strain [56].

Figure 2.18 (a) The 2D band of monolayer graphene unstrained, at 0.78% strain and with strain released. (b) The 2D band position as a function of applied strain for monolayer and trilayer graphene [55].
Ni et al. [55] deposited graphene onto the flexible PET film and applied the tensile strain up to ~0.8% in uniaxial direction. They found the 2D band shifted to lower frequency linearly the unaxial strain was applied, with the slope of ~-27.8 cm$^{-1}$/%, which is rather close to the value obtained by Huang et al. [27] (~-21 cm$^{-1}$/%). Figure 2.18 (a) shows the 2D bands at different states and (b) illustrates the shift rate for the monolayer and trilayer under uniaxial strain. They fitted the 2D band of trilayer graphene with a single peak and found the slope is approximately close to monolayer ~ -21.9 cm$^{-1}$/%, although generally the trilayer has a broader 2D peak. However, the 2D band slopes of graphene monolayer from Mohiuddin et al. and Tsoukleri et al. are about twice this value at ~-64 cm$^{-1}$/% and ~-59 cm$^{-1}$/% [26, 57]. The variation of slope values from different groups may be attributed to three factors: one is the structure of the sample and the others might be the difference of the substrate, and the final reason is that the topology of the sample surface is unsmooth. In most of the relevant papers, they deposit the graphene on a beam or film directly without any coating. Therefore, it might be a problem that when stretching or bending the sample, the stress cannot be transferred to the graphene efficiently, causing the small slope value. On the other hand, the material nature may play a significant role in which PDMS, PET and PMMA-SU-8 have different Poisson’s ratios.

Figure 2.19 Plot of the 2D band position of monolayer graphene as a function of tensile and compression strain. [57]

Tsoukleri et al. [57] also subjected the graphene on PMMA-SU-8 to compression. Figure 2.19 shows the 2D band position under tensile and compression conditions. In
tension, the frequency of 2D band decreases with applied strain. However, under the compression, the frequency goes up and subsequently have a plateau at \sim 0.6\% strain, resulting from the graphene flake collapsing at -0.6\% strain. It could be ascribed to the compression force detaching the graphene flake from the substrate. Furthermore, the strain at collapse can be reduced to a lower level by embedding the flake into a polymer matrix [57].

2.4.3.5 2D band splitting under uniaxial strain

As has been described in section 2.4.2, the G band undergoes splitting with applied uniaxial strain depending upon the relationship between the crystal orientation and the axis of the laser polarisation of strain, respectively. Similarly, the 2D band also splits when strain is applied on the graphene. However, the splitting mechanisms for both bands are different.

Figure 2.20 The 2D band features of monolayer under uniaxial tensile strain. The left and right panels were obtained with the incident light parallel and perpendicular to the strain axis, respectively [58].

Figure 2.20 illustrates the 2D band Raman features of a monolayer graphene under different strain levels and laser polarisations. Obviously, the 2D band shifts to lower frequencies and undergoes asymmetric distortion upon the tensile strain. Moreover, it
becomes more pronounced at high strain levels and can be divided into two Lorentzian peaks.

![Diagram of monolayer graphene with strain](image)

Figure 2.21 (a) Inner and outer DR processes. Reciprocal lattice diagram of monolayer graphene for (b) unstrained, (c) armchair-direction strained and (d) zigzag-direction strained. [59]

Huang et al. [53] suggested that the splitting of 2D band only exist in zigzag and armchair oriented samples and samples with intermediate orientations do not. Using a modified tight binding model [53, 60], it is understood that the Raman scattering path between Dirac point K and its three neighbour K’ points is distorted under the strain. The phonon with higher energy give rise to the $2D^+$ band and the lower energy corresponds to the $2D^-$ band. On the other hand, Frank et al. [58] and Yoon et al. [59] attributed the splitting of 2D band under strain to the inner and outer DR Raman scattering processes [61]. The Dirac point movements according for the 2D band broadening due to their modifying of the wave vector of the participating phonon [61-62]. As the strain increases, the three different K-K’ paths are induced Brillouin Zone asymmetry giving rise to three outer and three inner processes. Therefore, theoretically, it will give six components for the splitting, but two subbands are adequate enough. The inner process exhibit more strain-orientation-dependence than that of the outer process [58, 62]. In addition, the intensity of the $2D^+$ and $2D^-$ peaks depends on the polarisation of the incident light significantly [59].
References


Chapter 2 Raman Spectroscopy


Chapter 3 Experimental

3.1 Materials preparation

The graphene in this project was all prepared by mechanical cleavage from graphite crystals [1], followed by transferring it to different substrates for different characterization and deformation studies. Specimens were prepared in the form of both SiO$_2$/Si wafers and SU-8/PMMA beams.

The schematic diagram for graphene preparation is shown in Figure 3.1. Firstly, a small piece of HOPG flake or Natural Graphite flake was placed in the middle of Nitto Tape. Secondly, the graphite was peeled into thin graphene by folding the tape several times. Then the tape which was covered with a variety of different layers graphene which could be transferred to different substrates.

![Figure 3.1 Schematic diagrams for preparation of mechanically-cleavage graphene.](image)

3.1.1 Graphene on SiO$_2$/Si wafers

SiO$_2$/Si wafers are a general substrate used in graphene research [1-2]. The reason is graphene can be easily found under the optical microscope on a SiO$_2$ background. The SiO$_2$/Si wafers used in this project were supplied by IDB Technology Ltd. with a 300 nm SiO$_2$ layer on the Si substrate. Figure 3.2 shows the main route for preparing Graphene/SiO$_2$/Si wafer samples.
3.1.2 Graphene/PMMA composite

Similar to the graphene silicon oxide wafer route in section 3.1.1, the graphene was transferred onto a 5 mm thick PMMA beam from the tape. Two types of Graphene and PMMA composite were prepared. One is with a 50 nm PMMA layer on top of graphene; the other is no top layers. Both of them have a 300 nm thick SU-8 coating which is an epoxy-based negative photoresist between the PMMA beam surface and the graphene. The reason for the use of SU-8 is to make the graphene flakes visible. Figure 3.3 shows the structure of the two PMMA samples.

3.1.3 Graphene/SU-8 composite

SU-8 is a general propose highly transparent photoresist which is a very viscous epoxy based polymer that can be processed by spinning or spreading to a thin film. Exposure to ultraviolet light results in the molecular chains cross-linking to form a thermoset material [3]. Figure 3.4 illustrates the chemical structure of cross-linked SU-8.

The preparation route for graphene/SU-8 composite was as same as graphene/PMMA composite, replacing the PMMA top coating with a 300 nm SU-8 layer, forming a sandwich structure of SU-8/graphene/SU-8. Some of the graphene/SU-8 composite
specimens prepared in this way were kindly provided by Prof. Kostya Novoselov of the University of Manchester, Department of Physics and Astronomy. The structure of graphene/SU-8 composite is shown in Figure 3.5.

Figure 3.4 Chemical structures for cross-linked SU-8. [3]

Figure 3.5 Structure for Graphene/SU-8 composite.

3.2 Optical Microscopy (OM)

Optical microscopy was the first choice in identification the number, quality and area of graphene for study by the naked eye using an Olympus BH-2 microscope. The image was obtained by Zeiss Axiocam ICc3 camera and images were the analysed by the software Axiovision Rel. 4.8. The 100× and 50× objective lens were used to obtain high resolution images.

In the meanwhile, the Renishaw Raman spectrometers are equipped with OM as shown in Figure 3.6 to focus the laser beam. They were also used to obtain low resolution images.
3.3 Scanning Electron Microscopy (SEM)

A few specimens prepared on a SiO$_2$/Si wafer were selected to investigate the graphene surface morphology and quality. A Philips XL30 Field Emission Scanning Electron Microscopy operated at 5 kV instrument was used. The graphene deposited SiO$_2$/Si wafer was placed on an adhesive carbon tab then it was subjected onto an aluminium sample holder, following with thin gold sputter coated on the surface. A silver dag bridge was then applied over the edge of SiO$_2$/Si wafer and carbon tab to improve the discharge of the electrons generated by the electron beam.

3.4 Raman spectroscopy

3.4.1 Raman spectrometer

The Raman spectra were obtained using a Renishaw 1000 Raman spectroscopy system, equipped with a Ar$^+$ (514 nm) and near-infrared (785 nm) lasers, and a Renishaw 2000 Raman spectroscopy system fitted with a HeNe (633 nm) laser. Figure 3.6 illustrates the schematic diagram of the Raman spectrometer. The OM system was equipped with an Olympus BH-2 microscope.
The laser beam was focused on the sample using a 50× objective lens with the diameter of the laser spot of about 2 µm. A low laser power was selected, of ~1mW, to avoid the heating effects and damage by sample burning. In order to obtain a good resolution spectrum for monolayer and few-layer graphene, the exposure time was selected from 60 s to 120 s for different sample conditions, and the accumulation was generally set to 5 times using the extended mode.

Table 3.1 Polarised configurations with the various arrangements of the two half λ plates and the polariser [4].

<table>
<thead>
<tr>
<th>Incident beam direction</th>
<th>VN</th>
<th>VV</th>
<th>VH</th>
<th>HN</th>
<th>HH</th>
<th>HV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>//</td>
<td>//</td>
<td>//</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Scattered beam direction</td>
<td>No</td>
<td>//</td>
<td>↓</td>
<td>No</td>
<td>↓</td>
<td>//</td>
</tr>
<tr>
<td>Half λ, plate 1#</td>
<td>In</td>
<td>In</td>
<td>In</td>
<td>Out</td>
<td>Out</td>
<td>Out</td>
</tr>
<tr>
<td>Half λ, plate 2#</td>
<td>Out</td>
<td>Out</td>
<td>In</td>
<td>Out</td>
<td>In</td>
<td>Out</td>
</tr>
<tr>
<td>Polariser</td>
<td>Out</td>
<td>In</td>
<td>In</td>
<td>Out</td>
<td>In</td>
<td>In</td>
</tr>
</tbody>
</table>

Polarised Raman spectroscopy was used for the investigation of the G and 2D band splitting, accompanied by a rotation stage. Various polarisation configurations were obtained by adjusting the two half λ plates and the polariser. The details of the different arrangement of the optical components configurations are listed in Table 3.1. It should be noted that the horizontal axis in the schematic diagram was defined as the reference axis. “In” means the relative optical component is located in the path of the laser and “Out” defines the optical component is moved away from the path of the laser. In addition, the symbol “//” illustrates the laser is parallel to the reference axis, and “⊥” presents the laser is perpendicular to the reference axis [4].

3.4.2 Raman data analysis

The Raman spectra of monolayer were curve-fitted using a Lorentzian function to determine the information of the Raman bands precisely using the software of
OriginPro 8.1 or OriginPro 8.5. Bi- and trilayer graphene were similarly fitted with reasonable multiple peaks using this method. The equation is expressed as [5]:

\[
I = \frac{I_p W_p^2}{W_p^2 + (\Delta \nu - p)^2}
\]  

(3.1)

where \(I\) is the intensity of the peak between any given wavenumber \(\Delta \nu\), \(p\) is the peak position, \(I_p\) is the intensity at peak point and \(W_p\) is the full width at half maximum of the peak. All the fitting processes were made using Origin 8.1 or Origin 8.5 software. Figure 3.7 shows an example of a monolayer graphene 2D band fitted with a single Lorentzian peak with the Equation (3.1). The circle dots are the original data collected from the Raman signal whereas the black solid line is the fitted Lorentzian curve.

As mentioned before, the G band for graphene (regardless of the number of layers) was suitably fitted by one Lorentzian peak at around 1580 cm\(^{-1}\). In the case of the 2D band, monolayer has a single peak while bilayer and more than two layer graphene have a much more complicated broad peak which appropriately consists of four or more Lorentzian peaks [6].
3.4.3 Deformation analysis

For deformation analysis, the specimens were designed in the form of a 5 mm thick PMMA beam with a resistance strain gauge attached using a cyanoacrylate adhesive on the top surface as shown in Figure 3.8. Graphene is on the top surface or close to the surface of the beam (top coating specimens), thus it is easy to monitor the strain in graphene by the strain measurement of beam surface. The strain gauge was then connected to a multimeter with a pair of electric wires to measure the change in resistance. The calibration of the strain gauge is mainly referred to the manufacture technical value from Vishay.

![Graphene Strain Gauge PMMA Beam](image)

Figure 3.8 Four-point bending test sample.

![Four-point bending rig and diagram of test process](image)

Figure 3.9 Raman four-point bending rig and diagram of test process. [7]

The deformation process for graphene composites were carried out by employing a four-point bending rig, which leads to uniform tension or compression [8]. Figure 3.9 (a) shows the top view of the four-point bending rig where the specimen was placed
between the two pairs of bars. One pair is fixed whereas the other pair can be adjusted up and down by turning the load screw giving rise to the bending force derived from opposite movement of two pair bars at each surface of the beam as shown in Figure 3.8(b). It should be pointed out that the strain within the composite thin film was assumed to be the same as the strain at the surface of the beam. When the beam was subjected to the strain, it correspondingly causes the strain gauge to a same level strain, thus changing the resistance reading. Therefore, the value of the applied strain on the specimen surface could be calculated from the resistance of the strain gauge according to the following relation:

\[
\varepsilon_m = \frac{RS_i - RS_0}{S_{gf} \times RS_0} \times 100\%
\]

(3.2)

where \(\varepsilon_m\) is matrix surface strain, \(RS_0\) is strain gauge resistance without loading, \(RS_i\) is strain gauge resistance with loading, and \(S_{gf}\) is strain gauge factor, which is 2.080 ± 0.5 in this experiment as given by the strain gauge supplier.
References


Chapter 4  Characterisation of Graphene Using Raman Spectroscopy

4.1 Introduction

Raman spectroscopy is a powerful technique to characterise the mechanical and electronic properties of graphene. In addition, Raman spectroscopy can also be used to “count” the number of layers in graphene from the peak profiles and band position. In this chapter, the Raman spectra for undeformed mono-, bi-, tri- and few layer graphene will be presented and discussed in detail.

4.2 Monolayer graphene

The monolayer graphene, although only one atom thick, can be observed using optical microscopy on both the SiO$_2$/Si and PMMA substrates as prepared by the method described in Chapter 3. This is due to 2.3 ± 0.1 % of white light being absorbed by the graphene layer [1]. Figure 4.1 illustrates the Raman spectra obtained from monolayer on both types of substrates using different excitation lasers. The laser beam penetrates through the thin flake to the substrate so that the scattered signal from the substrate can also be collected. The SiO$_2$/Si substrate has no peaks in the range 1000 to 3000 cm$^{-1}$ so that the spectra within this range behave smoothly, whereas the PMMA/SU-8 based substrate has Raman bands in their region that affect the monolayer signal. Consequently, the monolayer spectrum in the case of the PMMA/SU-8 substrate is a combination of the signal from the monolayer, SU-8 and PMMA. It is providential that the 2D band of the monolayer does not overlap with the PMMA/SU-8 background under the three different laser sources. However, the G band is greatly affected and weakened by the background scattering particularly with the 633 nm laser where the SU-8 has a peak at 1580 cm$^{-1}$ overlapping the position of
the G band. Nevertheless, the G band signal can still be collected using the 514 nm and 785 nm lasers. Hence, the G band was only recorded and investigated using the 514 nm and 785 nm lasers but not with the 633 nm laser.

The G band of the monolayer graphene consists of a single and sharp peak located at ~1581 cm\(^{-1}\) at all the excitation laser energy and on both substrates. As mentioned before, the monolayer graphene the G band cannot be directly collected and is strongly affected by the SU-8 layer with the 633 nm laser. The 2D band of the monolayer graphene on the SiO\(_2\)/Si substrate gives a single peak (as shown in Figure 3.7 in Chapter 3) but the intensity is approximately twice high than that of the G band and becomes even stronger with the PMMA/SU-8 substrate implying that, the substrate reduces the signal of the G band but there is no reduction of the 2D band. Moreover, with both the 514 nm and 633 nm lasers, the 2D band position shifts to lower wavenumber (by ~11 cm\(^{-1}\)) when the substrate changes from the SiO\(_2\)/Si substrate to PMMA/SU-8 substrate. In reviewing the literature, this seems incompatible with the finding of Wang \textit{et al.} [2] who mentioned that the Raman features of graphene are independent of the substrate. However, another group found a similar phenomenon as in this project that the 2D bands shifts with different substrates [3]. As a matter of fact, the DR related 2D band position may depend on both the substrate and the preparation routes. Generally, the contact forces and the interface conditions between different substrates may vary. The mechanical cleavage prepared graphene sustained continual folding and cleaving. This may cause some residual strain after it is transferred to the substrate, leading to the shift of band position. However, the G band, reflects the vibration of carbon atoms in the \(sp^2\) carbon system [4], due to possibly an electronic effect, so the position at both cases does not change much as that of the 2D band which originates from the DR process. Combining the situation of the bilayer graphene discussed in the following section, it can be concluded here that the substrate plays a major role in the band position of the 2D band but not of the G band in both of the monolayer and bilayer (different situations for more than two layers graphene as discussed below).
Figure 4.1 Raman spectra for the monolayer graphene on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser.
The 2D band of the monolayer graphene also gives dispersion features with the laser excitation energy as shown in Figure 4.2. The 2D band position moves to high wavenumber (from 2580 to 2680 cm$^{-1}$) with the increasing of the excitation energy. It can be seen that the difference between the 2D band position for PMMA and SiO$_2$/Si substrates becomes larger as the laser energy increase. This may attribute to the heating effect of the lasers to both substrates being different. However the lineshape of both the G band and the 2D band remain as a single peak with different lasers. This project is mainly concerned with the micromechanical properties so the details of the electronic properties are not discussed further.

![Figure 4.2 The 2D band position of monolayer graphene as a function of laser excitation energy on different substrates.](image)

### 4.3 Bilayer graphene

The bilayer graphene prepared with the mechanical cleavage route generally gives materials with an AB stacking order. The bilayer graphene can be found under the optical microscopy with the different substrates by experience due to the light
adsorption from layer to layer [5]. Figure 4.3 shows the Raman spectra for the bilayer graphene on the SiO$_2$/Si substrate and PMMA substrate for different excitation lasers. Similar to the monolayer, the laser can still penetrate through the bilayer graphene so that these spectra still contain the substrate signals.

Analogous to monolayer graphene, bilayer graphene gives a clear and sharp single G band. Moreover, the intensity of the G band is similar to that of the 2D band, in respect that the strength of the E$_{2g}$ mode depends upon the thickness whereas the 2D band originates from the DR process [4, 6]. With an increase the number of layers, the G band intensity becomes stronger relative to the 2D band.

For the bilayer material, the G band located at ~1580 cm$^{-1}$ is close to that of the monolayer graphene and graphite. However, the 2D band of the bilayer graphene has a broadened structure. For comparison, it was curve-fitted to a mono-peak in determination of the peak position. In the case of the PMMA/SU-8 substrate, the centre of the 2D band is located at 2691.8 cm$^{-1}$, 2655.4 cm$^{-1}$ and 2612.3 cm$^{-1}$ at 514 nm, 633 nm and 785 nm, respectively, consistent with the dispersive behaviour. For the SiO$_2$/Si substrate, the 2D band lies at 2702 cm$^{-1}$ and 2662.5 cm$^{-1}$ as shown in Figure 4.3. Moreover, the 2D band of the bilayer shifts to higher wavenumber than that of the monolayer by ~20 cm$^{-1}$. Figure 4.4 shows the 2D band position dependence on the laser energy. Similar to the monolayer graphene, the gap between different substrates at the same laser energy may be due to the heating effect, and becomes even stronger when the laser energy increases.
Figure 4.3 Raman spectra for the bilayer graphene on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser.
Chapter 4 Characterisation of Graphene using Raman Spectroscopy

Figure 4.4 The 2D band position of the bilayer graphene as a function of laser excitation energy on different substrates.

Figure 4.5 An example for four Lorentzian components fit (green solid lines) to the 2D band with 633 nm laser for bilayer graphene on the SiO$_2$/Si substrate.
Chapter 4 Characterisation of Graphene using Raman Spectroscopy

The lineshape for the bilayer graphene is much more complex than for monolayer and broadened, and can be well-fitted into four Lorentzian components [4, 7] as shown in Figure 4.5. The black curve is the original data collected from bilayer graphene, and the red line is the well-fitted integration curve. The green curves denote the sub-peaks fitted comprising the 2D band. With the 633 nm laser, the four subbands located at 2618.1 cm\(^{-1}\), 2654.2 cm\(^{-1}\), 2681.4 cm\(^{-1}\) and 2704 cm\(^{-1}\), are termed the 2D\(_{1B}\), 2D\(_{1A}\), 2D\(_{2A}\) and 2D\(_{2B}\) bands, respectively [8]. These sub-bands were sourced from the four DR processes of the electrons and phonons near the Dirac point [8]. It is clear to see that the 2D\(_{1A}\) band has the strongest intensity, about twice to that of the 2D\(_{2A}\) sub-band. The 2D\(_{1B}\) and 2D\(_{2B}\) side bands exhibit the same level of intensity. It should be pointed out that the four combination sub-bands are a significant feature in identification of the bilayer graphene from the other thicknesses of graphene.

### 4.4 Trilayer graphene

Trilayer graphene prepared from the mechanical cleavage route generally keeps the ABA stacking order, and it can also be found clearly under the optical microscopy and further be identified by the Raman 2D band. Figure 4.6 shows the Raman spectra for the trilayer graphene on the SiO\(_2\)/Si substrate and PMMA substrate for different excitation lasers. Due to the transparency of the layers, the laser beams can still penetrate through to the substrate giving rise to the composite Raman spectrum.

The trilayer graphene has a single G band which is much stronger than the 2D band. Particularly, using the 633 nm and 785 nm lasers, the G band intensity is approximately three times that of the 2D band. This may provide another essential route to identify the number of the graphene layers from monolayer to trilayer by using the ratio of the intensity of the G and 2D bands, but it needs to be confirmed further. Since it needs various kinds of samples and various other characteristic techniques, this has not been investigated further in this project.
Figure 4.6 Raman spectra for the trilayer graphene on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser.
The G band position for the trilayer graphene is located at the same position as the monolayer, bilayer and HOPG, but the 2D band shifts to higher wavenumber by ~10 cm\(^{-1}\), compared with the bilayer graphene. Meanwhile, the 2D band of the trilayer also shows a linear dispersion behaviour with excitation laser energy as shown in Figure 4.7. It is interesting to mention that the 2D band position does not shift when the substrate is altered from the SiO\(_2\)/Si substrate to PMMA/SU-8 substrate, which was the case for the monolayer and bilayer. It was shown in Section 4.2 and 4.3 that the substrate plays an essential role in the Raman feature of the monolayer and bilayer graphene. Combining the situations of trilayer, few-layer (see below) and HOPG, it may be deduced that the substrate effect becomes negligible for the 2D band when the number of graphene layers is more than two.
Figure 4.8 Examples for (a) six Lorentzian components (green solid lines) and (b) four Lorentzian components fit (green solid lines) to the 2D band with the 633 nm laser for the trilayer graphene on the PMMA substrate.
The 2D band of the trilayer graphene has a flat-top and broaden peak and can be curve-fitted by six Lorentzian components [4]. As an example, Figure 4.8(a) indicates the 2D band of the trilayer graphene is well-fitted with six peaks. In comparison, Figure 4.8 (b) shows the 2D band fitted to four components. The 2D band of the trilayer graphene in theory can be fitted into 15 sub-peaks but is generally fitted simply with six peaks [4]. Furthermore, in contrast, when four peaks were selected to fit the trilayer 2D band as shown in Figure 4.8(b), it can be seen that the fitted overall line also matches the data well but not perfectly fitting on the small side shoulders as shown in Figure 4.8(b). The four-peak fit analysis is comparable to that of the fitted by six peaks owing to the peak positions and profiles being similar to the six-component fitted case. The two dominant peaks and the left side peak in both fitting are located in exactly the same position. Only the right side peak is changed slightly with a shift of ~5 cm$^{-1}$. This analysis result suggests that the trilayer could be simplified by fitting with four components, particularly in optimising the investigation of the 2D band shift dependence on strain.

It is easy to observe that the trilayer 2D band profile is definitely different from bilayer graphene. In the case of the bilayer graphene as shown in Figure 4.5 that a dominant peak curve lays at ~2654 cm$^{-1}$, and the other peaks have a lower intensity level. However, one aspect of trilayer graphene, as can be seen from Figure 4.8, is that the peak has a flat peak top and is relatively symmetric. Therefore, this is a significant feature for distinguishing between trilayer and bilayer graphene accurately, although their appearance are rather similar using optical microscopy.

**4.5 Few layer graphene**

The few layer graphene here is defined as graphene with a number of graphene layers between four and ~10. Their behaviour, such as electronic and mechanical properties, becomes closer to the performance of graphite with the increasing of the number of layers. Figure 4.9 shows the Raman spectra for the few layer graphene with the
different substrates using different excitation lasers. From the spectra of the PMMA/SU-8 substrate sample, an extremely strong signal from the substrate can still be collected, suggesting that the flake is still of nano-scale dimensions and the laser beam can easily penetrate through the graphene layers [5]. Hence, the spectra were still affected by the substrate scattering.

The few layer graphene gives a single sharp and high intensity G band which is located at \( \sim 1580 \, \text{cm}^{-1} \) for both substrates with the 514 nm, 633 nm and 785 nm lasers. In contrast, the 2D band is a much broader and has an asymmetric peak at 2711.9 cm\(^{-1}\), 2673.1 cm\(^{-1}\) and 2629.1 cm\(^{-1}\) in the case of the PMMA/SU-8 substrate, and 2710.9 cm\(^{-1}\), 2675.5 cm\(^{-1}\) with the SiO\(_2\)/Si substrate, respectively. Similar to the other thicknesses of graphene, the 2D band of the few layer graphene shows dispersion with excitation laser energy. Figure 4.10 indicates a linear dependence of the 2D band with laser energy. The substrate has no effect on the band position for both the G and 2D bands, it is concluded that substrate affects the 2D band position of the monolayer and bilayer graphene only. For a number of layers more than three, the substrate therefore plays a negligible role in controlling band position.

The 2D band of the few layer graphene has a much different peak profile than the other thickness graphene. The position of the 2D band is \( \sim 10 \, \text{cm}^{-1} \) higher that of the trilayer graphene. Figure 4.11 shows an example for the 2D band of the few layer graphene fitted by two Lorentzian peaks. It is interesting to see that the peak profile is quite close to that of graphite (as shown in the following Section, Figure 4.14) with a dominant shoulder at the higher wavenumber position.
Figure 4.9 Raman spectra for the few layer graphene on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser.
Figure 4.10 The 2D band position of the few layer graphene as a function of laser excitation energy on different substrates.

Figure 4.11 An example for two Lorentzian components fit (green solid lines) to the 2D band with the 633 nm laser for the few layer graphene on the SiO$_2$/Si substrate.

4.6 Highly Oriented Pyrolytic Graphite (HOPG)

Thick HOPG flakes, very shiny and clear under optical microscopy, were selected to be investigated on different substrates with the 514 nm, 633 nm and 785 nm wavelength lasers as shown in Figure 4.12. It should be noted that the fluorescence
effect from the SiO$_2$/Si substrate is still too strong to obtain a smooth and quality spectrum with the 785 nm laser, but there is no fluorescence effect with the PMMA based substrate. Two major bands, the G band and 2D band, can be clearly observed. Itkis et al. [9] proposed that the intensity ratio of the D band and G band relates to the quality of graphene based sample. Therefore, the good quality stacking order of HOPG provides spectra without any defect bands. The G band, generally located at ~1581 cm$^{-1}$ is independent of both the substrate effect and laser wavelengths. On the other hand, the 2D band position seems more sensitive to the excitation laser wavelength, which can be attributed to the dispersive behaviour of the electron and phonon vectors around the K point for the different laser excitation energy [10]. The G band has a sharp and symmetric structure and the intensity is around twice that of the 2D band. Moreover, the 2D band seems to be composed of two peaks where the degree of splitting of the 2D band is independent to the excitation laser energy. An example for the 2D band of HOPG fitted by two Lorentzian peaks is shown in Figure 4.14. The 2D peak position values labelled in Figure 4.12 are those of the higher wavenumber component. The 2D band position is also plotted against with the laser excitation energy as shown in Figure 4.13, showing good linear dispersion behaviour as with the other thicknesses of graphene. This behaviour is similar to few layer graphene in which the gap between both substrates is very small and it can be concluded that there is little substrate effect in HOPG.
Figure 4.12 Raman spectra for the HOPG on the SiO$_2$/Si and PMMA substrates obtained using the (a) 514 nm laser, (b) 633 nm laser and (c) 785 nm laser.
Figure 4.13 The 2D band position of HOPG as a function of the excitation energy on different substrates.

Figure 4.14 An example for two Lorentzian component fit (green solid lines) to the 2D band at 633 nm laser for HOPG on SiO$_2$/Si substrate.

### 4.7 Dependence of the 2D band position on the number of layers

In order to investigate the relationship between the number of graphene layers and the 2D Raman band position, Table 4.1 lists the positions of the 2D band for the different conditions in summary. Figure 4.15 indicates the relation between 2D band position and thickness of graphene visually. The monolayer graphene has the lowest 2D band
Raman wavenumber. With the increase of the number of layers, the 2D band Raman wavenumber increases to a higher value and reaches the highest Raman wavenumber in the case of HOPG. A complication is that it is hard to know the precise number of layers for the few layer graphene. Hence, Raman spectroscopy can be employed as a useful technique in determining the number of graphene layers rapidly and reliably.

Table 4.1 Various 2D band positions for the different number of graphene layers with different lasers and different substrates.

<table>
<thead>
<tr>
<th>Number of Layers</th>
<th>514 nm (cm(^{-1}))</th>
<th>633 nm (cm(^{-1}))</th>
<th>785 nm (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer</td>
<td>SiO(_2)/Si: 2682 ± 1</td>
<td>PMMA: 2671 ± 1</td>
<td>SiO(_2)/Si: 2637 ± 1</td>
</tr>
<tr>
<td>Bilayer</td>
<td>2702 ± 1</td>
<td>2692 ± 1</td>
<td>2662 ± 1</td>
</tr>
<tr>
<td>Trilayer</td>
<td>2705 ± 1</td>
<td>2704 ± 1</td>
<td>2665 ± 1</td>
</tr>
<tr>
<td>Few-layer</td>
<td>2711 ± 1</td>
<td>2712 ± 1</td>
<td>2675 ± 1</td>
</tr>
<tr>
<td>HOPG</td>
<td>2731 ± 1</td>
<td>2728 ± 1</td>
<td>2687 ± 1</td>
</tr>
</tbody>
</table>

Figure 4.15 The 2D band position dependence to the number of the graphene layers.
It is very valuable to modelling the number of graphene with the Raman 2D band position. However, this thesis is focusing on the mechanical properties of graphene reinforced nanocomposite. The precise relationship between the number of graphene layers and Raman 2D band position was not investigated further.

4.8 Conclusions

Raman spectroscopy has been shown to be one of the most reliable tools in characterisation the number of the graphene layers in a specimen.

The G band has been demonstrated a single and sharp peak independent to the substrate and laser excitation energy. In contrast, for the 2D band, which originates from the DR process of the electron and phonon interaction near the Dirac point, it has been validated that the peak profiles are independent to the substrate and laser excitation energy. However, the position of 2D band is strongly dependent upon the thickness of the graphene, the substrate and the laser excitation energy. The 2D Raman band position of the monolayer and bilayer graphene shifts with the change of the substrate and laser excitation energy. However, as the number of graphene layers is increased to more than two, the substrate effect becomes negligible whereas the excitation energy still affects the position of the 2D band significantly.

The 2D band of the monolayer graphene gives a single peak in contrast to the other thicknesses of graphene. The bilayer graphene gives a broad 2D peak which can be well fitted into four components associating with the DR process. The trilayer graphene in theory can be well fitted into six peaks but the fitting into four peaks does not influence on the sub-band position much compared with six-peak fitting. In the case of the few layer graphene, the 2D band was fitted into two components which is adequate for this project. In summary, characterising the Raman 2D band features is a useful way to distinguish between the graphene going from monolayer, bilayer, trilayer to few layers and HOPG.
Chapter 4 Characterisation of Graphene using Raman Spectroscopy

References


Chapter 5  Interfacial Stress Transfer in a Graphene Monolayer Nanocomposite†

5.1 Introduction

Graphene is one of the stiffest known materials, with a Young’s modulus of 1 TPa, making it an ideal candidate for use as a reinforcement in high-performance composites. However, being a one-atom thick crystalline material, graphene poses several fundamental questions: i) Can decades of research on carbon-based composites be applied to such an ultimately-thin crystalline material? ii) Is continuum mechanics used traditionally with composites still valid at the atomic level? iii) How does the matrix interact with the graphene crystals and what kind of theoretical description is appropriate? It will be demonstrated unambiguously that stress transfer takes place from the polymer matrix to monolayer graphene, showing that the graphene acts as a reinforcing phase. The behaviour using shear-lag theory will be modelled, showing that graphene monolayer nanocomposites can be analyzed using continuum mechanics. Additionally, the ability to monitor stress transfer efficiency and breakdown of the graphene/polymer interface will be demonstrated.

5.2 Materials and Methods

The specimen was prepared using a 5 mm thick poly(methyl methacrylate) beam spin-coated with 300 nm of SU-8 epoxy resin. The graphene, produced by the mechanical cleaving of graphite, was deposited on the surface of the SU-8. This method produced graphene with a range of different numbers of layers and the monolayers were identified both optically [1] and using Raman spectroscopy as

† This chapter is based upon a paper of “Interfacial Stress Transfer in a Graphene Monolayer Nanocomposite”, published in Advanced Materials 22(24) 2010, DOI 10.1002/adma.200904264.
discussed in Chapter 4. A thin 50 nm layer of PMMA was then spin-coated on top of the beam so that the graphene remained visible when sandwiched between the two coated polymer layers as shown in Figure 5.1(a).

The PMMA beam was deformed in 4-point bending and the strain monitored using a strain gauge attached to the beam surface. A well-defined Raman spectrum could be obtained through the PMMA coating using a low-power HeNe laser (1.96 eV and <1mW at the sample in a Renishaw 2000 spectrometer) and the deformation of the graphene in the composite was followed from the shift of the 2D band [2-5]. The laser beam polarization was always parallel to the tensile axis.

**5.3 Results and Discussion**

**5.3.1 Strain mapping**

![Figure 5.1 Single monolayer graphene composite. (a) Optical micrograph showing the monolayer graphene flake investigated. (b) Schematic diagram (not to scale) of a section through the composite.](image)
In this chapter, Raman spectroscopy is used to monitor stress transfer in a model composite consisting of a thin polymer matrix layer and a mechanically–cleaved single graphene monolayer, using the stress-sensitivity of the graphene 2D band. An optical micrograph of the specimen is shown in Figure 5.1(a) where the approximately diamond-shaped 12 µm × 30 µm graphene monolayer is indicated and Figure 5.1(b) shows a schematic diagram of the specimen.

![Diagram of Raman 2D Band](image)

Figure 5.2 Shifts of the Raman 2D band during loading and unloading of the monolayer graphene composite. (a) Change in the position of the 2D band with deformation. (b) Shift of the band peak position as a function of strain. (The blue circles indicate where the loading was halted to map the strain across the flake).
Raman spectra were obtained initially from the middle of the monolayer and Figure 5.2(a) shows the position of the 2D band before deformation, at 0.7% strain and then unloaded. It can be seen from Figure 5.2(b) that there is a large stress-induced shift of the 2D band. There was a linear shift of the band up to 0.4% strain when the stepwise deformation was halted to map the strain across the monolayer. It was then loaded up to 0.5% and 0.6% strain when further mapping was undertaken and finally the specimen was unloaded from 0.7% strain. It can be seen that there was some relaxation in the specimen following each of the mapping stages so that the band shifts became irregular. In addition, the slope of the unloading line from the highest strain level is significantly higher than that of the loading line. The slope of the unloading line is approximately -60 cm\(^{-1}\)/% strain, similar to the behavior found for the deformation of a free-standing monolayer on a substrate [2-3]. Moreover, the 2D band position after unloading is at a higher wavenumber than before loading. This behavior is consistent with the graphene undergoing slippage in the composite during the initial tensile deformation and then becoming subjected to in-plane compression on unloading.

Mapping the local strain in along a carbon fibre in a polymer matrix allows the level of adhesion between the fibre and matrix to be evaluated [6-7]. In a similar way mapping the strain across the graphene monolayer enables stress transfer from the polymer to the graphene to be followed. Figure 5.3 shows the local strain in the graphene monolayer determined from the stress-induced Raman band shifts at 0.4% matrix strain. The laser beam in the spectrometer was focussed to a spot around 2 \(\mu\)m which allows a spatial resolution of the order of 1 \(\mu\)m on the monolayer by taking overlapping measurements. Figure 5.3(a) shows the variation of axial strain across the monolayer in the direction parallel to the strain axis. It can be seen that the strain builds up from the edges and is constant across the middle of the monolayer where the strain in the monolayer equals the applied matrix strain (0.4%). This is completely analogous to the situation of a single discontinuous fibre in a model composite where there is good bonding between the fibre and matrix [6-7]. This behaviour has been
analysed using the well-established shear-lag theory [8-10] where it is assumed that there is elastic stress transfer from the matrix to the fibre through a shear stress at the fibre-matrix interface. It is relatively easy to modify the analysis for platelet rather than fibre reinforcement.

Figure 5.3 Distribution of strain in the graphene in the direction of the tensile axis ($x$) across a single monolayer at 0.4% strain. (a) Variation of axial fibre strain with position across the monolayer in the $x$-direction (The curve fitted to the data is Equation (5.15)). (b) Variation of graphene strain in the direction of the tensile axis ($x$) across a single monolayer at 0.6% matrix strain. (The solid lines are fitted to the data to guide the eye. The dashed curve is the shear-lag fit to the data in Figure 5.3(a) at 0.4% strain.)
5.3.2 Theoretical analysis

Figure 5.4 Deformation patterns for a discontinuous flake in a polymer matrix.

Figure 5.5 Balance of stresses acting on an element of length, dx, of the flake of thickness, t, in the composite.

In the case of discontinuous graphene flakes reinforcing a composite matrix, stress transfer from the matrix to the flake is assumed to take place through a shear stress at the flake/matrix interface as shown in Figure 5.4. Before deformation parallel lines perpendicular to the flake can be drawn before deformation from the matrix through the flake. When the system is subjected to axial stress, $\sigma_i$, parallel to the flake axis, the lines become distorted since the Young’s modulus of the matrix is much less than that of the flake. This induces a shear stress at the flake/matrix interface. The axial stress in the flake will build up from zero at the flake ends to a maximum value in the middle of the flake. The uniform strain assumption means that, if the flake is long
enough, in the middle of the flake the strain in the flake equals that in the matrix. Since the flakes have a much higher Young's modulus it means that the flakes carry most of the stress in the composite.

The relationship between the interfacial shear stress, \( \tau \), near the flake ends and the flake stress, \( \sigma_f \), can be determined by using a force balance of the shear forces at the interface and the tensile forces in a flake element as shown in Figure 5.5.

The main assumption is that the forces due to the shear stress at the interface, \( \tau \), is balanced by the force due to the variation of axial stress in the flake, \( d\sigma_f \), such that if the element shown in Figure 5.5 is of unit width

\[
\tau_i dx = -t d\sigma_f \quad (5.1)
\]

and so

\[
\frac{d\sigma_f}{dx} = -\frac{\tau_i}{t} \quad (5.2)
\]

where \( t \) is the thickness of the flake.

Figure 5.6 Model of a flake within a resin used in shear-lag theory. The shear stress, \( \tau \), acts at a radius \( \rho \) from the flake centre.

The behaviour of a discontinuous flake in a matrix can be modelled using shear lag theory in which it is assumed that the flake is surrounded by a layer of resin at a
distance, $z$, from the flake centre as shown in Figure 5.6. It is assumed that both the flake and matrix deform elastically and the flake-matrix interface remain intact. If $u$ is the displacement of the matrix in the flake axial direction at a distance, $z$, then the shear strain, $\gamma$, at that position is given by

$$\gamma = \frac{du}{dz} \quad (5.3)$$

The shear modulus of the matrix is defined as $G_m = \frac{\tau}{\gamma}$ hence

$$\frac{du}{dz} = \frac{\tau}{G_m} \quad (5.4)$$

The shear force per unit length carried by the matrix is transmitted to the flake surface through the layers of resin and so the shear strain at any distance $z$ is given by

$$\frac{du}{dz} = \frac{\tau_i}{G_m} \quad (5.5)$$

This equation can be integrated using the limits of the displacement at the flake surface ($z = t/2$) of $u = u_g$ and the displacement at $z = T/2$ of $u = u_T$

$$\int_{u_i}^{u_t} du = \left( \frac{\tau_i}{G_m} \right) \int_{t/2}^{T/2} dz \quad (5.6)$$

Hence

$$u_T - u_i = \left( \frac{\tau_i}{2G_m} \right) (T - t) \quad (5.7)$$

where $T$ is the thickness of the polymer layers.

It is possible to convert these displacements into strain since the flake strain, $\epsilon_g$, and matrix strain, $\epsilon_m$, can be approximated as $\epsilon_g \approx \frac{du_g}{dx}$ and $\epsilon_m \approx \frac{du_T}{dx}$. It should be noted that this shear-lag analysis is not rigorous but it serves as a simple illustration of the process of stress transfer from the matrix to a flake in a graphene-flake composite.

In addition, $\tau$ is given by Equation (5.2) and so differentiating Equation (5.7) with respect to $x$ leads to

$$\epsilon_g - \epsilon_m = -\frac{tT}{2G_m} \left( \frac{d^2 \sigma_i}{dx^2} \right) \quad (5.8)$$
since \( T >> t \). Multiplying through by the Young’s modulus of the graphene flake, \( E_g \), gives

\[
\frac{d^2 \sigma_t}{dx^2} = \frac{n^2}{t^2} (\sigma_t - \epsilon_m E_g) \tag{5.9}
\]

where

\[
n = \sqrt{\frac{2G_m}{E_g \left( \frac{t}{T} \right)}} \tag{5.10}
\]

This differential equation has the general solution

\[
\sigma_t = E_g \epsilon_m + C \sinh \left( \frac{nx}{t} \right) + D \cosh \left( \frac{nx}{t} \right)
\]

where \( C \) and \( D \) are constants of integration. This equation can be simplified and solved if it is assumed that the boundary conditions are that there is no stress transmitted across the flake ends, i.e. if \( x = 0 \) in the middle of the flake where \( \sigma_t = E_g \epsilon_m \) then \( \sigma_t = 0 \) at \( x = \pm l/2 \), where \( l \) is the length of the graphene flake in the \( x \) direction. This leads to \( C = 0 \) and

\[
D = -\frac{E_g \epsilon_m}{\cosh(nl/2t)}
\]

The final equation for the distribution of flake stress as a function of distance, \( x \) along the flake is then

\[
\sigma_t = E_g \epsilon_m \left[ 1 - \frac{\cosh(nx/t)}{\cosh(nl/2t)} \right] \tag{5.11}
\]

Finally it is possible to determine the distribution of interfacial shear stress along the flake using Equation (5.2) which leads to

\[
\tau_i = nE_g \epsilon_m \frac{\sinh(nx/t)}{\cosh(nl/2t)} \tag{5.12}
\]

It is convenient at this stage to introduce the concept of flake aspect ratio, \( s = l/t \) so that the two equations above can be rewritten as

\[
\sigma_t = E_g \epsilon_m \left[ 1 - \frac{\cosh \left( \frac{nsx}{l} \right)}{\cosh \left( \frac{ns}{2} \right)} \right] \tag{5.13}
\]
for the axial flake stress and as

$$\tau_i = nE_\varepsilon \varepsilon_m \frac{\sinh\left(\frac{ns x}{l}\right)}{\cosh(ns / 2)}$$

(5.14)

for the interfacial shear stress. The parameter $n$ is accepted widely as an effective measure of the interfacial stress transfer efficiency, so $ns$ depends on both the morphology of the graphene flake and the degree of interaction it has with the matrix.

It can be seen that the flake is most highly stressed, i.e. the most efficient flake reinforcement is obtained, when the product $ns$ is high. This implies that a high aspect ratio, $s$, is desirable along with a high value of $n$.

It is predicted from shear-lag analysis for the platelet that for a given level of matrix strain, $\varepsilon_m$, the variation of strain in the graphene flake, $\varepsilon_\varepsilon$, with position, $x$, across the monolayer will be of the form

$$\varepsilon_\varepsilon = \varepsilon_m \left[1 - \frac{\cosh\left(\frac{ns x}{l}\right)}{\cosh(ns / 2)}\right]$$

(5.15)

The curve in Figure 5.3(a) is a fit of Equation (5.15) to the experimental data using the parameter $ns$ as the fitting variable. The experimental data on the variation of graphene strain across the monolayer flake are fitted to the shear lag analysis derived above in Figure 5.7(a) and Figure 5.8. It can be seen that the fits of the theoretical shear-lag curves to the strain distribution are sensitive to the value of $ns$ chosen. Likewise the value interfacial shear stress at the flake ends is very sensitive to the values of $ns$ chosen. A reasonable fit was found for $ns \sim 20$ at $\varepsilon_m = 0.4\%$ showing that the interface between the polymer and graphene remained intact at this level of strain and that the behaviour could be modelled using the shear-lag approach.
Figure 5.7 (a) Distribution of strain in the graphene in direction of the tensile axis across a single monolayer at 0.4% strain. The curves are fits of Equation (5.13) using different values of parameter $ns$. (b) Variation of interfacial shear stress with position determined from Equation (5.14) for the values of $ns$ used in (a).

The variation of shear stress, $\tau_i$, at the polymer-graphene interface is given by Equation (5.14) and the maximum value of $\tau_i$ at the edges of the sheet for $ns = 20$ as shown in Figure 5.7(b) is found to be 2.3 MPa.
Equation (5.15) shows that the distribution of strain in the graphene monolayer in the $x$ direction in the elastic case depends upon length of the monolayer, $l$. It can be seen from Figure 5.1 that the flake tapers to a point in the $y$ direction and so the axial strain in the middle of the monolayer was mapped along the $y$ direction. The strain is fairly constant along most of the monolayer but falls to zero at the tip of the flake, $y = 0$. The distribution of axial graphene strain in the middle of the monolayer at $\varepsilon_m = 0.4\%$ determined using Equation (5.15) with $ns = 20$, taking into account the changing width by varying $l$ (and hence $s$). It was found that there is also excellent agreement between the measured and predicted variation of fibre strain with position on the monolayer using $ns = 20$, validating the use of the shear lag analysis.

![Graph of strain distribution](image)

Figure 5.8 Distribution of strain in the graphene in direction of the tensile axis across a single monolayer at 0.4% strain showing the variation of fibre strain with position across the monolayer in the vertical direction. The curves were calculated from Equation (5.13) using different values of $ns$.

When the matrix strain was increased to $\varepsilon_m = 0.6\%$ a different distribution of axial strain in the graphene monolayer was obtained as shown in Figure 5.3(b). In this case there appears to be an approximately linear variation of the graphene strain from the edges to the centre of the monolayer up to 0.6% strain ($= \varepsilon_m$) and a dip in the middle down to around 0.4% strain. In this case it appears that the interface between the
graphene and polymer has failed and stress transfer is taking place through interfacial friction [10]. The strain in the graphene does not fall to zero in the middle of the flake, however, showing that the flake remains intact unlike the behavior of carbon fibers undergoing fracture in the fragmentation test [6-7]. The interfacial shear stress, $\tau_i$, in this case can be determined from the slope of the lines in Figure 5.3(b) using the force balance equation

$$\frac{d\varepsilon_s}{dx} = -\frac{\tau_i}{E_s t}$$  \hspace{1cm} (5.16)

which gives an interfacial shear stress in the range 0.3-0.8 MPa for the lines of different slope.

**5.3.3 Implications**

There are important implications from this study for the use of graphene as a reinforcement in nanocomposites. The quality of fibre reinforcement is often described in terms of the ‘critical length’, $l_c$ – the parameter is small for strong interfaces and is defined as $2 \times$ the distance over which the strain rises from the fibre ends to the plateau level [10]. It can be seen from Figure 5.3(a) that the strain rises to about 90% of the plateau value over about 1.5 $\mu$m from the edge of the flake making the critical length of the graphene reinforcement of the order of 3 $\mu$m. It is generally thought that in order to obtain good reinforcement the fibre length should be $\sim 10l_c$. Hence, relatively large graphene flakes (>30 $\mu$m) will be needed before efficient reinforcement will take place. One process for efficiently exfoliating graphene to single layers reported recently produced monolayers of no larger than a few microns across [11-12]. The relatively poor level of adhesion between the graphene and polymer matrix is also reflected in the low level of interfacial shear stress, $\tau_i$, determined - carbon fibres composites have values of $\tau_i$ an order of magnitude higher ($\sim$ 20-40 MPa). However, in the graphene composite interfacial stress transfer will only be taking place though van der Waals bonding across an atomically smooth surface. The efficiency of reinforcement is also reflected in the value of the parameter
Interfacial Stress Transfer in a Graphene Monolayer Nanocomposite

Chapter 5

\[ n_s (\approx 20) \] in the shear lag analysis used to fit the experimental data. Since the graphene is so thin, the aspect ratio \( s \) will be large (12 \( \mu \text{m}/0.35 \text{ nm} = 3.5 \times 10^4 \)) making \( n \) small (6\( \times 10^{-4} \)). This value of \( n \) is a factor of 4 smaller than that determined by putting the values of \( G_m \approx 1 \text{ GPa}, E_g \approx 1 \text{ TPa} \) and \( t/T (\approx 0.35 \text{ nm}/100 \text{ nm}) \) into Equation (5.10) \( (n \approx 2.6 \times 10^{-3}) \), showing the limitation of the shear-lag analysis [9]. Nevertheless, the parameter \( n \) determined experimentally can be employed to monitor the efficiency of stress transfer across the graphene polymer interface, which in this case appears to be less than ideal.

5.4 Conclusions

This chapter has important implications for the use of graphene as a reinforcement in composites. As well as demonstrating for the first time that it is possible to follow the deformation of graphene monolayer in a polymer composite using Raman spectroscopy, a number of other issues also arise. Firstly, it is quite remarkable that a spectrum can be obtained from a reinforcement only one atom thick, allowing the mechanics of nano-reinforcement to be probed directly. Secondly, it appears that the continuum mechanics approach is also valid at the atomic level - a question widely asked in the field of nanocomposites - and that the composite micromechanics developed for the case of fibre reinforcement is also valid at the atomic level for graphene monolayers. It is expected that this technique will be used widely in the evaluation of graphene composites. This present chapter has concentrated upon pristine, untreated graphene. Chemical modification [13] of the surface or edges may significantly strengthen the interface between the graphene and a polymer, reducing the critical length and increasing \( n \). This technique should allow the effect of chemical modification to be evaluated. Moreover, if graphene is to be used in devices in electronic circuits, it will have to be encapsulated with a polymer. The technique will also allow the effect of encapsulation upon residual stresses in the material to be probed.
References


Chapter 6  Strain Mapping in a Graphene Monolayer Nanocomposite

6.1 Introduction

Model composite specimens have been prepared consisting of a graphene monolayer sandwiched between two thin layers of polymer on the surface of a poly(methyl methacrylate) beam. It has been found that well-defined Raman spectra can be obtained from the single graphene atomic layer and that stress-induced Raman band shifts enable the strain distribution in the monolayer to be mapped with a high degree of precision. It has been demonstrated that the distribution of strain across the graphene monolayer is relatively uniform at levels of applied strain up to 0.6% but that it becomes highly non-uniform above this strain. The change in the strain distributions have been shown to be due to a fragmentation process due to the development of cracks, most likely in the polymer coating layers, with the graphene remaining intact. The strain distributions in the graphene between the cracks are approximately triangular in shape, and the interfacial shear stress in the fragments is only about 0.25 MPa, which is an order of magnitude lower than the interfacial shear stress before fragmentation. This relatively poor level of adhesion between the graphene and polymer layers has important implications for the use of graphene in nanocomposites, and methods of strengthening the graphene-polymer interface are discussed.

‡ This chapter is based upon a paper of “Strain Mapping in a Graphene Monolayer Nanocomposite” in ACS Nano 5(4) 2011, DOI: 10.1021/nn2002079.
6.2 Materials and Methods

The specimen was prepared using a 5 mm thick poly(methyl methacrylate) beam spin-coated with 300 nm of SU-8 epoxy resin. The graphene was produced by mechanical cleaving of graphite and deposited on the surface of the SU-8 as described in Chapter 3. Well-defined Raman spectra could be obtained from the graphene monolayer using a low-power HeNe laser (1.96 eV and < 1 mW at the sample in a Renishaw 2000 spectrometer) and the deformation of the graphene in the composite was followed from the shift of the 2D band. The laser beam polarization was always parallel to the tensile axis and the spot size of the laser beam on the sample was approximately 2 µm using a 50x objective lens.

Raman spectra were obtained at different strain levels through mapping over the graphene monolayer in steps of between 2 and 5 µm by moving the x-y stage of the microscope manually and checking the position of the laser spot on the specimen relative to the image of the monolayer on the screen of the microscope. The strain at each measurement point was determined from the position of the 2D Raman band using the calibration in Figure 6.2 and strain maps of the monolayer were produced in the form of colored x-y contour maps using the OriginPro 8.1 graph-plotting software package, which interpolates the strain between the measurement points.

The beam was then unloaded and a thin 300 nm layer of SU-8 was then spin-coated on top so that the graphene remained visible when sandwiched between the two coated polymer layers. The beam was then reloaded initially up to 0.4% strain, unloaded and then reloaded to various other levels of strain. The strain in the graphene monolayer was mapped fully at each strain level as well as in the unloaded state.
6.3 Results and Discussion

An optical micrograph of the graphene monolayer on a polymer beam before deformation and spin-coating with the PMMA is shown in Figure 6.1. The long axis of the monolayer is aligned approximately parallel to the axis of tensile deformation (horizontal).

Figure 6.1 Optical micrograph of the graphene monolayer before deformation. (The faint straight lines in the background are from scratches on the PMMA beam.)

6.3.1 Strain calibration

The graphene monolayer gave a well-defined Raman spectrum characteristic of single layer graphene with a strong 2D band [1-2], a G band of around half the intensity of the 2D band and no D band (see Chapter 1 and 4). It was found that the 2D band shifted significantly as the beam was deformed in bending as shown in Figure 6.2. The shift rate (in terms of strain) was found to be \(-61 \pm 2 \text{ cm}^{-1}/\%\), which is similar to that the result in Chapter 4 and others in previous studies [3-5], showing good stress transfer between the underlying polymer and graphene monolayer. The slope of this line was used as a calibration for the subsequent mapping of strain in the monolayer.

It was found that as well as showing a large stress-induced band shift the 2D Raman band also underwent significant broadening during deformation which can been seen in Figure 6.2. It has been found recently that the 2D band can undergo broadening or even splitting depending on the angle between the axis of laser polarization and high-symmetry directions in the graphene [6]. It has been suggested that this could account for some of the discrepancies between band shift rates measured by different groups [3-7]. All of the measurements in this chapter, however, were undertaken with
the axis of laser polarization parallel to the strain axis in the same direction in the graphene monolayer. Hence the slope of the line in Figure 6.2 could be used as a calibration for the subsequent mapping of strain in the monolayer without needing to know the exact orientation of the symmetry axes in the graphene monolayer.

Figure 6.2 Position of the 2D Raman band in the uncoated graphene as a function of strain on the beam corresponding increasing FWHM.

6.3.2 Strain mapping

Figure 6.3 shows contour maps of the strain the graphene monolayer at different levels of strain applied in the horizontal direction along with a key showing the relationship between the contour colours and graphene strain. It was not always possible to make measurements close to the edge of the graphene due to the size of the laser spot (~2 µm), and so the outline of the flake (see Figure 6.1) is also given in each plot. The black dots also represent the points at which the measurements were taken.
Figure 6.3 Contour maps of strain over the graphene flake at 0% and 0.4% strain in the uncoated and coated states.

The first two contour plots show the strain maps for applied strains of 0% (i.e. undeformed) and 0.4% for graphene on the PMMA before the PMMA coating was applied. It can be seen that in both cases the strain in the graphene is relatively uniform with some evidence of a lower strain at the left-hand end at 0.4% strain. This is confirmed in Figure 6.4(a), which shows the distribution of strain over a linear region along the long axis of the flake. It shows that before deformation the strain in
the graphene approximately zero and at 0.4% strain it is uniform along the middle of the flake, falling away at the left-hand end and rising higher at the right-hand end.

![Graphene Strain Distribution](image)

Figure 6.4 Variation of the strain in the graphene along the monolayer both undeformed (0%) and at a strain of 0.4%. (a) Specimen uncoated and (b) following coating the with a SU-8 film. (The arrow indicates the point on the monolayer at which the calibration measurements were undertaken).

The specimen was unloaded, coated with SU-8, and reloaded to 0.4% and 0.6% strain, and contour maps are also shown in the loaded states following coating in Figure 6.3. It can be seen that at 0.4% strain the graphene strain distribution is virtually identical in both the uncoated and coated contour maps. This is confirmed in Figure 6.4(b) where there is still a lower level of strain at the left-hand end of the graphene.
monolayer at 0.4% applied strain following coating. Increasing the applied strain to 0.6% strain causes the strain in the graphene to increase to around 0.6% strain over most of the monolayer, with a lower level of strain at the left-hand end.

The drop off strain at the left-hand end of the monolayer is similar to the behaviour reported previously [7] for a graphene monolayer in a model composite under stress. Different behaviour is found at the right-hand (pointed) end, and it is possible to obtain some indication of what might be happening in the monolayer from the consideration of the deformation micromechanics of fibres in composites with differently shaped ends [8-9]. In the case of a square end in a cylindrical fibre there is a gradual decrease of fibre strain toward the end of the fibre, as is found at the left-hand end of the monolayer. In contrast, if the fibre has a pointed (e.g., conical) tip, then for high-modulus reinforcements the strain actually rises as the fibre tapers and drops to zero only very close to the end of the tip. The increase in strain seen in Figure 6.4 at the right-hand tip of the tapering monolayer may take place for a similar reason.

![Graph of 2D Position vs. Strain](image)

**Figure 6.5** Position of the 2D Raman band in the coated graphene as a function of strain on the beam during reloading to 0.8% and unloading.
Figure 6.6 Contour maps of strain over the coated graphene flake in the relaxed states and at 0.8% and 0.6% strain.

The specimen was unloaded from 0.6% strain, and it was found that a residual strain of the order of 0.15% due to creep of the PMMA beam that had undertaken under the long period of loading needed to undertake the extensive strain mapping. The coated specimen was then reloaded to an applied strain of 0.8%, and Figure 6.5 shows the variation of the 2D band position, measured at the point indicated by the arrow in Figure 6.4(a), as a function of strain. The reloading data are represented by the solid points and it can be seen that the slope of the reloading line is similar to that of initial loading line shown in Figure 6.2. The data fall close to the line up to about 0.76%
strain at which point the last two data points fall back to the 2D band starting position. This corresponds to the collapse of stress transfer to the graphene monolayer through the interfaces with the polymer films on the beam.

### 6.3.3 High strain deformation

Further information upon stress transfer to the graphene monolayer can be gleaned from the contour maps of the strain the graphene shown in Figure 6.6. The strain is relatively uniform at around 0.15% in the relaxed state, but when the applied strain is increased to 0.8%, it can be seen that the strain distribution becomes very non-uniform in the graphene flake. In particular there are three vertical regions of high strain across the monolayer, with other areas being subjected to lower levels of strain.

![Graph showing strain distribution](image)

Figure 6.7 Variation of graphene strain along the middle of the monolayer relaxed and reloaded to 0.6%. (The open triangles are the data points at 0.6% strain for the first loading in Figure 6.4(b).)
Figure 6.7 shows the variation of strain along the long axis of the graphene monolayer in the relaxed state and at 0.6% applied strain. The plot confirms that the monolayer is subjected to a relatively uniform strain of around 0.15% in the relaxed state as shown in Figure 6.6. When the applied strain is increased to 0.6%, it can be seen that the strain distribution becomes very nonuniform with a series of approximately triangular segments with the strain falling to around 0.2% between each one. The lengths of the segments are in the range 10 - 20 µm. This phenomenon is then further confirmed by reload the strain to 0.8%.

Figure 6.8 shows the variation of strain along the middle of the long axis of the graphene monolayer in the relaxed state and at 0.8% applied strain. The plot confirms that the monolayer is subjected to a relatively uniform strain of around 0.15% in the relaxed state as shown in Figure 6.6. When the applied strain is increased to 0.8% it can be seen that the strain distribution becomes very non-uniform with a series of approximately triangular segments with the strain falling to around 0.1% between each one. The lengths of the segments are also in the range 10 - 20 µm.

Figure 6.8 Variation of strain along the middle of the monolayer relaxed and reloaded to 0.8%.
Chapter 6 Strain Mapping in a Graphene Monolayer Nanocomposite

Figure 6.9 Schematic diagrams of the deformation of the graphene monolayer in the model composite. (a) Specimen before deformation, (b) graphene monolayer undergoing fragmentation and (c) cracking of both the PMMA and SU8 polymer coating. (Diagrams not to scale)

Figure 6.6 shows that when the specimen is relaxed again, the strain falls to around 0.1% but is rather less uniform than when it was relaxed originally. On further reloading to 0.6%, it can be seen that the strain is again non-uniform and the strain pattern is similar to that seen for the specimen when it was loaded to 0.8%. It appears that the specimen was damaged by loading up to 0.8% strain and this damage was retained on reloading to the lower strain. It should be noted that when the specimen was loaded initially to 0.6% strain the distribution of strain across the monolayer was relatively uniform (Figure 6.3), as can be seen from the open triangles in Figure 6.7.

It is clear from Figures 6.6 and 6.7 that loading to 0.8% strain causes damage to the interface between the graphene and polymer layers in the specimen. Figure 6.9 shows a schematic diagram of the model composite specimen and two possible failure mechanisms:

- fragmentation of the graphene monolayer or
- cracking of the PMMA and/or SU8 coatings

The strain distributions for the graphene monolayer obtained in Figures 6.6 and 6.7 would be consistent with either of these two processes taking place.
Figure 6.10 Optical micrograph of the specimen after deformation showing the formation of cracks in the coating that developed during loading. (The tensile axis is horizontal.)

Figure 6.11 SEM micrograph showing cracking on the surface of the polymer-coated specimen following deformation to 0.8%. (The straining direction is horizontal.)

In order to understand the damage mechanism the surface of the specimen was examined in a transmission optical microscope. A micrograph of the specimen is shown in Figure 6.10, and it can be seen that there is network of cracks (or possibly crazes) over the specimen surface – these cracks were not present in the specimen before deformation. The spacing of the cracks in the specimen is of the order of 20 µm and consistent with the pattern of deformation seen in Figure 6.7. Similar cracks are seen on the surface of the specimen following deformation as shown in Figure
6.11. It appears therefore that the cracks developed during deformation, although it is not possible to tell if they are in the coated polymer layers or extend into the surface of the PMMA beam. The craze strain of bulk PMMA is over 1% [10] and so it is most likely that cracking took place in the SU-8 and/or PMMA coatings. Hence it appears that the failure mechanism is that shown in Figure 6.9(c). The failure stress of graphene is in excess of 100 GPa and the failure strain over 20% [11] and so unlikely that the graphene monolayer would have fractured at an applied strain of only 0.8%.

6.3.4 Interfacial shear stress

The pattern of deformation seen at high strains in Figure 6.7 is reminiscent of that obtained during the fragmentation test with single-fibre composites [12-13]. In the case of fibre composites it is the fibre that undergoes failure rather than the matrix. It is possible, however, to use the same approach to estimate the shear stress, \( \tau_i \), at the interface between the graphene and polymer by assuming that the shear stress at the interface is balanced by the variation of strain, \( \varepsilon_g \) in the graphene monolayer, with distance along the fragments, \( x \), using the Equation (5.16) leading to a value of interfacial shear stress of the order of 0.25 MPa, using a Young’s modulus \( E_g \) of 1050 GPa for the graphene and a thickness \( t \) of 0.35 nm for the graphene.

It appears that the fragmentation process completely destroys the interfacial adhesion between the graphene and the polymers. The previous chapter showed that the initial level of interfacial shear stress in a similar specimen was of the order of 2 MPa but fell significantly once a triangular–shaped strain distribution developed at higher strain, again probably due to cracking of the polymer layers.

It is interesting to speculate why these values of interfacial shear stress for graphene monolayers in a polymer matrix are significantly lower than those of 20-40 MPa measured for carbon fibres [12-13]. The graphene is atomically smooth and the interactions can only be van der Waals in character. Computer simulations [14] and modelling [15] of the failure of graphene-polymer interfaces in shear predict values of
interfacial shear strength of the order of 100 MPa. Although these values are unrealistic since the polymer matrix will undergo shear yielding at around 50 MPa [10], there is clearly a discrepancy between the measured and predicted values. It is known that graphene surfaces can easily become contaminated with hydrocarbons and other matter in air [16]. This contamination may be one of the factors that are responsible for the poor adhesion with polymers.

Although the presence of holes and defects [17-18] leads to graphene oxide having mechanical properties that are significantly inferior to those of graphene [19-20], the presence of functional groups on the surface [21] may offer better interaction with polymers, particularly if they contain reactive groups such as in the case of epoxy resins. Significant levels of reinforcement have been reported in bulk composites reinforced with graphene oxide [22] and graphene oxide may therefore have the optimum combination of properties for use in nanocomposites, reasonable stiffness, and strength combined with the presence of reactive functional groups capable of forming a strong interface with the matrix polymer [23].

6.4 Conclusions

It has been demonstrated that the detailed strain distribution in the graphene monolayer can be mapped in a model composites specimen using Raman spectroscopy, and good stress transfer from the polymer matrix to the graphene monolayer has been demonstrated at matrix strain up to 0.6%. At higher strains fragmentation takes place in the polymer matrix and the interfacial shear stress in the fragments falls to as low as 0.25 MPa, indicating relatively poor adhesion at the graphene-polymer interface. There is clearly a need for more work to be undertaken upon improving the adhesion between the graphene and polymer matrix before the graphene can be employed a reinforcing phase in polymer nanocomposites for structural applications. This chapter has given a clear demonstration of a technique
that can be used to assess the levels of reinforcement in such systems with high precision.
Chapter 6 Strain Mapping in a Graphene Monolayer Nanocomposite

References


172


Chapter 7 Optimizing the Reinforcement of Polymer-Based Nanocomposites by Graphene

7.1 Introduction

The previous two chapters have shown that stress transfer to monolayer graphene is relatively well understood, the aim of this chapter is to evaluate and compare the levels of reinforcement in nanocomposites by exfoliated graphene flakes consisting of a different numbers of layers, paying particular attention to the behaviour of bilayer, trilayer and few-layer graphene materials. In one of the first investigations of the deformation of exfoliated graphene flakes, Ni et al.[1] found that the shift rate of trilayer graphene upon a polyester film was less than that of the monolayer material. Tsoukleri and coworkers [2] followed the deformation of polymer-coated graphene flakes upon a PMMA beam and found that the shift rate of the 2D band for few-layer material (that they termed “graphite”) was lower than that for monolayer graphene. Moreover, they found that the band-shift rate for the few-layer graphene without a top coat (i.e. a polymer interface on only one surface of the flake) was very low. Procter et al. [3] followed the shifts of the G and 2D bands of graphene, with different numbers of layers, supported uncoated upon the surface of 100 µm thick silicon wafers subjected to hydrostatic pressure. The graphene followed the biaxial compression of the surface of the silicon wafer during the pressurization since the thickness of the graphene was very much less than that of the silicon. Procter et al. [3] found that the highest rate of band shift (per unit pressure) was for a graphene monolayer. This band shift rate for bilayer graphene on the silicon substrate was slightly lower than that of the monolayer, whereas the shift rate of their “few-layer” graphene was only half that of the monolayer material. It was suggested [3] that this

§ This chapter is based upon a paper of “Optimizing the Reinforcement of Polymer-Based Nanocomposites by Graphene” in ACS Nano 6(4) 2012, DOI: 10.1021/nn203917d.
lower rate for few-layer material might be due to poor adhesion with the substrate. It is clear, therefore, that there is need for a systematic study to the effect of the number of layers in graphene upon its deformation behaviour and hence the ability to reinforce polymer matrices with graphene.

7.2 Materials and Methods

The specimens were prepared using 5 mm thick poly(methyl methacrylate) beams spin-coated with 300 nm of cured SU-8 epoxy resin as in Chapter 3. Well-defined Raman spectra could be obtained from the graphene with different numbers of layers, using either a low-power (< 1 mW at the sample) HeNe laser (1.96 eV) or near IR laser (1.58 eV) in Renishaw 1000 or 2000 spectrometers. The laser beam polarizations were always parallel to the tensile axis and the spot size of the laser beams on the sample was approximately 2 µm using a 50× objective lens.

One uncoated beam was unloaded after initial measurements had been made and then coated with a layer of cured SU-8. The beam was reloaded initially up to 0.4% strain, and the deformation of the monolayer and bilayer graphene on same flake on the surface of the beam was again followed from the shift of the 2D Raman band. The beam was then unloaded and then reloaded to various other levels of strain and the shift of a trilayer region on the same flake and a few-layer graphene flake was also followed from the shift of the 2D Raman band.

The strains in the graphene flake containing both monolayer and bilayer regions were mapped fully at each strain level as well as in the unloaded state. Raman spectra were obtained at different strain levels through mapping over the graphene monolayer in steps of between 2 µm and 5 µm by moving the x-y stage of the microscope manually and checking the position of the laser spot on the specimen relative to the image of the monolayer on the screen of the microscope. The strain at each measurement point was determined from the position of the 2D Raman band using the calibrations in Figure 7.1 and strain maps of the bilayer were produced in the form of coloured x-y contour
maps using the OriginPro 8.5 graph-plotting software package, which interpolates the strain between the measurement points.

7.3 Results and Discussion

7.3.1 Graphene deformation

Figure 7.1 Shift with strain of 2D Raman band of the graphene fitted to a single peak during deformation upon the PMMA beam (laser excitation 633 nm). (a) A graphene monolayer deformed before and after coating with SU-8. (b) A graphene bilayer deformed before and after coating with SU-8. (Schematic diagrams of the deformation of the uncoated (above) and coated (below) graphene are also included.)

Deformation of the graphene was undertaken by bending polymer beams on which flakes had been deposited. This leads to an axial strain in the graphene whereas the stress is somewhat biaxial in nature due to Poisson’s contraction effects. The crystallographic orientation of the flakes was not taken into account. Since all measurements were undertaken under similar conditions, all data are quoted in terms
of graphene strain and only the relative bands shifts during deformation were considered.

The shift of the 2D band with tensile strain for different monolayer and bilayer graphene flakes, deformed both before and after applying the SU-8 top-coat, is shown in Figure 7.1. The maximum strain in this case was 0.4% which is known to be below the level of strain at which debonding of the flakes or matrix polymer cracking can occur [4]. It can be seen from Figure 7.1(a) that the shift of the 2D Raman band for the graphene monolayer is -59 cm⁻¹/% strain and similar with and without the polymer top-coat. It is well established that the rate of shift per unit strain of the 2D Raman band for monolayer graphene depending upon the crystallographic orientation of the monolayer relative to the strain axis [5-7] and this value is within the range found by others, in both uncoated and coated specimens. In contrast, it is shown in Figure 7.1(b) that when the 2D Raman band is fitted to a single peak, the rate of shift per unit strain for an uncoated graphene bilayer (-31 cm⁻¹/% strain) is significantly less that of the same flake deformed after being coated (-53 cm⁻¹/% strain). The implications of this observation for the bilayer is that stress transfer between the polymer substrate and the graphene is relatively good, as has been found before [8], but that the efficiency of stress transfer between the lower and upper graphene layers is relatively poor. This is not an issue for the monolayer in Figure 7.1(a) where the presence of the top-coat makes no difference to the band shift rate.

The band-shift data in Figure 7.1(b) are for the 2D band for the bilayer graphene fitted to a single peak. It is well established [9-10] that the 2D band for the bilayer material can be fitted to four peaks as shown in Figure 7.2. Details of this band are also shown in Figure 7.2 before and after deformation to 0.4% strain for the specimen both uncoated and coated. It is found that the four peaks making up the band shift during deformation but remain otherwise unchanged (except for small relative intensity changes), demonstrating that the A-B Bernal stacking is maintained during the deformation of the specimen, in both the uncoated and coated states. Similar
behaviour has been reported by Frank et al. [11] although they did find evidence of local Bernal to non-Bernal transitions due possibly to cohesive failure of the few layer graphene.

Figure 7.2 Details of the 2D Raman band for the bilayer graphene both before and after deformation to 0.4% strain when it is either uncoated or coated. The fit of the band to four sub-bands is shown in each case in green and the fitted curve is shown in red (laser excitation 785 nm).

In order to gain a further insight into the behaviour of flakes with different numbers of graphene layers the deformation of a single coated flake containing distinct regions of monolayer, bilayer and trilayer graphene (identified before deformation) was first investigated. An optical micrograph of the flake is given in Figure 7.3(a) along with a schematic diagram in Figure 7.3(b) showing the different regions in the micrograph determined from both thickness contrast and Raman spectra. The 2D Raman spectra obtained from the monolayer, bilayer and trilayer regions are shown in Figure 7.3 (c)-(e) respectively. It can be seen that the monolayer 2D band comprises a single
peak whereas the bilayer and trilayer 2D bands can be fitted to four [9-10] and six [10] sub-bands respectively. In addition, a 2D band of a coated few-layer graphene flake (micrograph not shown) is given for reference in Figure 7.3(f). The band in this case is similar to that of graphite [10].

Figure 7.3 Graphene flake on a PMMA beam showing monolayer, bilayer and trilayer regions. (a) Optical micrograph (the fine straight lines are scratches on the surface of the beam). (b) Schematic diagram of the flake highlighting the different areas (the rectangle shows the area of the flake over which the strain was mapped). (c-f) Raman spectra of the 2D band part of the spectrum for the monolayer, bilayer (fitted to 4 peaks), trilayer regions (fitted to 6 peaks) and a few layer graphene flake, elsewhere on the beam (laser excitation 633 nm).

Figure 7.4 shows how the deformation of the middle of adjacent monolayer, bilayer and trilayer regions of the flake in Figure 7.3 up to 0.4% strain was followed from the shifts of their 2D Raman bands. The advantage of doing this on the same flake is that it can be ensured that the orientation of the graphene is identical in each region (A-B Bernal stacking is confirmed from the forms of the 2D bands [10] in Figure 7.3(c)-(f). The shift with strain of the four components of the bilayer graphene 2D band is shown in Figure 7.4(a). The shift of the adjacent monolayer region is shown for comparison. The 2D$_{1B}$ and 2D$_{2B}$ sub-bands (labelled) are relatively weak and therefore are
somewhat scattered but it can be seen that the slope of the two strong components 2D_{1A} and 2D_{2A}, are similar to each other, (-53 and -55 cm^{-1}/% strain respectively) and also similar to the slope of the adjacent monolayer region (-52 cm^{-1}/% strain).

Figure 7.4 (a) Shift with strain of the four components of the 2D Raman band of the bilayer graphene shown on the specimen in the Figure 7.3 along with the shift of the 2D band in an adjacent monolayer region on the same flake (laser excitation 633 nm).
(b) Shifts with strain of the 2D band for adjacent monolayer, bilayer and trilayers regions on the specimen in Figure 7.3, along with the shift with strain for the 2D band of a few layer flakes on the same specimen (all 2D bands were force fitted to a single Lorentzian peak).

The 2D band shifts with strain of the four different coated graphene structures is given in Figure 7.4(b), with 2D band force fitted to a single Lorentzian peak in each, for comparison purposes. The few layer graphene was from a different region of the specimen and the strain in trilayer was off-set since it was deformed after pre-loading of the beam to examine the behaviour other regions and so a permanent set had developed. The 2D Raman band positions at a given strain are off-set from each other.
due to differences in the band structure of the different forms of graphene, as has been shown elsewhere [9-10]. It can also be seen that the slopes of the plots are similar for the monolayer and bilayer material (-52 and -53 cm\(^{-1}\)/% strain respectively) but somewhat lower for trilayer at -44 cm\(^{-1}\)/% strain. In contrast, the slope for the few-layer graphene is significantly lower at around -8 cm\(^{-1}\)/% strain.

Figure 7.5 Three sets of data for the shift of the 2D Raman band with strain for uncoated monolayer graphene flakes (laser excitation 785 nm).

Although the data shown in Figures 7.1 & 7.4 suggest that the 2D band shifts rates vary with the number of layers in the graphene and the presence or of absence a polymer top coat, there is always the possibility that such variations may be due to inhomogeneities or uneven stress transfer due to slippage [11]. Variations in the band shift behaviour are also known to occur due differences in excitation wavelength, relative orientation of the graphene lattice to the straining direction and direction of laser polarisation [6-7, 12-13]. Because of this a systematic study was undertaken of the band shifts during deformation for more than 30 different graphene flakes on polymer beams in different orientations, consisting of different numbers of layers, both uncoated and with a polymer top coat. A different laser excitation was also employed (785 nm rather than 633 nm) and the data were carefully screened for
evidence of slippage. Details of this investigation are given as shown in Figure 7.5 & 7.6 and the relative 2D band shift rates with strain are summarized in Table 7.1.

The reproducibility of the band shift behaviour was first investigated in the case of an uncoated monolayer as shown in Figure 7.5. Three sets of data are presented and it can be seen that they all show a shift to lower wavenumber upon straining with two very close to each other. In one set of data, however, there is an abrupt shift to higher wavenumber at around 0.25-0.30% strain. This is due to slippage of the graphene on the polymer beam. In this case only the initial loading data were employed. All measurements of strain-induced band shifts were screened for similar effects and only data where no obvious slippage had taken place are presented in Table 7.1.

Figure 7.6 Representative shifts with strain of the 2D Raman bands band for different graphene flakes regions. (a) Uncoated condition. (b) Coated condition. Data were obtained from different flakes without and with an SU-8 coating. All 2D bands were force fitted to a single Lorentzian peak and the laser excitation was 785 nm.
Table 7.1 Measured 2D Raman band shift rates (with standard deviations) for the uncoated and coated graphene nanocomposite specimens described in Figure 7.5 & 7.6 (laser excitation 785 nm). All bands were fitted to a single Lorentzian peak and the number of flakes on which the measurements were made is indicated.

<table>
<thead>
<tr>
<th>Number of layers</th>
<th>Coating</th>
<th>$\frac{d\omega_{2D}}{d\epsilon}$ (cm$^{-1}$/% strain)</th>
<th>Number of flakes studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Uncoated</td>
<td>-48.8 ± 2.5</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Uncoated</td>
<td>-38.9 ± 2.4</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>Uncoated</td>
<td>-32.4 ± 0.4</td>
<td>2</td>
</tr>
<tr>
<td>&gt;3</td>
<td>Uncoated</td>
<td>-37.4 ± 8.2</td>
<td>3</td>
</tr>
<tr>
<td>Graphite</td>
<td>Uncoated</td>
<td>-3</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>Coated</td>
<td>-57.7 ± 7.8</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Coated</td>
<td>-53.9 ± 2.9</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Coated</td>
<td>-46.6 ± 9.0</td>
<td>6</td>
</tr>
<tr>
<td>&gt;3</td>
<td>Coated</td>
<td>-40.2 ± 14.2</td>
<td>7</td>
</tr>
<tr>
<td>Graphite</td>
<td>Coated</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 7.6 shows representative 2D band shifts with strain for graphene flakes, with and without an SU-8 coating, on a polymer beam. The data were all force fitted to single Lorentzian peaks. The number of layers in the graphene flakes was determined from the appearance of the graphene, the initial 2D band position and the form of the 2D peak. In some cases it was difficult to distinguish few-layer material from few-layer graphene or graphite. Data for the deformation of flakes of graphite on the beams are also given. The general shift of the data to higher wavenumber in the coated samples is most likely due to residual stresses induced by curing the SU-8
coating. The average slopes from measurements taken upon all flakes are given in Table 7.1.

For the uncoated specimens in Table 7.1, it can be seen that there is a decrease in the band shift rate for the flakes as the number of layers is increased from one to three. The shift rate data are more scattered for the few layer flakes as is impossible to know the exact number of layers in such flakes. The shift rate for a graphite flake on the same uncoated specimen is also very low. In contrast the band shift rates are generally higher in the case of the coated specimen. The monolayer and bilayer flakes in the coated specimen have the same band shift rate within the limits of experimental error and the band shift rate then decreases for the three layer and few layer flakes (again more scattered for the same reason as before). The shift rate for a graphite flake is again very low. The band shift behaviour shown in Figures 7.1 & 7.4 is completely consistent with the comprehensive set of data in Table 7.1. Similarly Procter et al. [3] found that the band shift rate for (uncoated) bilayer graphene on the silicon substrate under pressure was slightly lower than that of the monolayer, whereas the shift rate of their “few-layer” graphene was only half that of the monolayer material. Although they suggested that this lower rate for few-layer material could be due to poor adhesion with the substrate, the findings in Table 7.1 imply that it is more likely that this lower band shift rate is an inherent property of the few-layer material.

7.3.2 Theoretical analysis

It is well established that, to a first approximation, the band shift rates in Table 7.1 can be related to the efficiency of stress transfer to the graphene [8, 14-15]. All the data were obtained from the middle of the flakes and by eliminating any data showing slippage at the graphene-polymer interface. Differences with respect to the monolayer will therefore principally be a result of the efficiency of stress transfer between the different graphene layers (the effect of different crystallographic orientations of the graphene will lead to only minor differences) [6, 12]. This phenomenon is completely analogous to the efficiency of stress transfer between the different walls in multi
-walled carbon nanotubes (MWNTs) analyzed by Zalamea, Kim and Pipes [16]. They introduced a parameter $k_i$ that characterizes the efficiency of stress transfer; for perfect transfer between the walls, $k_i = 1$ and for no stress transfer, $k_i = 0$. This analysis has been used to successfully model [17] stress transfer between the outer and inner walls of double-walled carbon nanotubes (DWNTs), made by the pea-pod route [18], in a nanocomposite. It is relatively easy to adapt this theory to model stress transfer between the layers of few layer graphene. The effective Young’s modulus of a multi-walled nanotube (MWNT) is given by [16]:

$$E_{\text{eff}} = \frac{A_1}{(A_T + A_0)} E_g$$

(7.1)

where $E_g$ is the Young’s modulus of graphene, $k_i$ is the stress transfer efficiency factor, $A_1$ is the cross-sectional area of the outermost shell, $A_T$ is the total area of the MWNT excluding the annulus and central hole and $A_0$ is the combined area of the annulus between the layers and the centre of the nanotube. This equation can be easily adapted for few layer graphene assuming it to be flat rather than having a circular cross-section with a hole down the middle (i.e. $A_0 = 0$). It can be imagined that the MWNT can be split open and laid flat on the surface of the beam to give in the case of few layer graphene in the uncoated state,

$$E_{\text{eff}} = \frac{E_g}{n_l - k_i(n_l - 1)}$$

(7.2)

where $n_l$ is the number of layer of graphene in the few layer flake. The analogy is reasonable since a polymer matrix is only in contact with the outer walls of the nanotube and the polymer matrix is only in contact with one surface of the graphene for the few layer flake. The equation gives sensible prediction for the two extreme cases: if $k_i = 0$, then $E_{\text{eff}} = E_g/n_l$ and if $k_i = 1$, then $E_{\text{eff}} = E_g$.

Equation (7.2) needs to be adapted in the case of a coated specimen where the polymer matrix is in contact with the top and bottom surfaces of the few layer flake. In this case the stress transfer is mirrored either side of the flake and the number of
layers is effectively halved. Therefore for \( n_l \geq 2 \)

\[
E_{\text{eff}} = \frac{E_g}{\left[ \frac{n_l}{2} - k_i \left( \frac{n_l}{2} - 1 \right) \right]} \quad \text{(Coated)} \tag{7.3}
\]

It is known [19-20] that the shift of the 2D Raman band with strain is \( \frac{d\omega_{2D}}{d\varepsilon} \) is proportional to the effective Young’s modulus of the graphene and therefore the slopes of the lines in Figures 7.1, 7.4(b), Equation (7.1) & (7.3) are an indication of the efficiency of stress transfer. To a first approximation, therefore, the value of \( k_i \) can be determined in the case of the uncoated specimens by modifying Equation (7.2) to give

\[
(d\omega_{2D} / d\varepsilon)_{\text{Uncoated}} = \frac{(d\omega_{2D} / d\varepsilon)_{\text{Monolayer}}}{[n_l - k_i (n_l - 1)]} \tag{7.4}
\]

In the case of coated specimens, Equation (7.2) can be adapted to give

\[
(d\omega_{2D} / d\varepsilon)_{\text{Coated}} = \frac{(d\omega_{2D} / d\varepsilon)_{\text{Monolayer}}}{[(n_l / 2) - k_i ((n_l / 2) - 1)]} \tag{7.5}
\]

The data in Table 7.1 were all fitted to Equations (7.2) and (7.3) by assuming that the shift of the 2D Raman band with strain is \( d\omega_{2D}/d\varepsilon \) is proportional to the effective Young’s modulus of the graphene and the results are shown in Figure (7.7). In each case sets of lines are given for different values of the stress transfer efficiency factor, \( k_i \). It can be seen that in the case of the uncoated specimen the value of \( E_{\text{eff}}/E_g \) decreases as the number of graphene layers increases from one to three. The point for few-layer material has more scatter for the reasons outlined above. Overall the data fall closest to a stress transfer efficiency factor of around 0.8.

The behaviour for the coated samples is somewhat different. There is no significant decrease in \( E_{\text{eff}}/E_g \) between monolayer and bilayer material as predicted by the theory. The value of \( E_{\text{eff}}/E_g \) then decreases for three layer and few layer material and the behavior then follows the theoretical prediction for a stress transfer efficiency factor of around 0.6.
Figure 7.7 Derived values of $E_{\text{eff}}/E_g$ as a function of the numbers of layers, $n_l$, in the graphene. The theoretical lines are given using Equation (7.2) for the uncoated samples and Equation (7.3) for the coated ones. (The error bars for $E_{\text{eff}}/E_g$ represent one standard deviation).

Using equation (7.5) the data in Table 7.1 lead to $k_i \sim 0.6$ for stress transfer between the layers in few layer graphene. This analysis is rather simplistic but it demonstrates clearly that internal stress transfer is less than 100% efficient for both uncoated and coated graphene flakes. Moreover, it is known that each layer of the graphene absorbs 2.3% of the light [21] and so the Raman laser beam will only penetrate the outer layers of a few layer flake. Hence the measured band shift for the few-layer flake comes primarily from layers near the surface and this should be taken into account in a more thorough analysis.
The relatively-weak van der Waals bonding between the individual graphene layers of graphite allows sliding between the layers to take place relatively easily, like the shearing of a deck of cards, leading to the low-friction properties of graphite. The frictional characteristics of graphene have recently been investigated using friction force microscopy and it is found that the friction on SiC is reduced greatly by the presence of a graphene monolayer which is reduced by a further factor of two for bilayer graphene [22]. In a systematic investigation upon different graphene samples with up to four layers it was found that the friction decreased monotonically as the number of graphene layers increased [23] and tended towards the value for the bulk material value. It appears, therefore, that this easy shear between the graphene layers controls the dependence of both the frictional behaviour and efficiency of stress transfer upon the number of layers in a graphene flake.

It is worthwhile to consider the implications of these findings upon the design of graphene-based nanocomposites. If we take the parameter \((d\omega_{2D}/d\epsilon)_{\text{Measured}}\) as an indication of the ability of the graphene to reinforce a polymer matrix then the first finding is that bilayer graphene will be equally as good as monolayer graphene. Moreover, only around 15\% of the reinforcing efficiency is lost with trilayer graphene. In fact, if \(k_i\) is taken as 0.6, then it is only when \(n_l > 7\) that the reinforcing efficiency of the graphene falls to less than half of that of the monolayer material.

### 7.3.3 Variation of strain across the flake

As well as the number of layers in a graphene flake being important for reinforcement, it has already been established that lateral dimensions of the flake have a major effect as well [8]. Mapping of strains across a monolayer flake combined with shear-lag analysis has revealed that when a flake is deformed in a nanocomposite the strain builds up from zero at the edges to be the same as that in the matrix in the centre of the flake, if the flake is large enough (typically > 10 µm) [8]. Obtaining large exfoliated flakes in significant quantities remains something of a challenge [24]. Because of this, the strain was mapped in the bilayer region over the flake shown in
Figure 7.3 at different levels of matrix strain, $\varepsilon_m$, using the strong 2D$_{1A}$ component of the bilayer 2D band, and the results are given in Figure 7.8.

It can be seen that there is initially ($\varepsilon_m = 0.0\%$) a small amount of residual strain the bilayer graphene but that when $\varepsilon_m$ is increased to 0.4%, strain develops in the middle regions of the graphene bilayer, falling away at the edges. When the matrix strain is increased further, the distribution of strain in the graphene becomes less uniform and areas of both high and low strain develop in the middle regions of the flake.

![Figure 7.8 Maps of strain in the graphene bilayer regions of the flake shown in Figure 7.3, determined from the shift of the 2D$_{1A}$ component of the 2D Raman band, for different levels of matrix strain in the direction indicated by the arrow (laser excitation 633 nm). The black dots indicate where measurements were taken and the individual rows of data analyzed later are marked. The monolayer and trilayer regions in the flake have been masked out for clarity.](image-url)
Figure 7.9. Variation of strain in the graphene bilayer with position along row 2 (indicated in Figure 7.8), at different levels of matrix strain, $\varepsilon_m$, showing the development of a matrix crack (see schematic diagram).

The observation of the variation of strain across the flake at different strain levels gives further insight into the variety of deformation process of the bilayer in the nanocomposite. Figure 7.9 shows the variation of strain along row 2 (see Figure 7.8) at different levels of matrix strain $\varepsilon_m$. Initially there appears to be a residual strain at the left-hand end of the flake, possibly as a result of the fabrication process and...
coating. At $\varepsilon_m = 0.4\%$ the strain builds up to a plateau value of around 0.4% strain dipping down slightly in the middle of the flake. It then falls to zero at the right-hand end. The plots at $\varepsilon_m = 0.6\%$ and 0.8% strain are similar to each other, showing two triangular distributions across the flake, with the strain falling to zero at either end and also in the middle of the flake. This behaviour has been seen before for a large monolayer flake [4] and was attributed to the development of cracks in the SU-8 polymer coating although a recent study has suggested that it also could be due to cracking of the graphene [11]. Inspection of the map for $\varepsilon_m = 0.8\%$ in Figure 7.8 shows that similar large ‘peaks’ and deep ‘valleys’ have developed in the strain distribution for the graphene bilayer.

The triangular-shaped strain distributions are characteristic of frictional stress transfer at the graphene-polymer interface and it is possible to estimate the shear stress at this interface, $\tau$, from the slopes of the lines in Figure 7.9 using the force balance equation (5.16) as described in Chapter 5. Putting the measured slopes from Figure 7.9 into the equation gives a value of interfacial shear stress that increases from 0.15 MPa at 0.4% matrix strain to around 0.3 MPa at 0.8% matrix strain.

The variation of strain across the flake in the direction of tensile straining was also determined along rows of data points along the top of the flake where there are regions of adjacent monolayer and bilayer material (see Figure 7.3 (b)). Figure 7.10 (a) shows the strain variation in the bilayer and monolayer regions along row 13 at 0.6% matrix strain. The graphene strain was determined using the monolayer and bilayer calibrations from Figure 7.4 (b) and the graphene structure along the row is also shown in the schematic diagram in Figure 7.10. It can be seen that in this case there is a continuous variation of graphene strain along the row indicating elastic stress transfer across the graphene-polymer interface. The data points in Figure 10 (a) were fitted to shear lag theory using Equation (5.15) with fitting parameter $n_s$ of 10. The points all fall close to the theoretical line, giving further support to the observation that continuum mechanics is still applicable at the nano-scale, even though the strain
distributions may vary in detail between different places on the flake (c.f. Figure 7.9 & 7.10).

Figure 7.10 (a) Variation of strain in the monolayer and bilayer regions of graphene with position along row 13 (indicated in Figure 7.8) at an applied strain of 0.6%. The theoretical curve is a fit to the data points using Equation (5.15) derived from shear lag theory with $ns = 10$. (b) Correlation of measured strains in adjacent regions of the monolayer and bilayer graphene in rows 11-13 (Figure 7.8) at 0.6% applied strain. (The schematic diagram shows the variation of the number of graphene layers across the row).

The parameter $s$ is the aspect ratio of the flake equal to $l/t$, where $t$ is the flake thickness. It may be significant that in a previous study that mapped strain along a graphene monolayer flake, the data could be fitted best to Equation (5.15) using a
value of $n_s = 20$. This may be explained as being because the bilayer graphene is twice the thickness of monolayer graphene, the aspect ratio, $s$, will be halved for a flake of bilayer material of the same length, $l$. It should also be noted, however, that the value of $n$ depends upon $l^{1/2}$ and so this needs to be taken into account as well [8].

The continuity of strain between monolayer and bilayer regions was investigated further and similar measurements were also undertaken along rows 11 and 12 (Figure 7.8). Figure 7.10 (b) shows the correlation between the strain measured for adjacent points in rows 11-13 at a matrix strain of 0.6%. It can be seen that the data fall close to the line for uniform strain. This confirms the finding above that there is the same level of reinforcing efficiency for both monolayer and bilayer graphene.

### 7.3.4 Optimisation of reinforcement

![Diagram](image)

Figure 7.11 Schematic diagram of the microstructure of graphene-based nanocomposites based upon either monolayer or trilayer reinforcements. The interlayer spacing of the graphene is 0.34 nm and the effective thickness of the polymer coils is assumed to be to be around 2 nm.

At this stage it is worth considering the relative advantage of using bilayer graphene compared with the monolayer material. If we take two monolayer flakes dispersed well in a polymer matrix, the closest separation they can have will be of the order of the dimension of a polymer coil, i.e. at least several nm [25]. In contrast the
separation between the two atomic layers in bilayer graphene is only around 0.34 nm and so it will be easier to achieve higher loadings of the bilayer material in a polymer nanocomposite, leading to an improvement in reinforcement ability by up to a factor of two over the monolayer material.

Figure 7.12 (a) Effective graphene Young’s modulus, $E_{\text{eff}}$, and maximum graphene volume fraction for different indicated polymer layer thicknesses, as a function of the number of layers, $n_l$, in the graphene flakes. (b) The maximum nanocomposite modulus predicted for different indicated polymer layer thicknesses as a function of the number of layers, $n_l$, in the graphene flakes.
It is possible to determine the optimum number of layers need in the graphene flakes for the best levels of reinforcement in polymer-based nanocomposites. It was pointed out above that the effective Young’s modulus of monolayer and bilayer graphene is similar and that it decreases as the number of layers decreases. In high volume fraction nanocomposites it will be necessary to accommodate the polymer coils between the graphene flake and the coil dimensions will limit the separation of the flakes as shown schematically in Figure 7.11. Similar issues have been considered by Klein and Luckham [26] for polymer solutions between parallel mica platelets and also by de Gennes [27]. The minimum separation of the graphene flakes will depend upon the type of polymer (i.e. it chemical structure and molecular conformation) and its interaction with the graphene. It is unlikely that the minimum separation will be less than 1 nm and more likely that it will be several nm. The separation of the layers in few layer graphene, on the other hand, is of the order of 0.34 nm.

If a nanocomposite is assumed to be made up of parallel graphene flakes separated by thin polymer layer of the same uniform thickness (Figure 7.11), then it is possible to show that for a given polymer layer thickness, the maximum volume fraction of graphene in the nanocomposite will increase with the number of layers in the graphene, as shown in Figure 7.12(a). The Young’s modulus, $E_c$, of such a nanocomposite can be determined using the simple “rule-of-mixtures” model such as [25]

$$E_c = E_{\text{eff}} V_g + E_m V_m$$  \hspace{1cm} (7.5)

where $E_{\text{eff}}$ is the effective Young’s modulus of the few layer graphene, $E_m$ is the Young’s modulus of the polymer matrix (~3 GPa), and $V_g$ and $V_m$ are the volume fractions of the graphene and matrix respectively ($V_g + V_m = 1$). The maximum nanocomposite Young’s modulus can be determined using this equation along with the data in Figure 7.12(a) and is shown in Figure 7.12(b) as a function of $n_l$ for polymer layers of different thickness. It can be seen that it peaks at $n_l = 3$ for a polymer layer thickness of 1 nm and then decreases and the number of graphene layer in the flakes and polymer thickness increase. For a layer thickness of 4 nm the
maximum nanocomposite Young’s modulus is virtually constant for \( n_l > 5 \). This analysis assumes that the graphene flakes are infinitely long but the maximum Young’s modulus will be reduced for flakes of finite length because of shear-lag effects at the flake edge (Figure 7.12(a)). The exact form of plots such as Figure 7.12(b) and optimum value of \( n_l \) will depend upon value of the stress transfer efficiency factor, \( k_i \), but it serves as a useful design guide for graphene-based nanocomposites.

### 7.4 Conclusions

It has been demonstrated that although there is good stress transfer between a polymer matrix and monolayer graphene, monolayer graphene is not the optimum material to use for reinforcement in graphene-based polymer nanocomposites. There is also good stress transfer from the polymer matrix to the bilayer material and no slippage between the layers when it is fully encapsulated in a polymer matrix. Less efficient stress transfer has been found for trilayer and few-layer graphene due to slippage between the internal graphene layers, indicating that such materials will have a lower effective Young’s modulus than either monolayer or bilayer graphene in polymer-based nanocomposites. However, since the inter-layer spacing in few layer graphene is only 0.34 nm and so an order of magnitude less than the dimensions of polymer coils, higher volume fractions of graphene can be obtained for few layer material. There is therefore a balance to be struck in the design of graphene-based nanocomposites between the ability to achieve higher loadings of reinforcement and the reduction in effective Young’s modulus of the reinforcement, as the number of layers in the graphene is increased.
References


Chapter 8 Polarised Raman Study of Graphene Deformation

8.1 Introduction

The G band and 2D band of graphene are both strain sensitive since the band position moves to low frequency under the stress. Moreover, due to the large band shift during deformation, the 2D band has been used to investigate the micromechanical properties in graphene, particularly the stress transfer and the interface conditions between the graphene and its surrounding polymer matrix (see Chapter 5-7). However, both the G [1-2] and 2D bands [3-4] have been found in other studies to undergo splitting or asymmetric band broadening under the stress. Therefore, it is essential to understand the relationship between split subbands and their individual band shifts during deformation.

In this chapter, polarised Raman spectroscopy has been adopted as the main technique to monitor the graphene under deformation with different applied strain levels and polarisation configurations. It will be shown that the intensity ratio of $G/JG^+$ reveals the graphene crystallographic orientation with respect to the applied strain axis. Moreover, it has also been found that the intensities of the $2D^+$ and $2D^-$ bands are strongly dependent on the incident laser polarisation whereas it has no effect to the individual band position shift rates. Consequently, it implies that with a fixed strain axis and incident laser polarisation angle, a single peak fit of the 2D band is sufficient in the investigation of the strain or stress across the graphene flakes without any effect from the two individual subbands.
8.2 Materials and Methods

Graphene with various numbers of layers was prepared by the mechanical exfoliation from graphite and was deposited onto a ~300 nm thick SU-8 photoresist layer coated PMMA beam. Each graphene/PMMA beam was spin-coated with another SU-8 or SU-1805 layer on top. The beam was then attached with a strain gauge on the top surface to measure the strain on the beam using a digital voltmeter. Afterwards, the beam was subjected to bending by applying a four-point bending rig as described earlier.

Raman spectra were recorded with both 633 nm (1.96 eV) and 785 nm (1.58 eV) lasers. The laser power was set to the minimum at ~2 mW. A 50× objective lens was used, and the laser spot size is expected to be ~2 \( \mu \text{m}^2 \) in size. The laser was set to the VV configuration in the polarisation study, where both the incident and scattered lights were polarised parallel to the applied strain axis.

8.3 Determination of graphene crystallographic orientation

The crystallographic orientation of graphene flake is defined as the angle between the zig-zag direction and the applied strain direction. It is measured from the uniaxial strain-induced G band splitting [1-2]. Tensile strain induces the G band to shift to lower wavenumber. However, the G band splits into two components, which are termed \( G^- \) and \( G^+ \) respectively, when the strain is raised to a level high enough to distort the graphene symmetry [1-2, 5]. The shift rate for the \( G^- \) band (~30 cm\(^{-1}\)/% strain) is roughly three times to that of the \( G^+ \) band (~10 cm\(^{-1}\)/% strain). The value of \( d\omega_G^-/d\varepsilon \) and \( d\omega_G^+/d\varepsilon \) determined by various groups are summarised in Table 8.1.

The shift rate from Huang et al. [1] seems to be much lower than the other groups. It may mainly be attributed to the substrate they used, since the strain in non-free standing graphene is transferred from the substrate during deformation. Considering the Poisson’s ratio effect, the in-plane Poisson’s ratio for a graphene is ~0.13. The
Columbia researchers [1] selected PMDS as the studied substrate which has a rubbery structure with a larger Poisson’s ratio (~0.5). On the other hand, the others used acrylic substrates which are thermoplastic polymers with a lower Poisson’s ratio (~0.3). In addition, the method of strain calibration may also be another reason for a different shift rate [1].

Table 8.1 Summary of $d\omega_G/d\epsilon$ (cm$^{-1}$/% strain).

<table>
<thead>
<tr>
<th>References</th>
<th>$d\omega_G^-/d\epsilon$ (cm$^{-1}$/% strain)</th>
<th>$d\omega_G^+/d\epsilon$ (cm$^{-1}$/% strain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huang et al.[1]</td>
<td>-12.5</td>
<td>-5.6</td>
</tr>
<tr>
<td>Mohiuddin et al.[2]</td>
<td>-31.7</td>
<td>-10.8</td>
</tr>
<tr>
<td>Frank et al.[5]</td>
<td>-31.4</td>
<td>-9.6</td>
</tr>
<tr>
<td>Frank et al.[6]</td>
<td>-31.3</td>
<td>-9.9</td>
</tr>
<tr>
<td>Yoon et al.[4]</td>
<td>-33.4</td>
<td>-14.5</td>
</tr>
<tr>
<td></td>
<td>-33.0</td>
<td>-12.9</td>
</tr>
<tr>
<td>This work</td>
<td>-29.7, -28.8</td>
<td>-9.3, -11.7</td>
</tr>
</tbody>
</table>

Figure 8.1 illustrates the representative G band Raman spectra for a monolayer graphene flake as a function of applied unaxial strain. During loading, the G band moves to lower wavenumber with applied strain and moves back on unloading. Moreover, the splitting of the G band becomes pronounced when the strain reaches 0.7%. Below 0.7% strain, the G band just appears broaden with the increasing applied strain. Beyond 0.7% strain, the G band splits into two components which are designated as $G^-$ and $G^+$ respectively [1-2], related to the $E_{2g}^-$ and $E_{2g}^+$ phonon movements, where the $E_{2g}^-$ phonon is parallel to the applied strain whereas the $E_{2g}^+$ phonon is perpendicular to the applied strain. An example of two-peak curve-fit is shown in Figure 8.2. It is easy to understand that these two subbands shift with different rate when the unaxial strain is applied. The $E_{2g}^+$ phonon undergoes a smaller shift rate as the parallel phonon has much more contributions from the parallel strain, giving rise to a greater shift rate. As a matter of fact, it should be noted here that the
$E_{2g}^1$ phonon is affected by both the tensile and compression strain components due to the Poisson’s ratio effect of the applied tensile strain.

Figure 8.1 The Raman G band peaks under various uniaxial strains. (a) Tensile loading. (b) Tensile unloading.

Figure 8.2 An example for Two Lorentzian peaks fit (green solid lines) to the Raman G band. The black dots are the original data and the red solid line is the sum of the fitting peaks.
Figure 8.3 Plots of the G⁻ and G⁺ bands as a function of applied uniaxial strain. (a) Loading plots. (b) Unloading plots.

Figure 8.3 shows plots of the G⁻ and G⁺ bands as a function of applied strain in a loading and an unloading cycle. Except for 0% strain, all the G band spectra were curve fitted by two Lorentzian peaks. It seems that, below 0.3% strain, the positions of the G⁻ and G⁺ bands are scattered to a high wavenumber position, possibly due to the residual strain in the graphene flakes which may be attributed to either the preparation process or shrinkage during the polymer top-coat curing. Moreover, as a result of possible poor surface interaction of the graphene and undersurface SU-8 resin, slippage may occur between the graphene and the surrounded polymer layers, which may explain in the low strain loading case why the band position moves up rather than down. Afterwards, owing to the roughness of the resin surface, the graphene was “locked” to the polymer substrate or coating layer and followed the strain deformation with polymer, consequently, leading the bands to move towards low wavenumber. This is therefore further evidence that graphene can improve the mechanical performance of composites. Above 0.3% strain, the Raman wavenumber for both the G⁻ and G⁺ decrease linearly to a high strain without any slippage or
interfacial failure. As predicted theoretically [1-2], the $G^-$ band has larger shift slope than the $G^+$ band.

![Figure 8.4](image)

**Figure 8.4** Schematic diagram of angles between strain axis, graphene zigzag direction and laser polarisation.

The crystallographic orientation of graphene was calculated from the intensity ratio of the $G/G^+$ peaks at a high strain level when the $G$ band has an obvious splitting as shown in Figure 8.2. The electrons excited by the laser interact and resonate with phonons in the graphene that are sensitive to the crystal lattice and strain axis [7]. The intensities of both subbands are given by [1-2]

$$I_{G^-} \propto \sin^2(\theta_i + \theta_o + 3\varphi_s)$$  \hspace{1cm} (8.1)

$$I_{G^+} \propto \cos^2(\theta_i + \theta_o + 3\varphi_s)$$  \hspace{1cm} (8.2)

where $\theta_i$ is the incident light and $\theta_o$ is the scattered laser polarisation with respect to the strain axis, and $\varphi_s$ is an arbitrary angle between the strain axis and the graphene crystallographic axis (the zigzag axis). The definition of these angular relations is given in Figure 8.4. The Raman spectrometer was set with the VV configuration parallel to the applied tensile strain. Therefore, both the incident and scattered light angles with respect to strain are $0^\circ$. In this case, Equations (8.1) and (8.2) are simplified as

$$I_{G^-} \propto \sin^2(3\varphi_s)$$  \hspace{1cm} (8.3)

$$I_{G^+} \propto \cos^2(3\varphi_s)$$  \hspace{1cm} (8.4)
Combining these two formulae into the expression of intensity ratio between the $G^-$ and $G^+$ gives

$$
\frac{I_{G^-}}{I_{G^+}} = \tan^2(3\varphi_s)
$$

(8.5)

Hence, the graphene crystal orientation with respect to the strain axis can be simply measured from the intensity ratio of the $G^-$ and $G^+$ bands. The crystal orientation for the monolayer graphene flake in this specimen therefore is calculated to be $12.5 \pm 0.2^\circ$ (with respect to the zigzag direction and strain axis).

### 8.4 2D band splitting

![Graph showing 2D band splitting](image)

Figure 8.5 The Raman 2D band features for a monolayer graphene with various strains. (a) Tensile loading. (b) Tensile Unloading.

The 2D band splitting depends on the crystallographic orientation with respect to the strain axis [4, 8]. Figure 8.5 shows several representative 2D Raman spectra from the same flake with the same orientation investigated in Section 8.3 as a function of the applied tensile strain. Obviously, in both the loading and unloading cases, the 2D band moves to lower wavenumber as the strain increases, accompanied by
asymmetric band broadening. Moreover, the 2D band splits more notably at higher strain levels ($\varepsilon \geq 0.6\%$). It is also reversible as the 2D band returns to a single band when the monolayer graphene is unloaded to a relaxed state. The asymmetric 2D band feature can be appropriately fitted by two Lorentzian components, even at low strains when it appears as a single peak, designated as 2D$^-$ and 2D$^+$ according to their wavenumber. Huang et al. [8] claimed that monolayer with a non-zigzag crystallographic orientation or armchair orientation undergoes 2D band broadening but no splitting. These findings are inconsistent with the results presented here in which the crystal orientation of the monolayer specimen shown in Figure 8.5 is $12.5 \pm 0.2^\circ$ as described in the earlier section.

Figure 8.6 shows the 2D peak shift rate can be fitted with two peaks under tensile strain. For the loading case, the shift rates are quite linear with the values of -55.8 and -33.2 cm$^{-1}$/% for the 2D$^-$ and 2D$^+$ respectively. Whereas on releasing the applied strain, the 2D$^-$ shift rate increases to >-60 cm$^{-1}$/% while the shift rate of the 2D$^+$
remains in the same level. This phenomenon is consistent with the previous report [9]. Unlike the flakes studied in the previous chapters, the maximum strain in this case reaches 0.7% strain without debonding, instead there is a linear and smooth trend at high strain levels. This means the interface between this monolayer graphene flake and the surrounding polymer matrix is relatively good. Therefore, on releasing the strain, the monolayer graphene reverses to the original condition prior to deformation. The evidence can be found in Figure 8.6 that the original point at 0% applied strain seems to be the same for both the loading and unloading cases.

![Figure 8.7 Schematic diagrams for reciprocal lattice of the graphene Brillouin zone. (a) Unstrained. (b) Under strain with a 12.5° orientation angle.](image)

It is well established that the 2D band of graphene stems from the double resonance Raman scattering mechanism, involving an electron and phonon interaction near the Dirac K-point in the Brillouin zone [10-11]. The splitting of 2D band is attributed to the inner and outer Raman scattering processes due to the strain-induced movement of the Dirac cones [3-4, 8]. Near the K-point, there are three neighbouring Dirac point which are all termed as K_1’, K_2’, K_3’-points as shows in Figure 8.7. In the unstrained state, the phonon scattering momentum between the three K-K_1’, K-K_2’, K-K_3’ points in the Brillouin zone is highly equivalent, giving rise to a single 2D peak. On the other hand, the application of tensile strain induces the reciprocal lattice to become distorted asymmetrically. In the case of the strain axis parallel to armchair orientation, one of K’ points moves away while the other two K’ points move toward to the K
point. There is an opposite effect for the applied strain in the zigzag direction. The two K’ points move away with same momenta and one K’ point moves close to the K point. Consequently, in both of these two extreme cases, two different phonon scattering processes are involved, corresponding to two different 2D mode frequencies thus leading to a 2D band splitting. Therefore, it is easy to understand that when the applied strain is at an intermediate angle, the contribution of three unequal K’-K lines leads to the 2D band consisting of three subbands contributing to the 2D band [3]. However, due to the relatively low strain levels, two of the subbands are often overlapping and hard to distinguish. Therefore, it is hard to fit the strained 2D band with three peaks. This interpretation can also be validated from the intensity of the 2D band. The arbitrary intensity of the 2D band at 0% strain is 11000 with a FWHM of 26.5 cm$^{-1}$ as shown in Figure 8.8. At 0.7% strain, the arbitrary intensities of the fitted two peaks are 4720 and 3470 with 28.6 cm$^{-1}$ and 30.7 cm$^{-1}$ FWHMs, respectively. Considering the strain-induced band broadening, the broader subband with a FWHM of 30.7 cm$^{-1}$ may actually consist of two peaks.

![Figure 8.8](image)

Figure 8.8 The arbitrary intensities of the 2D band at 0%, and the 2D$^{-}$ and 2D$^{+}$ bands at 0.7% applied strain.
Huang et al. [8] proposed a model for the 2D− and 2D+ band intensity polarisation dependence for the zigzag and armchair orientations of graphene with respect to the incident and scattered lights, given by

\[ I_{Z}^{2D-} \propto \left( \sin^3 \left( \frac{2\pi}{3} - \theta \right) \sin^3 \left( \frac{2\pi}{3} - \theta_i - \theta_o \right) + \sin^3 \theta_i - \theta_i - \theta_o \right) \] (8.6)

\[ I_{Z}^{2D+} \propto \sin^2 \theta_i \sin^2 (\theta_i + \theta_o) \] (8.7)

for the zigzag orientation sample, and

\[ I_{A}^{2D-} \propto \cos^2 \theta_i \cos^2 (\theta_i + \theta_o) \] (8.8)

\[ I_{A}^{2D+} \propto \left( \cos^2 \left( \frac{2\pi}{3} - \theta \right) \cos^2 \left( \frac{2\pi}{3} - \theta_i - \theta_o \right) + \cos^2 \theta_i - \theta_i - \theta_o \right) \] (8.9)

for the armchair orientation sample. \( \theta_i \) is designated as the angle between the incident light polarisation direction and the strain axis and \( \theta_o \) is denoted as the angle of polarisation of the scattered light with respect to the incident light, respectively. These two cases are restricted to the extreme orientations which are not suitable for a graphene monolayer sample with an intermediate orientation. Hence, here an expression is proposed which can be applied appropriately to all sample orientations. Taking into account of both the components contribution from the zigzag and armchair cases, the intensities of the 2D− and 2D+ bands at \( \phi_o \) orientation are then derived as

\[ I_{2D}^{\phi_o} \propto \left( \sin^2 \left( \frac{2\pi}{3} - \theta \right) \sin^2 \left( \frac{2\pi}{3} - \theta_i - \theta_o \right) + \right) \cos 3\phi_o + \cos^2 \theta_i \cos^2 (\theta_i + \theta_o) \sin 3\phi_o \] (8.10)

\[ I_{2D}^{\phi_o} \propto \sin^2 \theta_i \sin^2 (\theta_i + \theta_o) \cos 3\phi_o + \left( \cos^2 \left( \frac{2\pi}{3} - \theta \right) \cos^2 \left( \frac{2\pi}{3} - \theta_i - \theta_o \right) + \right) \cos^2 \theta_i - \theta_i - \theta_o \sin 3\phi_o \] (8.11)

In the VV configuration, the incident light and scattered light are parallel to each other, i.e. \( \theta_o = 0 \). Therefore, Equation (8.10) and (8.11) can be simplified, giving
\[ I_{2D^-} \propto \cos^4 \theta_i \sin 3\varphi_s + \left( \sin^4 \left( \frac{2\pi}{3} - \theta_i \right) + \sin^4 \left( \frac{4\pi}{3} - \theta_i \right) \right) \cos 3\varphi_s \] (8.12)

\[ I_{2D^+} \propto \sin^4 \theta_i \cos 3\varphi_s + \left( \cos^4 \left( \frac{2\pi}{3} - \theta_i \right) + \cos^4 \left( \frac{4\pi}{3} - \theta_i \right) \right) \sin 3\varphi_s \] (8.13)

Figure 8.9 shows the arbitrary intensities of the 2D\(^-\) and 2D\(^+\) bands as a function of angles between the incident light and applied strain axis. The solid lines are the curves fitted using Equations (8.12) and (8.13) by defining the crystallographic orientation angle \( \varphi_s \) equal to 12.5°. The theoretical curves fit the experiment data well and the 2D\(^-\) band has maximum intensity when \( \theta_i = 0°, 180° \) and 360°, respectively and, a minimum at \( \theta_i = 90° \) and 270°. On the other hand, the 2D\(^+\) band has the opposite trend-line in the form of an “M” shape as expected from the theory.

Figure 8.9 Arbitrary intensities of (a) the 2D\(^-\) and (b) 2D\(^+\) peaks as a function of angle of incident light with respect to the strain axis. Solid lines were curve-fits using Equation (8.12) and (8.13).
Figure 8.10 Intensity ratio of (a) $I_{2D^+}/I_{2D^-}$ and (b) $I_{2D^-}/I_{2D^+}$ peaks as a function of $\theta_i$.

In order to further compare the intensity dispersion of the $2D^-$ and $2D^+$ bands, the intensity ratios of the $2D^+$ and $2D^-$ bands are plotted as shown in Figure 8.10. The $2D^+$ band dominates at range of $38^\circ$ to $142^\circ$ and $218^\circ$ to $322^\circ$. At $\theta_i = 38^\circ$, $142^\circ$, $218^\circ$ and $322^\circ$, the $2D^+$ and $2D^-$ peaks have the equal intensity. From the maximum intensity ratio of the $2D^+/2D^-$ ($\sim 7$) and $2D^-/2D^+$ ($\sim 2.5$), the applied strain at the orientation angle $\phi_s = 12.5^\circ$ gives a higher contribution to the $2D^+$ band than that of the $2D^-$ band. The solid lines in Figure 8.10 are derived from the Equation (8.12) and (8.13) which fit the experimental data well. It is still not clearly understood what process contributes to the higher wavenumber Raman peak (here is $2D^+$ band) intensity. Kürti et al. [12] calculated and predicted that the highest intensity comes from the outer Double resonance activation involving phonon branches along K-M direction.
8.5 Raman shift rate dependence upon polarisation

New samples with a top SU-8 coat were analysed to study the Raman shift rate dependence upon laser polarisation. From the intensity ratio of the G and G' peaks, the crystallographic orientation was found to be 21.0 ± 0.5° (with respect to the zigzag direction). In the Raman measurement, the incident and scattered light were kept parallel to each other (VV configuration), and the sample was subjected to bend by fixing upon a four-point bending rig which was set on a rotary stage. The rig was rotated by an interval of 10° or 15° at different strain levels, enabling with the Raman spectroscopy test to be followed in situ.

8.5.1 2D band shift rate dependence upon polarisation direction

![Graph](image)

Figure 8.11 Monolayer graphene Raman 2D band shift rate as a function of θi. (a) Single Lorentzian peak fit. (b) Two Lorentzian peaks fit.
Figure 8.12 The monolayer graphene Raman 2D band line shapes for different incident laser polarisation at the 0.7% applied strain. The black curve is the original data collected from the graphene, the red curve presents its single-peak curve fitting and the blue curves are the two-peak fittings.

Figure 8.11(a) shows the 2D band position using single peak fit whereas the data in Figure 8.11(b) shows a monolayer graphene two-peak fit of the Raman 2D band position with the various incident light polarisation angles. It can be clearly seen that single peak fit band shift has an upward trend when changing the angle between the strain axis and the incident light. However, the individual 2D+ and 2D− bands shift rates do not change much. Frank et al. [3] reported that the strain shift rates depend on the incident light polarisation angle. It may now be able to explain the concept that the single peak fit of the monolayer graphene depends on the incident laser polarisation. Actually, from Figure 8.11(b), the individual 2D+ and 2D− band shift rates change little with different incident laser polarisations. Care has to be taken with fitting to a single peak since the relative intensities of the individual components of the peak can
change with angle. This can be further confirmed by the original lineshape of the 2D band and the fitting quality. Figure 8.12 shows the corresponding monolayer graphene Raman 2D band at 0.7% applied strain for different incident laser polarisations. At $\theta_i = 0^\circ$, the 2D band is mainly dominated by the 2D$^-$ band whereas the 2D$^+$ subband is very weak and can be neglected as a contribution to the sum 2D band fitting. As a result, the single peak fitting band shift is close to the band shift rate of the 2D$^-$ band as shown in Figure 8.11. When the incident laser light changes to $15^\circ$ or more, the original 2D band curve is outgrown by a small shoulder at high wavenumber due to the intensity of the 2D$^+$ band increasing. Therefore, in the case of a single peak fit, the fitted peak centre was affected by the 2D$^+$ subband, giving rise to the 2D band shift rate moves toward to the value of 2D$^+$ band shift. In this case, the intensity of 2D$^+$ band increases as $\theta_i$ increases. Eventually, the 2D$^+$ band dominates the 2D band at $90^\circ$. As a result, the shift rate for a single fitting is strongly influenced by the 2D$^+$ subband as presented in Figure 8.11(a). Accordingly, both the shift rate as shown in Figure 8.11 and profile of a single peak fit for the monolayer graphene as shown in Figure 8.12 is a combination of the 2D$^+$ and 2D$^-$ band values which vary with different incident laser polarisations.

8.5.2 G band shift rate dependence upon polarisation

As a comparison, the G band shift rate was also investigated in this section. Figure 8.13 shows the monolayer graphene Raman G band shift rate as a function of incident laser polarisation angle. In the case of two-peak fitting, the shift rates of both the G$^-$ and G$^+$ are stable at $\sim -30 \text{ cm}^{-1}/\%$ and $\sim -11.5 \text{ cm}^{-1}/\%$. It can be assumed that the G$^-$ and G$^+$ bands shift rates remain constant for a fixed crystal orientation at different laser polarisations. However, in contrast, in the case of a single peak fit, the G band shift rates change from $\sim -30 \text{ cm}^{-1}/\%$ to $-10 \text{ cm}^{-1}/\%$ dramatically as the incident light changes with angle to the strain axis. Above $\sim 45^\circ$, it changes back quickly to $\sim 30 \text{ cm}^{-1}/\%$ as $\theta_i$ increases to $90^\circ$. This is an analogous interpretation to the observation that the single peak fit of the G band switches from the G$^-$ band to the G$^+$ band every
quarter cycle [1-2]. Therefore, the shift rate of single peak fit follows the intensities of the subband with the dominant intensity. In other words, the single peak fit of the G band is inadequate to explain the band shift rate in different laser polarisations. A single peak fit for the G band is a combination of the G\(^-\) and G\(^+\) bands. With an angle difference between the applied strain axis and the incident light polarisation, the single peak fit shift rate alters greatly. It reveals that the best way to investigate the Raman G band shifts is the two-peak fitting method.

![Figure 8.13 Monolayer graphene Raman G band shift rate as a function of \(\theta_i\). (a) Two Lorentzian peaks fit. (b) Single Lorentzian peak fit.](image)

Hence, although the single peak fitted shift rate for both G and 2D bands depends on the laser polarisation angle, all the subbands maintain the same relative intensity level. For a fixed angle between the strain axis and laser polarisation as studied in Chapter 5-7, the strain distribution mapping by a monolayer graphene 2D band was investigated to evaluate whether the two-peak fit and single-peak fit match with each other or not.
8.6 2D band strain mapping

Figure 8.14 Optical micrograph of the monolayer graphene. (The red dot square is the selected mapping area).

Figure 8.15 Contour strain maps at 0.5% applied strain of a selected monolayer area. (a) Single peak fit. (b) The 2D$^-$ band. (c) The 2D$^+$ band.

The monolayer graphene specimen is shown in Figure 8.14, and the 2D band shifts are $-51.5\ \text{cm}^{-1}/\%$, $-55.8\ \text{cm}^{-1}/\%$ and $-33.2\ \text{cm}^{-1}/\%$ for fits to a single peak or 2D$^-$ and 2D$^+$, respectively. The middle square was selected to investigate the strain distribution.
obtained by the two fitting approaches in detail. The specimen was first loaded to 0.5% strain in the horizontal direction by the four-point bending rig, following with a measurement of the strain distribution by using Raman spectroscopy. The contour maps for single-peak fit, 2D\textsuperscript{-} and 2D\textsuperscript{+} bands are shown precisely in Figure 8.15. It can be seen that at 0.5% applied matrix strain the graphene strain distribution tracked by the separate 2D\textsuperscript{-}, 2D\textsuperscript{+} bands and single-peak fit are similar. The strain reaches the same level of the applied strain in the middle of the flake which is similar to the previous studies as shown in Chapter 5-7 in model graphene composites under stress. The distribution of the strain is quite uniform across the monolayer sheet on the whole. In the top of selected area, there is an interfacial failure strain valley which is also distinguished simultaneously by the three different strain monitoring strategies. This can possibly be understood as local poor interfacial adhesion leading to stress transfer failure between the polymer matrix and the graphene.

![Contour strain maps at 0.7% applied strain of a selected monolayer area. (a) Single peak fit. (b) The 2D\textsuperscript{-} band. (c) The 2D\textsuperscript{+} band.](image)

The monolayer specimen was further loaded up to a higher strain level of 0.7%. It was found that the strain distribution maps were also identical when measuring strain over the graphene flake either by a two-peak fit or single-peak fit as shown in Figure 8.16 of the contour strain maps for variation of strain over the monolayer graphene square.
It was found that the strain distribution is still relatively uniform in the middle, but near the edges of the area, it becomes nonuniform with an obviously vertical interfacial failure band, possibly as matrix cracking occurring [13]. All these features were clearly distinguished by measuring the 2D⁻, 2D⁺ and single-peak fitted 2D band positions. Moreover, the magnitude of the strain across the graphene flake is also the same in the three different monitor approaches with the order of 0.7% strain. Finally, it can be concluded that the strain distribution monitored by the single-peak fitting of the 2D band resembles to the two-peak fitted method in the particular fixed strain axis and the incident laser polarisation. The contour map implies that the single peak fit could simply and adequately reveal the comprehensive mechanical properties over the graphene monolayer. Therefore, in the investigation of strain distribution maps and the stress transfer efficiency, it should be sufficient to use single-peak fit in measuring the position of the 2D band and there is no need for multi-fit for strain mapping. Nevertheless, the strain must be calibrated with the strain axis, the graphene and the laser polarisation in a fixed orientation.

**8.7 Conclusions**

Polarised Raman spectroscopy has been applied to determine the crystallographic orientation of monolayer graphene on a PMMA beam based nanocomposite. It has been demonstrated that the G band of the monolayer graphene splits into two peaks under stress. The intensity of each subband is polarisation dependent that can be used to identify the precisely crystal lattice orientation by measuring the intensity ratio of the G/G⁺ bands.

Analogously, the 2D band also undergoes strain-induced splitting. The 2D⁻ band has a significantly higher Raman shift rate than that of the 2D⁺ band. It is well established that the Raman signal intensities of the 2D⁻ and 2D⁺ are strongly dependent upon the angles between the strain axis, the incident laser polarisation orientation and the crystal orientation axis.
It has also been proved that the shift rate for the $G^-$, $G^+$, 2D$^-$ and 2D$^+$ bands are independent to the laser polarisation although the nature of the G or 2D bands may seem to alter with the laser polarisation. In fact, the profiles of the G or 2D bands oscillates between the $G^-$ and $G^+$ or the 2D$^-$ and 2D$^+$ components with increasing incident laser polarisation angle, and the resultant band is a combination of these subbands. It has further been proved that the single-peak fit for the monolayer graphene 2D band is adequate in measuring the strain distribution over a graphene flake.
References


Chapter 9 Conclusions and Future Work

9.1 Conclusions

Graphene nanocomposite was successfully prepared in the form of a sandwich structure of the PMMA/graphene/SU-8 in this study. It has been proved that Raman spectroscopy is a powerful technique for the identification of the number of the graphene layers and also in monitoring the stress transfer from the matrix to the reinforcing graphene flakes by using the 2D band. In this study, the G band and 2D band of graphene were mainly studied. In particular, the 2D band was employed to investigate the deformation of the graphene composites. It has been found that monolayer, bilayer, trilayer and few-layer graphene have different lineshapes and frequencies for the 2D band. Monolayer has a single and sharp peak, bilayer graphene has a much more asymmetric broad peak at a higher wavenumber which can be fitted with four components, and there is a complex 2D band for tri- and few-layer graphene under even 0% strain. Moreover, the 2D Raman bands of the different number of the graphene layers also give linear dispersion behaviour with different laser excitation energies.

9.1.1 Monolayer graphene reinforced nanocomposites

The 2D band of the monolayer graphene has been used in the investigation of stress transfer in graphene reinforcing nanocomposite. It has been demonstrated that the 2D band moves towards low frequency linearly under stress, which is a significant signal in monitoring the strain in graphene in a deformed specimen. The Raman spectroscopy behaviour under deformation validates that the monolayer graphene acts as a reinforcement in nanocomposites even though it is only one atom thick. Furthermore, it appears that the continuum mechanics approach is also feasible at the
atomic level. It has been indicated that composite micromechanics developed for fibre reinforcement is also valid in the case of graphene monolayers.

In the study of strain distribution in monolayer graphene composites, it has been found that the strain builds up from the edges of the monolayer and is constant across the middle where the strain in the monolayer equals to the applied matrix strain, proving the graphene reinforces the composite. A shear-lag model was successfully developed in analysing the stress transfer mechanism at the graphene-matrix interface.

When the deformation of the graphene composite is higher than 0.4% strain, the graphene-polymer interface can breakdown with an interfacial shear stress of the order of ~1 MPa and valley line-shapes of strain distributions develop. The efficiency of reinforcement by graphene monolayer is reflected in the value of parameter $ns$ which corresponds both the morphology of the graphene flake and the degree of interaction it has with polymer matrix.

Furthermore, the strain distribution in a single graphene atomic layer sandwiched between two thin layers of polymer on the surface of a PMMA beam could be mapped in two dimensions with a high degree of precision from Raman band shifts. It has been found that the distribution of strain across the graphene monolayer was relatively uniform even with level of matrix strain up to 0.6%. Afterwards, it becomes highly non-uniform which trends a zig-zag lineshape across the graphene monolayer. The change in strain distribution was shown to be due to a fragmentation process as a result of the development of cracks, probably in the polymer coating layers, with the graphene appearing to remain intact. The strain distribution in the graphene between the cracks were approximately triangular in shape and the interfacial shear stress, $\tau_i$, in the fragments was found to be only ~0.25 MPa, an order of magnitude lower than the interfacial shear stress before fragmentation.
9.1.2 Bilayer, trilayer and few-layer graphene reinforced nanocomposite

A systematic investigation of deformation of bilayer, trilayer and few-layer graphene has been undertaken in a view to determining the optimum number of layers for the reinforcement of nanocomposites. It has been found that the rate of the 2D band shift for uncoated bilayer graphene on a PMMA beam was lower than that for a monolayer, indicating relatively poor stress transfer between the two layers. In contrast, in the case of coat graphene, the shifts of the two strong component $2D_{1A}$ and $2D_{2A}$ of the 2D band, are similar to each other, and also similar to the slope of the adjacent monolayer region, implying that bilayer graphene could give reinforcement equally as good as monolayer graphene. Moreover, the slopes of 2D band for the monolayer and bilayer graphene are similar but somewhat lower for the trilayer. In contrast, the shift rate for the few-layer graphene behaves significantly lower. It has been demonstrated that there is good stress transfer at the polymer-graphene interface but poorer levels of stress transfer between the graphene layers.

In modelling the behaviour of the stress transfer efficiency using the theory of Zalamea et al. [1], it has been illustrated that bilayer has an equal performance quality in reinforcement as monolayer. Less efficient stress transfer has been found for trilayer and few-layer graphene due to slippage between the internal graphene layers, indicating that such materials will have a lower effective Young’s modulus than either monolayer or bilayer graphene in polymer-based nanocomposites. An optimum approach has been further developed in designing a good reinforcement composite with an appropriate number of graphene layers.

9.1.3 Polarisation dependence of Raman band

Both the G and 2D bands have been found undergo splitting under high strain level or asymmetric band broadening in lower strained deformation. The G band polarisation property has been adopted to determine the crystallographic orientation of monolayer graphene by measuring the intensity ratio of $G^-/G^+$ bands. Analogously, the 2D band
also undergoes strain-induced splitting where the 2D− band has higher Raman shift rate than that of the 2D+ band. It is well established that the Raman signal intensity of the 2D− and 2D+ are strongly angular dependent to the angle between strain axis and incident laser polarisation and the crystal orientation direction.

It has also been demonstrated that the shift rates for the G−, G+, 2D− and 2D+ bands are independent to the laser polarisation. The profile of the G or 2D bands oscillates between the G− and G+ or the 2D− and 2D+ with a change of the incident laser polarisation angle, as they are a combination effect of these subbands. Consequently, the strain mapping study of monolayer graphene by both single- and two-peak fits implies that the single-peak fit for the monolayer graphene 2D band is good enough to measure the strain distribution over a graphene flake.

9.2 Future work

9.2.1 Inner-layer stress transfer in the tri- and few-layer graphene

In a sandwich structure graphene composite, as has been reported, monolayer and bilayer graphene have equal stress transfer efficiency and no inner layer graphene slippages occurs during the deformation tests. Therefore, the 2D band lineshapes for the monolayer and bilayer remain the same or broaden slightly as shown in Figure 9.1. However, in the case of the number of graphene layer more than two layers, the 2D band shift rate decreases. It has been concluded that good stress transfer at the polymer-graphene interface but poorer between the graphene layers. Hence, a possible reason could be attributed to the slippage between the graphene layers that might even change the crystal lattice structure of the tri- or few-layer graphene from AB Bernal stacking order to a non-AB stacking order. It is well known that the non-AB stacking graphene leads to a single symmetric 2D peak [2], so a question is put forward is that will the 2D band feature for the tri- or few-layer graphene change to a single peak?
Figure 9.1 The Raman 2D bands for (a) the monolayer and (b) bilayer graphene under various applied strains.

Figure 9.2 (a) The Raman 2D band for the trilayer graphene under various applied strains. (b) The trilayer FWHMs as a function of the applied strain.
Chapter 9 Conclusions and Future Work

Figure 9.2(a) shows the 2D band of a trilayer graphene under different applied matrix strains. It can be clearly seen that the lineshape remains the same at 0% and 0.2% strain, but becomes a single peak when the strain increases to 0.4%. This is consistent with the prediction of a lineshape change due to a losing of AB stacking order. It is further found for the band width of trilayer graphene decreases as the strain increases, which is quite different from monolayer and bilayer where their FWHMs increase under stress.

Furthermore, it is interesting to find that the lineshape transformation reverses to the original feature when the specimen was unloaded to a relaxed state. This phenomenon suggests that the interface between the inner graphene layers was not permanently damaged and remained intact after being loaded to 0.4% strain level. As reported in the previous study [3], the shear stress at the edge of graphene is higher than that in the middle. Therefore, a strain map over a tri- and few-layer graphene is accordingly needs to be investigated and a study of comparing the 2D band lineshapes in the middle of the flake and the edge need to be studied in succession to establish a prospect of local stress slippage distribution across the flake. Excitingly, it gives rise the challenging task of determining the stress needed to shear a layer of graphene off bulk graphite.

9.2.2 Defect monitoring in graphene nanocomposite

Strain maps in a monolayer graphene nanocomposite was investigated and reported that the distribution of strain across the graphene monolayer was relatively uniform under the low level of strain. It behaves a triangular form which was attributed to a fragmentation process in the surrounding polymer matrix. Franck et al. [4] however supposed that it is the crack formation in a monolayer flake itself rather than its adjacent polymer matrix. Therefore, one appropriate approach is to monitor the D band over the graphene flakes at 0% strain and the strain level when the fragmentation process occurs. Eventually, the D band map could be a feasible strategy in revealing the reason for the formation and mechanism of fragmentation process.
9.2.3 Graphene oxide and functionalised graphene sheet reinforced nanocomposites

Graphene oxide was developed from graphite oxide which has been studied for a hundred years, and it can be further exfoliated by sonication to produce suspended graphene oxide sheets [5]. Its production can be scaled up and it can be widely used particularly in the application of composite. In addition, the properties of graphene oxide can be modified through reduction and functionalisation for specific purposes. Functionalised graphene oxide embedded into polymer forming chemical bonded interface between graphene sheet and matrix improves the reinforcement more efficiently than the pristine graphene sheets. Graphene oxide has a well deformed Raman spectrum showing D and G band (Figure 1.8) and it could be interesting to know if it is possible to obtain Raman band shifts under stress for GO micromechanics analysis.
References


