Low Temperature Synthesis of Graphene as an Alternative Transparent Electrode for Large Area Organic Photovoltaics

by

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BSc (Physics); MSc (Physics)

A thesis submitted in fulfilment of the requirements of the degree of Doctor of Philosophy in Physical Science School of Mathematical and Physical Sciences The University of Newcastle, Australia July 2020



Statement of originality

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision. The thesis contains no material which has been accepted, or is being examined, for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968 and any approved embargo.

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Acknowledgment of authorship

I hereby certify that the work embodied in this thesis contains published paper/s/scholarly work of which I am a joint author. I have included as part of the thesis a written declaration endorsed in writing by my supervisor, attesting to my contribution to the joint publication/s/scholarly work.

By signing below, I confirm that **Alaa Yousif Ali** contributed to the papers/ publications entitled "Matrix assisted low temperature growth of graphene" by:

- Fabrication and characterisation of CVD graphene at low temperature growth.
- Preparation and optimisation of graphene films with different growth conditions.
- Conduct different characterisation measurements for the quality of graphene films.

Paul dastoor December 2019 "For the soul of my father and brother 'Muthanna', to my mother, family and my wife 'Zubaidah'"

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List of publications

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- Kasman Sulaiman, Alaa Y. Ali, Daniel Elkington, Krishna Feron, Kenrick F. Anderson, Warwick Belcher, Paul Dastoor, Xiaojing Zhou "Matrix assisted low temperature growth of graphene", Carbon, 2016. <u>http://www.sciencedirect.com/science/article/pii/</u> S0008622316304468
- Alaa Y. Ali, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Paul Dastoor, Xiaojing Zhou. "Low Temperature CVD-Grown Graphene as Transparent Electrode for Organic Photovoltaics", draft paper, pending.
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- 6. Alaa Y. Ali, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Paul Dastoor and Xiaojing Zhou. "Low Temperature Synthesis of Graphene as an Alternative Transparent Electrode for Large Area Organic Photovoltaics", Participated THREE MINUTE THESIS presentation, Faculty of Science, University of Newcastle, Australia, 2017.

- 7. Alaa Y. Ali, presented in the inaugural postgraduate Art in MAPS exhibition held on the 23rd of May 2017, won second prize in the art night event, Newcastle University, Australia.
- 8. Alaa Y. Ali, John Holdsworth, Warwick Belcher, Paul Dastoor and Xiaojing Zhou, "Synthesis of Graphene Thin Films at the Low Temperature as an Alternative Transparent Electrode for Organic Photovoltaics", Smart Future Cities 2015 (SFC2015) Conference was held at the Newcastle City Hall on the 1-2 October 2015, Abstract has been submitted. I won the prize for having presented the best poster at the smart future cities 2015 conference, Newcastle, Australia.

Abstract

This thesis presents a systematic study of the fabrication and optimisation of graphene films as an alternative electrode for large area organic photovoltaics (OPVs). It is mainly focused on the growth of graphene layers at low temperatures (below 700 °C) using chemical vapour deposition (CVD) method. A routine procedure was developed to produce large-area graphene films of centimetre size.

Firstly, we demonstrated that we could fabricate multi-layers of graphene films utilising organic solvent residual in a polymer film matrix as the carbon source. The polymer matrix is poly (methyl methacrylate) (PMMA), which can be dissolved in a polar solvent, such as, chlorobenzene. When PMMA is dissolved in chlorobenzene and drop-cast as a film into a quartz slide, a small amount of chlorobenzene is trapped in the PMMA. When heating up the quartz slide to 180 °C, chlorobenzene molecules evaporate and land on copper foils, which is maintained at much high temperature in the growth zone in the CVD system. Copper (Cu) catalytically promotes chlorobenzene dissociation and formation of micron-sized graphene domains at the different growth temperature. After a parametric study, we found that at 75 sccm (standard cubic centimeters per minute) of H₂ flow during the growth while maintaining the Cu foil at 600 °C, produced the optimal graphene growth conditions.

We also compared PMMA dissolved in other organic solvents and as carbon sources at lowtemperature growth ~450 °C for deposition of the graphene layers onto a Cu catalyst. An optimisation process was carried out to see the effects of other carbon sources on the quality of graphene films. The carbon sources studied were both aliphatic solvents (dichloromethane, chloroform, acetone) and aromatic solvents (p-xylene, toluene, o-xylene, chlorobenzene, dichlorobenzene), to probe the growth mechanism of graphene formation. However, none of the other solvents produced a better quality of graphene than chlorobenzene.

Lastly, graphene films were used to replace indium tin oxide (ITO) in the OPV device fabrication. The results showed that working devices were successfully made for both small and large areas OPVs.

Table of contents

Statement of originality	I
Acknowledgment of authorship	II
Acknowledgments	IV
List of publications	V
Conference presentations	VI
Abstract	VIII
Table of contents	IX
List of abbreviations and symbols	XIII
List of figures	XVIII
List of tables	XXVII
1. Chapter one: Introduction to graphene	1
1.1 Overview	1
1.2 Defining graphene	1
1.3 Properties of graphene	4
1.3.1 Electronic properties	5
1.3.2 Optical properties	6
1.3.3 Thermal properties	8
1.3.4 Mechanical properties	
1.4 Synthesis methods of graphene	
1.4.1 Mechanical cleavage	
1.4.2 Epitaxial growth	
1.4.3 Chemical synthesis	
1.4.4 Chemical vapour deposition (CVD)	
1.5 Large single-crystal monolayer and bilayer graphene	
1.6 Graphene device applications	
1.7 Graphene electrodes in OPV devices	
1.8 Basics of organic photovoltaics (OPVs)	
1.8.1 OPV architecture	
1.8.2 Bulk heterojunction OPV operation principles	
1.8.3 The efficiency of OPV	
2. Chapter two: Fabrication and characterisation of graphene electrodes	
2.1 Overview	
2.2 Fabrication of graphene film	
2.2.1 Catalyst	

2.2.2 Carbon source	
2.2.3 Graphene growth	40
2.2.4 Transfer process for graphene film	41
2.3 Fabrication of OPV based on graphene electrode	42
2.4 Characterisation of graphene film	43
2.4.1 Optical microscopy	43
2.4.2 Atomic force microscopy (AFM)	43
2.4.3 X-Ray diffraction (XRD)	44
2.4.4 X-ray photoelectron spectroscopy (XPS)	45
2.4.5 Raman spectroscopy	47
2.4.6 UV-Vis spectroscopy	48
2.4.7 Four-point probe conductivity	49
2.4.8 Scanning electron microscopy (SEM)	52
2.4.9 Transmission electron microscopy (TEM)	53
2.4.10 Thermogravimetric analysis (TGA)	54
2.4.11 Fourier transform infrared spectroscopy (FTIR)	55
2.4.12 UV photoelectron spectroscopy (UPS)	56
2.4.13 Profilometer	57
2.4.14 OPV device characterisation	57
3. Chapter three: Low temperature CVD growth of multi-layered graphene chlorobenzene-PMMA film as the carbon source	using
3.1 Overview	
3.2 Introduction	
3.3 Carbon sources for graphene growth	60
3.3.1 Thermal degradation of PMMA	61
3.3.2 Thermal degradation of chlorobenzene-PMMA	
3.4 Catalyst preparation	63
3.4.1 The morphology of Cu foil	63
3.4.2 The purification of Cu foil	64
3.4.3 The structure of Cu foil as a function of annealing temperature	66
3.5 Graphene growth optimisation	
3.5.1 The effect of Tgrowth on graphene growth	68
3.5.2 The effect of H ₂ flow rate on graphene growth	71
3.6 Factors affecting graphene deposition	73
3.7 Highly oriented pyrolytic graphite (HOPG)	75
3.8 The honeycomb structure of graphene	76

3.9 Identifying single-layer graphene	78
3.10 Conclusion	80
4. Chapter four: Low temperature CVD graphene growth via organic solve retention in PMMA film	nt 81
4.1 Overview	81
4.2 Introduction	82
4.3 Using organic solvents as carbon sources	82
4.4 Residual organic solvents within the PMMA film	83
4.5 Quantification of residual organic solvents within the PMMA film	87
4.6 The thermal analysis of organic solvents retained in PMMA matrices	
4.7 Graphene quality dependence on carbon source	91
4.8 The growth mechanism of graphene via aromatic and aliphatic sources	94
4.9 Transmission electron microscopy of the graphene flakes	97
4.10 The uniformity of graphene domains	101
4.11 The effect of carbon source on sheet resistance and transparency of grapher	ne films 103
4.12 The effect of carbon sources containing heteroatoms upon CVD-graphene	
4.12.1 The analysis of graphene films based on heterocarbon sources	
4.12.2 Chemical bond analysis of graphene films	
4.13 Conclusion	
5. Chapter five: Low temperature CVD-grown graphene as a transparent e for organic photovoltaic cells	lectrode
5.1 Overview	113
5.2 Introduction	113
5.3 Architecture of OPVs	114
5.3.1 Device substrate	115
5.3.2 Graphene film	115
5.3.3 OPV anode electrodes	116
5.4 The resistance and transparency of graphene electrodes	117
5.5 The work function of graphene electrode	120
5.5.1 The work function of the graphene electrode on a Si substrate	120
5.5.2 The work function of graphene electrodes on an ITO substrate	121
5.6 The quality of graphene electrode on an OPV substrate	
5.7 The morphology of the graphene electrode	
5.8 The carbon bonding of the graphene electrode	127
5.9 Elemental analysis of the graphene electrode	
5.10 The optimisation of bulk heterojunction OPV	131

5.10.1 The structure of OPV	131
5.10.2 Benchmarking OPV fabrication	133
5.10.3 The effect of thermal annealing on OPV performance	135
5.10.4 The optimisation study of the PEDOT:PSS layer in OPVs	137
5.11 Conclusion	140
6. Chapter six: Large area graphene as an alternate transparent electrode for or photovoltaic cells	:ganic 141
6.1 Overview	141
6.2 Introduction	141
6.3 Transfer of large area graphene films onto a target substrate	142
6.4 The morphology of large area graphene	145
6.5 The resistance and optical transmission of large area graphene	147
6.6 The quality of large area graphene	151
6.7 The performance of large area OPV based on a graphene electrode	153
6.8 OPVs based on graphene films as a transparent electrode	155
6.8.1 The J-V characterisation of OPVs	155
6.8.2 The external quantum efficiency of OPVs	159
6.8.3 The resistance of OPV electrodes	162
6.9 Assessment of OPVs based on graphene and PEDOT:PSS as window electrodes	164
6.10 The effect of masked electrode area on the performance of graphene electrodes	166
6.11 The fabrication of inverted OPV based on graphene electrode	170
6.12 The performance of silver nanowire with the graphene electrode	173
6.13 Conclusion	177
7. Chapter seven: Conclusion and future work	178
7.1 CVD growth of multi-layer graphene at low temperature	178
7.2 Using residual organic solvents in a PMMA matrix as the carbon source for low temperature growth	178
7.3 The performance of graphene electrodes applied to OPV cells	179
7.4 CVD graphene grown at low temperature as alternative window electrodes on OI	PVs
	180
7.5 Future work	181
Appendix: Conferences and awards	183
References	186

List of abbreviations and symbols

а	Length
А	Absorbance of incident light
AFM	Atomic force microscopy
Ag	Sliver
Al	Aluminium
AM1.5	Air Mass 1.5: Reference Solar Spectrum for OPV characterisation
Ar	Argon gas
Au	Gold
AuCl ₃	Gold chloride
BCP	Bathocuproine
BE	Binding energy
BHJ	Bulk Heterojunction
BN	Boron nitride
BSE	Backscattered electron
c	Light speed
С	Carbon
C (b/s,a/b)	Additional dimensionless correction factor
C (b/s,a/b) C ₁₂ H ₂₂ O ₁₁	Additional dimensionless correction factor Sucrose
C (b/s,a/b) C ₁₂ H ₂₂ O ₁₁ C ₁₃ H ₁₀	Additional dimensionless correction factor Sucrose Fluorene
C (b/s,a/b) C ₁₂ H ₂₂ O ₁₁ C ₁₃ H ₁₀ C ₂ H ₂	Additional dimensionless correction factor Sucrose Fluorene Acetylene
C (b/s,a/b) C ₁₂ H ₂₂ O ₁₁ C ₁₃ H ₁₀ C ₂ H ₂ C ₂ H ₄	Additional dimensionless correction factor Sucrose Fluorene Acetylene Ethylene
C (b/s,a/b) C ₁₂ H ₂₂ O ₁₁ C ₁₃ H ₁₀ C ₂ H ₂ C ₂ H ₄ C ₅ H ₅ N	Additional dimensionless correction factor Sucrose Fluorene Acetylene Ethylene Pyridine
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C (b/s,a/b) $C_{12}H_{22}O_{11}$ $C_{13}H_{10}$ $C_{2}H_{2}$ $C_{2}H_{4}$ $C_{5}H_{5}N$ C_{60} Ca $CH_{3}OH$	Additional dimensionless correction factor Sucrose Fluorene Acetylene Ethylene Pyridine Buckminsterfullerene Calcium
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CuPc	Copper phthalocyanine
CVD	Chemical vapour deposition
d	Width
DCB	Dichlorobenzene
DI	Deionised water
DSSCs	Dye-sensitized solar cells
e	Electron charge
ED	Energy denoted
ED	Electron diffraction
EDS	Energy dispersive X-ray spectroscopy
E _F	Fermi energy
EQE	External quantum efficiency
ETL	Electron transporting layer
eV	Electron volt
Fe	Iron
Fe (NO ₃) ₃	Iron nitrate
FET	Field effect transistors
FF	Filling factor
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
G	Graphene
G(s,t)	Proportionality constant depending upon the geometry of sample
GNRs	Graphene nanoribbons
GO	Graphene oxide
h	Planck's constant
H ₂	Hydrogen gas
HC1	Hydrochloric acid
НОМО	Highest occupied molecular orbital
HOPG	Highly ordered pyrolytic graphite
HTL	Hole transporting layer
Ι	Electrical current
IH	Hydrogen iodine
IPA	Isopropanol

IPCE	Incident photon to current efficiency
IQE	Internal quantum efficiency
Ir	Iridium
I _{SC}	Short circuit current
ITO	Indium Tin Oxide
J_{sc}	Short-circuit photocurrent density
J-V	Current density-Voltage
LCD	Liquid crystal displays
LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital
MEH-PPV	Poly (2-methoxy-5-(2'-ethyl-hexyloxy)- 1,4-phenylene vinylene)
MLG	Multilayers of graphene
MoO ₃	Molybdenum trioxide
MoS_2	Molybdenum di-sulphide
MWCNT	Multiwall carbon nanotube
Ν	Number of Layers
n	Integer
n GL	Number of layers of graphene
N_2	Nitrogen gas
NaBH ₄	Sodium borohydride
NEXAFS	Near-edge X-ray absorption fine structure
Ni	Nickel
O ₂	Oxygen
OLEDs	Organic light emitting diodes
OPV	Organic photovoltaic
РЗНТ	Poly(3-hexylthiophene)
PBASE	Pyrene buanoic acid succidymidylester
PC	Bisphenol A carbonate
PCBM	Phenyl-C61-butyric acid methyl ester
PCE	Power convention efficiency
Pd	Palladium
PDMS	Polydimethylsiloxane
PEDOT-PSS	Poly(3,4-ethylenedioxithiophene):poly(styrenesulfonate)

PET	Polyethylene terephthalate
PI	Polyimide
P _{max}	Maximum Power Point of I-V Curve
PMMA	Poly(methyl methacrylate)
Pt	Platinum
PV	Photovoltaic
QDSSC	Quantum dot sensitized solar cell
R	Reflectance of light
Rs	Series resistance
Rsh	Shunt resistance
R _{sheet}	Sheet resistance
Ru	Ruthenium
S	Distance between two neighbouring tungsten pins
SAED	Single area electron diffraction
sccm	Standard cubic centimeter per minute
SE	Secondary electron
SEM	Scanning electron microscopy
SG	Single layer of graphene
Si	Silicon
Si ₃ N ₄	Silicon nitride
SiC	Silicon carbide
SiO ₂	Silicon dioxide
SNW	Sliver nanowire
STXM	Scanning Transmission X-ray Microscopy
SWCNT	Single-wall carbon nanotube
Т	Optical transmittance
T _{500nm}	Transmission of light at wavelength of 500nm
TCNQ	Tetracyanoquinodimethane
TEM	Transmission electron microscopy
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
TAnnealing	Temperature annealing
Tgrowth	Temperature growth

T _{source}	Temperature source
UPS	UV photoelectron spectroscopy
UV-vis	Ultraviolet-visible
V	Voltage
Voc	Open-circuit voltage
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray diffraction
ZnO	Zinc oxide
η	Solar cell power conversion efficiency
η_c	Carrier collection efficiency
η _e	Energy conversion efficiency
λ	Wavelength
ρ	Sheet resistivity
σ	Conductivity
2D	Two dimensional
3D	Three dimensional

List of figures

Figure 1.2: (a) Schematic of the in-plane σ -bonds and π orbitals perpendicular to the plane of the graphene sheets, and (b) electronic band structure of single layer graphene showing the energy dispersion curve, upper and lower surface covalent and valence bands respectively while the K_x- and K_y-axes denote wave vectors in respective x and y directions . Reproduced from Ref.,³⁻⁵ with permission from IOP publishing and the Royal Society of Chemistry.3

Figure 1.8: (a) SEM image of a graphene sheet spanning an array of circular holes (scale bar = 3mm). (b) Schematic of nano-indentation on suspended graphene. Reproduced from Ref.,¹² with permission from American Association for the Advancement of Science......10

 Figure 1.12: SEM images of (a) carbon nanotube (b) diamond on Cu (111) and (c) photographs of Cu foils are covered with fully grown graphene Cu/Gr. Reproduced from Ref.¹¹⁹⁻¹²² with permission from Elsevier Science, Scientific Reports and American Chemical Society......17

Figure 1.15: (a) SEM image of hexagonal graphene grains grown on Cu substrate, and (b) schematic of Cu tube, suppression of loss of Cu by evaporation and redeposition in a confined space during growth of CVD graphene, Reproduced from Ref.,^{105,149} with permission from Macmillan publishers limited and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. ..25

Figure 1.17: Schematic depicting graphene-containing OPV device architecture and band structure. It is reproduced from Ref.,¹⁸⁵ with permission from American Chemical Society. 30

Figure 1.21: Comparison of the world reports between OPVs and thin film PV technia-Si from 1985 to present. ²⁰¹	ologies of 34
Figure 2.1: Schematic depicting the electrochemical polishing of Cu foil	
Figure 2.2: Atomate CVD system for the growth of graphene films	

Figure 2.3: The chemical structure of MMA and PMMA. ²⁰³
Figure 2.4: Schematic of CVD tube showing heater zones in the system. The carbon source is a drop cast film of PMMA dissolved in organic solvent
Figure 2.5: Schematic depicting the wet transfer method of graphene films
Figure 2.6: Schematic of AFM system used for the characterisation of thin films44
Figure 2.7: (a) Philips X'Pert MPD XRD equipment, (b) schematic depicting the X-ray diffraction principle
Figure 2.8: A schematic depicting electrons absorbing X-rays and being ejected from their orbitals
Figure 2.9: Schematic of XPS system46
Figure 2.10: The Renishaw inVia Raman spectrometer47
Figure 2.11: A schematic of the Raman spectrometer light path48
Figure 2.12: UV-Vis spectrophotometer
Figure 2.13: (a) Four-point probe sheet resistance equipment, (b) schematic of four-point probe measurement for thin film
Figure 2.14: Four-point probe of large area graphene (custom built)52
Figure 2.15: Schematic of the SEM electron gun and optics
Figure 2.16: TEM performed on a Jeol 210054
Figure 2.17: Perkin-Elmer Diamond TG/DTA used for characterising the thermal evolution of solvents in PMMA matrix
Figure 2.18: Perkin Elmer Spectrum Two FTIR spectrometer
Figure 2.19: Photoelectron Spectrometer model AC-2, manufactured by Riken Keiki
Figure 2.20: Current density-voltage (J-V) curve for an organic solar cell under dark (black) and illumination (red). ²¹⁴
Figure 3.1: TGA curve of pure PMMA powder61
Figure 3.2: TGA curves of chlorobenzene-PMMA films. The curves represent 180 °C dried, air-dried and, drop cast wet film
Figure 3.3: AFM images of copper foil (a) before and (b) after polishing at 3 V for 60 sec63

Figure 3.4: Images of Cu foil after staged cleaning of the surface (a) new sample surface of raw Cu foil, (b) Cu foil surface after electro-polishing process and (c) Cu foil surface after thermal annealing inside CVD furnace tube, images at magnification scale of $700 \times 1000 \ \mu m$
Figure 3.5: XPS spectrum of the Cu foil (a) unannealed and (b) annealed65
Figure 3.6: XPS spectra of the O 1s peak on the surface of the Cu foil before and after thermal annealing at 900 °C for 1 hour in the CVD under H ₂
Figure 3.7: XRD patterns of the Cu foil samples annealed at different temperatures for 1 h. 67
Figure 3.8: XRD patterns of the annealed Cu foil samples
Figure 3.9: Raman spectra of graphene thin films grown with varied T _{growth} 69
Figure 3.10: I_G/I_{2D} ratio as a function of growth temperature. Error bar (0.1)70
Figure 3.11: Raman spectra of graphene grown at different H ₂ flow rates and T _{growth} of 600 °C.
Figure 3.12: I_G/I_{2D} ratio as a function of H_2 flow rate. Error bar (0.1)
Figure 3.13: (a) Spatial map of graphene film Raman G/2D peak ratio over a $100 \times 100 \mu\text{m}$ area (T _{growth} : 600 °C, H ₂ flow rate 75 sccm), and (b) associated optical image of mapped area73
Figure 3.14: (a) and (b) show optical images of graphene films on Cu foil74
Figure 3.15: Raman spectra of Graphene films growth at 600 °C for 1 minute with H ₂ =75 sccm.
Figure 3.16: Raman specters of HOPG flecks on SiO ₂ with their optical images including G/2D ratio of Raman specters
Figure 3.17: (a) TEM image of graphene layers suspended on Cu grid and (b) the electron diffraction pattern of the carbon atoms of graphene
Figure 3.18: (a) TEM image of graphene multi-layers on the edge of film and, (b) the pattern of electronic diffraction of graphene layers suspended on Cu grid
Figure 3.19: AFM image of CVD graphene grown at 600 °C with H ₂ flow rate of 75 sccm79
Figure 3.20: AFM image spanning the edge of a graphene film transferred onto a Si substrate by the wet transfer method
Figure 4.1: FTIR spectra of PMMA dissolved by (a) p-xylene, (b) toluene, (c) o-xylene and (d) chlorobenzene. Insets depict magnified regions of interest. The spectrum of PMMA powder is also provided in a-d for comparative purposes

Figure 4.5: TGA profiles of different organic solvents inside the PMMA matrix......91

Figure 4.10: TEM images of graphene films suspended on copper grid grown from (a) acetone-PMMA, (b) chlorobenzene-PMMA (c) chloroform-PMMA and (d) electron diffraction pattern collected from the centre of (c) with Miller-Bravais indices. A 2 nm scale bar is shown......98

Figure 4.14: (a) TEM image of graphene layers grown at T_{growth} 450 °C transferred onto Cu grid and, (b) graphene layers suspended on Cu grid were grown at T_{growth} 600 °C.103

Figure 4.15: (a) Sheet resistance of graphene films from each type of carbon sources (error bar from p-xylene to acetone are 130.4, 128.2, 59.9, 87.5, 126.7, 112.7, 191.8 and 314.9, respectively) and (b) Raman map (100×100 µm) of the intensity ratio between G to 2D for a Figure 4.16: Transmission of visible light of wavelength 500 nm of graphene films from each type of carbon source (error bars from p-xylene to acetone represent 12.2, 13.2, 12, 7.7, 7.1, Figure 4.17: Mechanism growth of graphene domains using pyridine solvent as carbon source Figure 4.18: Raman spectra of CVD graphene grown on Cu foils by (a) pyridine-PMMA, and Figure 4.19: Transmission and sheet resistance of graphene films grown via pyridine-PMMA Figure 4.20: XPS spectra of graphene film on Cu foil at T_{growth} of 450 °C for 1 min using pyridine-PMMA as carbon source.....110 Figure 4.21 XPS spectra of graphene film on Cu foil grown using methanol-PMMA as carbon source at T_{growth}......111 Figure 5.1: The architecture of an OPV device with a CVD graphene film as transparent electrode (anode).....114 Figure 5.2: Schematic for preparation of OPV substrate based on graphene electrode.115 Figure 5.3: Optical micrograph depicting the graphene film attached through ITO finger for Figure 5.4: Photograph and schematic of an OPV based on graphene electrode with Al Figure 5.5: Representative UV-Vis light transmission spectra for graphene thin films with sheet Figure 5.6: UV-vis spectra of graphene films and their sheet resistance grown under the same conditions......119 Figure 5.7: UPS plot for the determination of the work function of graphene film transferred onto Si substrate.....120 Figure 5.8: UPS plot for the determination of the work function of CVD-graphene grown at

Figure 5.9: Raman spectrum of graphene electrode transferred onto OPV substrate. Inset showing optical micrograph
Figure 5.10: Raman spectral analysis of another area of the same graphene electrode transferred onto OPV substrate as Figure 5.9. Inset showing optical micrograph
Figure 5.11: SEM images of graphene film grown at $T_{growth} 600 ^{\circ}\text{C}$ for 1 min with $H_2 = 75$ sccm on annealed Cu foil
Figure 5.12: SEM image of graphene film transferred onto Si substrate via the wet transfer method
Figure 5.13: Survey XPS spectrum showing elemental electron configuration contributions on the Cu foil after graphene growth
Figure 5.14: C 1s energy band of graphene film grown on Cu foil at T _{growth} 600 °C128
Figure 5.15: (a) Energy dispersive X-ray spectroscopy (EDS) spectrum of graphene grown on the annealed Cu catalytic foil, prepared at $T_{annealled}$ 900 °C for 1 h, and (b) associated SEM image of the area analysed with EDS
Figure 5.16: (a) EDS spectrum of the graphene film transferred onto an Si substrate, and (b) SEM image of graphene film marked with the EDS analysis region at the green cross130
Figure 5.17: The structure of OPV based on an ITO electrode
Figure 5.18: The efficiency of OPVs prepared in different atmosphere conditions. The red and blue line present the average value of efficiency (2.12 % and 2.47 %)
Figure 5.19: The fill factor of OPVs fabricated in two atmosphere conditions. The red and blue line present the average value of FF (0.51 and 0.57)
Figure 5.20: The diagram of OPV efficiencies in dried and thermal annealed condition. The red and blue line shows the average value of efficiency (1.58 % and 2.5 %)
Figure 5.21: (a) Efficiencies, and (b) fill factors of OPVs arising from the thermal annealing conditions before and after the deposition of Al/Ca electrodes. The line are shown the average value of efficiency (2.5 % and 1.61 %) and FF (0.56 and 0.51)
Figure 5.22: J-V curves of OPVs based on buffer layer of (a) PEDOT: PSS-PH1000, and (b) PEDOT: PSS-Al 4083. The measurement was completed inside a nitrogen atmosphere box
Figure 6.1: Large area of graphene films laminated onto PET substrates before Cu foil etching.
Figure 6.2: Large area graphene film (~10 cm×5 cm) transferred onto PET substrate via the direct method without polymer film support

Figure 6.3: Graphene film from large area procedure transferred into SiO₂ substrate without mechanical film supporting. AFM imaging technique at scale bar of (900×700 µm)......145 Figure 6.4: Optical images of large area graphene film transferred onto PET substrate......147 Figure 6.5: UV-vis transmission and sheet resistance of large area graphene films transferred Figure 6.6: UV-vis transmission spectrum of large area graphene film on PET substrate....150 Figure 6.7: UV-vis transmission spectrum and sheet resistance of large area graphene film on Figure 6.8: Raman spectra of large area of graphene film transferred onto flexible PET substrate Figure 6.9: (a) Raman spectra of large area graphene on a glass substrate, and (b) optical micrograph of the graphene film for determination of the Raman analysis regions.152 Figure 6.10: (a) I_G/I_{2D} and (b) I_{2D} of large area graphene grown on Cu foil at low temperature Figure 6.11: (a) Optical image of the contact between graphene electrode and ITO for I-V characterisation, and (b) the structure of the OPV based on graphene electrode using ITO Figure 6.12: AFM image of graphene electrode transferred onto Si substrate for thickness Figure 6.13: Current density – voltage (J-V) characteristics of OPV cells made from P3HT: PC₆₁BM blend films, based on (a) graphene and (b) ITO.157 Figure 6.14: Optical micrograph of PEDOT: PSS (Al 4083) spin-coated on the graphene Figure 6.15: EQE spectra of OPV cells using graphene and ITO as transparent electrode. This is for four devices of OPV/G comparing with control standard device of OPV/ITO......160 Figure 6.16: EQE and IQE spectra of OPV made from P3HT: PCBM blend films, based on a Figure 6.17: Nyquist plots of OPV devices based on (a) graphene and (b) ITO as transparent electrode, (c) the equivalent AC circuit of OPV......163 Figure 6.18: (a) Dispersion of total real part resistance of impedance versus frequency for OPVs based on graphene and ITO as window electrodes, and (b) the linear J variations vs V for Graphene-based device, and ITO-based OPV device......164 Figure 6.19: J-V characterisation of OPVs based on electrodes of (a) graphene and (b) PEDOT:

Figure 6.20: J-V characterisation of OPV based on graphene electrode at full area and mask area of the device
Figure 6.21: Diagram relationship between PCE and Rs of OPVs based on graphene electrodes and scale areas devices
Figure 6.22: J-V characterisation of OPV based on graphene film as a transparent electrode at different scale area
Figure 6.23: Device architecture of inverted OPV based on graphene film as a transparent electrode
Figure 6.24: J-V characterisation of inverted OPVs based on transparent electrodes of (a) ITO, and (b) graphene
Figure 6.25: Schematic of the OPV structure of P3HT: PCBM active layer based on a graphene/SNW window electrode
Figure 6.26: (a) SEM micrograph, and (b) EDS of G-SNW deposited onto the surface of graphene electrode then transferred onto Si substrate, respectively174
Figure 6.27: (a) UV-Vis light transmission spectra and sheet resistance of G-SNW film in before and after deposited of SNW network layer, (b) current density – voltage (J-V) characteristics of OPV cell made from P3HT: PCBM blend films, based on G-SNW electrode,

and (c) based on graphene electrode......176

List of tables

Table 1-1: Graphene material thickness associated with the number of layers4
Table 1-2: Comparison of graphene fabrication methods. Permission from American Association for the Advancement of Science, Nature publishing group and Macmillan publishers limited.
Table 1-3 shows the summary of CVD conditions for deposition of graphene films
Table 2-1: Correction factor for the measurement of sheet resistance with the four-point probe method
Table 3-1: Characteristic values of the Raman spectra G and 2D band positions, the intensity ratio between them, and, the 2D peak width, 2D _{FWHM} . ²³²⁻²³³
Table 3-2 Raman characterisation of graphene at T_{growth} 600 °C for four H ₂ flow rates. ²³²⁻²³³
Table 4-1: FTIR analysis is shown of fingerprint and shift peaks for organic solvents-PMMA.
Table 4-2: Thermal analysis shows of organic solvents inside the PMMA matrix
Table 4-3: Characteristic values from Raman analysis, G and 2D position, the intensity ratio between them, and the 2D _{FWHM} are shown. ²³²⁻²³³
Table 5-1: Figure of merit (FoM) for several graphene films in UV-vis transmission with sheet resistance
Table 5-2: shows OPVs characterisation using two types of PEDOT:PSS in the fabrication.
Table 6-1: Figure of merit for several large area graphene films (~4 to 10 cm ²) based on UV- vis transmission with sheet resistance
Table 6-2: J-V characterisation of OPVs made from P3HT: PCBM blend films as active layer,based on electrode of ITO and graphene film
Table 6-3: J-V characterisation of OPVs based on graphene and PEDOT:PSS as transparent electrodes. 165
Table 6-4: J-V analysis of OPV based on graphene electrode at different scale area
Table 6-5 J-V characterisation of inverted OPVs based on electrodes of ITO and graphene.
Table 6-6: J-V characterisation of OPVs based on graphene and graphene with SNW as window electrodes. 175

1. Chapter one: Introduction to graphene

1.1 Overview

This chapter establishes a necessary explanation of graphene as a single sheet of carbon. Then increases the detail, describing the properties of graphene when viewed as a two dimensional material with excellent potential to be a transparent electrode for organic photovoltaics (OPVs). A brief overview of modern graphene applications in organic electronics is provided. The methods and mechanisms of graphene growth have been carefully summarised to contextualise the research plan with the goal of achieving low temperature graphene electrodes for large area OPVs.

1.2 Defining graphene

Graphene is a pure carbon compound formed by a single, ideally flat atomic layer which is infinite in extent, with sp²-bonded carbon atoms. These arranged into a hexagonal honeycomb crystal lattice. As such, graphene is now recognised widely as a nanocarbon material.¹ The hexagonal array can fold upon itself and close into three-dimensional crystalline nanomaterials such as "spherical" Buckminsterfullerene "buckyballs" (or elongated larger allotropes), as well as into carbon nanotubes of a wide variety of size and arrangement. All these carbon allotropes feature the same identifiable hexagonal basis unit shown in Figure 1.1.¹⁻² Figure 1.1 demonstrates how carbon nanotubes may form from subsets of the infinite hexagonal array. It also shows how the more jagged subgroups of the range may develop into the spherical and elongated ball structures. Relatively weak Van-der-Waals forces connect graphene layers between adjacent layers meaning that it is possible to extract graphene through exfoliation of graphite.



Figure 1.1: Single layer graphene. Bottom from left to right: a nanometer size jagged graphene fragment self-forming into Buckminsterfullerene (C_{60}), cylinders forming from defined sections of graphene to create a carbon nanotube, and a stack of graphene layers forming graphite. Reproduced from Ref.,¹ with permission from Nature publishing group.

In the atomic structure of carbon, four valence electrons occupy three hybridised sp^2 orbitals and one P_z orbital for each single carbon atom with an electronic ground state shell of [He] 2s²2p². For graphene, the carbon-carbon bonds are created from the hybridised orbitals. It generated by the superposition of the 2s orbital with the $2p_x$ and $2p_y$ orbitals. Three in-plane covalent σ -bonds correspond with the deep filled valence band, organised by three sp² orbitals. By contrast, the π -bonding and π^* -antibonding states remain perpendicular to the plane formed by the σ -bonds; these are created by the remaining P_z orbital. Furthermore, bonding and antibonding states contribute to the highest occupied valence band and the lowest unoccupied conduction band. Figure 1.2a shows the three in-plane σ -bonds per atom and π orbitals perpendicular to the plane. In the structure, the interaction between different graphene layers is controlled via the out of plane π -bonds.³⁻⁴ In the Brillouin zone, at the k-point (centre of edge), the graphene valence and conduction bands touch each other as shown in Figure 1.2b.⁵ The energy of the electrons is equal to the Fermi energy (E_F) . The touching point between valence and conduction bands is called the Dirac point. In the energy regions near zero, the dispersion curve is linear and, in this zone, the effective mass of electrons and holes in graphene is zero, leading to exceptional conductivity properties.



Figure 1.2: (a) Schematic of the in-plane σ -bonds and π orbitals perpendicular to the plane of the graphene sheets, and (b) electronic band structure of single layer graphene showing the energy dispersion curve, upper and lower surface covalent and valence bands respectively while the K_x- and K_y-axes denote wave vectors in respective x and y directions . Reproduced from Ref.,³⁻⁵ with permission from IOP publishing and the Royal Society of Chemistry.

The structure of graphene is a 2D atomic crystal. Before the discovery of graphene, the majority of scientists believed no long-range ordering 2D structure could be stable at any finite temperatures. Novoselov and Geim disproved this hypothesis through the process of repeatedly sticking and tearing graphite with Scotch tape.⁶ When each action occurred, the graphite was exfoliated, and the sheets of graphite became thinner and thinner. This process ended with one single layer of graphite, graphene, as illustrated in Figure 1.3.⁷⁻⁸



Figure 1.3: Schematics of graphene structure. Reproduced from Ref.,⁷⁻⁸ with permission from Nature publishing group.

The distinction between a graphene film and graphite can be loosely made at around 8 to 10 layers. However, the behaviour observed in graphene films shows significant changes by even the formation of a bi-layer.⁹ Different types of multi-layer graphene materials can be defined by the number of layers and the terminology ascribed to the different thickness and numbers of layers is listed in Table 1-1.

Thickness	Number of Layers (N)
multi-layer	N > 1
bi-layer	2
tri-layer	3
few-layer	4 < N < 10

Table 1-1: Graphene material thickness associated with the number of layers ¹⁰.

1.3 Properties of graphene

The extraordinary physical structure of graphene has been attracting extensive study since 2004. Graphene has been found to display; remarkable electronic and thermal properties; unique optical properties and; mechanical strength.^{1, 6, 11-14} Deservedly, the 2010 Noble Prize in Physics was awarded to A. Geim and K. Novoselov ¹⁵ for their groundbreaking work on graphene and the exfoliation technique. The exfoliation technique has been used extensively for the production of two dimensional atomic layers containing not only graphene but also other 2D materials, such as molybdenum di-sulphide (MoS₂) and boron nitride (BN).^{6, 16} The properties of graphene make it highly suited to being an electrode for organic solar cells because of the advantages of the materials high hole transport mobility, low resistivity, excellent optical transmittance and high mechanical strength. Graphene would also be an excellent replacement for flexible transport conductors in touch screens, flexible displays, solid-state lighting and printable electronics.¹⁷

1.3.1 Electronic properties

Graphene has a carbon-carbon bond length of 0.142 nm. It has a layer thickness of ~ 0.35 nm,¹⁸ parameters that give it electrical properties which make it considered to be a semi-metal or zero-bandgap semiconductor. Specifically, the charge carriers in single layer graphene maybe tuned continuously between electron and holes in concentrations of 10^{13} /cm² with an ambipolar electric field.^{6, 19-20} The carrier mobility of graphene can be up to 200,000 cm² V⁻¹ s⁻¹ when it is transferred onto a clean surface, which is desirable for optoelectronics and ultrafast electronics.²¹ Results from transport measurements of graphene detail its high electron mobility at room temperature.¹ Novoselov et al. reported values over 15,000 cm² V⁻¹ s⁻¹, with a close to identical mobility for electrons and holes.¹ However, in reality, the movement within graphene can be limited to 2,000-15,000 cm² V⁻¹ s⁻¹ by defects in the crystal lattice, scattering, and the presence of tiny ripples.^{1, 6, 22}

A low defect density in the graphene crystal lattice will increase its conductivity as defects in the lattice structure work as scattering sites and block charge transport by limiting the mean free path of electrons. The conductivity of pristine graphene is affected by several intrinsic factors that arise from the valance and conduction bands intersecting at the two-inequivalent points k and k'. The energies of the group are degenerate and form zero energy bandgap (see Figure 1.4b). This band overlap is why graphene is considered a key material for the future generations of electronic devices. However, the zero bandgaps is a disadvantage of graphene when it is used as electronic material in logic applications that require frequent on/off switching. The quantum Hall effect has been shown in graphene even at room temperature because of the high charge mobility and the unique behaviour of its charge carriers as massless relativistic particles (Dirac fermions).²³⁻²⁴ The band structure of single-layer graphene and bilayer graphene are shown in Figure 1.4.²⁵



Figure 1.4: Illustration of the band gap in graphene and schematic diagrams of the lattice structures (a) monolayer and (b) bilayer of graphene. Reproduced from Ref.,²⁴ with permission from Nature publishing group.

1.3.2 Optical properties

Graphene has characteristic high transparency which one the reason for its demand in multiple applications, particularly photonic devices that require conductive and transparent thin films. The absorption of graphene over the visible spectrum averages to 2.3 % and the transmittance linearly reduces with increasing numbers of graphene layers (see Figure 1.5a,b).¹⁴



Figure 1.5: (a) UV-Vis transmittance of single layer and multi-layer graphene, (b) optical micrograph of graphene (single layer and bilayer). Reproduced from Ref.,¹³ with permission from American Association for the Advancement of Science.

Graphene has a high-frequency conductivity of Dirac fermions in the infrared to the visible range of the electromagnetic spectrum that is constant and given by: ²⁶⁻²⁷

$$\delta = \pi e^2 / 2h \tag{1.1}$$

The optical transmittance (T) and reflectance (R) in normal incidence light are given by: ¹⁴

$$T = (1 + \frac{1}{2}\pi\alpha)^{-2}$$
(1.2)

$$R = \frac{1}{4}\pi^2 \alpha^2 T \tag{1.3}$$

Where:

$$\alpha = 2\pi e^2 / hc \approx 1/137 \tag{1.4}$$

e is the electron charge, c the light speed and h is Planck's constant. Combining equations (1.2) and (1.4) allows determination of the opacity of graphene: ¹⁴

$$(1-T) \approx \pi \alpha \approx 2.3\% \tag{1.5}$$

Thus, for chemical vapour deposition (CVD)-grown graphene, the optical transmittance decreases by ~2.3 % for each additional layer, as shown in Figure 1.6a.²⁸ In this figure, the peak at ~250 nm (UV region) belongs to the inter-band electronic transition from unoccupied π -states.²⁸ Optical microscopy enhanced by interference contrast has allowed monolayer graphene to be imaged on SiO₂ where the distinction is based on the thickness of the SiO₂ on a Si substrate, the wavelength of light used ²⁹ and the angle of illumination.³⁰ Panels b and c in Figure 1.6 illustrate optical micrographs of increased layer numbers of CVD graphene on the SiO₂ substrate with point reflection intensity analysis in Figure 1.6c.³¹ The transparency of graphene layers in comparison to indium-tin-oxide (ITO) coated glass has been studied by Kalita et al. (2010).³² Graphene was transparent in the range 250 nm to 2000 nm while ITO glass is transparent from 300 nm – 1100 nm (see Figure 1.6d).³² Additionally, ion diffusion of ITO into the polymer layers of organic solar cells, the intrinsic chemical degradation of ITO under acid/base conditions and the poor transparency of ITO films in near-infrared regions is increasingly problematic for its utility, especially considering future uses in electronics.³³⁻³⁴



Figure 1.6: (a) Transmittance spectra of graphene films roll-to-roll layer-by-layer transferred onto quartz substrates. (b) Optical image of graphene film with one, two, three, and four layers on SiO₂/Si substrate. (c) Contrast optical micrograph of CVD graphene transferred to SiO₂ substrate and histograms of reflected light intensity from marked regions of optical image. (d) UV-spectra of large area graphene sheets fabricated using different amount of camphor and transferred onto glass. Reproduced from Ref.²⁷⁻³¹ with permission from Macmillan Publishers Limited, American Chemical Society, American Institute of Physics and American Chemical Society.

1.3.3 Thermal properties

High performance and reliability of future electronic components depend on heat transfer and extraction from the active devices. Carbon allotropes such as graphite, diamond and carbon nanotubes with strong covalent bonds exhibit phonon scattering and have lower thermal conductivities as a result.²⁴ Little or no phonon scattering occurs in two-dimensional graphene and, in general, heat transfer occurs via the low energy phonons. Transport properties of phonons, such as scattering rates and energy dispersion, were shown to be substantially different in graphene compared to 3D graphite in both theory and experiment.³⁵ According to
the Wiedemann-Franz law, electron contribution is negligible in thermal conductivity due to a relativity low carrier density in pristine graphene.³⁶ In few-layer graphene, the primary heat carriers are acoustic phonons at room temperature.^{35, 37} The thermal conductivity of single-wall carbon nanotube (SWCNT) and multiwall carbon nanotube (MWCNT) have values of about 3500W/mK and 3000 W/mK respectively at room temperature.^{24, 38-40} However, the highest intrinsic thermal conductivity that has ever been found in any material has been in a single layer of graphene. Balandin et al. investigated the first measurement of graphene thermal conductivity at room temperature. It was found to be as high as 5300 W/mK for a single layer of graphene.¹² CVD-graphene has a lower thermal conductivity of about 2500 W/mK.⁴¹ The number of layers present in the graphene and the type of structure, such as AA or AB type, can control its thermal conductivity. The highest in-plane thermal conductivity in any known material about 2000-4000 W/mK is few-layers graphene for freely suspended samples at room temperature. It is lower than the single layer (see Figure 1.7a,b).^{17, 42-43}



Figure 1.7: (a) Thermal conductivity as a function of temperature and (b) thermal conductivity (at room temperature ranges) of diamond, graphite, carbon nanotubes (CNTs), graphene and graphene nanoribbons (GNRs). Reproduced from Ref.^{16,41-42} with permission from American Chemical Society and Nature publishing group.

1.3.4 Mechanical properties

The lifetime and performance of electronic devices can be negatively affected by unwanted strain. Generally, the application of external stress will induce changes in the material interatomic distances. This cause a redistribution of local electronic charge, which subsequently alters the electron transport properties by the generation of a bandgap in the electronic structure. Graphene has strong mechanical properties while remaining very flexible, attributed to the high strength of the carbon-carbon bond. The elastic properties and intrinsic breaking strength of monolayer graphene are measured by nano-indentation using atomic-force microscopy (Figure 1.8 a and b). This experiment has established the graphene as the highest elastic modulus and strength material that have been reported.¹³

Young's modulus has been measured for a single layer, defect-free graphene at 1 TPa with an intrinsic fracture strength of 130 GPa. The presence of defects and wrinkles, the chirality and edge functionalization all affect Young's modulus of graphene.⁴⁴⁻⁴⁶ Graphene oxide has also been studied. In this experiment, the highest fracture strength obtained and the average elastic modulus was approximately 120 MPa and 32 GPa for graphene oxide and graphene, respectively.⁴⁷ The overall reduction of Young's modulus is caused by the defects produced during the chemical reaction.⁴⁸ This chemical reaction was achieved by a modified Hummers method using the natural graphite powder.



Figure 1.8: (a) SEM image of a graphene sheet spanning an array of circular holes (scale bar = 3mm). (b) Schematic of nano-indentation on suspended graphene. Reproduced from Ref.,¹² with permission from American Association for the Advancement of Science.

1.4 Synthesis methods of graphene

Several ways exist for the preparation of graphene thin films and their transfer to rigid or flexible substrates before use in devices. The first method for the production of graphene was developed by Geim and Novoselov in 2004 when they used micromechanical exfoliation of graphite to produce graphene sheets.⁶ Following this, there have been further methods of exfoliating graphite established and, several ways of linear graphene growth, including the epitaxial growth on SiC, chemical synthesis and chemical vapour deposition (CVD).^{1, 22, 49-52} These methods have improved the production and quality of mono-, bi- and tri-layer graphene.

1.4.1 Mechanical cleavage

Mechanical cleavage is considered the first recognised technique and associated with graphene synthesis and is a top-down technique in nanotechnology. The small lattice spacing and strong bonding in the hexagonal lattice plane compared to the large lattice spacing in the perpendicular direction. Weak bonding allows graphene sheets to be exfoliated from graphite. This method is the most commonly used to achieve few-layer graphene on the desired substrate for production. The technique is also the cheapest for producing high-quality graphene. However, it is not suitable for large-scale production of graphene because, in the process of industrial application, small flakes will be scattered randomly on the substrate.

Mechanical exfoliation was used for the first time by the Ruoff group in 1999. They were able to peel the graphene planes from graphite by using an atomic force microscopy (AFM) tip, and small pillars patterned into highly ordered pyrolytic graphite (HOPG) (by plasma etching) as illustrated in Figure 1.9a.⁵³ Geim and co-workers made the first report of isolated graphene on SiO₂ substrates by mechanical exfoliation in 2004. Geim and Novoselov prepared the single layer of graphene (SG) in this method from HOPG (Figure 1.9b).⁶ In 2005, Kim and co-workers used a similar technique and reported electrical properties.⁵⁴



Figure 1.9: (a) SEM depicting graphene generated from early attempts at mechanical exfoliation using graphite pillars by Ruoff's peeled away layer with AFM tip, and (b) AFM image of single layer graphene. Reproduced from Ref.,^{6,52} with permission from American Association for the Advancement of Science and IOP publishing.

1.4.2 Epitaxial growth

Epitaxial growth of graphene on silicon carbide (SiC) substrate via vacuum graphitisation is another promising method of graphene production. It is an effective bottom-up technique to prepare carbon-based electrodes and output is possible on a wafer scale.⁵⁵ High-quality graphene and with a very high carrier mobility (~10000 cm²/Vs) are viable by epitaxial growth of graphene on SiC.^{51, 56-58} Graphene production using this method requires the thermal decomposition of SiC at high temperatures, between 1200 °C and 2000 °C. Here, growth temperature, growth time and other parameters of the growth process affect the number of graphene layers formed.⁵⁷⁻⁵⁸ The growth of ultrathin graphite or a few layers of graphene on the Si-terminated surface may be obtained by thermally annealing single crystal SiC under ultrahigh vacuum. The layer thickness is determined by the annealing temperature. ⁵⁹⁻⁶⁰ Thermal desorption of Si produces SG films on a Si-terminated (0001) face of single crystal 6H-SiC.^{58,} ⁶¹⁻⁶² Bostwick et al. (2009) achieved the growth of both graphene and bilayer graphene on SiC.⁶³ In particular, epitaxial graphene on SiC has been used for high-performance devices such as field-effect transistors,⁶⁴ photodetectors ⁶⁵ and chemical sensors.⁶⁶ The C-terminated and Si-terminated (0001) surfaces are suitable catalysts for epitaxial growth of graphene, with the graphene films prepared much faster on the carbon face.⁶⁷ The strong and weak coupling

of both the substrate and successive graphene layers are the main difference between graphene formed on the C-terminated and the Si-terminated surfaces.⁴ Moreover, patterned caps are used to select the synthesis of epitaxial graphene on a template substrate.⁶⁸ However, transferring graphene films on SiC onto other substrates is difficult. Consequently, the high cost of single-crystal SiC wafers limits the industrial scalability of graphene growth on SiC.

1.4.3 Chemical synthesis

Top-down, indirect graphene synthesis was the first method to demonstrate graphene production by a chemical route. Single-layer graphene was produced by Ruoff and coworkers using a solution-assisted process.⁵² The initial graphite feedstock was chemically modified to obtain a water-dispersible graphitic intermediate in this experiment. Layered stacks of puckered sheets form from the graphitic oxide, and these sheets are entirely exfoliated on the addition of mechanical energy.⁶⁹ This shedding is facilitated by the strength of interactions between the oxygen-containing (hydroxyl and epoxide) functionalities and water present in the basal plane through oxidation. The sheets disperse as individual units due to their hydrophilic nature which allows water to intercalate between them readily. Ruoff et al. showed that hydrazine hydrate was the best reagent to eliminate oxidation during the removal and formation of epoxide complexes.⁵² Low cost and massive scalability are the most exciting advantages of the chemical synthesis method. For example, graphite as a pure material can be used in the chemical synthesis to prepare a large amount of chemically derived graphene dispersed in a liquid.^{47, 70} Furthermore, graphene oxide (GO) is also considered a suitable material to produce graphene via the reduction of the graphene oxide. GO reduced in solution, or after film deposition on a substrate, can lead to increased electrical conductivity of graphene, as shown in Figure 1.10.^{24, 52, 71}



Figure 1.10: Oxidation of graphite to GO and reduction to reduce GO. Reproduced from Ref.,²³ with permission from Elsevier.

Several different reduction methods have been used, including sodium borohydride (NaBH₄),⁷² hydrogen iodine (IH),⁷³ hydroquinone,⁷⁴ dimethylhydrazines ⁷⁵ and hydrazine.²⁴ The removal of oxygenated groups from GO creates sheets with less hydrophilicity and these instantly aggregate in the solution. As mentioned previously hydrazine hydrate is the best process to prepare fragile and delicate graphite sheets. The removal of oxygen atoms leads to a reduction in hydrophilicity in GO, and the reaction pathway could contribute to the re-establishment of the conjugated graphene network (see Figure 1.10).^{24, 52} However, hydrazine is considered highly toxic and potentially explosive, so caution must be exercised when using it.

1.4.4 Chemical vapour deposition (CVD)

Chemical vapour deposition (CVD) is the most popular method for the filing of high-quality graphene onto transition metal catalysts such as Ni,⁷⁶⁻⁷⁸ Pd,⁷⁹ Ir,⁸⁰ Co⁸¹ or Cu^{49, 82-84} films/foils. This promising, low cost and readily accessible approach have been used to produce large areas of graphene thin film.⁸⁵ In particular, the metal substrate, which is most widely used in CVD is copper (Cu) foil. This preference is because of copper's low carbon solubility, inexpensive

processing cost, the absence of copper carbide (C₂Cu₂) and its surficial self-limiting regime when used for graphene synthesis.⁸⁶⁻⁸⁸ In 2009, Li et al. were the first to use CVD growth over a large area using polycrystalline Cu foil as a catalyst. High-quality centimetre-size graphene films of predominantly monolayers (~95 %) were produced, showing carrier mobility of up to 4050 cm² V⁻¹ s⁻¹.⁴⁹ Li et al. also demonstrated a sheet resistance of a four-layer graphene film of 350 Ω/\Box with relatively high transmittance of about 90 %.⁸⁹ Cai et al. report that the sheet resistance of a few layers of graphene has measurements as low as $200 \Omega/\Box$ with a transmittance of 85 %.90 Furthermore, the range of typical sheet resistance for as-grown graphene film by CVD is 100-300 Ω/\Box -cm which were obtained by Anchal et al. in 2010.⁹¹ Hussain et al. have demonstrated different conditions for H₂ flow in CVD with variations in the value of charge carrier densities and the resistivity of graphene thin films, also showing the transmittance values at 550 nm for a monolayer graphene (~97.1 %).⁸⁴ In the last few years, many reports have demonstrated large area, high-quality graphene thin film growth by CVD. These reports show the suitability of the graphene as a transparent electrode for organic solar cells is dependent on the sheet resistance. The transmittance is influenced by the number of layers and the thickness of the thin film. Despite these successful reports, there are still many problems to be solved. It is always a significant challenge for researchers to investigate the graphene growth mechanism and its compatibility with organic solar cell device fabrication.

1.4.4.1 Thermal CVD on copper

Thermal chemical vapour deposition (CVD) is one of the most promising techniques for graphene growth and has proven to be one of the best processes for large scale graphene fabrication. In CVD, the thickness, size and the quality of graphene can be controlled by the experimental parameters, such as catalyst, carbon source, gas flow rate, pressure, growth temperature, growth duration, cooling rate, etc.^{49, 92} This process relies on carbon saturation of a transition metal with exposure to a hydrocarbon gas at a very high temperature. It was pioneered by researchers at the Massachusetts Institute of Technology (MIT) and Samsung Advanced Institute of Technology.⁷⁶⁻⁷⁷ The solubility of carbon in the transition metal surface. Hydrocarbon sources such as ethylene, acetylene, methane and benzene have been investigated, and these materials decompose on different transition metal substrates such as Ni, Cu, Co and Au.^{49, 76-78, 81-82}

The thermal CVD approach uses thin foils of Ni or Cu as catalysts for the decomposition of organic compounds at high temperature. Forming a large area of graphene film, the atoms of carbon form layers on the catalysts surface; this process leads to bonding together in a hexagonal lattice which produces the graphene film.⁴⁹ Several research groups have described methods where CVD deposits graphene on a Cu catalyst surface ^{49-50, 93-95} and the technique has a unique attraction for extensive area synthesis. The promising feature of Cu is the relative solubility of carbon in Cu which is critical to facilitate uniform growth of a single layer and a large area of graphene.^{93-94, 96-101} At high temperature (≥900 °C), Cu reveals relatively low carbon solubility (0.04 %) compared to Ni (2.7 %), and the solubility of carbon reduces as the temperature decreases.¹⁰² The attractive interaction between carbon (C) adatoms on the flat Cu surface during the adsorption process allows for fast growth of graphene from initial islands.¹⁰³⁻ ¹⁰⁵ Previous research has provided evidence that the CVD growth of graphene results in larger sizes and good quality single-layer graphene, even on polycrystalline Cu.^{28, 106-107} Through the thermal CVD growth, the carbon atoms are influenced by the surface structure and bond more readily at the Cu grain boundary (as this region supports grain boundary defects).^{103-104, 108} After rapid cooling, the diffusion of carbon atoms occurs on the surface during a segregation and precipitation mechanism resulting in the formation of mono-or few-layer graphene; a process that is dependent upon the cooling rate (see Figure 1.11).^{49, 77, 109}



Figure 1.11: Transmission electron microscopy images of graphene on transition metal substrates depicting the edges of film regions consisting of one (a), three (b) and four (c) graphene layers during the growth process of the CVD. Reproduced from Ref.,⁴⁸ with permission from American Chemical Society.

A range of different growth mechanisms has described the graphene growth process. Hot filament thermal chemical vapour deposition on a Cu substrate has been demonstrated by Singh et al.¹¹⁰ Kim et al. have produced films of graphene on Cu substrates for use as transparent electrodes in stretchable, flexible and foldable electronics.²⁸ The most common CVD growth of graphene has been on Cu ¹¹¹⁻¹¹² and Ni ^{77, 113-114} substrates. The growth of large areas of graphene was first attempted using a Ni substrate.^{76-77, 113} Because of the slow cooling rate, the carbon atoms have sufficient time for diffusion through the bulk Ni without segregation on the surface. At this higher rate, the carbon atoms are segregated out of the Ni, forming a defective graphitic structure. However, the segregation of carbon atoms and graphene formation are achieving at a moderate cooling rate.¹⁰⁹ Reina et al. (2009) report that the thickness and quality of graphene on polycrystalline Ni surfaces is affected by the cooling rate.¹¹⁵ While Ni segregation contributes to the growth of graphene films, the relatively low carbon solubility found in Cu leads to improved graphene formation. The mechanism of graphene growth on Cu substrates is different from that of Ni. The concentration of carbon atoms primarily affects the growth of graphene on Cu, which predominantly depends on the vapour pressure in the thermal CVD. The Cu substrate has the potential for carbon growth in almost all forms, such as diamond,¹¹⁶ carbon nanotubes,¹¹⁷ graphite ¹¹⁸ and most recently graphene ¹¹⁹ as illustrated in Figure 1.12. At high temperatures (~900 °C), multi-layer and initially single-layer graphene have been prepared on varied (100), (110), (111) and (210) copper surfaces by out-diffusion of carbon dissolution in the precipitation mechanism.¹²⁰⁻¹²³



Figure 1.12: SEM images of (a) carbon nanotube (b) diamond on Cu (111) and (c) photographs of Cu foils are covered with fully grown graphene Cu/Gr. Reproduced from Ref.¹¹⁹⁻¹²² with permission from Elsevier Science, Scientific Reports and American Chemical Society.

The fabrication of monolayer and large area graphene has been achieved by a roll-to-roll method.²⁸ This process was implemented using CVD on Cu foil. Bea et al. described this method in 2010 ²⁸ following an earlier report by Li et al.⁸⁹ In the thermal CVD reactor, the foil becomes roll-on cylindrical quartz, allowing the formation of large-area graphene within a tube reactor. Bea et al. prepared the deposition of graphene on a roll of Cu with dimensions of up to 30 inches. The resultant uniformly high quality and large area graphene showed high mobility up to 7350 cm² V⁻¹ s⁻¹.²⁸ In low-temperature growth, large-area monolayers graphene film has measured the hole and electron mobility which are 811 and 190 cm²/V.s, respectively.¹²⁴

To achieve high-quality graphene films, Borysiak ¹²⁵ and Li et al.^{49, 99} focused on preparing a monolayer of graphene on a 25 μ m thick Cu substrate. Evidence that higher preparation temperature leads to increased growth rate with generally more top quality graphene morphology was demonstrated. The mechanism of graphene growth was shown to depend on C adsorption at the surface. In 2013, Kobayashi T. et al. fabricated a high quality, 100 m length of graphene with a low sheet resistance of 150 Ω/\Box by using the roll-to-roll method on Cu foil, followed by a transfer process.¹²⁶ However, these examples are exceptions and in general, fabricating large-area graphene via a simple process, with high stability is still proving to be complicated. Table 1-2 shows a summary of the relative advantages and disadvantages of the synthesis methods discussed.

Table 1-2: Comparison of graphene fabrication methods. Permission from American Association for the Advancement of Science, Nature publishing group and Macmillan publishers limited.

Method	Images	Advantage	Disadvantage	References
Mechanical exfoliation	<u>20 μm</u>	Fewer defects	Not suitable for mass production	6, 16
Epitaxial growth		No defects for every single graphene island	Discontinuous	127
Chemical Synthesis	No.	Large scale production at low cost	Low quality of graphene	128
CVD	šjuni Syni (High quality and significant area of film graphene	Complex transfer process for thin film	76

1.4.4.2 Growth mechanism of graphene in the CVD method

One of the significant modes of film deposition for the semiconductor industry is CVD as it can produce a high throughput of high-quality film at a relatively low cost. In the CVD process, volatile precursors inside a reactor chamber are transferred into the vapour phase for decomposition on a heated substrate. During this process, several reaction steps, phase changes and material transportations coincide. The thermodynamic process contributing to the structure quality of the final film is very complex, involving the surface adsorption of carbon on a transition metal substrate. Graphene growth can occur on a metal surface by carbon segregation on the surface of hydrocarbon decomposition at raised temperatures. The epitaxial graphene metallic single crystal is similar to this process, but CVD grown graphene on metal requires relatively higher growth pressure than epitaxially grown graphene and also requires a high temperature, typically 1000 °C.^{28, 49-50, 129} Growth at low temperature is highly desirable because it is more convenient, economical and feasible for industrial application.

Recently, the growth of graphene has been demonstrated by coating polymethylmethacrylate (PMMA) or other stable hydrocarbon sources on Cu or Ni substrates and subsequently annealing above 800 °C.¹³⁰ Nevertheless, the growth of graphene at significantly lower temperatures is a challenge. PMMA was used as a carbon source because of its low thermal decomposition temperature.¹³¹ Previous reporters have studied PMMA degradation at low temperature.¹³²⁻¹³⁴ Kashiwagi et al. first observed that the PMMA weight loss was initiated by scissions of the head to head linkages (H-H) around 165 °C.¹³⁵ Using solid PMMA or polystyrene as a carbon source centimetre scale of monolayer graphene of excellent quality has been achieved at growth temperatures above 800 °C.^{130, 136-137} Graphene can be produced even when the temperature growth is decreased to below 400 °C. However, the quality of the graphene film is low. The growth of graphene at a temperature as low as 300 °C requires benzene or toluene as the hydrocarbon source; these procedures obtain high-quality monolayer graphene as small flakes.^{124, 136, 138} Graphene can also be deposited from different carbonaceous gases such as acetylene (C₂H₂) ¹³⁹ and ethylene (C₂H₄)¹³⁹⁻¹⁴⁰, but the preferable carbon precursor is methane (CH₄).

Figure 1.13a, the diagram shows a standard setup for the CVD system for graphene growth on Cu foils. It is provided by three heating coil zones, a quartz tube, a mass flow controller and three ultra-high purity gases including CH₄, hydrogen (H₂) and argon (Ar). The initial step of this synthesis process is heating the substrates under a H₂ and Ar atmosphere to achieve annealing, which allows for temperature stabilisation and metal grain growth. The procedure of graphene growth on Cu foil (25 μ m in thickness and 2×2 cm² in size) is described as follows: the sample is positioned in the middle of a quartz tube. Then the pumping system is started to evacuate the machine and then fill it with Ar gas until it reaches atmospheric pressure. The temperature of the Cu foil is increased in the furnace to 850-1000 °C with the addition of Ar and H₂ under pressure. This process reductively cleans the Cu foil and is followed by the addition of CH₄ for the graphene growth. The ratio between H₂ and CH₄ is chosen to be ~1:17.⁴⁹ At the end of this process, both H₂ and CH₄ flows are shut down, and the substrate is cooled down to room temperature. Research groups have adopted this process ^{93, 141-143} and mass production of monolayer graphene films have been scaled up to the industrial level.²⁸ Figure 1.13b shows a typical schematic of the process of graphene deposition in which growth

parameters have been optimised factors by systematically observing their influence on graphene quality. These parameters include the thermal annealing and growth temperature (900-1000 °C), annealing time (15-60 min), the ratio between H₂/CH₄ (0-10) during growth, growth time (2-30 min) and the gas phase composition during the cooling stage (with or without H₂).¹⁴⁴



Figure 1.13: (a) Schematic depicting a CVD system for graphene synthesis, (b) timing protocol demonstrating the key steps in CVD graphene synthesis. Typically, the thermal annealing and growth temperature was 950 °C with continuous H₂ flow (10 sccm for the whole process), 50 sccm CH₄ was introduced for 15 min during growth stage. Reproduced from Ref.,¹⁴³ with permission from Springer and IOP Publishing.

Of the hydrocarbon-based reactants, CH₄ is the most common carbon (C) source because of the strong C-H bonds in methane molecules (440 kJ/mol). The mechanism of graphene growth from the H₂/CH₄ mixture starts with the transportation of reactants by forced convection, as shown in Figure 1.14.¹⁴⁵ After this step, thermal activation and homogeneous gas reactions can occur within the diffusing gas stream as controlled by the kinetic parameters. The third step is the transportation of the reactants from the main gas stream, through the boundary layer, and then the adsorption of reactants occurs on the substrate surface. After that, dissolution and bulk diffusion occur on and in the metal, substrate as dictated by the solubility and physical properties of the substrate. The sixth stage in this reaction is the thermal activation of surface chemical decomposition of by-products from the surface, then the transport of these by-

products by diffusion through the boundary layer and back to the main gas stream. Finally, these materials are transported by forced convection away from the deposition region.



Figure 1.14: Schematic diagram of thermal CVD process in the case of graphene growth from CH_4/H_2 mixtures. Reproduced from Ref.,¹⁴⁴ with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Yu et al. demonstrated the growth of few-layer graphene sheets on polycrystalline Ni foils. These foils were annealed in hydrogen and then exposed to a CH_4 -Ar- H_2 environment at a temperature of 1000 °C under atmospheric pressure for 20 min. The foils were then cooled at different rates of between 20 °C/s and 0.1 °C/s. The cooling speed is affected by the thickness of graphene layers, and few-layer graphene (3-4 layers) start forming with a cooling rate of 10 °C/s.¹⁰⁹ Li et al. also used a similar process to fabricate large scale monolayer graphene on copper foils. The 25 µm foil was first heated to 1000 °C in a flow of 2 sccm (standard cubic centimetres per minute) of hydrogen at low pressure and then introduced to a methane flow of 35 sccm at a pressure of 500 mTorr. Scanning electron microscopy (SEM) imaging and Raman spectroscopy were used to confirm the graphene film to be primarily monolayer and monolayer formation that was shown to be independent of growth time.⁴⁹ These and other studies for specific growth parameters on (Cu, Ni) substrates by CVD are provided in Table 1-3.

	Pre-annealing Conditions		Growth Conditions		
Substrate	Gas Source	TAnnealing (°C)	Carbon Source	TGrowth (°C)	References
Cu foil	Ar:H ₂ (10:1sccm)	1050	Polystyrene + halogen lamp- (Ar:H ₂)	950-1050	137
Cu (foil, film)	Ar:H ₂ (~200-940:10- 100sccm)	800-1100	CH ₄ :H ₂ :Ar (~0.025-300:1- 100:30-860 sccm)	950-1075	96, 98, 100, 106- 107, 120, 142, 146-148
Cu foil	H ₂ N ₂ [10 sccm]	1025	H ₂ N ₂ :CH ₄ [10 sccm: 40 sccm]	1025	95
Cu (foil, film)	H ₂ (~2-500sccm)	800-1070	CH4:H2 (~0.15-70:2- 100sccm)	900-1070	28, 49-50, 93-94, 97, 99, 101, 111, 125, 129, 141, 144, 149-151
Cu foil	Dried film in Vacuum	70	PMMA 4% in anisole -Ar:H ₂ (500:50sccm)	800-1000	130
Cu foil	Ar/H ₂ : 400sccm	Heating up to 950	Hexane(C_6H_{14}) (4mL/h)-(Ar/H ₂)	950	91
Cu foil	$Ar: H_2$	1000	C ₂ H ₄ :H ₂ (20:50sccm)	700	121
Cu foil	Ar:H ₂ (80:20sccm)	800	CH ₄ :H ₂ :Ar (10:20-50:80sccm) -Hot Filament Thermal	600	110
Cu foil	Ar:H ₂ (100:50sccm)	900	PMMA in chlorobenzene- Ar:H ₂ (100:50sccm)	450	131
Cu foil	low-pressure	igniting the plasma	(CH ₄ :H ₂ : N ₂)+ Plasma Power (40W)	~425	152
Cu foil	H ₂ :100sccm	1000	Benzene, PMMA, polystyrene	200-1000	136-138
Ni (foil, film)	Ar,H ₂	900-1000	CH ₄ :H ₂ :Ar (~15-550:50- 100:200sccm)	900-1000	76, 109, 114
Ni film	Ar:H ₂ (500-600:400- 500sccm)	900-1000	CH4:H2 (5-25:1500sccm)	900-1000	77, 115, 143
Ni film	Ar:H ₂ (150:50sccm)	750	C ₂ H ₄ (1sccm),H ₂ :Ar (50:150 sccm)	750	113

Table 1-3 shows the summary of CVD conditions for deposition of graphene films.

1.5 Large single-crystal monolayer and bilayer graphene

Being able to control the number of layers grown during the fabrication of graphene is critical to the application of graphene as a large-scale electrode. Specifically, integrated graphene devices require the availability of ultra-large graphene single crystals. The availability of these materials is paving the way to scalable photonic and electronic devices that utilise graphene materials. As demonstrated previously, large area mono- or bi-layer graphene can be achieved using the CVD process on catalyst substrates, for example, Cu or Ni. Indeed, production of continuous mono- or few-layer graphene with sizes measured of square meters has been obtained by using the CVD approach.²⁸ As such, controlling the growth and nucleation of graphene during CVD processes have produced large, high-quality single crystals. However, the quality of CVD graphene is still not as high as those exfoliated from graphite, due to the smaller grain size. This smaller grain size results in the production of increased grain boundaries and defects. Reducing the number of nucleation sites has improved the number of graphene domains via preparation of Cu surface since the Cu grain boundaries, impurities and surface roughness associated with the nucleation sites.¹⁵³ Therefore, the critical method to enhance the quality of polycrystalline CVD graphene is increasing the grain size of graphene domains. The size of graphene domains has improved due to electro-polishing of Cu foils.⁹⁶

In 2011, Yu et al. prepared hexagonal monolayer graphene single crystals on Cu with a grain size of ~15 μ m, utilising Ar-diluted CH₄ as the carbon source (see Figure 1.15a).¹⁰⁶ The welldefined zigzag edges produced the hexagonal crystallite shape of the graphene grains, which showed interesting electronic properties.¹⁵⁴ The physical and chemical properties of graphene are reduced with a higher density of grain boundaries. Thus, to minimise the impact of defects that are found at grain boundaries, a tremendous single-crystal metal catalyst was prepared. Previously researchers have achieved millimetre size single-crystal graphene on noble metals such as Pt¹⁵⁵ of Ru(0001),¹⁵⁶ or Ni(111).¹⁵⁷ For industrial-scale implementation; a costeffective method must be used. Sub-millimetre size (~0.5 mm) single-crystal graphene deposited on polycrystalline Cu has been reported by a few researchers and can be obtained by low-pressure CVD in a Cu enclosure 93 or by ambient pressure CVD and suppressing nucleation through annealing.¹⁴⁷ By using Polystyrene as a carbon source to trigger the growth, Wu et al. have fabricated ~1.2 mm sized hexagonal monolayer graphene grains on mechanically, electrically polished and atmospherically annealed Cu foils.¹³⁷ The Ruoff group presented an improved method that can be used for the growth of large single-crystal graphene. In this case, they reported the growth of ~2 mm single crystal monolayer graphene grains inside

of a Cu tube (Figure 1.15b).¹⁵⁰ Before being rolled in the CVD tube the Cu foil was electrochemically polished. The authors explored the suppression of graphene nucleation on the inside of Cu tube substrate, which was helping the Cu inner surface remain flat with nucleation on inner surface which led to the formation of millimetre-sized graphene single crystals. A method of two-step processing in which Cu is melted and solidified as the substrate and then \sim 1 mm sized hexagonal monolayer graphene grains were successfully grown was demonstrated by Mohsin et al.¹⁴⁸



Figure 1.15: (a) SEM image of hexagonal graphene grains grown on Cu substrate, and (b) schematic of Cu tube, suppression of loss of Cu by evaporation and redeposition in a confined space during growth of CVD graphene, Reproduced from Ref.,^{105,149} with permission from Macmillan publishers limited and WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

A different pathway to producing millimetre-sized single-crystal graphene grains has been reported by Duan et al.¹⁵¹. The authors annealed Cu foils in a non-reducing gas (Ar) to maintain a catalytically inactive copper oxide (Cu₂O) layer. The authors then were able to synthesise \sim 5 mm sized hexagonal monolayer graphene grains with straight edges after 48 h of growth. After that, the Luo ¹⁵⁸ and Ruoff ¹⁵⁹ laboratories also have reported the suppression of graphene nucleation by oxygen-rich Cu. The Ruoff group prepared centimetre scale single-crystal graphene grains from thorough oxygen treatment of the Cu foil before graphene growth.¹⁵⁹

1.6 Graphene device applications

The substantial increase in literature on graphene is primarily driven by the prospect of graphene's many possible electronic applications. ITO has been widely used as a transparent conductive electrode for flat panel displays, liquid crystal displays (LCD), touch panels and solar cells. However, limited supply, high cost and the brittle nature of the mixed indium oxide, limits its use in flexible substrate applications. These limitations have encouraged research into high conductivity and high transparency thin-film alternatives. The extraordinary mechanical, thermal and chemical stability of graphene coupled with its high transparency and thin-film nature make graphene a promising candidate for transparent conducting electrode applications. Consequently, graphene is expected to become one of the most sought-after materials for transparent electrodes in optoelectronic devices such as LCDs and solar cells.^{33, 76, 160} Also, graphene is also one of the most promising materials for flexible and reliable electronic applications.^{28, 76, 161-164} As such, the next generation of transparent conductive material is considered to be graphene.

Several reports are demonstrating the use of graphene as a flexible, transparent electrode in organic photovoltaics ¹⁶⁵⁻¹⁶⁷ and also using graphene in the device photoactive layer.¹⁶⁸ Graphene has been used as a transparent electrode material in multiple types of inorganic, organic and dye-sensitized solar cells (DSSCs), and can also be used as a counter electrode in DSSCs, as illustrated in Figure 1.16.¹⁶⁹ The light absorber in a quantum dot sensitized solar cell (QDSSC) and a network of graphene.⁷⁶⁻⁷⁷ Wang et al. have also reported the application of graphene as a transparent electrode for DSSCs;³³ the DSSC had an open-circuit voltage (V_{oc}) of 0.7 V, short-circuit photocurrent density (J_{sc}) of 1.01 mA/cm² and calculated filling factor (FF) of 0.36 with the overall power conversion efficiency (PCE) is 0.26 %. This low efficiency for a DSSC was attributed to the low quality of graphene film. Graphene has also been used as a counter electrode with Poly(3,4-, ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT-PSS), yielding a high transmittance (>80 %) with high electro-catalytic activity. In this case a device, the efficiency was of 4.5 % was achieved.¹⁷⁰



Figure 1.16: Schematic depicting various types of graphene film based solar cells: (a) inorganic, (b) organic and (c) dye-sensitized solar cells (DSSCs). Reproduced from Ref.,¹⁶⁸ with permission from Macmillan publishers limited.

An option for improving the efficiency of graphene-based organic photovoltaics is to control the morphology of the graphene sheet and functionalize the graphene.¹⁷¹ Functionalized graphene has been combined with various organic and inorganic materials including Gold chloride (AuCl₃),¹⁷² butylamines,¹⁷³ pyrenebutyrate,¹⁷¹ poly(3-hexylthiophene) (P3HT)¹⁷⁴ before using it as an electrode of BHJ solar cells. Highly doped multilayer CVD graphene as an anode has been described in recent reports using P3HT: PCBM as the active layer in flexible OPVs. These provide a maximum of PCE of 3.2 % with excellent bending stability.¹⁷⁵⁻¹⁷⁶

Another potential application of graphene is as a transparent conductive layer for the touch screens that have been adopted in different electronic devices such as cell phones and e-books. Typically, an electric short between the top and bottom transparent conducting films is used in this type of touch screen. Films were required with a sheet resistance of up to 550 Ω/\Box and an optical transmittance of over 90 % at a 550 nm wavelength. Graphene films for resistive touch screens can be formed on flexible polyethylene terephthalate (PET) substrates.²⁸ Graphene

films are also an attractive material for use as a transparent conductive electrode in organic light-emitting diodes (OLEDs) because of their electrical conductivity, controllable transparency and tunable work function. Several OLEDs based on CVD graphene films have been reported. ¹⁷⁷⁻¹⁷⁸ These devices utilising graphene films from copper foil have incredibly high performance compared with devices based on ITO. Han et al. modified the work function and sheet resistance of graphene to describe a promising method for improving the performance of flexible OLEDs.¹⁷⁹ A four-layered graphene film was produced with a sheet resistance of 40 Ω/\Box and a transmittance of 90 % by applying a conducting polymer with a gradient work function. This device showed a high current efficiency (30.2 and 98.1 cd/A) and luminous efficiency (37.2 and 102.7 lm/W).

Graphene anodes could replace ITO in the production of high performance flexible organic optoelectronic devices. Graphene is suitable for photodetectors which respond rapidly across a broad visible spectrum to the infrared region. Flexible photodetectors that obtain photoresponsivities of the order of 10^7 A/W with excellent bending stability have been fabricated using CVD-grown graphene and PbS quantum dots.¹⁸⁰ In transistors, graphene films that are synthesised by CVD or other methods can provide excellent continuity to the alignment of channel material over the electrodes and become a bottom gate structure for a polymer-based transistor.¹⁸¹⁻¹⁸⁴ Field-effect transistors (FET) have also been fabricated using graphene. The first reported FET using graphene was created by Novoselov et al. in 2004. In this report, they show that graphene-based FETs have ambipolar characteristics with mobility up to ~ 10000 cm² V⁻¹ s⁻¹ and an electron and hole concentrations of 3×10^{13} /cm² at room temperature.⁶ It is promising results for using graphene film in electronic applications.

1.7 Graphene electrodes in OPV devices

Organic photovoltaics (OPV) has many advantages and high potential as a renewable energy source. Specifically, OPV has attracted immense attention in the last few years due to their low material cost, low weight and flexibility. Device cost is one of the essential criteria for the commercialisation of OPV. As a result, improvements must be made not only to the power conversion efficiency (PCE) but also the fabrication cost of the device. ITO is one of the most expensive components in organic photovoltaics because indium is a rare material. It is not an ideal choice for an optically transparent electrode in these devices. However, many electronic applications including LCDs, touch screens and organic photovoltaics have used this rare

material due to its low resistance (<100 Ω/\Box), high mobility and high transparency (visible transmittance of >80 %). The replacement of ITO is a considerable challenge, but the development of low-cost graphene films could meet this challenge. In organic photovoltaics, the great interest for future applications in graphene films because of its high three-dimensional aspect ratio, remarkable optical transmittance, extraordinary thermal resilience, large specific surface area, superior mechanical stiffness, excellent electron/hole transport properties and flexibility. Graphene can be used as an interfacial layer and a transparent window/counter electrode in an OPV.

Many research groups have used graphene films as transparent electrodes for both organic and dye-sensitised solar cells.¹⁶⁴⁻¹⁶⁶ The performance has to date been inferior to that of devices with ITO electrodes since the conductivity of graphene electrodes once incorporated into a device is relatively low. Arco et al. reported a 75 mm² flexible organic solar cell with a graphene electrode with a PCE up to 1.3 %.¹⁶⁴ Park et al. also reported organic solar cells with Au-doped graphene electrodes (1.21 mm²) that showed a maximum PCE of 1.63 %.¹⁷² Another organic solar cell that used a graphene electrode anode (4 mm²), reported by Wang et al. in 2011, reached a PCE of 2.5 %.¹⁸⁵ Hsu et al. demonstrated a maximum PCE of 2.58 % in organic photovoltaics (area: 10 mm²) with sandwiched graphene/tetracyanoquinodimethane (TCNQ)/graphene stacked films as transparent electrodes, as shown in Figure 1.17.186 Recently, PCEs of 2.7 % in semitransparent OPVs with highly doped single-layer graphene electrodes have been reported by Liu et al.¹⁶⁵ Liu also fabricated flexible OPVs on polyimide (PI) substrates with P3HT: PCBM as the active layer and highly doped multilayer CVD graphene. The top transparent electrodes (anode); these devices showed a maximum PCE of 3.2 % under AM1.5 conditions.¹⁷⁵ These reports have demonstrated gradually improved device performance by using chemically doped graphene films or stacked multilayer graphene. This trend demonstrates that graphene is a promising material for transparent electrodes in organic solar cells.



Figure 1.17: Schematic depicting graphene-containing OPV device architecture and band structure. It is reproduced from Ref.,¹⁸⁵ with permission from American Chemical Society.

1.8 Basics of organic photovoltaics (OPVs)

1.8.1 OPV architecture

Organic photovoltaics (OPVs) are usually classified according to the type of donor-acceptor materials employed and the layer structure: single layer, bilayer and bulk-heterojunction. A typical OPV architecture is depicted in Figure 1.18 with five layers. The substrate in this device which is the first layer in its construction is made of materials such as quartz, glass, polyester, PET. The second layer in this structure is ITO that is deposited on the substrate and patterned, producing the anode (in a conventional device architecture). A hole transport material, such as poly (3, 4-ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS), is deposited on ITO as the third layer. The active layer which is commonly a binary blend of electron donor material and electron acceptor material, such as poly (3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM), is then deposited as the fourth layer. The fifth layer in this conventional architecture device is then a conductive metal cathode of aluminium (Al), silver (Ag), or gold (Au). ITO and Al in this device are used to collect holes and electrons respectively as shown in Figure 1.18.¹⁸⁷⁻¹⁸⁹



Figure 1.18: Device architecture of a bulk heterojunction organic photovoltaic with spin-coated PEDOT: PSS and P3HT-PCBM layers and thermally evaporated aluminium.

1.8.2 Bulk heterojunction OPV operation principles

In organic photovoltaics (OPVs), free charge carriers are generated from sunlight by organic semiconductor materials. Single component photoactive layer organic photovoltaics are unsuitable candidates for future applications due to their high recombination of free charges and, therefore, low efficiencies. However, a new era emerged for organic photovoltaic cells after the discovery of the bulk heterojunction architecture in 1995 by Yu et al.¹⁹⁰. The improvement was in energy conversion efficiency (η_e) and the carrier collection efficiency (η_c) as a consequence of the new architecture produced by mixing the semiconducting polymer with C₆₀ or its functionalized derivatives. The efficient charge separation arises from photoinduced electron transfer from poly (2-methoxy-5-(2'-ethyl-hexyloxy)- 1,4-phenylene vinylene) (MEH-PPV) (as a donor) to C₆₀ (as acceptor).¹⁹⁰

Generally, the free charge carriers at interfaces in OPVs are generated by the dissociation of excitons into holes and electrons. The recombination rate is lower for bulk heterojunction solar cells when compared with single-component solar cells because domains of both electron-donating and electron-accepting materials exist in the active layer, which facilitates charge transport. The organic semiconductor has a band structure similar to an inorganic semiconductor. In this structure, the conduction band is ordinarily free of electrons, but the group that is typically filled with electrons in the valence band. Thus, the lowest unoccupied

molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) on organic devices are analogues to the conduction band and valence band respectively.¹⁹¹⁻¹⁹²

An exciton (bound electron-hole pair) is generated when an organic semiconductor absorbs light, and an electron is promoted from the HOMO to the LUMO, as depicted in Figure 1.19. The second process is exciton diffusion, and this process is limited by the exciton diffusion length in the selected semiconductors. Exciton dissociation occurs at donor-acceptor interfaces in the bulk heterojunction photoactive layer generating a hole in the donor material and an electron in the acceptor material. Thus, free charges are produced when the lifetime of the exciton is sufficient to reach an interface between the electron donor material and the electron acceptor material. The energy level offset of the two elements at the interface drives the dissociation of a free electron and hole. Finally, charge transport occurs within the active layer and, when charges reach the appropriate electrode, charge collection occurs, as illustrated in Figure 1.19.¹⁹³⁻¹⁹⁵



Figure 1.19: Energy level diagram of an organic solar cell depicting the steps of exciton generation with a donor-acceptor interface: (1) exciton generation, (2) exciton diffusion, (3) exciton dissociation, (4) charge transport.¹⁹⁴

The working principle for bulk heterojunction solar cells is depicted in Figure 1.20. The morphology of the donor material and acceptor material of the bulk heterojunction layer sandwiched between the two electrodes is drawn as a typical example in this figure. The separation of charge occurs at the interface of donor and acceptor material domains. Transportation of charge occurs via conduction paths (represented by red and green lines) which are formed within the respective material phases to their electrodes.¹⁹⁶



Figure 1.20: Schematic of bulk heterojunction solar cells demonstrating the working principle: (1) generating an exciton by light absorption, (2) diffusion of the exciton to an interface of the donor (blue) and acceptor (yellow) material, (3) dissociation of the exciton, (4) free carrier charge transport to the cathode and anode, (5) charge collection at the cathode and anode. Permission from the Annual Review of Chemical and Biomolecular Engineering.¹⁹⁵

1.8.3 The efficiency of OPV

Organic photovoltaics (OPVs) are typically characterised under AM 1.5 solar spectrum with 1000 W/m² light.¹⁹⁷ In solar cells, the extent of the energy conversion efficiency depends on the thermodynamical losses. Energy conversion is generated by the absorption of photons, which have energy more massive than the bandgap of the photovoltaic material. Another contribution of photons power is the thermalising of the charge carriers. Frenkel excitons control the absorption in organic materials; the banding energy in these excitons is about 0.3 eV. According to the fundamental investigation of Shockley and Queisser, which considered spectral losses alone, a solar cell for materials with an energy gap around 1.1 eV has a peak

theoretical efficiency of 48 %.¹⁹⁸ In single junction organic photovoltaics, an efficiency of approximately 11 % is expected based on a donor having bandgap energy of 1.5 eV with 0.6 eV loss in the open-circuit voltage (V_{oc}). The internal quantum efficiency (IQE) is limitation assuming (external quantum efficiency (EQE) = 65 %).¹⁹⁹ In 2011, Mitsubishi Chemical certified by Newport had recorded a new efficiency of ~10 % from solutions of small molecules.²⁰⁰ Zhang S. et al. reported that OPV efficiency had reached over 14 % for a polymer solar cell enabled via a chlorinated polymer donor.²⁰¹ Figure 1.21 shows the historical trend for PV efficiency, highlighting the significant performance gap between organic photovoltaic and competitive thin-film photovoltaic (PV) technologies.²⁰²



Figure 1.21: Comparison of the world reports between OPVs and thin film PV technologies of a-Si from 1985 to present.²⁰¹

2. Chapter two: Fabrication and characterisation of graphene electrodes

2.1 Overview

This chapter details the procedure for the growth of graphene via chemical vapour deposition (CVD), the post-growth transfer process, characterisation of graphene films and fabrication of organic photovoltaic devices (OPVs) incorporating graphene. For the CVD growth of graphene, selecting the catalyst based on its physical and chemical properties is the critical first step. Cleaning of the catalyst surface to remove surface contamination is also then essential in obtaining high-quality graphene. The purity of the catalyst was tested using X-ray photoelectron spectroscopy (XPS) before the growth of graphene. Raman spectroscopy was utilised before transferring the grown graphene to determine the quality of the graphene while still on the copper (Cu) catalyst. Further characterisations of transferred graphene then included a conductivity measurement via four-point probe, UV-Visible spectroscopy and UV photoelectron spectroscopy before utilisation of the graphene as a window electrode in an OPV.

2.2 Fabrication of graphene film

The fabrication of CVD graphene on a Cu foil catalyst is a promising method for preparing a high-quality transparent electrode as discussed in Chapter 1.⁸⁹ Furthermore, producing low-cost CVD grown graphene at low temperature using a liquid carbon source has significant potential applications in the electronics industry. However, low temperature graphene growth is a complicated method with further work to be completed in understanding the growth mechanism. The aim of this project is low temperature CVD fabrication and assessment of a transparent graphene electrode for OPV.

2.2.1 Catalyst

An essential factor in the preparation of graphene using CVD is the catalyst. Cu foil (Sigma-Aldrich, 349208 Aldrich, 99.98 % purity, 1.673 Ω cm⁻¹, 20 °C resistivity, 25 μ m thickness and density 8.94 g/mL at 25 °C) was utilised as a catalyst in this procedure.

The as-received Cu foil substrate has a native oxide layer from reaction with air. In addition, the surface can contain some level of contamination and surface deformation from fabrication, storage and handling. Surface defects and non-uniform surface morphology can exist due to the cold rolling of the Cu to foil thickness during manufacture. Before removing the native oxide layer by thermal annealing in the CVD system, the surface of the Cu foil must be cleaned and a low-roughness, flat surface prepared. The cleaning procedures below were performed for each CVD growth attempt to achieve the highest quality of graphene.

2.2.1.1 Washing of Cu foil

After cutting, the Cu foil was washed to remove surface contaminants originating from storage. The first solvent used to clean the surface of the catalyst was acetone. The foil substrates were submerged in acetone for 5 min, followed by a slow rinse in isopropanol (IPA). Deionised (DI) water was then used to removing any organic solvent remaining on the surface of the catalyst. Finally, the catalyst surface was dried with a stream of nitrogen (N₂) gas. This procedure was adequate for removing the majority of surface contaminants on the Cu foil originating from the rolling process during manufacture.

2.2.1.2 The electropolishing of Cu foil

Electropolishing was used to further smooth and clean the Cu Surface. An electrochemical cell was set up with Cu foil (25 μ m thick) as the anode and a large Cu plate as the cathode, as illustrated in Figure 2.1. The electropolishing electrolyte solution consisted of 600 mL water, 300 mL ethanol, 60 mL isopropyl alcohol, 300 mL ortho-phosphoric acid, and 6 g urea. The electrodes of the electrochemical cell were inserted into the solution, and a DC power supply was used to apply a constant voltage. A range of voltages between 3 V and 6 V was supplied for different periods of times (10 to 120 s) to optimise polishing. Subsequently, the condition was used at 3V for 30 s as minimised the surface roughness of the sample.



Figure 2.1: Schematic depicting the electrochemical polishing of Cu foil.

The chemical reactions for the electro-polishing of Cu foil in ortho-phosphoric acid are as follows: ²⁰³

$$Cu \to Cu^{+} + e^{-}$$
(2.1)

$$2Cu + 2OH^{-} \to Cu_{2}(OH)_{2} + 2e^{-}$$
(2.2)

$$Cu^{+} + 2OH^{-} \to CuO + H_{2}O + e^{-}$$
(2.3)

$$3Cu_{2}(OH) + H_{3}PO_{4} \to 2Cu(OH)_{3}PO_{4} + 4Cu^{o} + 3H^{+} + 3e^{-}$$
(2.3)

$$3CuO + 2H_{3}PO_{4} \to Cu_{3}(PO_{4})_{2} \cdot 3H_{2}O$$
(2.4)

$$Cu(OH)_{3}PO_{4} + 3Cu^{o} + H_{2}PO_{4}^{-} \to Cu_{3}(PO_{4})_{2}Cu(OH)_{2} + H_{3}O^{+} + 2e^{-}$$
(2.4)

The reaction of oxygen evolution:

$$20H^{-} \rightarrow \frac{1}{2}O_{2} + H_{2}O + 2e^{-}$$
(2.5)

Ultimately, the technique cleans and smooths the Cu Surface and reduces the oxide layer thickness. At the end of the process, the Cu foil was washed with deionised water (DI) followed by ethanol, then dried with nitrogen (N_2) gas.

2.2.1.3 Thermal annealing of Cu foil

The chemical vapour deposition (CVD) system used for the preparation of graphene on Cu foils was an Automate CVD system. The system also has a coil heater element of NiCr, which allows temperatures of up to 1100 °C as may be seen in Figure 2.2.



Figure 2.2: Atomate CVD system for the growth of graphene films.

After electropolishing the Cu catalysts, thermal annealing CVD was performed for three essential purposes. Firstly, a high-temperature treatment of the catalyst in the CVD system under an H₂ and Ar atmosphere is a proper technique for completely removing any oxide layer on the surface. The Cu foils were annealed at different temperatures. The mixture of gases in the CVD system was optimised to find the best overall conditions for achieving a high quality of graphene (as shown in Chapter 3). Optimal oxide removal occurred when foils were annealed at 900 °C for 1 hour under H₂ 50 sccm, Ar 0.1 SLM (standard litre per minute) and a system pressure ~ 0.5 Torr. ⁹⁶ Secondly, the most significant factor affecting the roughness of the catalyst is the grain size of Cu. A high temperature ~ 900 °C anneal of the Cu foil leads to increased grain size, reducing the number of defects in the substrate. ^{96, 98}

Finally, thermal annealing can also increase the purity of the Cu foil via the removal of any contamination remaining from the cleaning process. Hence, thermal annealing is considered the final stage of cleaning before graphene growth. Furthermore, since the annealing takes place inside the CVD system, the possibility of reoxidation and contamination of the Cu surface is limited.

2.2.2 Carbon source

Different types of carbon sources have been utilised for the growth of graphene, including gases, liquids and solids (such as polymers).¹³⁰ The nature of the carbon source is a critical parameter in graphene growth due to the energy required for bond-breaking and the deposition of suitable carbon moieties onto the catalyst. Utilising the low C-H bond energy of the carbon source could be a possible route to reduce the energy required for the synthesis of graphene. Organic solvents entrapped in a PMMA matrix were used as a carbon source in this project. PMMA can be used as a stable carbon source with the decomposition of the polymer back into monomer units providing the mobile carbon. Alternatively, solvents trapped within the PMMA film may act as the carbon source. The structure of PMMA and the MMA (methyl methacrylate) monomer are shown in Figure 2.3.²⁰⁴ PMMA is an amorphous polymer, with the methyl side groups restricting the ability of the polymer to pack in an ordered dense array.



Figure 2.3: The chemical structure of MMA and PMMA.²⁰³

PMMA has as glass transition temperature (T_g) range of 110 to 120 °C, a density of 1.18 g/cm³ at room temperature, and a melting point of 220-240 °C.²⁰⁴⁻²⁰⁵ The thermal decomposition temperature of PMMA ranges over 300-400 °C. The annealed Cu foils were located in Zone 3 of the CVD tube, (See Figure 2.4 below) which was heated to 300-800 °C inside the 2-inch diameter CVD system quartz tube furnace. PMMA dissolved in various organic solvents with concentration (100 mg/ml) was drop-cast as a film onto a glass substrate that was loaded into Zone 1 as the carbon source. This zone was then heated to 180 °C. Zone 2 was left at room temperature to minimise heat leak from Zone 3 to Zone 1.

2.2.3 Graphene growth

The CVD system has three heating zones with individual temperature control. In the procedure developed, Zone 1 was used as the carbon source heating zone with $T_{source} = 180$ °C. Zone 3 was used as the growth area and contained the catalyst substrate, as shown in Figure 2.4 with typically, $T_{growth} = 450$ °C or 600 °C.



Figure 2.4: Schematic of CVD tube showing heater zones in the system. The carbon source is a drop cast film of PMMA dissolved in organic solvent.

 H_2 gas was used to exclude oxygen (O₂) from the growth zone to reduce amorphous carbon formation. ¹⁴² The set growth time was short, 1 min, to minimise the number of graphene layers grown. Graphene on the Cu foil was identified via Raman spectroscopy before the transfer process, with measurements conducted on a Renishaw inVia Raman spectrometer. Graphene layers were then transferred from Cu foil onto a target substrate via a wet transfer method, as reported elsewhere. ⁸⁹ Section 2.2.4 describes this transfer process in full.

Three heating coil zones with 8 inches distance between each zone surrounded the CVD tube. Quartz boat holders inside the tube furnace were used for holding the catalyst and carbon source. Full software computer controlling is available with many variables controlled such as heating profiles for each zone, gas flow rates and overall system pressure.

2.2.4 Transfer process for graphene film

Graphene layers were transferred from Cu foil to target substrates via a wet transfer method (see Figure 2.5). Etching of the Cu substrate in this method was utilised to leave a graphene film floating on DI water surface. This process required mechanical support of the graphene layer from a polymer film/membrane.



Figure 2.5: Schematic depicting the wet transfer method of graphene films.

To create mechanical support for the graphene films, PMMA was dissolved in chlorobenzene (50 mg/ml) and was spin-coated (4000 rpm for 1 min) onto the graphene: Cu foil surface. Following this step the PMMA adheres firmly to the graphene film, enabling the etching away of the Cu foil without impacting the morphology of the graphene layers due to the polymer support. An aqueous iron nitrate (Fe (NO₃)₃) solution (0.05 g/ml) was used as the etching solution to separate the sandwich of PMMA/graphene from the Cu foil over a period over 48 hours. Washing the released PMMA/graphene film in a petri dish with DI water removed any iron solution left on the surface. The PMMA/graphene film was left floating on DI water until transfer onto the desired substrate by lifting it from the water surface. Three rinses removed

the polymer film with acetone and isopropanol. It followed by an overnight soaking of the graphene film in a chloroform solvent bath to remove any contamination from the transfer method. The graphene film on the target substrate was then dried using a stream of N_2 gas.

2.3 Fabrication of OPV based on graphene electrode

Graphene films were picked up from the water surface by glass substrates after etching away the Cu catalyst. According to AFM measurements discussed in chapter 5, the graphene electrode was ~ 1 to 2 nm in thickness, indicative of a single layer of carbon. A thin film of PEDOT:PSS (~30 nm) was spin-coated onto the graphene-coated glass substrate at 4000 rpm for 1 min. This material is available commercially as an aqueous dispersion (low conductivity poly(3,4-ethylene dioxythiophene-poly(styrene sulfonate)) (PVP AI4083 (purchased from Heraeus)). The PEDOT:PSS film was dried at 140 °C for 30 min to remove water. The glass/graphene/PEDOT:PSS substrate was then directly moved into a N₂ atmosphere for photoactive layer film deposition. A blend solution of poly(3-hexylthiophene-2,5diyl):(phenyl-C₆₁-butyric acid methyl ester) (P3HT:PCBM) was prepared at a concentration ratio of 1:0.8 (20 mg: 16 mg) by dissolving in 1057 µL of anhydrous 1,2-dichlorobenzene. This polymer-fullerene solution was sonicated at room temperature for 1 hour, followed by stirring overnight for complete dissolution. The P3HT:PCBM active layer was spin-coated onto the PEDOT:PSS layer at 900 rpm for 1 min (thickness ~ 200 nm) under a nitrogen (N_2) atmosphere. Pre-annealing (before cathode deposition) of the active layer was conducted on a hot plate under a N₂ atmosphere at 140 °C for 4 min. An interfacial layer of calcium (Ca) (~30 nm) was thermally evaporated onto this active layer. It followed by thermally evaporating a metal cathode of aluminium (Al) (120 nm) utilising an Angstrom Engineering evaporator under vacuum to 10^{-7} bar pressure. Devices were then transferred to a N_2 glovebox to measure photoresponse J-V curves by a Keithley 2400 meter. The devices were illuminated under an AM1.5 Newport class A solar simulator calibrated via a Si photodiode.

2.4 Characterisation of graphene film

Graphene films were analysed by Raman spectroscopy to evaluate their quality. Atomic force microscopy (AFM) and optical microscopy were utilised to investigate the efficiency of the transfer method. Graphene films were also characterised following the transfer onto target substrates by ultraviolet-visible (UV-Vis) spectroscopy, four-point probe, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and photo-electron spectrometry. The graphene-based OPV device performance was determined by J-V measurement.

2.4.1 Optical microscopy

Optical microscopy is a valuable tool for analysing the morphology and topography of samples. The surface morphology of graphene films and Cu foil catalyst were examined using a Carl Zeiss West Germany (467085, NT 6V/10W stab) optical microscope, with images recorded in transmission mode.

2.4.2 Atomic force microscopy (AFM)

AFM has been widely used since its discovery in 1986 by Binning et al. ²⁰⁶ for the investigation of the morphology of material surfaces at the nano-scale in many fields of science. In this thesis, an Asylum Research Cypher AFM was utilised to analyse the surface topography of graphene layers. Also, AFM was used to determine the thickness of graphene samples, as well as the roughness of the Cu catalyst surface following the cleaning process. AFM operates via measuring the forces acting between a sharp tip and a sample surface. An excellent tip is connected to a cantilever, which is raster scanned across the sample surface to generate a 3D image. According to Hooke's law, repulsive and attractive forces originating from the interaction between the tip and the sample surface when the tip is very close to the surface (within a few nanometres) cause the cantilever to bend. This force will generate a positive or negative bending of the cantilever, which is monitored by directing a laser spot onto the cantilever and detecting the reflected light with a photodiode array as depicted in Figure 2.6.



Figure 2.6: Schematic of AFM system used for the characterisation of thin films.

2.4.3 X-Ray diffraction (XRD)

The crystallographic structure of a material can be probed via X-ray diffraction. This technique was utilised to study the crystalline domain formation of the Cu catalyst, with measurements of both unannealed and annealed catalysts being performed. X-ray diffraction was performed using a Philips X'Pert MPD XRD (Figure 2.7a). XRD measurements were made with the sample tilted at 45° and the source emitting Cu K α radiation at 1.5405 Å. A diffraction pattern can be measured following X-ray scattering from regular planes in the sample crystal lattice. Max von Laue described this diffraction pattern in 1912, and then in 1913 William L. Bragg and his father William H. Bragg assumed Bragg's law to explain the patterns: ²⁰⁷

$$n\lambda = 2dsin\theta \tag{2.6}$$

Where n is an integer, λ represents the wavelength of the incident light, d describes the spacing between the planes in the atomic lattice and θ is the angle between the incident X-rays and the scattering planes (Figure 2.7b). Information relating to the atomic-level structure of materials is provided by analysis of X-ray diffraction patterns.


Figure 2.7: (a) Philips X'Pert MPD XRD equipment, (b) schematic depicting the X-ray diffraction principle.

2.4.4 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is an excellent technique for studying chemical compositions at the surface of a wide range of materials. Samples are irradiated with a non-monochromatic X-ray beam and photoelectrons emitted are detected and analysed. The photoelectron production results from electrons initially bound to an atom at its core levels (see Figure 2.8). The kinetic energy of the emitted electrons is given by: ²⁰⁸

$$KE = h\nu - BE - \phi_s \tag{2.7}$$

Where hv represents the energy of the X-ray photons, BE is the binding energy of the atomic orbital and ϕ_s is the spectrometer work function. Based on the binding energy of electrons, it is unique to each element in a specific shell of an atom. Components can be identified, and the relative composition of elements based on their chemical shifts at the material surface can be probed (other than hydrogen (H₂) and helium (He)). Spectral lines of XPS are identified via the electron emission from the core elemental shells (1s, 2s, 2p, 3s, 3p, 3d, etc.).



Figure 2.8: A schematic depicting electrons absorbing X-rays and being ejected from their orbitals.

A non-monochromatic X-ray source (Omnivac) using Al K α (1486.6 eV) was used for this thesis, and the photoemission was collected by a SES2002 analyser (Scienta). XPS surface analysis was utilised to gain information on the chemical states and the elemental compositions of samples. The hemispherical analyser is used to determine the kinetic energies of photoelectrons in most modern XPS instruments, as shown in Figure 2.9. XPS is known to be a surface-sensitive technique, probing the top ~10 nm of film surfaces. In XPS, the yield of electrons produced as a function of the impacting photon energy enables the measurement of the quantitative chemical composition of the sample surface.



Figure 2.9: Schematic of XPS system.

2.4.5 Raman spectroscopy

Characterisation of sp² hybridised carbon systems ranging from graphene to carbon nanotubes has been widely achieved via Raman spectroscopy. The Raman spectral features of material can identify changes in the Fermi level and breaks in lattice symmetry. Raman spectroscopy can be used to characterise graphene layers due to changes in vibrational energy bands which are representative of film quality.²⁰⁹ Raman spectroscopy is a non-linear scattering phenomenon where the incident photon scatters from a virtual state to a vibrational level of the molecule under study or the phonon manifold of bulk material.²¹⁰ A Renishaw inVia Raman spectrometer was used in this thesis (Figure 2.10). This spectrometer was equipped with several lasers, including 325 nm (Helium-Cadmium), 514 nm (Argon-Ion) and 633 nm (Helium-Neon).



Figure 2.10: The Renishaw inVia Raman spectrometer.

The interaction between an incident laser and the sample produces predominantly Rayleigh scatter, and a much weaker Raman scatter signal. The combined scatter is then filtered, via a notch filter, to remove the Rayleigh component. The weak Raman signal is dispersed in a grating spectrometer to measure its constituent wavelengths as shown in Figure 2.11. For Raman mapping, an XploRA PLUS Raman microscope from HORIBA Scientific was used to identify the quality of graphene layers up to $100 \times 100 \,\mu\text{m}$ in dimension. This instrument has a high-performance atomic force microscope (AFM) functionality with laser wavelength 532 nm (green), power 20 mW, N NA 0.7 lens, spot size 400 nm and step size 1 nm.



Figure 2.11: A schematic of the Raman spectrometer light path.

2.4.6 UV-Vis spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy is the measurement of the photon energies absorbed by a molecule arising from electron transitions from the ground states of the molecules to excited states of the molecule. ²¹¹ UV-Vis spectroscopy was used to determine the transmission of graphene films at selected wavelengths from 200 to 900 nm. Beer-Lambert's law represents the absorbance (A) of incident light: ²¹²

$$A = -\log\left(\frac{l}{l_0}\right) \tag{2.8}$$

Where the transmittance is described as the ratio between the intensity of transmitted light and the intensity of incident light (I/I_0) .

A Varian Cary 6000i UV-Vis-NIR spectrophotometer was utilised to measure the transmittance of graphene films on glass substrates (Figure 2.12). The most critical component of the UV-Vis spectrometer is the light source. The source must allow measurement of a complete absorption spectrum in the UV-Vis range of 175 to 1800 nm. The Varian Cary 6000i instrument has two light sources covering this entire UV-Vis region. The first source is a deuterium lamp covering the UV spectrum from 175 to 350 nm. The second source is a quartz tungsten halogen bulb emitting the higher wavelengths.



Figure 2.12: UV-Vis spectrophotometer.

2.4.7 Four-point probe conductivity

The four-point probe method is widely used to determine the resistivity of semiconductor and conductor material films. The measurement of resistance between probe tips in contact with a film is based on applying a constant current (I) between two outer probes and measuring the potential difference (V) using two inner probes (Figure 2.13a). A two-point probe electrical setup is usually used for general purpose resistance and current-voltage measurements. However, for more accurate analysis, the four-point probe method is used as it avoids contact resistances between the probe and material surface. This equipment (Figure 2.13b) has four tungsten pins, which contact the graphene film with 2 mm spacing and 100 µm radii. High flexibility springs hold the tungsten pins for limiting sample destruction through probing. The low resistivity of graphene requires a high current in external probes to achieve a suitable voltage recording.



Figure 2.13: (a) Four-point probe sheet resistance equipment, (b) schematic of four-point probe measurement for thin film.

In this analysis, the sheet resistance is given by the equation:

$$R_s = \frac{V}{I} C\left(\frac{a}{d}; \frac{d}{s}\right)$$
(2.9)

Where R_s is the sheet resistivity, a length of the film, d width of the film, and s the distance between two neighbouring tungsten pins (2 mm).

 $C\left(\frac{a}{d};\frac{d}{s}\right)$ is the correction factor based on a, d and s values. This factor is determined based on values in Table 2-1.²¹³

Table 2-1: Correction factor for the measurement of sheet resistance with the four-point probe method.

d/s	Circle	a/d=1	a/d=2	a/d=3	a/d≥4
	utatii u/s				
1				0.9988	0.9994
1.25				1.2467	1.2248
1.5			1.4788	1.4893	1.4893
1.75			1.7196	1.7238	1.7238
2			1.9454	1.9475	1.9475
2.5			2.3532	2.3541	2.3541
3	2.2662	2.4575	2.7000	2.7005	2.7005
4	2.9289	3.1137	3.2246	3.2248	3.2248
5	3.3625	3.5098	3.5749	3.5750	3.5750
7.5	3.9273	4.0095	4.0361	4.0362	4.0362
10	4.1710	4.2209	4.2357	4.2357	4.2357
15	4.3646	4.3882	4.3947	4.3947	4.3947
20	4.4364	4.4516	4.4553	4.4553	4.4553
40	4.5076	4.5120	4.5129	4.5120	4.5129
x	4.5324	4.5324	4.5324	4.5325	4.5324

For large area sample measurements, a custom-built four-point probe setup with soft conductive rubber connections was used (Figure 2.14). This system had a measurement error of $\pm 1 \Omega/\Box$.



Figure 2.14: Four-point probe of large area graphene (custom built).

2.4.8 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is considered to be one of the most useful techniques for the imaging and analysis of microstructural characteristics of solid films. The high resolution of SEM (sub-nanometre) is a primary reason for the frequent use of SEM in the field of nanotechnology. In SEM, an electron beam is incident upon a sample surface and produces several modes for imaging including X-ray, Auger electron, cathode luminescence, backscattered electron (BSE) and secondary electron (SE). Generating images in SEM is via the selective collection of these signals with an array of detectors. In our work, graphene films were transferred onto conductive silicon (Si) substrates to assess film morphology via SEM on a Zeiss Sigma VP SEM (Figure 2.15). The resolution of this SEM is 1.3, 1.5 and 2.8 nm at operating voltages of 20, 15 and 1 kV, respectively. The electron beam passes through magnetic lenses and scanning coils that focus and raster the shaft on the sample surface.



Figure 2.15: Schematic of the SEM electron gun and optics.

2.4.9 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was utilised to image the structural shape of graphene and the number of layers. High-resolution TEM has a resolution limit of 0.1 - 0.2 nm, making it a handy tool for measuring nanomaterials such as graphene. Single area electron diffraction (SAED) was utilised to collect diffraction patterns on selected graphene areas. In this project, TEM was performed on a Jeol 2100 with an operating voltage of 80 - 200 kV and varying magnification ranges (10,000 to 100,000 x) (Figure 2.16). Graphene layers were suspended on copper (Cu) grid substrates (GCu100, Pro Sci-Tech, 100 mesh square) following the PMMA transfer method.



Figure 2.16: TEM performed on a Jeol 2100.

2.4.10 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) characterises the change in mass of a material as a function of time and temperature. TGA can give information on endothermic and exothermic phase transitions, including those that involve the absorption or evolution of gases from the sample. The mass resolution of TGA is at one μg . ²¹⁴ In this thesis, a Perkin-Elmer Diamond TG/DTA (Figure 2.17) was used for characterisation of the decomposition of, and gas evolution from, PMMA-solvent matrices. PMMA-solvent matrices were heated to 600 °C with a heating rate of 10 °C/min under a nitrogen (N₂) atmosphere. Primarily, this instrument includes a microbalance covered via a furnace; the mass gains or losses are recorded over time.



Figure 2.17: Perkin-Elmer Diamond TG/DTA used for characterising the thermal evolution of solvents in PMMA matrix.

2.4.11 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is an analytical chemistry technique for measuring the intensity of infrared absorption as a function of wavenumber. The IR spectrum is divided into three wavelength regions: near-infrared (NIR: 750-2500 nm), mid-infrared (MIR: 2500-25000 nm) and far-infrared (25-1000 μ m). FTIR spectroscopy probes vibrational modes of atoms in organic molecule functional groups and is very important in identifying the functional groups present in organic molecules. In our analysis, PMMA polymer dissolved via organic solvents (film, liquid) as samples. These were characterised using a Perkin Elmer Spectrum Two with a total range of 8300 to 350 cm⁻¹ at a best resolution of 0.5 cm⁻¹ (see Figure 2.18).



Figure 2.18: Perkin Elmer Spectrum Two FTIR spectrometer.

2.4.12 UV photoelectron spectroscopy (UPS)

The work function of graphene films was measured via UPS on a Photoelectron Spectrometer model AC-2 (manufactured by Riken Keiki) (see Figure 2.19). This model has a UV source with a unique electron detector that can operate at atmospheric pressure. The AC-2 model instrument can measure work function, ionisation potential and density of states. The excitation energy by a UV source in this analysis is of 3.40-6.20 eV.



Figure 2.19: Photoelectron Spectrometer model AC-2, manufactured by Riken Keiki.

2.4.13 Profilometer

Thickness of all films in the thesis was measured using a Stylus Profilometer (Bruker Dektak XT). All films were spin-coated onto glass substrates. This profilometer uses a diamond tip stylus for contacting the sample surface.

2.4.14 OPV device characterisation

Power conversion efficiency (PCE) is considered to be the key performance indicator of solar cells. The current-voltage characteristics of a solar cell determines the PCE, which can be calculated using equation 2.11. The curves shown in Figure 2.20 represent the dark and illuminated current density-voltage (J-V) characteristics of a solar cell.²¹⁵



Figure 2.20: Current density-voltage (J-V) curve for an organic solar cell under dark (black) and illumination (red).²¹⁴

This J-V curve demonstrates a diodic behaviour in the dark and under illumination solar cell. Three keys figures characterise the illuminated J-V curve are short circuit current, open-circuit voltage and maximum powerpoint. The short circuit current (I_{SC}) is defined as the current at zero applied voltage. It represents the number of charge carriers that are generated and collected per unit time by the electrodes under short circuit conditions. The open-circuit voltage (V_{OC}) is the maximum photo-voltage which can be produced by a solar cell when the current under illumination becomes zero in the cell. In organic solar cells, V_{OC} is linearly dependent on different between the HOMO level of the donor and LUMO level of the acceptor. ²¹⁶

The maximum point of the electrical power that represents the value of maximum power to an external load in the solar cell is called the maximum power point in Figure 2.20. The ratio between the maximum electrical power P_{max} and the product of the open-circuit voltage (V_{OC}) and short circuit current (I_{SC}) is defined as the fill factor (FF): ²¹⁷

$$FF = \frac{Vm\,Im}{V_{oc}\,I_{sc}} \tag{2.10}$$

Ideally, the fill factor would be 1, but losses from recombination and transport result in values between 0.2-0.7 for organic photovoltaics. The solar cell power conversion efficiency (η) can be calculated for a given incident power of light according to: ²¹⁸

$$PCE (\%) = \eta = \frac{P_{out}}{P_{in}} = \frac{V_{oc}I_{sc}}{P_{in}Area} FF$$
(2.11)

 P_{in} is the power density of the incident light. Light with an intensity of 1000 W/m² and spectral intensity distribution is called an AM 1.5 spectrum, and the spectral intensity matches that of the sun on the earth's surface at an incident angle of 48.2°. ²¹⁹ This light spectrum has been used as standard for OPV characterisation. Two other valuable figures of merit to assess OPV performance are external quantum efficiency (EQE) and internal quantum efficiency (IQE). The EQE, also known as the incident photon to current efficiency (IPCE), represents the spectral quantity as a ratio between the number of extracted electrons and the number of incident photons. The IQE is a quantum efficiency that deals only with processes of the absorbed photons within the active photovoltaic layer and ignores any losses from transmission and reflection. A tungsten halogen lamp passed through an Oriel Cornerstone 130 monochromator was utilised to measure the efficiency of OPV devices as a function of the wavelength of light to reveal EQE of OPV. A homemade photomask was used to define the photo active area of devices. In addition, in this study the effect of conductive substrate electrodes, the dark Nyquist plots of the devices based on ITO and prepared graphene electrodes were analysed by an LCR meter (Keysight E4980A) within the frequency range of 20-106 Hz under dark.

3. Chapter three: Low temperature CVD growth of multi-layered graphene using chlorobenzene-PMMA film as the carbon source

3.1 Overview

The growth of high-quality graphene in a CVD instrument requires a careful interplay of a range of materials and processes. The materials include a carbon source, a carrier gas (to transport the active carbon to the substrate surface) and a catalytic growth substrate. The CVD is comprised of a thermally controlled zone for introducing the carbon source, a system for controlling the flow rate and pressure of the carrier gas and a thermally controlled growth zone; allowing for thermal annealing of the substrate and heating during graphene growth. This chapter describes the synthesis and growth of graphene via low temperature CVD. An optimisation study has been completed to show the influence of each parameter, such as growth temperature (T_{growth}) and H₂ gas flow rate. The goal of this study is to determine a parameter set providing improved graphene quality when utilising low temperature growth from a liquid carbon source entrapped in a polymer matrix.

3.2 Introduction

Several types of precursors can be used to prepare graphene, including gas, liquid and solid sources. Available carbon sources to grow graphene are usually hydrocarbon gases due to their high purity as compared to solid and liquid sources.²²⁰ In recent years, there has been a growing interest in liquid carbon sources due to their ease of handling and low-cost in comparison with gaseous carbon sources.²²¹⁻²²² The decomposition temperature of the carbon source can be selected based on the C-X bond energy in the source molecule. For example, the growth of graphene using a methane (CH₄) carbon source occurs at a high temperature of ~ 1000 °C due to the high C-H bond energy (440 kJ mol⁻¹).¹⁴⁵ However, using other solid and liquid hydrocarbon sources such as polymethylmethacrylate (PMMA), benzene and, PMMA with entrapped chlorobenzene has proven to be a successful means of growing graphene, potentially at low temperatures.^{136, 223} However, graphene grown with reduced temperature CVD has been shown to have an increased number of defects, affecting the physical properties of the graphene.^{130, 136, 224} The use of metallic catalytic substrates in the CVD growth process is thought to enable a lowered growth temperature.²²⁵

The carbon solubility of metals is essential when making the selection of an appropriate catalyst for graphene synthesis, with a low carbon solubility ideal. Different substrate metals including Cu, Ni, Co, Fe, Ir and Ru²²⁶ have been tested for low solubility. The most promising of these catalytic substrates for growing large areas of graphene at relatively low cost are Co, Fe, Cu and Ni. Although Co, Ni and Fe are considered to be sufficiently strong catalysts for graphene growth, these substrates have been proven in the past unsuitable due to a difficulty in controlling the thickness of the growing film.²²¹ For example, graphite films several micrometres thick have been created due to the saturation of 50 µm nickel foils by carbon at 1000 °C.⁹⁹ A Cu catalyst, however, exhibits weak catalytic action for methane (CH₄) and a low carbon solubility for growth of few-layer graphene films and has emerged as the most promising substrate for growing thin films of graphene. In this work, Cu foil has been used as the catalyst to synthesise graphene.

3.3 Carbon sources for graphene growth

Previous work in this laboratory has shown that a chlorobenzene-PMMA matrix can act as a suitable graphene growth carbon source with a low decomposition temperature; revealing an interplay between the source C-X bond energy and the molecular structure. In addition, the growth temperature used in graphene fabrication is known to produce a variation in the dissociation and deposition mechanisms.¹⁴⁵ For example, Nandamuri et al. used ethylene and acetylene as gaseous carbon sources, instead of CH₄, for low-temperature graphene growth due to their lower C-C pyrolysis temperature compared to CH₄.²²⁷

Both graphene and benzene possess an aromatic hexagonal arrangement of carbon atoms in their atomic structure. Due to benzene's low activation energy, and for small scales of fabrication, benzene has been used to synthesise graphene layers at a growth temperature of \sim 300 °C. However, this process produced poorly conducting films.^{105, 136} Large area, monolayer graphene films have been grown continuously on Cu foil using benzene as the carbon source in CVD at 100-300 °C and ambient pressure.¹³⁸ In our previous work, multilayer graphene was grown using chlorobenzene in PMMA matrix, and the selected range temperature of growth was 300-500 °C.²²³ The focus of this work was to further understand the low-temperature growth process and hence produce optimised better quality graphene layers.

3.3.1 Thermal degradation of PMMA

PMMA polymer films were used in this procedure for two purposes. Firstly, the PMMA polymer film formed a matrix to retain and slowly release solvent molecules as a carbon source. Secondly, the polymer itself could constitute a carbon source at higher source temperatures when T_{source} exceeded the polymer decomposition temperature. A thermal decomposition study of pure PMMA powder was carried out using TGA, with thermal pyrolysis was conducted over a temperature range from 30 to 520 °C. Figure 3.1 shows the thermal decomposition profile of pure PMMA powder under a nitrogen (N₂) atmosphere.



Figure 3.1: TGA curve of pure PMMA powder.

In Figure 3.1, PMMA initially starts to lose mass at ~219.5 °C, with a reduction to 98.93 % of the starting mass. Scission commences at unsaturated ends, which result from termination by deprotonation. The random scission of the polymer chain is the last step of degradation starting at ~350 °C.²²⁸ The phase of thermal degradation in PMMA at around 350 - 400 °C was thought to be dominated by scission of a methoxycarbonyl side group rather than through random scission of the main chain.²²⁹ More recently, the degradation process at 350 - 400 °C is thought to consist of two separate phases related to simultaneous scissions of end groups with the random breaking of chains.²³⁰

3.3.2 Thermal degradation of chlorobenzene-PMMA

TGA was used to characterise the degradation of PMMA films drop cast from a chlorobenzene solution, under N_2 gas atmosphere, with the results presented in Figure 3.2.



Figure 3.2: TGA curves of chlorobenzene-PMMA films. The curves represent 180 °C dried, air-dried and, drop cast wet film.

Drop cast PMMA films were prepared under three conditions for thermal analysis, (1) dried at 180 °C, (2) air dried, and (3) no drying (drop cast). Thermal pyrolysis was then conducted over a temperature range from 30 to 520 °C. Different degradation behaviour was observed between pure PMMA and drop cast PMMA films, with the onset of mass loss beginning at various temperatures. The sample conditions of 180 °C dried, air-dried and drop cast were selected as representative of the carbon source state during insertion into the CVD tube furnace. For the 180 °C dried sample, the content of chlorobenzene molecules residing in the polymer film was high, which is shown by the sharp drop of the TGA profile leading up to the 130 °C boiling point of chlorobenzene. The majority of this mass loss was below 130 °C as the vapour pressure of the solvent is high, and the N₂ flow rate in the TGA system causes the solution to vaporise continually. The carbon source after a 180 °C drying treatment revealed a pure PMMA decomposition behaviour around ~350 °C (Figure 3.1). As discussed, there is a random scission degradation of PMMA released by homolytic scission of a methoxycarbonyl side group, then β scission at about 350-400 °C.²³⁰ However, the properties of the polymer film incorporating the organic solvent could differ from the original bulk polymer since solvent molecules tend to be trapped between the polymer chains; resulting in a reduction of the α relaxation due to the influence of plasticising.²²⁸

3.4 Catalyst preparation

Cu foil was chosen as a catalyst to prepare graphene films before transfer to the target substrate. Cu is a promising catalyst for making CVD graphene due to its low carbon solubility, low cost and a high-degree of self-limited growth regime of Cu foil when used for graphene synthesis.⁷⁸

3.4.1 The morphology of Cu foil

The washed Cu surface shows a high roughness under atomic force microscopy (AFM) (Figure 3.3). Micron-sized bumps and depressions are evident from microscopy analysis, which would prove detrimental to graphene growth. To improve the smoothness of the Cu surface, several nanometres of Cu was removed by electropolishing, which was shown to be a suitable method for achieving smooth and clean metal surfaces (Figure 3.3). This work was performed in a custom-built electro-polishing cell for the Cu foil.



Figure 3.3: AFM images of copper foil (a) before and (b) after polishing at 3 V for 60 sec.

Optical microscopy was used to investigate the morphology further and optical micrographs of the Cu foil after the various stages in the cleaning process are shown in Figure 3.4. Lines on the surface from the production rolling mill are evident and reducing the catalytic surface roughness is required (Figure 3.4a). Mechanical surface polishing, followed by electrochemical polishing, decreased the severity and achieved a smoother topographical surface (Figure 3.4b).

Thermal annealing plays another role in achieving a smoother Cu foil surface. This process removes most of the defects on the surface by growing domains of crystalline Cu on the foil, as shown in Figure 3.4. The line boundaries and domains on the Cu foil are more explicit after these cleaning steps demonstrating a flatter and smoother surface when compared to the raw sample.



Figure 3.4: Images of Cu foil after staged cleaning of the surface (a) new sample surface of raw Cu foil, (b) Cu foil surface after electro-polishing process and (c) Cu foil surface after thermal annealing inside CVD furnace tube, images at magnification scale of $700 \times 1000 \,\mu\text{m}$.

3.4.2 The purification of Cu foil

The purity of the Cu foil surface was influenced by both oxidation and contamination from the rolling factory. The Cu foil was annealed at 900 °C for 1 hour under a gas mixture of H_2 and Ar. This thermal treatment with a high purity gas atmosphere was aimed at reducing the oxidation level on the surface of the Cu catalyst, which was probed with XPS (Figure 3.5).



Figure 3.5: XPS spectrum of the Cu foil (a) unannealed and (b) annealed.

Figure 3.5 shows the XPS spectra of both annealed and raw Cu foil, featuring peaks at binding energies ~284.4, 537 and 75.4 eV representative of C 1s, O 1s and Cu 3p, respectively. After thermal annealing, the C 1s peak shifts 1.1 eV in comparison to as-received Cu foil, and the peak intensity reduces due to a reduction into the level of amorphous carbon. Under the same conditions, the height of the O 1s peak is decreased after treatment, and the peak position shifted by 2.9 eV relative to the standard sample. This analysis provides good evidence for the success of the thermal annealing step in the Cu foil cleaning process. Figure 3.6 shows a focused area XPS scan for the O 1s peak to investigate the change in the level of oxygen in the Cu surface with thermal annealing. After thermal annealing, the height of oxygen level decreased (by 76.48 %) as shown in Figure 3.6.



Figure 3.6: XPS spectra of the O 1s peak on the surface of the Cu foil before and after thermal annealing at 900 °C for 1 hour in the CVD under H_2 .

3.4.3 The structure of Cu foil as a function of annealing temperature

The thermal annealing of Cu in a reducing atmosphere of H_2 and Ar gases is ideal for removing the oxide layer from the catalyst surface. The grain size of Cu increased during annealing, which results in a corresponding decrease in grain boundaries, as shown by X-ray diffraction (XRD) analysis (Figure 3.7). The process reduces the defect density on the surface and lowers the amount of oxygen present in the Cu surface. This purification process is critical in preparing a surface catalyst for graphene growth.

XRD has investigated the crystal structure of Cu foil after annealing at four different temperatures from 600 - 900 °C. Figure 3.7 clearly shows an increase in Cu crystallinity after annealing (as indicated by the rise in diffraction peaks due to the (200) plane). The annealing at higher temperatures seems to result in greater crystallinity. The relative intensities follow the trend; 900 °C ≈ 800 °C > 700 °C > 600 °C, which in turn should promote high-quality graphene growth. It could be concluded that the grain size of Cu foil increases with annealing temperature for the (200) orientation.²³¹⁻²³²



Figure 3.7: XRD patterns of the Cu foil samples annealed at different temperatures for 1 h.

The diffraction peaks of the (111), (100) and (022) planes have a much lower intensity compared to the significantly stronger (200) diffraction peak,²³² as illustrated in Figure 3.8, indicating that the (200) plane crystal orientation is more prevalent. After annealing at 900 °C, the (200) plane intensity is more prevalent, ascribed to re-crystallisation, with a much larger grain size within the Cu foil. The (022) peak demonstrated the opposite behaviour with increasing annealing temperature due to the crystallisation altering the orientation planes. It is expected that the phase growth of crystalline planes in the Cu foil will reduce the number of grain boundaries and adequately prepare a catalyst surface with fewer defects. Since there is evidence of systematically increasing Cu crystallinity as a function of annealing temperature, an annealing temperature of 900 °C was chosen as optimal for subsequent experiments.



Figure 3.8: XRD patterns of the annealed Cu foil samples.

3.5 Graphene growth optimisation

3.5.1 The effect of T_{growth} on graphene growth

Graphene layers were deposited on cleaned Cu foil, annealed at 900 °C at a variety of growth temperatures, T_{growth} 400 to 800 °C. An H₂ flow rate of 50 sccm and the carbon source heated to 180 °C (T_{source}).²²³ These conditions were optimised based on our previous work and other reviews.^{114, 223} The quality of the graphene synthesised was established by Raman spectroscopy before the wet transfer method was used to lift the films from the substrate. This qualitative analysis is based on the intensity ratio of between two peaks I_G/I_{2D}^{233} , which are the most significant features in the Raman spectrum of graphene shown in Figure 3.9. The G peak is located at ~1580 cm⁻¹ (assigned to 1582 cm⁻¹), and the 2D peak (assigned to 2690 cm⁻¹) is situated at ~2700 cm⁻¹. It is also a powerful technique to determine the number of layers of graphene identifies the presence and quality of graphene layers on the Cu foil before film transfer onto the target substrate. From Raman characterisation, G and 2D bands were identified at ~ 1582 cm⁻¹ and 2690 cm⁻¹, respectively. Additionally, the Raman spectrum D

band located at ~1350 cm⁻¹ is a measure of the defects, such as domain boundaries in graphene, and hence is an additional indicator of material quality. Notably, in Figure 3.9, the D peak intensity is weak compared to other peaks for all temperatures. Table 3-1 shows that the highest quality graphene, i.e. which has the lowest G to the 2D ratio of 0.50, obtained with a T_{growth} of 600 °C, while both more upper and more moderate temperatures increased the rate.



Figure 3.9: Raman spectra of graphene thin films grown with varied T_{growth}.

Table 3-1: Characteristic values of the Raman spectra G and 2D band positions, the intensity ratio between them, and, the 2D peak width, $2D_{FWHM}$.²³³⁻²³⁴

Tgrowth (°C)	G position (cm ⁻¹)	2D position (cm ⁻¹)	IG/I2D	2 D FWHM (ст ⁻¹)	n GL~
400	1591.76	2724.25	1.12	47.02	14
500	1591.76	2724.25	0.94	49.31	7
600	1585.78	2712.6	0.50	49.85	3
700	1585.78	2716.48	1.70	73.04	26
800	1587.27	2717.78	1.05	48.47	11

The dehydrogenation of benzene molecules from PMMA-chlorobenzene requires low activation energy on Cu (111) of ~ 1.47 eV for the growth of graphene domains.²³⁵ However, it has been reported that using benzene as the graphene layer carbon source does not lead to large graphene domains and continuous graphene films.^{105, 136} A T_{growth} of 600 °C will provide sufficient thermal energy to enable dehydrogenation of benzene molecules and C-C bond formation as required for graphene growth. Li et al. showed that the quality and domains of graphene were improved at a growth temperature of ~500 °C rather than at lower temperatures.¹³⁶ This observation was believed to be due to the reduced activation of benzene at low temperature. The elementary reactions for the combination of CH groups and the incorporation of atomic carbon into the graphene structure have activation energies between 1 -2 eV.²³⁶⁻²³⁷ Thus, at temperatures of 500 – 600 °C, sufficient thermal energy is present for the deposition of carbon atoms on a catalyst.²³⁸ This hypothesis is supported by the fact that it has been shown that most carbon atom sources start depositing, and form soft bonds with a Cu catalyst, at temperatures around 600 °C.²²⁵ This conclusion is supported by the data in Figure 3.10 that shows that the intensity ratio of I_G/I_{2D} was somewhat variable across the temperature range examined, but that graphene growth is observed at all temperatures and is optimal at 600°C.



Figure 3.10: I_G/I_{2D} ratio as a function of growth temperature. Error bar (0.1).

3.5.2 The effect of H₂ flow rate on graphene growth

Hydrogen (H₂) gas flow rate has proven to be a significant parameter in the synthesis of graphene via CVD.¹¹⁴ After the T_{growth} optimisation study, the influence of H₂ flow rate was studied to improve the graphene quality. Graphene films were deposited on Cu foil at a T_{growth} of 600 °C with a range of H₂ flow rates from 25 to 100 sccm. Raman spectra of the resultant graphene growth are shown in Figure 3.11. The full peak width at half maximum (FWHM) of the 2D band of 53.37 cm⁻¹ indicates a good quality of graphene at T_{growth} of 600 °C with an H₂ flow rate of 75 sccm. Compared to other conditions of H₂ flow rate, the relative intensity ratio of G to the 2D band is an excellent 0.21. It indicates a few layers of graphene for this growth condition (n GL~2).^{146, 233} The intensity ratio of D to G band was also 0.21. This ratio is used in typical CVD-derived graphene samples to quantify defects such as domain boundaries, where the lower the ratio, the fewer defects in the graphene layer.⁷⁷



Figure 3.11: Raman spectra of graphene grown at different H₂ flow rates and T_{growth} of 600 °C.

The H₂ flow rate thermodynamically affects the graphene growth rate through nucleation, influences the number of graphene layers,^{50, 239} and has been identified to have an essential role in the estimated graphene domain size.¹⁴² The above result is significant and indicates that control of the graphene growth rate through H₂ flow rate is possible. It has been reported that the density of wrinkles in the graphene layers increases with increasing H₂ flow rate up to 300sccm, which affected the quality of graphene film.²³⁹

In this work, the number of graphene layers increased at an H_2 flow rate of 50 sccm, and the variety and quantity of graphene layers exhibited a visible improvement when the H_2 flow was increased to 75 sccm. (Table 3-2 ²³³⁻²³⁴) The 75 sccm H_2 flow rate provided the optimum low-temperature graphene growth conditions (Figure 3.12).

H ₂ flow rate (sccm)	G position (cm ⁻¹)	2D position (cm ⁻¹)	Ig/I2d	2D _{FWHM} (ст ⁻¹)	n GL ~
25	1579	2694	1.16	64.56	15
50	1581	2707	1.5	71.7	25
75	1581	2685	0.21	53.37	2
100	1584	2711	2.11	80.71	28

Table 3-2 Raman cha	racterisation of gra	aphene at T _{growth}	600 °C for	four H ₂ flow	rates. ²³³⁻²³⁴



Figure 3.12: I_G/I_{2D} ratio as a function of H_2 flow rate. Error bar (0.1).

For large scale graphene (grown on Cu foil, at 600 °C under 75 sccm H₂ flow), the film quality was further characterised by Raman mapping, as illustrated in Figure 3.13a, where the Raman G/2D peak ratio is mapped over the surface.¹⁴⁹ This map shows the multi-layered graphene flake is micron-sized, as is evident in the associated optical image (Figure 3.13b) and covers ~60 % of the Cu foil surface.

Equally, it is clear that 40 % of the surface does not have graphene on it, and the Raman map reveals amorphous carbon on the surface. Further investigation into the presence and location of amorphous carbon are the subject of the next section.



Figure 3.13: (a) Spatial map of graphene film Raman G/2D peak ratio over a $100 \times 100 \,\mu\text{m}$ area (T_{growth}: 600 °C, H₂ flow rate 75 sccm), and (b) associated optical image of mapped area.

3.6 Factors affecting graphene deposition

The growth and film quality of single-layer graphene can be affected by oxygen (O_2), present in the reaction chamber of CVD or residual O_2 on the catalyst surface after cleaning or incorporated into the carbon source.^{138, 142}

We have shown that H_2 flow rate is a prime factor in controlling the quality of graphene layers during the growth process. In particular, to combat defects due to the presence of O_2 , H_2 flow is used to remove it from the growth chamber. Catalyst surface and H_2 consequently influences the graphene morphology grown on catalyst via the CVD method.²⁴⁰ It is also used to contribute to the edge structure and shape structure of graphene domains at low-pressure CVD growth.¹¹⁴

Figure 3.14 shows multi-layer graphene grown on Cu foil by low temperature growth at 600°C, using the CVD system. Two distinct regions are observed, with bright and dark areas present on the Cu foil which overlay the visible Cu domains. These different graphene regions correspond to the thickness of the grown graphene films. According to this explanation, bright areas correspond to the graphene thin film (monolayer graphene) while dark regions relate to a thicker growth of graphene film (multi-layers).²⁴¹⁻²⁴²



Figure 3.14: (a) and (b) show optical images of graphene films on Cu foil.

For confirmation, Raman spectra from the two different regions are shown in Figure 3.15. In general, the bright area regions exhibit smaller carbon signals compared to the dark region. By contrast, the dark region shows a high-intensity 2D band (~2700 cm⁻¹) which indicates more graphene layers. In addition, the number of defects increases with the number of layers based on the size of the D band at around 1350 cm⁻¹. The intensity of the G band is located at a higher value than usual at about 1600 cm⁻¹. This behaviour indicates an appreciable coupling between the catalyst substrate and the graphene layers.²⁴³ The sharper increased 2D band peak in the dark region could be due to the formation of multi-layer graphene having typical Bernal stacking ²⁴⁴ or a turbostratic multilayer.³¹



Figure 3.15: Raman spectra of Graphene films growth at 600 °C for 1 minute with H₂=75 sccm.

3.7 Highly oriented pyrolytic graphite (HOPG)

HOPG is an artificially grown graphite with an almost perfect alignment perpendicular to the carbon planes.²⁴⁵ For characterisation, HOPG (HOPG grade ZYH 434HP-AB from SPI supplies) was used as a control sample to compare with the Raman spectra of CVD grown graphene samples. Small flecks of graphene were prepared by mechanical exfoliation from the HOPG bulk material and subsequently transferred to a SiO₂ substrate for Raman analysis (located at the cross symbol in the optical images shown in Figure 3.16). The Raman spectra 2D band intensities were consistent with multi-layered graphene on SiO₂. The G/2D ratio of HOPG Raman spectra is shown in the figure. Comparative analysis between the best samples in Section 3.5 and the HOPG samples reveals that the quality of graphene films grown at low temperature (~600 °C) is better than graphene peeled from the HOPG; in part, due to the difficulty in obtaining single-layer graphene via exfoliation.



Figure 3.16: Raman specters of HOPG flecks on SiO₂ with their optical images including G/2D ratio of Raman specters.

3.8 The honeycomb structure of graphene

Graphene layers were transferred onto Cu grid substrates after being etched off of their Cu foil growth substrate for imaging with TEM. Figure 3.17a shows a TEM image of patterned graphene layers collected at an accelerating voltage of 200 kV using a Jeol 2100 TEM. From this TEM image, there is a bright contrast for the carbon atoms in front of the focal plane and dark contrast for the carbon atoms behind the focal plane. The topological defects in graphene layers frequently come from the mechanical transfer method. It can be challenging to remove the PMMA mechanical support film from graphene layers altogether. Consequently, these defects and the residual PMMA are visible when imaging graphene at the atomic scale.²⁴⁶ The

nuclear resolution of TEM reveals the honeycomb structure of graphene.²⁴⁷ The electron diffraction (ED) accompanying the TEM was used to probe the atomic arrangement of graphene and is shown in Figure 3.17b. This image exhibits a six-fold symmetry as expected from graphene.²⁴⁸ The diffraction pattern relates directly to the Miller-Bravais (h k i l) indices, showing this graphene sheet to be a single layer.



Figure 3.17: (a) TEM image of graphene layers suspended on Cu grid and (b) the electron diffraction pattern of the carbon atoms of graphene.

Inspection of the TEM images revealed an area between two distinct graphene flakes, as illustrated in Figure 3.18. Measuring the interatomic distance in this region gave a range of 0.26 nm at the edge of the graphene layer (see Figure 3.18a). The graphene flakes were somewhat disordered and wrinkled by the wet transfer method and did not show the classic hexagonal diffraction pattern expected for graphene. The image shows superimposed diffraction patterns due to multi-layering of the graphene sheets and variation from the hexagonal, which is often observed with the presence of defects and amorphous carbon on the graphene films (Figure 3.18b).



Figure 3.18: (a) TEM image of graphene multi-layers on the edge of film and, (b) the pattern of electronic diffraction of graphene layers suspended on Cu grid.

3.9 Identifying single-layer graphene

The topography of graphene films is affected by the growth mechanism and transfer technique used and can affect their viability for use in OPV and other electronic applications. Furthermore, the thickness of the graphene film is a significant factor when considering its application as a transparent electrode for OPV. The growth conditions in CVD, namely deposition time, H_2 flow rate and T_{growth} directly affect this parameter. The surface morphology and thickness of graphene films (~1 nm per layer of graphene) can be measured by AFM, as shown in Figure 3.19. The presence of several circular features which are significantly higher than the substrate is apparent. These features are ascribed to residual contamination of the PMMA used to support the graphene film during the transfer process mechanically. PMMA was removed in an acetone solution, but some residue of PMMA remains on the graphene film and can influence the optical and electrical properties of graphene.²⁴⁹ However, it is clear from the thickness measurement taken across the edge of the graphene flake (marked by the dotted line) that single-layer graphene is also present.



Figure 3.19: AFM image of CVD graphene grown at 600 °C with H₂ flow rate of 75 sccm.

Other measurements at graphene edges showed that the presence of single-layer graphene is not uniform and that there is bilayer and higher layer graphene present, as illustrated in Figure 3.20. Contamination from the transfer method left on the surface of the graphene increases the roughness of the film surface and potentially may cause defects in the graphene layers. The measured thickness was more than 2 nm with a rough topography of the graphene film which had been transferred onto a clean atomically flat Si substrate. Reducing the roughness of the graphene film surface is one of the enormous challenges following the wet transfer method.



Figure 3.20: AFM image spanning the edge of a graphene film transferred onto a Si substrate by the wet transfer method.

3.10 Conclusion

In this work, graphene was synthesised at low temperature over a Cu foil catalyst using chemical vapour deposition (CVD). The flow rate of H₂ gas and the T_{growth} optimised to improve the quality of graphene. The selected carbon source, PMMA-chlorobenzene, showed a differing decomposition behaviour at 180 °C compared to bulk pristine PMMA or chlorobenzene solvent. It was the slow release of chlorobenzene vapour from the PMMA-chlorobenzene that formed the carbon source. Low T_{growth} of 600 °C has proven to provide sufficient thermal energy for breaking bonds in the aromatic carbon source and allowed for deposition of carbon atoms onto the catalyst surface. Graphene domains possess a honeycomb structure, often surrounded and covered by amorphous carbon, as evidenced by Raman mapping. Increasing the size of these domains is a promising but necessary path to improving the electrical properties of graphene films.
4. Chapter four: Low temperature CVD graphene growth via organic solvent retention in PMMA film

4.1 Overview

In this chapter, a range of organic solvents was utilised as the carbon sources for graphene films grown on Cu foil via the CVD method, where these solvents had been incorporated within a matrix polymer poly (methyl methacrylate) (PMMA). The carbon sources studied were p-xylene, toluene, o-xylene, chlorobenzene, dichlorobenzene, dichloromethane, chloroform and acetone. Besides, two more carbon sources were included in this study to probe the effect of incorporating heteroatoms into the carbon source structure; pyridine and methanol. This study is designed to investigate the mechanism of low temperature graphene growth on Cu and, once this understanding is achieved, allow a full optimisation of growth carbon source and conditions to produce high-quality graphene.

Using organic solvents for decreasing the decomposition temperature, it has been shown a sufficient formation growth of graphene layers via the heterogeneous source of PMMA film as matrix polymer containing aromatic and aliphatic carbon sources. In this chapter, we report the growth of graphene from different carbon sources using a low temperature procedure, T_{growth} = 450 °C and T_{source} = 180 °C. PMMA served as a matrix polymer to hold a variety of organic solvents, the solvents forming the carbon source for CVD graphene synthesis. The carbon sources studied were both aliphatic solvents (dichloromethane, chloroform, acetone) and aromatic solvents (p-xylene, toluene, o-xylene, chlorobenzene, dichlorobenzene), to probe the mechanism of graphene formation. This is a comparing analysis of carbon source based on the quality of graphene films. It was a clear point of the influence of benzene ring structure in carbon molecules for depositing a better quality of graphene layers on Cu foil. To confirm that the solvent was indeed acting as the carbon source, FTIR was used to identify solvent fingerprint peaks in the drop cast films, and the T_{source} was held below the decomposition temperature of the PMMA matrix. The quality of the deposited graphene, as gauged by the Raman spectrum G/2D intensity ratio, four-point probe, UV-vis spectroscopy and TEM, does differ with the carbon system source and these results are characterised and discussed below.

4.2 Introduction

Utilising different carbon sources for graphene synthesis by CVD allows determination of graphene quality as a function of the thermal energy of hydrocarbon decomposition required for the particular carbon source used.^{235, 250} Molecules with low C-H bond energy, including sucrose (C₁₂H₂₂O₁₁), fluorene (C₁₃H₁₀) and polystyrene have been used to prepare high-quality graphene films.^{130, 136-137} Gadipelli and coworkers used benzene and methanol liquids as carbon sources to develop good quality graphene via CVD onto Cu foil.²⁵¹ These molecules are readily available and economical carbon sources and provide the potential for an inexpensive and straightforward method of graphene fabrication. Methanol was also observed to inhibit amorphous carbon growth.²⁵¹ Monolayer graphene was also produced from a range of other alcohols; ethanol, propanol and methanol in CVD as well as from methane gas. ²⁵² In this report, the authors show that monolayer and bi-layer graphene flakes can be grown from organic solvent molecules adsorbed onto a clean Cu surface at a reaction temperature of 850 °C. The quality of this graphene was measured to be equivalent to graphene grown using methane (CH₄) gas as a carbon source.

Ethanol is now one of the most common liquid carbon sources used in CVD due to an observed faster graphene growth rate and full growth coverage of the whole catalyst surface by monolayer graphene.^{220, 253} A lower graphene growth reaction temperature of 300 °C, was shown to be possible with benzene liquid as the carbon source.¹³⁸ Subsequent work has identified that organic solutions can act as a carbon source in CVD when using a catalytic surface at the low growth temperature.²²³

4.3 Using organic solvents as carbon sources

With the goal of developing carbon sources with low C-H bond energy, ¹⁴⁵ PMMA dissolved in, and deposited from, a variety of organic solvents (p-xylene, toluene, o-xylene, chlorobenzene, dichlorobenzene, dichloromethane, chloroform and acetone) was examined and assessed as carbon providers for CVD growth. The CVD system available has three heating zones with separately controllable temperatures. The first zone, zone 1, was used to host the carbon source. Zone 3 was used as the carbon deposition and graphene growth section and contained the catalytic substrate on which the graphene forms (Figure 2.4).

The carbon source material (consisting of PMMA dissolved in the selected solvent) was dropcast onto a quartz slide which was inserted in zone 1. The cleaned Cu foil was placed in zone 3 in a quartz boat. Zone 2 is where the CVD gas mixture (H₂, Ar) flows into the chamber before entering the heated deposition tube which is maintained at a pressure of ~ 0.5 Torr during both the ramp-up to temperature phase and the graphene growth phase.

As a reducing gas, H_2 gas can scavenge atomic and molecular oxygen from the growth region as it is released from the oxide layer on the Cu foil, helping to reduce the amorphous carbon surface content and thus improve the quality of grown graphene film.¹⁴² Ar gas assists with the bombardment of the oxide layer and the overall cleaning of the Cu surface during the ramp-up to the growth temperature desired and provides an inert carrier for the carbon source. As the end goal is monolayer graphene, the time required for growth was limited to ~1 min. More extended periods deposit excess carbon on the surface and may result in multiple layers of graphene. The cool-down time was ~2 hours, allowing for the reactor vessel to cool and for the cu foil was characterised via Raman spectroscopy before the wet transfer method⁸⁹ was performed.

Samples of the PMMA dissolved in each different organic solvent were studied to determine the presence and amount of entrenched solvent. PMMA deposited from p-xylene, toluene, oxylene, chlorobenzene, dichlorobenzene, dichloromethane, chloroform and acetone were deposited onto a quartz slide and placed in a Fourier transform infrared (FTIR) spectrometer (PerkinElmer Spectrum Two). The spectra of both the liquid solution (in cuvette) and dropcast films were recorded. The purpose of the FTIR study was to provide evidence for the existence of residual solvent in the PMMA film to act as the carbon source, as evidenced by both the presence of solvent peaks and also shifts in the PMMA peaks due to solvent-matrix interactions.

4.4 Residual organic solvents within the PMMA film

The FTIR characterisation of films of PMMA deposited from organic solution is presented in Figure 4.1 and Figure 4.2. The discussion of this analysis will be based on each type of organic solvent individually. The FTIR analysis aimed to confirm the presence of residual solvent as the carbon source for graphene growth via CVD at low temperatures. Using different organic

solvents within PMMA as a carbon source in CVD at a low temperature then may provide a further understanding of the mechanism of growth of graphene layers. The first organic solvent studied was p-xylene, FTIR analysis of a drop-cast p-xylene-PMMA film shows there are no solvent fingerprint peaks or shifting in PMMA peaks (Figure 4.1a). However, for the solvent toluene, a fingerprint peak attributed to C=C was identified at 1605 cm⁻¹ (Figure 4.1b), but no peak shifts were observed for PMMA. The procedure with o-xylene as solvent found that the C=C (1605 cm⁻¹) fingerprint peak evident was in the FTIR analysis of the drop-cast film (Figure 4.1c). However, no shift in the PMMA peaks was observed for the o-xylene-PMMA drop-cast film. FTIR analysis of PMMA dissolved via chlorobenzene showed clear fingerprint peaks for chlorobenzene retained in the drop cast film. Two fingerprint peaks were identified; the first peak attributed to C=C was located at 1584 cm⁻¹, the second peak associated with C-Cl was located at 469 cm⁻¹ (Figure 4.1d).



Figure 4.1: FTIR spectra of PMMA dissolved by (a) p-xylene, (b) toluene, (c) o-xylene and (d) chlorobenzene. Insets depict magnified regions of interest. The spectrum of PMMA powder is also provided in a-d for comparative purposes.

Fingerprint peaks for C=C and C-Cl at 1574 and 484 cm⁻¹, respectively (Figure 4.2a) were also observed in the analysis with dichlorobenzene as the solvent. The dichloromethane drop-cast film spectra in Figure 4.2b showed no solvent fingerprint peak or peak shift for PMMA. This absence may be related to the low solvent boiling point temperature similar to the acetone solvent,²⁵⁴ discussed below.

For chloroform, the FTIR spectrum for the chloroform-PMMA drop-cast film in Figure 4.2c contains the fingerprint peak for C-Cl at 667 cm⁻¹, but no PMMA peak shifts. Acetone, $(CH_3)_2CO$ is an organic solvent which has bands for C=O, C-C and C-H, overlapping with the PMMA bands of C=O, C-O, C-C and C-H. The lack of an acetone fingerprint peak in Figure 4.2d may be due to the low ~ 56 °C boiling point of acetone and thus the higher likelihood of solvent release from the film at room temperature. In PMMA, the C-H stretch peak is at 2951 cm⁻¹, in liquid acetone the C-H stretch peak is located at 3006 cm⁻¹. The dissolved solution of PMMA in acetone, as a liquid, shifts the C-H stretch peak location to 2999 cm⁻¹ and a drop cast film turns the C-H stretch band to 2915 cm⁻¹. The drop cast film has a small peak appearing at 2849 cm⁻¹ also associated with the C-H stretch. Table 4-1 shows the fingerprint and shift peaks of FTIR analysis for the different organic solvent-PMMA matrix combinations.



Figure 4.2: FTIR of PMMA dissolved via (a) dichlorobenzene, (b) dichloromethane, (c) chloroform and (c) acetone. Insets depict magnified regions of interest. The spectrum of PMMA powder is also provided in a-d for comparative purposes.

The results presented show that the residual solvent is retained in the PMMA matrix for all solutions except dichloromethane and p-xylene. The dichloromethane result is, perhaps, not surprising owing to the low boiling point of the solvent. However, it is unclear why no residual p-xylene is observed using this technique. To further determine solvent presence thermal analysis of the drop-cast films were conducted to detect mass loss at temperatures associated with each solvent, Section 4.6.

Solvent-PMMA matrix	Fingerprint peak	Peak location (cm ⁻¹)	Peak shift	Peak lo (cm	c location cm ⁻¹)	
				Original	Shifted	
p-xylene	N/A	N/A	N/A	N/A	N/A	
Toluene	C=C	1605	N/A	N/A	N/A	
o-xylene	C=C	1605	N/A	N/A	N/A	
Chlorobenzene	C=C and C-Cl	1584 & 687	N/A	N/A	N/A	
Dichlorobenzene	C=C and C-Cl	1574 & 659	N/A	N/A	N/A	
Dichloromethane	N/A	N/A	N/A	N/A	N/A	
Chloroform	C-Cl	667	N/A	N/A	N/A	
Acetone	N/A	N/A	C-H stretch	2999	2915	

Table 4-1: FTIR analysis is shown of fingerprint and shift peaks for organic solvents-PMMA.

4.5 Quantification of residual organic solvents within the PMMA film

Further to the investigation above, a study of PMMA concentration in a chlorobenzene solution (100 mg/ml to 500 mg/ml) was undertaken to be able to quantify solvent retention via FTIR. The residual organic solvent is predicted to interact with the PMMA matrix through weak bonding interactions such as H-bonding, Van der Waal's or π -interactions.²⁵⁵ It would be a significant point to establish the molecular bonding of the solvent component inside the polymer matrix as part of a quantification study.²⁵⁶ To gain more information on the solvent retention, the intensity of critical peaks in their dichlorobenzene and PMMA FTIR spectra were determined as a function of the concentration of PMMA in the solvent.

Figure 4.3 shows the C=O and C=C FTIR peak transmittance for the different solution concentrations of PMMA in dichlorobenzene (DCB) solvent. The C=O peak is attributed to PMMA polymer while the C=C spike is attributed to the DCB solvent.²⁵⁷⁻²⁵⁸ There is an apparent decrease in transmittance of IR light at ~1730 cm⁻¹, assigned to the C=O peak, with increasing PMMA concentration. The C=C bond located at ~1574 cm⁻¹ also shows a corresponding increase in transmittance with increasing PMMA concentration; with this

feature associated with the presence of the DCB solvent. This data can be used for calibration purposes for identifying the amount of the carbon source inside the polymer matrix.



Figure 4.3: C=O and C=C FTIR spectra (transmittance) for different concentrations of PMMA dissolved in DCB solvent.

Figure 4.4 replots the data in Figure 4.3 to compare the intensity and area of the FTIR C=O PMMA and C=C DCB peaks of interest. The percentage ratio allows a measure of the retention of DCB inside a drop-cast PMMA film. The percentage of solvent per solution mass shows a negative slope with increasing PMMA concentration, as expected and is plotted to provide a reference point. For the C=C/C=O ratio of the intensity of FTIR transmission peaks, we observe a positive slope with increasing PMMA concentration (Figure 4.4a). For the C=C/C=O ratio of FTIR peak area, a negative slope is found, representing the reduction in the solvent with the increase in PMMA solution concentration (Figure 4.4b). Based on the observed trends, this method can be a useful path for determining the amount of the carbon source trapped inside the polymer matrix.



Figure 4.4: (a) The intensity transmission, and (b) the area ratio of C=C/C=O peak FTIR with a percentage of solvent per mass solution as a function of PMMA concentration for the DCB: PMMA matrix combination.

4.6 The thermal analysis of organic solvents retained in PMMA matrices

The thermal profile of drop-cast PMMA films prepared from the selected range of organic solvents was studied by thermogravimetric analysis (TGA). The TGA curves of PMMA dissolved in the different organic solvents (at a concentration of 100 mg/ml) that is drop-cast films are presented in Figure 4.5, and this data was used to determine the source temperature (T_{source}) for graphene growth using each organic solvent. The TGA data provides conclusive evidence for solvent retention in the drop-cast PMMA films and implies that if the source temperature is kept between the temperatures for solvent release and PMMA decomposition of the films then these solvent molecules must be the carbon source responsible for the low-temperature formation of graphene layers. The TGA data also indicates a possible shift in evaporation temperature for these molecules inside the PMMA film compared to the boiling point²⁵⁹ of each pure organic solvent as listed in Table 4-2.

The thermal decomposition of PMMA occurs at ~ $350 \,^{\circ}$ C .²⁶⁰ However, the PMMA side-chain bonds may degrade at a lower temperature via the chain transfer process that determined the initiate thermal degradation of polymer based on observed results,²⁶¹ being one of the two main

decomposition processes occurring above 220 °C. The second process, C-C scission in the polymer backbone, occurs around 300 °C.^{229, 262} Because of the strong interactions between the PMMA macromolecules and Cl atoms in some organic solvents,²⁶³ evaporation temperatures are often shifted higher, as observed for chloroform and dichloromethane in Table 4-2. Furthermore, this interaction was shown in FTIR data, as illustrated in Figure 4.1 and Figure 4.2.

Solvent-PMMA matrix	Boiling point (°C)	Evaporation temperature measured with TGA (°C)		
p-xylene	138	135		
Toluene	111	111		
o-xylene	144	142		
Chlorobenzene	132	128		
Dichlorobenzene	181	174		
Dichloromethane	40	65		
Chloroform	61	117		
Acetone	56	60		

Table 4-2: Thermal analysis shows of organic solvents inside the PMMA matrix.

The TGA data provides clear evidence of residual solvents inside the PMMA matrix, which can be contrasted to TGA data of pure PMMA in chapter 3, as shown in Figure 3.1. Patra et al. reported that the polymer backbone and conformational structure have a substantial effect on the molecular motion of solvents trapped within the film due to bond formation, including H-bonding, between solvent and polymer. ²⁶³ For example, chlorobenzene exists in PMMA in a distinct state with different rotational freedom dynamics.²⁶⁴ The chlorobenzene molecules can exist as clusters or pools in the PMMA matrix, with a distinct boiling point different from a pure organic solvent.^{223, 265} The thermomechanical properties of the solvent molecules are thus strongly influenced by the polymer matrix.



Figure 4.5: TGA profiles of different organic solvents inside the PMMA matrix.

4.7 Graphene quality dependence on carbon source

Having established that the organic solvents are retained in the PMMA matrix and can be selected as the carbon source by accurate selection of the source temperature, low temperature graphene films were grown at low temperature ($T_{growth} = 450 \text{ °C}$ and $T_{source} = 180 \text{ °C}$) on Cu catalysts and analysed using Raman spectroscopy. Raman spectroscopy is a quick and precise technique for identifying the quality and number of graphene layers and has been used as a qualitative measure of graphene films grown from these carbon sources. It allows determination of the graphene signature peaks at G (~1580 cm⁻¹) and 2D (~2700 cm⁻¹). An excitation wavelength of 514 nm was used for Raman measurements on a Renishaw inVia Raman spectrometer.

It has been previously demonstrated that the number of graphene layers can be quantified based on the ratio of the critical peak intensities, I_G/I_{2D} , and the shape of the 2D band.²⁶⁶ Also, the enhancement of the D band (~1350 cm⁻¹) indicates defects created through the growth and transfer process. Figure 4.6 shows the Raman spectra of graphene grown from the various carbon sources, where, for the most part, an influential G band at 1580 cm⁻¹ is observed, indicating that the graphene film consists of multiple carbon layers. Using the full width at half-maximum (FWHM) of the 2D band, and the peak height ratio, the graphene film quality from different carbon sources may be quantified, as shown in Table 4-3.



Figure 4.6: Raman spectra of graphene films on Cu foil grown at T_{growth} of 450 °C with an H₂ flow rate of 50 sccm using different carbon sources.

Table 4-3: Characteristic values from Raman analysis, G and 2D position, the intensity ratio between them, and the $2D_{FWHM}$ are shown.²³³⁻²³⁴

Carbon source	G position (cm ⁻¹)	2D position (cm ⁻¹)	IG/I2D	n GL~	2D FWHM (ст ⁻¹)
p-xylene-PMMA	1581.35	2716.54	2.53	28	83.57
Toluene-PMMA	1584.34	2697.08	1.48	14	56.8
o-xylene-PMMA	1585.84	2676.27	0.99	8	65.55
Chlorobenzene-PMMA	1585.84	2691.88	0.19	2	50.98
Dichlorobenzene-PMMA	1584.34	2708.76	1.62	16	81.74
Dichloromethane-PMMA	1587.33	2700.98	1.66	18	70.86
Chloroform-PMMA	1581.35	2697.08	1.04	10	72.24
Acetone-PMMA	1588.83	2700.98	4.98	48	76.11

The 50.98 cm⁻¹ graphene 2D peak FWHM at 2691.88 cm⁻¹ grown from the chlorobenzene-PMMA source with an I_G/I_{2D} intensity ratio of ~ 0.19 with n GL~ 2 layers (Table 4-3), is the best quality graphene measured from the sources due to a bilayer of graphene. The spectra identify the presence of a "bilayer" graphene deposition from chlorobenzene-PMMA source at the low growth temperature.²³³ Compared with the chlorobenzene-PMMA source, the next best graphene film (prepared via the o-xylene-PMMA source) was of lower quality; corresponding to a higher number of graphene layers instead of monolayer/bilayer growth. The FWHM of the 2D peak is ~65.55 cm⁻¹ with an I_G/I_{2D} intensity ratio of ~ 0.99 for the o-xylene-PMMA source. By comparison, there are a few layers of graphene deposited on Cu foil from the chloroform-PMMA source. The intensity of the I_G/I_{2D} ratio is ~ 1.04 in this growth condition. Chloroform is, therefore, another possible carbon source for the growth of more than single graphene layers. Other carbon sources that gave an I_G/I_{2D} ratio of more than one are typically considered to be multilayers of graphene.²³³ Further investigation of the morphology of the flakes of graphene created from these differing low-temperature carbon CVD sources is continued using TEM in Section 4.9.

The quality of the graphene layers is clearly shown by the ratio intensity of I_G/I_{2D} in these spectra (see Figure 4.7 and Table 4-3). The ratio changes massively depending on the carbon source. Therefore, these results clearly show that, under the experimental conditions used, the carbon source for graphene growth is a major influencing factor in this work. The number of graphene layers varies from bilayers to multi-layers of atomic carbon based on the source condition. Chlorobenzene produces a bilayers to a few layers of graphene. However, by contrast, multilayered graphene is formed using an acetone source. This analysis demonstrates that chlorobenzene is the best source for low-temperature growth graphene in this work.



Figure 4.7: Variation of the Raman I_G/I_{2D} peak ratio as a function of the carbon source material. The error bars of each ratio from p-xylene to acetone are 0.33, 0.12, 0.09, 0.14, 0.08, 0.11, 0.09 and 0.8, respectively. The number of graphene layers (n GL) referred by black points in the figure.

4.8 The growth mechanism of graphene via aromatic and aliphatic sources

There are two parameters which have been shown to affect the quality of graphene in this work. Firstly, each carbon source has different bond energies within the molecules which require different amounts of activation energy to decompose to give suitable carbon moieties in the growth region.²⁵ Secondly, the interaction between the liquid source and polymer matrix controls the release of molecules of solvent as the carbon source for CVD growth. Investigation of low temperature graphene growth and the quality of the resulting graphene is a promising path for understanding the mechanism of growth with different sources and may allow optimisation of low temperature graphene. An example in point is the quality of graphene growth based on chlorobenzene-PMMA and dichlorobenzene-PMMA as carbon sources. Lower quality of graphene films is observed for dichlorobenzene-PMMA. This observation must be related to the characteristics of the organic solvent. In particular, the boiling point of dichlorobenzene is higher than chlorobenzene occurs at a higher temperature, thus requiring more energy. Furthermore, chlorobenzene generates an aromatic benzene fragment on the catalyst in a more straightforward manner than dichlorobenzene, which must pass through a

chlorobenzene moiety or undergo a direct production of benzene fragments.²⁶⁸ Moreover, the dehydrogenation of the adsorbed carbon source molecules at the catalyst surface is dependent on the potential energy barrier specific to the carbon source.⁴⁴

Figure 4.8 shows a schematic of the mechanical process of graphene flakes grown from chlorobenzene-PMMA as the carbon source. Firstly, the growth phase starts with heating the carbon source to move the chlorobenzene molecules to the growth zone and the Cu catalyst. Secondly, based on the bonding dissociation energy of molecules, the first bond broken is C-H due to having the lowest activation energy of 337.2 kJ/mol. ²⁶⁹ Then at the third phase, the C-Cl bond is broken with a bond energy of 397 kJ/mol. However, the C-C bond with an energy of 607 kJ/mol for benzene rings is retained and thus performed C₆ benzene fragments contribute to the growth of the graphene domains.²⁶⁹ Model simulations of liquid chlorobenzene as a carbon source shows significant interaction of the six-member aromatic rings at ~25 °C. This interaction leads to an agglomeration of molecules of chlorobenzene acting as an early step in graphene formation.²⁷⁰ The next stage involves the reaction of the Cu catalyst to produce cuprous chloride (CuCl) on the surface.²⁷¹ Consequently, at this stage, as shown in Figure 4.8, the chlorobenzene source more readily provides a 'naked' benzene fragment compared with a dichlorobenzene source that must lose two Cl atoms. This requirement could result in smaller graphene domains using dichlorobenzene source. As a result of the weakening of the C-H bonds that occurs upon interaction with the catalyst surface, benzene ring degradation is governed by a low potential energy barrier of only 145.69 kJ/mol; facilitating graphene growth at low temperature.¹⁰⁵ Then the metal copper atoms on the surface interact with the π -system of the benzene rings,²⁷² weakening the C-H and C-Cl bonds, facilitating the breaking of these bonds and releasing free H and Cl atoms on the surface.

Consequently, we might expect graphene growth to be more facile for non-halogenated benzene rings and for growth to become less facile as additional Cl atoms are introduced. Thus, chlorobenzene behaves better than dichlorobenzene as a carbon source. Furthermore, since preformed C_6 moieties are formed on the catalyst surface, aromatic carbon sources might be expected to perform better than aliphatic sources where moiety growth is required (see Figure 4.9). In the case of acetone, which contains C=O bond with a very high bond strength of 749 kJ/mol,²⁶⁹ the oxygen is likely retained in the graphene structure, causing defects. Indeed, these oxygen atoms do cause more amorphous carbon¹³⁸ in graphene layers as is clear from the relatively large G peak in the Raman spectrum (Figure 4.6).



Figure 4.8 Molecular structure of chlorobenzene with schematic representation the mechanism of graphene growth: (1) moving of the chlorobenzene molecules, (2) bonding dissociation energy of molecules; bond broken of C-H, (3) bond broken of C-Cl and produce cuprous chloride (CuCl), (4) the surface interact of Cu with the π -system of the benzene rings for the growth of the graphene domains.

C-C bonds typically have a bond strength weaker than C-H bonds in aromatic structures. ²⁷³ However, we would expect aliphatic substituted aromatic rings such as, toluene and xylenes to produce poorer quality graphene than the chlorinated aromatics since, whether the C-C bond is broken to form a C₆ moiety (and free C atoms) or remains attached, it seems reasonable to speculate that the aliphatic carbons will provide a source of defects in the hexagonal structure. Indeed, the results in Table 4-3 and Figure 4.7 support this hypothesis. According to the Raman spectra (Figure 4.6), organic solvents, which have high boiling point temperatures, close to source temperature and which have a benzene ring in their chemical structure (aromatic sources), give a better quality of graphene at low-temperature growth.^{25,32} The preforming of C₆ moieties, the weakness of the C-Cl bonds associated with aromatic chlorocarbon sources explain the relative quality of graphene films grown at low temperatures.



Figure 4.9: Schematic diagram shows the mechanism growth of graphene using dichloromethane-PMMA as carbon source. The mechanism: (1) moving of the carbon source molecules, (2) C-H bond broken, (3) C-Cl bond broken and produce free atoms, (4) C atoms calibrate for ring structure to contribute in graphene growth, (5) C fragment is bonding for graphene domains.

4.9 Transmission electron microscopy of the graphene flakes

To provide information about the graphene quality down at the atomic level, TEM imaging of graphene films grown at low temperature was recorded at and electron beam energy of 200 kV. This energy was required to minimise radiation damage to the sample,²⁷⁴ especially crucial for specimens consisting of light elements such as carbon.²⁷⁵⁻²⁷⁶ In this work, TEM was performed on a Jeol 2100 instrument with an operating voltage of 200 kV and varying magnification from 10,000 times to 100,000 times. Graphene layers were transferred onto a 100-mesh square copper grid (GCu100, ProSciTech). Figure 4.10 shows the TEM images of graphene flakes for three carbon sources: acetone, chlorobenzene and chloroform. The high-resolution TEM could image the typical honeycomb lattice of small domains of graphene in these samples. The graphene layers in Figure 4.10a provide clear evidence of a graphene hexagonal structure in the domain measured, as well as the presence of amorphous carbon. As is evident, the graphene films grown under these conditions are not one continuous layer of carbon atoms, but they consist of small domains of graphene connecting through zones of amorphous carbon. It appears that factors such as the mechanical transfer method have caused numerous defects and contamination on the surface of the graphene layers (Figure 4.10b). The flatness of the sample surface is an important parameter to achieve for obtaining a clear electron diffraction pattern, as illustrated in Figure 4.10c, keeping in mind that ideally, this is monolayer diffraction. In the

electron diffraction pattern in Figure 4.10d, there is clear evidence for the hexagonal atomic arrangement of the carbon atoms. The darkness of this crystallographic image conveys that it is a region of high electron density due to the amplitude of transmitted electrons scattered from the field potential of the crystal (see Figure 4.10d) and, as such, this image infers that a multi-layer graphene sample was grown.



Figure 4.10: TEM images of graphene films suspended on copper grid grown from (a) acetone-PMMA, (b) chlorobenzene-PMMA (c) chloroform-PMMA and (d) electron diffraction pattern collected from the centre of (c) with Miller-Bravais indices. A 2 nm scale bar is shown.

Multi-layer graphene from the other carbon sources was transferred for TEM analysis. As is evident in Figure 4.11a, the graphene layer is not sufficiently flat to give a clear image depicting the structure. However, it does convey the overall structure of graphene, with flakes of randomly orientated graphene, with amorphous carbon surrounding these hexagonal structures. The armchair and zigzag edges are known to both provide an electron energy bandgap that scales as the inverse of the ribbon width.²⁷⁷ The graphene nanoribbons with zigzag-shaped edges could have a narrow band-edge state of the Fermi energy (E_F).²⁷⁸ The nature of the graphene edges plays a key role in determining the electronic structure of films and, as such, affects the magnetic, electric and chemical activity at the graphene edges. For example, scattering of the electron wave results in interference at armchair edges whereas a nonbonding edge state that is localized at the zigzag-shaped edges is created.²⁷⁹ The existence of defects in graphene layers (as shown in the centre of the inset in Figure 4.11b) disrupts electron transfer and will lead to induced charge localisation and insulating states. Also, a bright honeycomb structure is observed in this TEM image, which is the electronic diffraction of carbon atoms. Figure 4.11c shows a complete graphene domain at the edge of the layers revealing a clear armchair structure with some defects inside the atomic structure. The aromatic armchair edges are considered to be more energetically stabilised comparing with zigzag edges.²⁷⁹ The edge structure is predicted to play a critical role in the physical performance of graphene layers.⁷ Indeed, different edge states in graphene nanoribbons and graphene quantum dots can be selected to influence the overall electronic properties.

Change et al. demonstrated that it is possible to control the edge state (from zigzag to armchair structure) by altering the reaction growth processes to ensure the growth rate for the armchair state is faster than the zigzag edge.²⁸⁰ Moreover, defects can be topological, vacancy and impurity defects. Topological defects involve a rotation in bonding angles between the carbon atoms, but the atom is not removed from the lattice (Figure 4.11d). The TEM image indicates that there are some morphology defects coming from the wet transfer method; moving the carbon atoms from their atomic position in the hexagonal orientation. This process could create a structural defect in the atomic layer of graphene. Furthermore, one or more fragments were removed from the atomic lattice as vacancy defects. An impurity defect is identified as one carbon atom in lattice structure being replaced via another atom of a different element.



Figure 4.11: TEM images of graphene films suspended on copper grid grown via (a) dichlorobenzene-PMMA, (b) dichloromethane-PMMA (c) o-xylene-PMMA and (d) p-xylene-PMMA as carbon sources. A 2 nm scale bar is shown.

Multilayer flakes overlapping each other is illustrated in Figure 4.12a. This image also shows apparent hexagonal structure showing that these are individual randomly aligned graphene flakes. The multi-layers of graphene are evident as shown by the electron diffraction pattern in Figure 4.12b where many active diffraction spots with a six-fold symmetry of the carbon hexagonal plane are visible,²⁸¹ resembling a polycrystalline diffraction pattern. Overall, these TEM images show that for all carbon sources, small randomly orientated graphene flakes are formed, with amorphous carbon surrounding these domains. In most cases, these flakes are multilayer and are only a few tens of nanometers in size.



Figure 4.12: (a) TEM image of graphene layers fabricated using Toluene-PMMA as carbon source and (b) electron diffraction pattern of multi-layered graphene. A 2 nm scale bar is shown.

4.10 The uniformity of graphene domains

Raman spectroscopy was utilised to investigate the homogeneity of the graphene layers on the catalyst, combined with imaging to provide more detail on the graphene surface at macroscale resolution, as shown in Figure 4.13a and b. Twelve replicate measurements (red crosses) were recorded across one graphene sample that was grown on Cu foil via PMMA-dichlorobenzene as a carbon source at T_{growth} of 450°C and H_2 flow 50 sccm. The optical micrographs show that multiple graphene domains have grown in different shapes and without constant size on the Cu foil (Figure 4.13b). The Raman analysis indicates that the graphene layers are non-uniform based on the intensity of the 2D peak. The graphene domains size varied on regions of Cu foil after growth condition. There were also some initial signs of a high level of amorphous carbon on the graphene layers are non-continuous and do not exist in some regions. In these regions, only the G peak was present, indicative of amorphous carbon on the Cu surface, rather than graphene layers. There remained some defects on graphene layers (D peak) even after the process of cleaning.





Figure 4.13: (a) Raman spectra shows of graphene film sample grown on Cu foil at 450 °C by PMMA-dichlorobenzene (baseline shifted to 2000 a.u of first line (1) and up to 260000 a.u of last line (12)) and, (b) optical micrographs taken at 20 μ m scale bar magnification of graphene layers on Cu foil for each measurement.

The growth temperature could be playing a significant role in the formation of these graphene domains and, in particular, affecting the growth rate of the graphene.²⁸² Higher growth temperatures could be reducing the nucleation density of carbon atoms and increasing the growth rate. Figure 4.14 indicates the phase of carbon atoms at different growth temperatures ($T_{growt} = 450 \text{ °C}$ and 600 °C). The graphene layers were deposited on Cu foil at low temperature using PMMA-chlorobenzene as carbon source. Then the graphene layers were suspended on Cu grids for TEM analysis. Clearly, for $T_{growth} = 450 \text{ °C}$, graphene domains could not reach the

coalescence phase for creating a lattice of large graphene domains (Figure 4.14a). In Figure 4.14b, the carbon atoms have received sufficient activation energy to achieve a clear honeycomb structure of graphene domains at $T_{growth} = 600$ °C. Increasing the available energy in this way could reduce the defects and amorphous carbon on graphene films and result in the growth of more continuous domains.



Figure 4.14: (a) TEM image of graphene layers grown at T_{growth} 450 °C transferred onto Cu grid and, (b) graphene layers suspended on Cu grid were grown at T_{growth} 600 °C.

4.11 The effect of carbon source on sheet resistance and transparency of graphene films

A four-point probe is widely used to determine the resistivity of any semiconductor film. The measurement of resistance between probe tips on the film is based on the constant current between two probes while analysis of the potential difference on the surface is recorded between another two probes. A two-point electrical measurement is usually sufficient in general-purpose resistance and current-voltage measurements, however, the more accurate tool for resistance analysis is a four-point probe. The sheet resistance of graphene films from each growth condition was measured via the four-point investigation with the results plotted in Figure 4.15a. The conductivity of graphene is still low due to the small domain size of graphene and non-continuous layers (as shown in Figure 4.15b, where many sub-10 nm graphene flakes can be seen).

The transmittance of graphene films on the glass substrate was measured for each growth condition (see Figure 4.16). The optical transmittance for the best film was ~ 70 % at 500 nm wavelength, while the best sheet resistance of the film grown from toluene-PMMA¹²⁴ was ~ 493 Ω/\Box . As a result of the transfer method, graphene films have multiple defects and possible contamination even after a comprehensive cleaning process. Moreover, the transparency of graphene films reduced due to the number of layers of graphene, and possibly residual PMMA on the transfer support (a 70 % transmission suggests an average of 10 layers of graphene).

In conclusion, these factors led to an increase in sheet resistance and a reduction in the transmittance of graphene films. However, being able to control graphene film quality by using different carbon sources is a unique path for the development of graphene fabrication. Raman mapping of the ratio of I_G/I_{2D} of graphene layers grown from a chlorobenzene-PMMA source is shown in Figure 4.15b. It maps the quality of the graphene layer, indicating that the coating is not continuous and that amorphous carbon is present. These two factors combine to be the main effect on the electrical and optical properties of graphene films.



Figure 4.15: (a) Sheet resistance of graphene films from each type of carbon sources (error bar from p-xylene to acetone are 130.4, 128.2, 59.9, 87.5, 126.7, 112.7, 191.8 and 314.9, respectively) and (b) Raman map ($100 \times 100 \mu m$) of the intensity ratio between G to 2D for a graphene film produced from chlorobenzene-PMMA source.

Graphene films from different organic solvents as carbon source show similar optical properties according to the range of transmittance values, 50 to 80 % (Figure 4.16). All of the solvents used act as adequate carbon sources in the PMMA matrix and the matrix source is not a limiting condition to the amount of carbon atoms involved in the graphene growth. The conductivity of low-temperature CVD graphene was compared to that of graphene grown at a high-temperature growth (350 Ω/\Box at a transmittance of about 90 %).^{89, 91} The best graphene film, based on sheet resistance data, was grown from the toluene-PMMA source, but the best combinations for the low-temperature graphene were films with 500 Ω/\Box at a transmittance of about 70 %. These numbers are not too far removed from those obtained for high-temperature growth.^{76, 283} Furthermore, the honeycomb structure of graphene was identified in all graphene growth conditions. However, there were some defects and non-uniform layers introduced to the films due to the mechanical transfer method. Based on this analysis, organic solvent sources which have high boiling point close to source temperature and aromatic base structures could be optimised to give a better quality of graphene at low-temperature growth.^{136, 138}



Figure 4.16: Transmission of visible light of wavelength 500 nm of graphene films from each type of carbon source (error bars from p-xylene to acetone represent 12.2, 13.2, 12, 7.7, 7.1, 14.4, 16.2 and 8.7, respectively).

4.12 The effect of carbon sources containing heteroatoms upon CVDgraphene

In this section, we compare the graphene growth of carbon sources which incorporate heteroatoms to determine if doping or defects arising from the source structure affecting the graphene properties. Carbon sources comprising pyridine and methanol solvent – PMMA matrices were investigated in this chapter for graphene synthesis. The PMMA matrix is regarded as a promising source for optimising the quality of the graphene film because it enables the different organic solvents as carbon sources in CVD to be investigated when operating at a T_{source} below the decomposition temperature of PMMA.

4.12.1 The analysis of graphene films based on heterocarbon sources

In this synthesis, we used the same graphene growth procedure as previously, but with N- and O- containing organic solvents. An additional two organic solvents were chosen as carbon sources. The first carbon source was pyridine-PMMA that has structure related to benzene with one C-H replaced by a nitrogen atom.²⁸⁴ Pyridine with chemical formula C₅H₅N has a sixmembered aromatic heterocycle similar to the benzene structure (see Figure 4.17). In theory, this structure could be considered a carbon source with less bond energy required to break C-H bonds and thus more suitable for reduced growth temperature.¹³⁷ As such, this is a promising structure to grow graphene at low temperature in the CVD method.²⁷¹ However, a nitrogen atom in the benzene ring that has a high electronegativity affects the resonance situation limits and hence the formation of the graphene hexagonal substructure. It will potentially cause defects in the carbon structure.²⁸⁵ Pyridine has been used as a liquid source for the growth of graphene film with N-doped at a high temperature in CVD.²⁸⁶

Figure 4.17 proposes a mechanism of 'graphene' growth using pyridine as an atom source. The N atom forms two σ -bonds with C atoms and donates one electron to the aromatic π -system.²⁸⁷ The dissociation energy of the C-N bond is high at 770 kJ/mol.²⁶⁹ Consequently, the aromatic C₅N ring will be retained during 'graphene' growth and the N atom will replace a C atom within the graphene structure. The N atoms replacement generates vacancy defects and causes large holes in the hexagonal structure with more missing C atoms ²⁸⁸ (see Figure 4.17). Other nitrogen containing carbon sources have been used to grow graphene; such as dimethylformamide by Gao et al. ²⁸⁷ and melamine by Wang et al.,²⁸⁹ but neither of these sources contained a preformed aromatic ring structure. Hence the mechanism of graphene

growth will be quite different to that from pyridine, the carbon source have used here. Thus the quality of graphene is likely to differ.



Figure 4.17: Mechanism growth of graphene domains using pyridine solvent as carbon source at T_{growth} of 450 °C.

The other carbon source used in this analysis was methanol-PMMA. Methanol consists of a methyl group linked to a hydroxyl group, with a formula of CH₃OH.²⁹⁰ In a simple and effective syntheses, a liquid methanol was used as carbon source to grow graphene by immersing the catalyst in the liquid source and then heating up ~ 850 °C.²²⁰ The procedures used in this study were heating the PMMA matrix trapped source up to 180°C (T_{source}) and a 450 °C heating of the catalyst (T_{growth}). Raman spectroscopy (Renishaw inVia) with a 514 nm pump laser was used to identify graphene film on Cu foil after the growth process for both heteroatom carbon sources. Figure 4.18 shows the quality of graphene utilising both procedures at T_{growth}.



Figure 4.18: Raman spectra of CVD graphene grown on Cu foils by (a) pyridine-PMMA, and (b) methanol-PMMA as carbon sources.

The Raman analysis gives some evidence of graphene domain formation using pyridine-PMMA as carbon source. A 2D band was bright for the growth of graphene under these conditions. This observation demonstrates that graphene growth occurs at low T_{growth} when utilising pyridine within a polymer matrix as the source, even if a low quality of graphene film results. There are defects in the film as shown from the D feature located around 1350 cm⁻¹. In addition, as a result of amorphous carbon deposited on the catalyst, the G peak located ~ 1580 cm⁻¹ is the highest compared with other bands. This analysis shows that graphene film has more amorphous carbon than all the previous aromatic carbon sources, with non-continuous graphene layers.

In the case of methanol as a source, the Raman spectrum shows a high amount of amorphous carbon with no graphene on the Cu foil using methanol-PMMA as carbon source. The C-O bond strength is higher than that of a C-C bond ²⁶⁹ and even if the C-O bond is broken, the stoichiometric amount of O on the catalyst surface (one O for each C) will preferentially cause the formation of amorphous carbon.

For more characterisation, UV-vis analysis and four point-probe measurements on the graphene films after the wet transfer method are shown in Figure 4.19. The data shows a slightly better quality of graphene grown via the pyridine-PMMA source with a sheet resistance of 989 Ω/\Box and transmission of 64 % at 500 nm wavelength. However, a sheet resistance of 1.42 k Ω/\Box with the transmission of 71 % at 500 nm wavelength is obtained for the methanol-PMMA, showing that little, if any graphene is formed in this case.

Thus, it would appear that the incorporation of N or O into a carbon source results in imperfect quality graphene with a high proportion of defects (if the heteroatom is retained in the structure) or preferential formation of amorphous carbon.



Figure 4.19: Transmission and sheet resistance of graphene films grown via pyridine-PMMA (989 Ω/\Box) (dashed line) and methanol-PMMA (1.42 k Ω/\Box) (dotted line).

4.12.2 Chemical bond analysis of graphene films

XPS characterisation was carried out for identification of the chemical bonding in the graphene/Cu foils that were grown using both pyridine and methanol as carbon sources. Samples of graphene grown from pyridine-PMMA and methanol-PMMA sources were immediately moved into the XPS system following synthesis. The C-1s XPS spectrum of graphene films produced by pyridine-PMMA is shown in Figure 4.20, while that grown from methanol-PMMA is shown in Figure 4.21.

XPS peaks relate to the chemical environment of atoms on the material surface. As such, a significant summit due to sp² C-C bonding would be expected for graphene. The spectra were fitted with known elemental core level peaks and a background. A core level peak is related to a specific chemical or electronic binding of the element.²⁹¹ The sub-spectra of sp² C-C, π - π *, sp³ C-C, C-O, C=O, O-C=O and C-F are assigned at energies of 284.53, 291.03, 284.83, 286.33, 287.83, 289.33 and 293.61 eV, respectively. It was expected that XPS scanning would identify the existing of C-C, C-N and C-O bonds in the graphene films. Previous work has shown that incorporation of small amounts of N into the graphene structure can lead to doping and increasing of the conductivity.²⁹² However in our work, where N is incorporated at a 1:5 ratio with C and at low temperatures high conductivity materials are not observed.

In both cases, the most intense peak in the XPS spectrum is due to sp^2 C-C bonding (86 % and 74 % for the pyridine and methanol respectively) with a broader peak assigned to sp^3 C-C also present (4 % and 16 %). The sp^3 peak is mainly contributed to by amorphous carbon.²⁹³ These peaks suggest that there is considerable graphene-like material in these films and that, as expected, there is more amorphous carbon in the film grown from methanol-PMMA. Interestingly no peak due to C-N bonds are observed in the pyridine case, and only a small peak corresponding to C-O bonding (2.7 %) is seen in the methanol case (for comparison the corresponding peak in the pyridine spectrum is 1 % of the area). It is possible that these elements are removed as ammonia and water, respectively, by the reducing carrier gas (H₂) or that it is buried under a layer of graphene and amorphous carbon.



Figure 4.20: XPS spectra of graphene film on Cu foil at T_{growth} of 450 °C for 1 min using pyridine-PMMA as carbon source.

These results confirm that the inclusion of N or O in the carbon source leads to poor graphene quality (or no graphene growth at all) and that the pyridine-PMMA source results in better graphene quality with less amorphous carbon than that observed in graphene films based on methanol. This result is further evidence that a pyridine-PMMA source could be used in low-temperature graphene growth but with small graphene domains resulting. After this analysis, it is clear that a lot of the surface material in both cases is amorphous carbon, with no N signal observed. As a result, it is impossible to determine if N or O are retained during the "graphene" growth.



Figure 4.21 XPS spectra of graphene film on Cu foil grown using methanol-PMMA as carbon source at T_{growth} .

4.13 Conclusion

Using PMMA films as the matrix for residual organic solvents is a successful procedure for the growth of graphene films. PMMA entrapped organic solvents were used as carbon sources in the CVD system. The overall graphene quality is more reduced than that achieved at higher temperatures. There is significant evidence to conclude that aromatic solvent sources grow better quality graphene when compared to aliphatic sources and that this result is associated with the relative decomposition mechanisms for aromatic and aliphatic materials. Based on Raman spectral data, we identify chlorobenzene-PMMA as the best carbon source in this work at low temperature growth. The graphene films were single or bilayer; as determined by Raman spectroscopy. However, the domain of graphene was small (tens of nanometres at most for all carbon sources) for low temperature growth. Consequently, a film of multilayer graphene flakes is formed, not a single uniform graphene sheet and this limits the conductivity of the graphene film. Solvents containing O and N heteroatoms were found to produce imperfect quality graphene (or no graphene at all), with the methanol source creating a high proportion of amorphous carbon on the Cu foil surface. However, overall decreasing growth temperature and using entrenched aromatic carbon sources for preparing graphene layers by the CVD method has been shown to be successful. This work offers a new understanding of graphene growth and a potential pathway to improve the fabrication of graphene making it suitable for applications in industry and within the environment.

5. Chapter five: Low temperature CVD-grown graphene as a transparent electrode for organic photovoltaic cells

5.1 Overview

This chapter reports the characterisation of transparent layers of graphene fabricated by chemical vapour deposition (CVD) at low temperature (T_{growth} 600 °C) and evaluates their suitability as a transparent electrode in organic photovoltaic (OPV) cells. The graphene films are catalytically grown on copper (Cu) foil substrates, as detailed in Chapter 2, at low growth temperatures across the T_{growth} range from 400 to 800 °C, which were investigated in Chapter 3. Chlorobenzene trapped in poly (methyl methacrylate) (PMMA) polymer is used as the carbon source ($T_{source} = 180$ °C) as outlined in Chapter 4, with the graphene quality characterised by Raman spectroscopy. In Chapter 5, the OPV device construction is brought into focus and P3HT (poly (3-hexylthiophene-2, 5-diyl)): PCBM (phenyl-C₆₁-butyric acid methyl ester) OPV devices are optimised. These bulk heterojunction solar cells are prepared with the goal of fabricating OPVs based on graphene as the window electrode instead of indium tin oxide (ITO).

5.2 Introduction

Graphene is a single layer, two-dimensional sheet of sp² hybridised carbon atoms arranged in a hexagonal lattice structure and displays extraordinary electronic and thermal properties, unique optical properties and hardy mechanical strength.^{1, 6, 11-14} These properties, along with an abundance of the carbon source material, make graphene highly suited for replacing the scarce ITO as a transparent electrode material for organic electronics.^{164, 185, 249, 283, 294-297} Additionally, the use of graphene would eliminate the degradation pathway of indium ion diffusion into organic solar cell polymer layers arising from the intrinsic chemistry of ITO in acid/base reactions.²⁹⁸⁻²⁹⁹ Furthermore, the reduced transparency of ITO in near-infrared regions causes a reduction in the device efficiency when using low bandgap materials as active layer, a problem which could be eliminated by the use of graphene.³³⁻³⁴

5.3 Architecture of OPVs

The graphene electrode OPV is a new design for OPVs and here will be compared to the performance and characteristics of standard ITO-electrode OPV devices in the conventional architecture. Consequently, both types of devices were fabricated using the same procedure and a graphene-based OPV with the architecture depicted in Figure 5.1 was produced. Graphene was transferred onto commercially available 0.7 mm thick glass substrate (XINYAN Technology Limited, XY15S) as the transparent anode, to which was added a low conductivity layer of poly(3,4-ethylene dioxythiophene-poly(styrene sulfonate) (PEDOT:PSS) as the hole transport layer (HTL). The active layer consisted of blended poly(3-hexylthiophene-2,5-diyl) and phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM) with a calcium (Ca) layer as the electron transport layer (ETL) and aluminium (Al) as the back-electrode (cathode). ITO based devices were fabricated using the same procedure except the glass substrate had a pre-patterned ITO electrode with a sheet resistance 15 Ω / \Box deposited on the glass slide. For the graphene devices, the layer of ITO was eliminated.



Figure 5.1: The architecture of an OPV device with a CVD graphene film as transparent electrode (anode).

The graphene electrode could vary in thickness depending on the number of layers deposited, but monolayer graphene of thickness ~ 1 nm was targeted. The PEDOT:PSS HTL and the active layer thicknesses were within ±5 nm and controlled by modifying the parameters of the spin coating deposition. The ETL and cathode layers were thermally evaporated under vacuum.

5.3.1 Device substrate

The glass substrates used were sized at 17.5 mm \times 12.5 mm \times 0.7 mm and had three ITO fingers of a width of 2 mm, spaced at 1 mm on each long side and a 3.5 mm wide central electrical contact finger on one short edge, allowing six devices to be prepared at the same time. For the transfer of the CVD grown graphene onto the substrate, an area of ~4 mm \times 4 mm of ITO was removed by etching with an aqueous HCl solution of 37 vol % concentration as illustrated in Figure 5.2. The extremities of the ITO fingers ~2 mm were retained as an electrical contact for ease of measurement and this region was protected from etching by a positive photoresist (ELECTROLUBE PRP) layer. After etching, the photoresist was removed by solvent (acetone), and the substrate was cleaned with deionised (DI) water and isopropanol. Substrates modified in this way were then used to fabricate the transparent graphene electrode-based OPV devices, with electrical connection to the graphene film made via the remaining ITO pads on the substrate.



Figure 5.2: Schematic for preparation of OPV substrate based on graphene electrode.

5.3.2 Graphene film

Transferring the graphene, from the Cu catalytic surface on which it was grown, to the glass substrate was accomplished by the wet transfer method. As discussed previously (Chapter 4), this process increases the mechanical defects within the graphene, with the most common defects evident being the graphene grain boundaries, wrinkling of the surface, folding of the

film and point defects, as shown in Figure 5.3. These defects are expected to affect the graphene electrode performance when forming part of an OPV device. Additionally, there was a concern that the remaining ITO (left to establish the electrical contact following etching) was not sharp-edged nor sufficiently flat to allow a good electrical connection with the transferred graphene film. These additional defects could potentially create vacancy defects in the graphene structure, which in turn would increase the transparent electrode sheet resistance. Nonetheless, the graphene electrode was successfully inserted into the OPV structure and assessed as a window electrode for replacing ITO.



Figure 5.3: Optical micrograph depicting the graphene film attached through ITO finger for electrical contact.

5.3.3 OPV anode electrodes

It is essential to discuss the role OPV electrodes play in achieving power conversion efficiencies near to the theoretically expected value. The optimisation of the electrode structure can yield a higher efficiency due to a higher charge carrier extraction. The engineering of interfaces with the transparent graphene film, which is acting as the hole extraction electrode, are significant and vital to provide the maximum charge output from the device. Generally, most OPVs consist of a polymer layer sandwiched between an ITO anode electrode and an Al cathode electrode as a single layer of organic semiconductor. If an electrode is replaced, there will be measurable performance differences between the old and new structures.
One method attempted for using graphene as the transparent conductive electrode, was to apply the film directly to an ordinary glass substrate of similar size to the OPV standard substrate. Aluminium (Al) electrode contact fingers of $2 \text{ mm} \times 1 \text{ mm}$ and $4 \text{ mm} \times 1 \text{ mm}$ dimensions were evaporated onto the graphene film after transfer to the glass substrate, as shown in Figure 5.4.



Figure 5.4: Photograph and schematic of an OPV based on graphene electrode with Al electrical contact fingers.

The graphene was cleaned well and dried under a N₂ gas stream to prevent oxidisation after Al deposition. In testing this design, it was noticed that the ohmic contact between the graphene film and the Al fingers was not very well impedance matched when compared to ITO. Additionally, the opportunities for contamination were increased due to the long fabrication process, meaning it was highly probable to have some oxidisation of the Al contact electrodes. During OPV characterisation via I-V measurement, short circuits between the cathode and anode electrodes were commonly observed in this design. Consequently, this architecture was discarded.

5.4 The resistance and transparency of graphene electrodes

The transmittance and resistance of four graphene film samples were measured to determine the quality of each film for OPV device applications, with the results shown in Figure 5.5. The average sheet resistance of the graphene films was ~294 Ω/\Box with optical transparency of ~65% at 500 nm, suggesting these are ~12-layer graphene films. The variation in the sheet resistance of graphene film from 235 to 376 Ω/\Box is likely due to the small domain size of the graphene attributed to the morphology of the Cu catalyst, as discussed previously in Chapter 3. Furthermore, undesirable impurities and defects in the transferred graphene films will cause a reduction in conductivity and transmission of graphene, where amorphous carbon exists between the graphene domains from the low temperature growth process. A lower defect density of the graphene crystal lattice is expected to increase its conductivity as the defects in the lattice structure act as scattering sites and block charge transport by limiting the mean free path of the conducting electrons.²⁴



Figure 5.5: Representative UV-Vis light transmission spectra for graphene thin films with sheet resistance provided in legend.

Indicators of electrode quality for utilisation as a transparent OPV electrode are logically based on the optical transparency and the electrical conductivity as well as the D band of the Raman spectrum for amorphous carbon contamination. Figure 5.6 illustrates samples grown at T_{growth} 600 °C with ~60 to 80 % optical transparency (at a λ of 500 nm), and sheet resistances of 500 to 1200 Ω/\Box . This set of graphene film samples were considerably more transparent to the naked eye, indicating that there was less amorphous carbon and contamination from the wet transfer method and also fewer defects on the film. This improvement led to improved light transparency through the electrode and, with a more effortless flow of carriers, good conductivity.



Figure 5.6: UV-vis spectra of graphene films and their sheet resistance grown under the same conditions.

A figure of merit (FoM) for potential graphene electrodes was established, which was the ratio of graphene transmission to sheet resistance, with a higher value implying higher quality graphene. This FoM allows us to quickly compare films and gauge the suitability of a graphene sheet for OPV applications. The FoM for several graphene films made at different times under the same 600 °C growth conditions are illustrated in Table 5-1. There is a significant variance in the values due to the graphene samples being comprised of small flakes and the presence of defects left over from the wet transferred method. This FoM was used in subsequent selection of graphene films for OPV fabrication.

Table 5-1: Figure of merit (FoM) for several graphene films in UV-vis transmission with sheet resistance.

T (%) at 500 nm	R (Ω∕□)	FoM	
72	1200	0.06	
66.9	514	0.13	
72.1	906	0.07	
80.4	850	0.09	
66.9	784	0.08	
68.9	637	0.1	
67.1	850	0.07	
55.1	563	0.09	
Averag	0.086		
Standard de	0.021		

5.5 The work function of graphene electrode

The surface work function is defined as the minimum energy required for extracting an electron from the bulk material to an infinite distance. Based on quantum mechanics, the work function is calculated via the difference between the Fermi level (E_f) and the vacuum level (V_0).³⁰⁰ The work function of an electrode is a critical parameter since the difference between electrode work functions determines the internal voltage of a device.

5.5.1 The work function of the graphene electrode on a Si substrate

Multi-layers of graphene grown on Cu foil were transferred, by utilising PMMA as a support layer during the wet etching of the Cu substrate, to conductive silicon substrates for characterisation of the graphene work function. Figure 5.7 shows the UPS spectrum of the work function of a graphene film on a silicon (Si) substrate where the graphene work function is calculated to be ~ 4.98 eV, while the work function of Si is ~ 4.67-4.92 eV.³⁰¹ The 4.65 eV work function of ITO,¹⁶⁰ is sufficiently close that graphene film can be utilised as a replacement transparent electrode in organic photovoltaics (OPVs), which has been done for both organic and dye-sensitised solar cells.^{164, 166} The modification of graphene's work function and sheet resistance (to match more closely that of ITO) could be a promising method for improving the performance of flexible organic light-emitting diodes (OLEDs) and OPV devices.¹⁷⁹



Figure 5.7: UPS plot for the determination of the work function of graphene film transferred onto Si substrate.

The work function of single-layer graphene has been reported to be in the range of 4.55-4.57 eV,³⁰²⁻³⁰³ with a separate report of 5.11 eV.³⁰⁴ Besides, some experiments have shown the work function of monolayers graphene up to approximately 4.8 eV.³⁰⁵⁻³⁰⁶ A change in Fermi level has been identified as the principal cause of a change in the work function value, where this Fermi level may be altered by doping with aromatic and gas molecules or ultraviolet irradiation.³⁰⁷⁻³⁰⁸ Riedl et al. found that the substrate could affect the electronic properties of the graphene layer in a theoretical simulation,³⁰⁹ and this change was a function of the graphene film thickness, with an increase in work function with increasing the graphene film thickness.³⁰⁴ In Figure 5.7, the measured work function was higher than the generally expected value for a single layer of graphene due to the extent of amorphous carbon on the surface of graphene in this film.³¹⁰

Based on values of work function, this graphene film could be used as an alternative transparent electrode in OPVs for improving the band structure alignment at the interface layers of OPVs. The achievement of producing low temperature graphene electrodes is considered to be an excellent opportunity for the development of a new type of window electrode that has a more flexible work function.³¹¹ It is a beneficial way of improving the stability of a transparent electrode for different electronic devices, as compared with ITO electrodes.³¹² For example, ITO is a typical window oxide electrode and exhibits limited work function tenability (~0.5 eV). The Fermi level of ITO electrode changes once deposited onto a different substrate.³¹³ However, the graphene electrode is more stable and considered a novel active electrode with unique properties and a potentially tunable work function. This ability in graphene electrode means that could be possible to generate a window electrode matching the electrical characteristics of OPVs.

5.5.2 The work function of graphene electrodes on an ITO substrate

Currently, efficient OPVs require the use of electron or hole blocking layers to control the transport of charge to the electrodes. Tailoring the work function of a graphene film electrode could overcome the significant work function mismatch between the photoactive layers and better match the lowest unoccupied and highest occupied molecular orbitals of the photoactive layers of OPVs. The large area of a graphene electrode can support a smaller barrier for charge tunnelling in the device and thus could reduce the energy loss from carrier thermalisation,³¹⁴ creating a highly conductive, flexible and transparent electrode which does not require a hole

transport layer (HTL) when applied in OPVs. This observation provides an exciting opportunity to develop new electronic applications of graphene, so the work functions for large area (up to $\sim 1 \text{ cm}^2$) graphene films transferred onto ITO substrates were measured, with results as illustrated in Figure 5.8.



Figure 5.8: UPS plot for the determination of the work function of CVD-graphene grown at low temperature (600 °C) transferred onto an ITO substrate.

The characterisation shows a work function value of ~5.02 eV, which is higher than the work function of ITO.¹⁶⁰ Graphene with this work function is a suitable replacement electrode for ITO once quality can be improved. Generally, the range of work function measured for multilayers of graphene was ~ 4.89 - 5.16 eV, which is higher than the theoretical value of ~ 4.5 eV.³¹⁵⁻³¹⁶ These different values for the graphene work function are affected by the contact resistance with the substrate electrode.³¹⁷ The work function of graphene has been determined using a modified electric field, to be within the range of 4.65 to 4.75 eV for bilayer graphene and 4.5 to 4.8 eV for monolayer graphene in ambient and dry nitrogen.³⁰² In this work, we measure a work function for multilayers graphene grown at T_{growth}. Preparing a novel low-temperature CVD grown graphene electrode, a strategically crucial alternative electrode based on its work function, was successfully achieved.

5.6 The quality of graphene electrode on an OPV substrate

As discussed in detail earlier, Raman spectral analysis using 514 nm and 532 nm wavelength sources to measure the G 1582.72 cm⁻¹ and 2D 2696.98 cm⁻¹ peak intensities and their ratio is a measure of film quality, purity and thickness. Figure 5.9 shows the Raman spectrum of graphene electrode fabricated at T_{growth} . The spectrum allows calculation of the number of graphene layers on the glass substrate and observation that the film has high defect density due to the wet transfer process with a large amount of amorphous carbon present.



Figure 5.9: Raman spectrum of graphene electrode transferred onto OPV substrate. Inset showing optical micrograph.

The Raman spectrum G/2D ratio of 0.88 indicates ~ 6 graphene layers on the glass substrate.²³³ It is beneficial to increase the graphene layer number up to the point where the properties are significantly altered and around six layers was determined to be a right balance between the sheet resistance and the light transmission of the electrode. There are still defects and wrinkles in the graphene film even after the cleaning process as determined from the intensity of the 1350 cm⁻¹ D band. The strength and FWHM of the G band are low compared to the 2D band, revealing clear evidence for moderate amounts of amorphous carbon in the graphene honeycomb structure. The high intensity and FWHM of the 2D band (which is the most significant Raman peak) indicates good quality graphene. Based on this Raman analysis, the graphene electrode quality should be suitable as an OPV window electrode.

Raman characterisation of another region of the same sample is illustrated in Figure 5.10. In this analysis, it shows that the amorphous carbon is more in the hexagonal structure of graphene in the selected area. The 1350 cm⁻¹ D peak is increased while the G band has a higher intensity, with lower FWHM, and is shifted in location compared with the earlier analysis. The FWHM of the 2D peak, now located at 2687.88 cm⁻¹, is more than the previous measurement (see Figure 5.9) with lower intensity. This observation indicates that the localised quality of this area is not high as in the last analysis with more amorphous carbon and increased graphene defects. The G/2D ratio is 1.5 showing ~ 19 carbon layers.²³³⁻²³⁴ This film is still usable as a transparent OPV electrode, but not as ideal, and we would expect the transmission of this region to be lower (only ~40 %). In both figures, the optical micrographs of the graphene electrode are presented, showing the morphology of the sample, which is explored further in the next section.



Figure 5.10: Raman spectral analysis of another area of the same graphene electrode transferred onto OPV substrate as Figure 5.9. Inset showing optical micrograph.

5.7 The morphology of the graphene electrode

The study of graphene morphology achieved following wet transfer onto the glass substrate can provide more insight into its performance as a transparent electrode. Here we use scanning electron microscopy (SEM) to obtain high resolution (sub-micron) images of our graphene films.

The roughness of the graphene surface after the cleaning process and associated defects affect the performance of the graphene electrode and are one of the reasons for poor electrode conductivity. Figure 5.11 shows two SEM images (scale bars 2 μ m and one μ m for a and b, respectively) of a graphene film grown at T_{growth} for 1 min under the same conditions as the fabricated graphene electrodes. It can be observed that the surface is not flat and consists of a random aggregation of carbon layers in a thin layer on the Cu foil. The image reveals zones of fragile, wrinkled sheets of graphene with clear evidence of darker amorphous carbon zones. Furthermore, darker contrast flat regions are observed which are ascribed to multilayer graphene. At higher magnification in the SEM image in Figure 5.11b (scale bar 1 μ m), white features close to the wrinkled carbon structure are evident and are ascribed to point defects left from PMMA contamination. The grain boundaries of the Cu foil are expected to influence the formation of electrode film, and the larger patterns in the film are ascribed to the underlying foil. The comparison between this and the earlier measurement in Figure 5.12 indicate a less uniform graphene morphology after transfer onto the Si substrate.



Figure 5.11: SEM images of graphene film grown at T_{growth} 600 °C for 1 min with $H_2 = 75$ sccm on annealed Cu foil.

After the wet transfer process, the graphene morphology is affected by the defects and material left on the surface. Figure 5.12 depicts an SEM image of a graphene film transferred onto a Si substrate following washing with DI water, acetone and isopropanol, respectively. The graphene film appears to consist of continuous layers of graphitic carbon with some defects left over from the transfer process. There are wrinkles in the sheets and some polymer contamination of the surface that arises from the mechanical support to the film during the transfer method. The amount of amorphous carbon on the graphene surface is reduced after the cleaning process (as compared with Figure 5.11). The image also shows clearly the topography of the surface with strong evidence of defects such as cracks and wrinkle in the graphene electrode. These defects influence the performance of the OPV window electrode and eliminating these defects is difficult when the device involves many steps of fabrication.



Figure 5.12: SEM image of graphene film transferred onto Si substrate via the wet transfer method.

5.8 The carbon bonding of the graphene electrode

X-ray photoelectron spectroscopy (XPS) analysis allows characterisation of the bonding environment within the graphene film over large areas. An XPS image of a graphene film grown on Cu foil at T_{growth} 600 °C is shown in Figure 5.13. The analysis identifies the existence of carbon along with functional groups and other materials on the Cu foil. Figure 5.13 characterises the bond energy of carbon present with contributions from O species. The most common element other than carbon atoms is oxygen, which is not surprising, as the cleaning procedure does not remove all the oxygen species from the catalyst surface. The surface of the Cu foil is quite reactive to oxygen in the air.¹³⁸



Figure 5.13: Survey XPS spectrum showing elemental electron configuration contributions on the Cu foil after graphene growth.

XPS identifies the chemical bonds of the carbonaceous material in and on the graphene films as the binding energy of a core level electron peak is affected by the outer electron distribution of the element. The binding energy for a C 1s level in an sp² configuration is ~284.3 eV,³¹⁸ while a carbon sp³ core level peak is 284.9 eV. This peak is dominant indicating the presence of graphene, as shown in Figure 5.14. In XPS characterisation, a C 1s region scan can be successfully fitted with an asymmetric peak corresponding to the sp² bonded graphene, and asymmetric peak corresponding to sp³ defects or contaminants.²⁹³ The main peak is fitted with a Doniach-Sunjic function with an asymmetry factor of 0.10 which minimises the residual and

is in good agreement with the literature.³¹⁸⁻³²⁰ Approximately 95 % of the carbon is in the sp² bonded state, indicating good conversion to graphene. In general, analysis of the XPS data is indicative of the sp² hybridisation of the carbon when in graphene layers. The sp³ hybridisation is attributed to oxygen bonding with carbon as oxidised species, such as ketones and carboxylic acid peripheral groups, and amorphous carbon associated with contamination and defects in the graphene films.³²¹



Figure 5.14: C 1s energy band of graphene film grown on Cu foil at T_{growth} 600 °C.

As shown in Figure 5.14, the observed XPS spectrum of low temperature grown CVD graphene has C1s at 284 eV with a contribution from C-C and C=C bonds arising from graphite and graphene.³²² The XPS peak at ~ 547 eV in Figure 5.13 indicates small oxygen contamination of the graphene. The main sp² component feature located at 284.3 eV corresponds to a combination of graphene and amorphous carbon. However, the second energy band sp³ at 284.9eV is ascribed to amorphous carbon. Increasing the sp³ bond energy is attributed to existing defects in graphene layers such as structural vacancies, grain boundaries left from Cu foil substrate and C-H bonds in hydrogenated graphene.²⁹³ This factor is considered as one of the main reasons for the increased sheet resistance in the graphene electrode and is unable to be removed by cleaning overnight by alcohol solvent bath as it is a structural feature of the graphene flakes, rather than a surface contamination.

5.9 Elemental analysis of the graphene electrode

Energy-dispersive X-ray spectroscopy (EDS) is a useful technique for elemental analysis in a minimal volume of material, down to a few cubic micrometres. It offers a determination of elemental composition at individual points or can give a map of elements over a specific region of a film,³²³ and has sufficient sensitivity to identify changes in the chemical structure on the Cu surface after deposition. For this work, EDS was used to determine the chemical composition of the CVD grown carbon film on the Cu foil. Figure 5.15 shows the EDS spectrum of the carbon film on the foil catalyst showing the presence of C, O and underlying Cu, after CVD growth. The EDS spectrum in Figure 5.15a was collected with an electron beam energy of 10 keV from a micron-sized area of graphene layers on Cu foil before, and repeated after, the transfer method. The EDS investigation showed elemental carbon deposition on to the Cu substrate at the green cross point illustrated in the SEM image (see Figure 5.15b) and a dominant Cu L peak in the region between ~ 0.8 to 1.0 keV. There is elemental oxygen on the Cu Surface, or in the graphene layer, corresponding to O K-line at ~ 0.5 keV and the from the CVD, either as graphene layers or amorphous carbon, with a K-line at 0.2 keV.³²⁴



Figure 5.15: (a) Energy dispersive X-ray spectroscopy (EDS) spectrum of graphene grown on the annealed Cu catalytic foil, prepared at $T_{annealled}$ 900 °C for 1 h, and (b) associated SEM image of the area analysed with EDS.

The EDS spectrum of the graphene film after transfer onto the target Si substrate is identical with the typical peaks for each element in the sample, but now a Si peak is present, and the Cu peak is absent. Figure 5.16 shows the EDS spectrum corresponding to the graphene film transferred onto the Si substrate. After the wet transfer method, the Cu peak is absent, indicating complete removal of Cu contamination from the foil via the etching solution. A similar level intensity of oxygen is present arising from either oxygen species present in the carbon layer or the native oxide on the Si. The relative level intensity of the carbon peak is reduced a small amount compared with the carbon level on the Cu foil, possibly due to the cleaning process after the wet transfer method removing amorphous carbon. The peak at ~ 1.7 keV is the Si K-line due to the Si substrate after the transferred process.³²⁴ This characterisation confirms the efficiency of the assigned procedure for producing the graphene electrode without any Cu contamination.



Figure 5.16: (a) EDS spectrum of the graphene film transferred onto an Si substrate, and (b) SEM image of graphene film marked with the EDS analysis region at the green cross.

5.10 The optimisation of bulk heterojunction OPV

OPVs can contribute as part of an environmentally friendly energy source. In general, OPVs are devices which convert sunlight into electricity by utilising organic semiconductor materials. One of the challenges with the production of silicon photovoltaic cells is the significant material costs and energy-intensive processes ³²⁵ associated with the cells. OPVs, by comparison, have much lower cost materials and recyclable polymers. In terms of stability and performance, OPVs at present are a relatively new type of thin-film solar cell. To assess OPV devices with a graphene anode (as are discussed in Chapter 6), first literature standard ITO electrode P3HT: PCBM OPV devices were fabricated and characterised to use as a benchmark for comparison. The following sections detail this process.

5.10.1 The structure of OPV

In this optimisation process, the first organic film layer deposited to interface with the photoactive organic polymer films is PEDOT:PSS. This conducting polymer usually covers the ITO layer on the substrate and works as a hole transporting layer (HTL), blocking electrons from recombining with holes during hole transport to the OPV anode electrode. This process enhances the photo-induced voltage generated and the charge collection of the OPV system.³²⁶ The most common organic materials used in OPV devices, are PCBM and P3HT, as an electron acceptor and donor, respectively.³²⁷ These organic semiconductor materials were selected based on the energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels.³²⁸ The optimisation of the polymer material blend was chosen to increase the light absorption, improve the charge transport and enhance the exciton pair dissociation to free charges.³²⁹ In general, donor and acceptor molecules should be intimately mixed, so that the exciton pair mean free path length matches the exciton pair diffusion distance to an interface between the acceptor fullerene and donor polymer. Figure 5.17 illustrates the layered structure of a conventional architecture OPV that allows pathways for charge carriers moving respectively towards anode and cathode electrodes for collection. Improving device performance is associated with increasing the charge transport efficiency through the OPV stack. The top layer of the ITO electrode-based OPV has an evaporated Al metal cathode electrode with thickness ~ 120 nm and a Ca is an interfacial layer of ~ 30 nm.



Figure 5.17: The structure of OPV based on an ITO electrode.

The blending of P3HT and PCBM improves the OPV charge extraction. In particular, the bulk heterojunction structure enhances exciton dissociation by creating a large interfacial area ³³⁰⁻³³¹ within the diffusion length of the exciton.¹⁹⁰ The mixture results in exciton dissociation at the interface of the donor P3HT polymer and the acceptor PCBM molecule with the latter transferring electrons to the metallic electrode. The blend has a functional absorption band overlap with the electromagnetic solar emission spectrum.³³² The P3HT crystalline morphology and high molecular weight improve the mobility of holes along the polymer chain.

The active layer of P3HT: PCBM was spin-coated as a layer between the transparent anode (ITO) with significant work function ~4.65 eV 160 and a cathode (Al) with small work function ~4.25 eV 333 for charge transfer through the OPV structure and to the electrodes. The optimised structure of ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al generally function well and are widely reported in the literature.

5.10.2 Benchmarking OPV fabrication

The stability of OPV is affected by many degradation mechanisms which happen under different environmental conditions, one of which is humidity causing electrode oxidation. Photo-oxidation of the P3HT and PCBM active layer has been identified as affecting the OPV leading to a 70 % reduction in the short circuit current and reducing ground state absorption by 2 %.³³⁴ Over time, both water and oxygen molecules increase in concentration within encapsulated OPVs by diffusion through seals and barrier films, and these relate directly to the underlying degradation pathways.³³⁵ The stability of OPVs may be improved by removing oxygen and water from the fabrication atmosphere (Figure 5.18).



Figure 5.18: The efficiency of OPVs prepared in different atmosphere conditions. The red and blue line present the average value of efficiency (2.12 % and 2.47 %).

The diffusion of oxygen and water atoms into the OPV layers may cause chemical reactions leading to the formation of defects in the active layer and corrosion to the electrode interfaces.³³⁶ In this work, there were two preparation environments used. The fabrication of active layers (P3HT:PCBM) was processed in a laboratory fume hood under an ambient atmosphere or in a clean room with a glove box under a nitrogen (N₂) atmosphere. Figure 5.18 clearly shows the influence of the preparation environment on OPV efficiency, as determined by the current-voltage characteristics. In the wet laboratory, OPVs materials were exposed to humidity and oxygen at room temperature, ~ 27 °C. By contrast, devices fabricated in the cleanroom were prepared in the absence of water, oxygen and dust. Consequently, devices fabricated in the wet laboratory are of lower efficiency due to oxidative degradation. This result also highlights the importance of device encapsulation in increasing the stability and lifetime of OPV devices.

The fabrication of OPVs under a N₂ atmosphere inside an inert atmosphere, glove-box minimises the undesired degradation of devices. The power conversion efficiency (PCE) values were increased with more stable devices, and the device fill factor shows overall device quality in Figure 5.19. This plot reveals a higher and more consistent performance within the cleanroom fabricated devices compared to the wet laboratory environment. Exposure of P3HT to oxygen atoms has been found to cause damage to the polymer structure and the deterioration of its properties.³²⁵ The humidity in the wet laboratory can also cause degradation of the PEDOT:PSS and this leads to a short lifetime of the OPV device.³³⁶ The key for future solar energy development in organic electronics is to address these stability and degradation issues.³³⁴



Figure 5.19: The fill factor of OPVs fabricated in two atmosphere conditions. The red and blue line present the average value of FF (0.51 and 0.57).

5.10.3 The effect of thermal annealing on OPV performance

Thermal annealing is a means by which the morphology of active layers may be modified to enhance the device performance. This factor is a remarkable performance-enhancing step for OPVs using polymer materials as active layers.³³⁷ For example, the thermal annealing of OPV blends of P3HT:PCBM at 80 °C for 5min was shown to lead to the formation of crystalline domains of P3HT because of a more ordered packing of the polymer chains.³³⁸ This morphological change increased the photoconductivity and enhanced the hole mobility in the crystalline domains of P3HT which improved from 0.0056 cm²/Vs for the non-annealed sample to 0.044 cm²/Vs for the annealed sample.³³⁸

The reason for improved performance is the increase in crystallinity of the P3HT achieved via thermal annealing, and this leads to better charge transport properties in the polymer blend, enhancing the short circuit current density (J_{sc}), the open-circuit voltage (V_{oc}) and the fill factor (FF) for the annealed devices. For the P3HT: fullerene system, thermal annealing at 55°C for 30 minutes improves the efficiency of OPV devices 3-4-fold, compared to a reference device.³³⁹ After thermal evaporation of OPV electrodes, the annealing temperature increases the measured power outcomes of P3HT:PCBM devices from 0.4 % efficiency in the reference device to 2.5% in the annealed device.³³⁹ The annealing also usually leads to a modification of the size and composition of donor and acceptor domains, hence affecting exciton dissociation, charge separation and charge extraction.³³⁷

The optimisation of the annealing step in the fabrication of OPVs can lead to significantly better morphology and performance of P3HT:PCBM devices. Following annealing of P3HT:PCBM films, the main P3HT polymer chain backbones change orientation to align parallel, and the side chains orient themselves perpendicular to the substrate, while the PCBM forms crystallites with the PCBM diffusing from the mixed polymer film to create these phases. ³⁴⁰ Figure 5.20 shows the corresponding efficiencies for two thermal annealing conditions studied. Devices were dried at 60 °C for 4 minutes, and other devices were annealed at 140 °C for 4 minutes, both before thermal evaporation of the Al/Ca electrode onto the structure.



Figure 5.20: The diagram of OPV efficiencies in dried and thermal annealed condition. The red and blue line shows the average value of efficiency (1.58 % and 2.5 %).

Another benefit of annealing is a reduction of moisture within the OPV devices due to the higher temperature increasing water evaporation and ultimately preventing active layer oxidation in the polymer structure and electrode oxidation. Moreover, annealing before Al deposition prevents additional electrode oxidisation. The annealing of P3HT:PCBM devices can improve performance if done either before or after deposition of Al/Ca.³⁴¹ Figure 5.21 illustrates the device enhancement that occurs when thermal annealing is performed before electrode deposition compared to after. In Figure 5.21a, the efficiencies of OPVs annealed before Al electrode deposition was higher; they exhibited a higher FF (see Figure 5.21b) and were more stable than devices annealed after Al electrode deposition. Based upon these results annealing conditions of 140 °C for 4 minutes were chosen for optimal device fabrication.



Figure 5.21: (a) Efficiencies, and (b) fill factors of OPVs arising from the thermal annealing conditions before and after the deposition of Al/Ca electrodes. The line are shown the average value of efficiency (2.5 % and 1.61 %) and FF (0.56 and 0.51).

5.10.4 The optimisation study of the PEDOT:PSS layer in OPVs

Poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) is applied as a polymer electrolyte containing an excess of positive charge, i.e. p-doped material in the PEDOT chains, with the negative matching charge located in the PSS, to ensure charge neutrality. The PSS contribution is also as a polymer surfactant that effectively stabilises and disperses PEDOT in water and other solvents. PEDOT has been demonstrated to be the most successful hole-transport layer in large scale printing applications for OPV,³⁴² and, in general, has been widely used as an anode buffer layer in polymer solar cells electrodes.³⁴³⁻³⁴⁴ The PEDOT:PSS aqueous dispersion has, as one of its desirable polymer solar cell properties, high optical transparency in the visible light region. Besides, the work function of PEDOT:PSS is

reported to be between 4.8 and 5.2 eV, a value that can allow the formation of ohmic contact with donor polymers.³⁴⁵

An essential requirement for the PEDOT: PSS layer in ohmic contact is to avoid energy barriers at the OPV ITO interface. All P3HT:PCBM conventional solar cell performance parameters show a definite improvement with a PEDOT:PSS interlayer at the ITO/active layer interface.³⁴⁶ Two types of commercially available PEDOT:PSS was used in the fabrication of OPVs in this work. PEDOT:PSS aqueous solution Clevios PH1000 purchased from Heraeus formed a high conductivity OPV buffer layer, while PEDOT:PSS-Al 4083 yielded a less conductive polymer film. Table 5-2 records the power and efficiency metrics for devices using both types of PEDOT:PSS.

PEDOT:PSS Type	PCE (%)	Voc (V)	Isc (A)	FF	Cell Area (mm ²)	J _{SC} (mA/cm ²)
PEDOT:PSS-PH1000	3.14	0.55	-6.18E-04	0.46	5	-12.36
PEDOT:PSS-PH1000	2.76	0.54	-3.53E-04	0.55	3.8	-9.3
PEDOT:PSS-Al 4083	3.06	0.55	-4.19E-04	0.66	5	-8.38
PEDOT:PSS-Al 4083	3.04	0.55	-3.01E-04	0.7	3.8	-7.92

Table 5-2: shows OPVs characterisation using two types of PEDOT:PSS in the fabrication.

It is evident that OPVs fabricated with PEDOT:PSS-PH1000 had a lower average performance than PEDOT: PSS-Al4083. The PCE reduced markedly with a decrease in masked device area from 5 mm² to 3.8 mm² for OPVs based on PH1000 due almost exclusively to J_{SC} , as shown in Figure 5.22a. The values for OPVs based on Al4083 were more stable with a mask compared to devices based on PH1000 (see Figure 5.22b). There is a sharp drop point in the J_{sc} in devices based on PEDOT:PSS-PH1000 as buffer layers after applying mask area ~3.8 mm², suggesting that there may be photo charge being collected from outside the direct illumination area. The results indicated that PEDOT:PSS-Al4083 would be best in using in conjunction with graphene electrode in OPVs. The density of dark current is also more stable with PEDOT:PSS-Al4083 compared with PH1000 condition (see Figure 5.22a and b). The dark current density of the OPV based PH1000 type is not stable, and a leakage current occurs under dark conditions which contributes more sheet resistance to OPV substrate (see Figure 5.22b). This observation could also correspond to less mismatch of interface-layer between the buffer and active layers of OPV due to the uniformity of PEDOT:PSS-PH1000. This work provides a road map to applying the best type of PEDOT:PSS for use with a graphene window electrode in OPVs in Chapter 6. From this data, it is clear that ITO-based P3HT:PCBM devices of \sim 3 % are optimal under these fabrication conditions and for the materials used. This efficiency will then provide a benchmark for devices prepared with graphene electrodes in Chapter 6.



Figure 5.22: J-V curves of OPVs based on buffer layer of (a) PEDOT: PSS-PH1000, and (b) PEDOT: PSS-A1 4083. The measurement was completed inside a nitrogen atmosphere box.

5.11 Conclusion

Preparing a high-quality graphene electrode via low temperature CVD to be the transparent electrode in an OPV was the challenge addressed in this thesis chapter. The conductivity of graphene was lower than that of ITO, due to the small domain size of graphene achieved and defects from the transfer method. The growth temperature affected the quality of the graphene electrode, as was identified from Raman analysis in Chapter 3. The graphene electrode prepared at T_{growth} 600 °C with 75 sccm H₂ flow rate performed the best. Understanding the operation of low-temperature graphene-based OPV devices and investigating the polymer formation on these graphene surfaces remain areas of great interest to create new approaches to preparing environmentally friendly, economic, conductive electrodes.

6. Chapter six: Large area graphene as an alternate transparent electrode for organic photovoltaic cells

6.1 Overview

This chapter will focus on low temperature CVD-grown graphene films with an area greater than 1 cm² with the overarching goal of creating an alternate transparent electrode for OPV cells. The electrical sheet resistance and optical transmission have been measured for all films, as well as the graphene layer uniformity and the overall morphology was measured by atomic force microscopy (AFM) over areas of several square micrometres. Raman spectroscopy has been used to identify the graphene layer quality, as detailed previously. Raman mapping has also been used to provide information on regions of graphene film up to 100 μ m² in area.

6.2 Introduction

Small area graphene has been used in several applications such as sensors, transistors, transparent conducting films and as window electrodes for OPV.^{164, 347-349} However, much larger area graphene films are required for significant production applications. The CVD method is considered to be the most promising technique by which large area, high-quality graphene may be fabricated, due to the transferability of the films and the cost effectiveness of the approach and equipment. ^{28, 350} Using CH₄ as the carbon source and under high temperature (~1000 °C) growth conditions, large area graphene films, on the scale of 25 to 750 mm², have been produced for electronic device applications. ^{28, 76-77} Under these growth conditions, the continuous fabrication of graphene layers for use as a transparent electrode for large scale electronic devices has been shown to be possible.^{185, 351-352}

The ideal transparent electrode should have low sheet resistance (<100 Ω/\Box), high transparency (>80 %) and a work function in the range 4.5-5.2 eV for use as an ITO electrode replacement. Wang et al. ²⁸³ reported that large areas of graphene, produced by high temperature (~1000 °C) CVD, could be utilised as transparent electrodes in OPVs, where the average sheet resistance varied from 1350 to 210 Ω/\Box and the optical transparency ranged from 72 % to 91 % in the visible wavelength range. The performance of this OPV, using a graphene electrode with pyrene buanoic acid succidymidylester (PBASE) that altered the surface wettability without degrading the conductivity,²⁸³ resulted in a PCE of 1.71 %. However, the corresponding control

device (based on an ITO electrode) was around 3.1 % of PCE for ITO/poly(3,4– ethylenedioxythiophene):poly(styrenesulfonate)/poly(3-hexyl)thiophene: phenyl-C61-butyric acid methyl ester/LiF/A1 device structure. Despite these advances, reducing the graphene growth temperature whilst creating large area (up to 300 mm wide by 100 metre long) electrodes for printed flexible organic photovoltaic cells remains a significant, challenge for researchers.

6.3 Transfer of large area graphene films onto a target substrate

A common transfer method for graphene films uses a mechanical PMMA polymer support layer which adheres to, and protects, the graphene layer while the Cu foil is etched away. The PMMA/graphene film may then be moved to a new substrate, before the PMMA is dissolved using an alcohol solvent. This technique has been used in this work to apply graphene film on to a range of different substrates. However, we observe that when using this transfer process, it becomes more difficult to achieve a high quality transferred film as the area of graphene increases.

The PMMA polymer, spin-coated onto the graphene covered Cu catalyst, often does not dissolve completely, leaving some residual contamination on the graphene surface. This problem arises because of the long residual polymer chains aligning via π - π interactions with the sp² carbon bonds in the graphene layer.³⁵³⁻³⁵⁴ In addition, more residual PMMA and other contaminants are expected on the graphene morphology because of the carboxyl groups in the PMMA film reacting at the graphene domain boundaries.³⁵⁵ Even after the use of cleaning processes such as: activated carbon treatment, plasma treatment, heat treatment under specific gas atmosphere or overnight soaking in an organic solvent bath, ³⁵⁵⁻³⁵⁶ removal of these residues remains a problem and a surface completely clean of these residues cannot be achieved. Additional cleaning steps to improve the cleaning process outcomes can also increase defects within the graphene film. This contamination then directly affects the electrical properties of the graphene sheet. Furthermore, the wet transfer process for large area graphene can cause cracks and wrinkles which are considered to be key conductivity degradation pathways as they decrease the charge transport channels .³⁵⁷ An et al.³⁵⁸ reported the successful transfer method of graphene via PMMA as support layer and HCl solution as the Fe etchant. The key role of the polymer layer is supporting graphene layers at a necessary step for wet transfer method. Dry transfer using polydimethylsiloxane (PDMS) stamp as the supporting layer has also been

developed.³⁵⁹ To avoid film cracking after removing, Li et al. added a second PMMA coating layer after the PMMA/graphene has been placed on a target substrate.⁸⁹ Little cracking was observed with this method since the second PMMA layer provides additional film support once the Cu substrate has been removed with the PMMA support subsequently dissolved by acetone. This second layer process could be useful for large scale graphene production, with other polymer support layers, such as poly(bisphenol A carbonate) (PC), successfully used for wet transfer.³⁶⁰

In this work, a direct transfer method for large area graphene has been developed where the lamination of graphene with a flexible substrate, as illustrated in Figure 6.1, allows for the transfer of large areas of film. This method has yielded improved transferral of graphene electrodes with high purity as outlined in the sections below. Graphene films were transferred in two ways with adhesive PET substrates: (a) one opposite face between the graphene film and PET substrate and (b) with another one between the Cu foil and the PET substrate. In the Cu foil stack to PET flexible film transfer, PMMA was spin-coated as a mechanical support for the graphene layers following etching of the Cu foil.



Figure 6.1: Large area of graphene films laminated onto PET substrates before Cu foil etching.

Two methods were developed for the transfer of graphene at large scale onto PET substrates. The first methods moves the graphene film onto the target substrate without a mechanical polymer support using plastic sheeting typically used in screen protection. The other process used an additional polymer film support. We have found that as the area of the graphene film increases it becomes increasingly desirable to transfer the graphene film onto PET without a PMMA support. The process involves three stages; in the first stage the graphene/Cu is adhered onto the PET substrate via face to face adhesion between graphene layers to PET surface. Then the sandwich structure of Cu/graphene/PET is dipped completely into a bath solution of iron nitrate Fe (NO₃)₃. The Cu metal is oxidised to Cu^{2+} ions and the Fe³⁺ ions are reduced to Fe²⁺. The time required to dissolve Cu catalyst is more than 48 hours due to the large area and to ensure that any Cu contamination is fully removed. After the etching process, the graphene film on the PET substrate was cleaned using the same process as for small area graphene; resulting in a supported graphene film, as shown in Figure 6.2. The large area graphene is now free from polymer residue but there appear defects such as cracks and wrinkles, which form in the solution bath. The crack formation results from the reduced mechanical film support in this method. Nonetheless, this method opens an avenue for the formation of low cost flexible large area graphene at low temperature growth for electronic applications.



Figure 6.2: Large area graphene film (~10 cm×5 cm) transferred onto PET substrate via the direct method without polymer film support.

6.4 The morphology of large area graphene

The morphology of graphene layers over large areas is critically affected by the deposition and addition of carbon atoms on the catalyst surface at low growth temperatures. To determine the surface appearance after transfer, a region of large area graphene was transferred onto a SiO_2 substrate and imaged using AFM as shown in Figure 6.3.



Figure 6.3: Graphene film from large area procedure transferred into SiO_2 substrate without mechanical film supporting. AFM imaging technique at scale bar of (900×700 µm).

The image shows that the graphene layer is not continuous but instead is made up of individual graphene flakes which are defined by the grain boundaries of the Cu foil catalyst. This result is somewhat expected, since using an organic solvent as the carbon source has been shown to allow the synthesis of graphene at low temperature growth due to its low activation energy, but does not lead to the formation of large scale of continuous graphene films. ^{124, 136} Previous studies have shown that using a hot pressing method for transferring large areas of graphene improves the morphology of large scale areas of graphene in comparison with the laminated by roll to roll method.³⁶¹ In particular, the surface of large scale graphene has fewer wrinkles and defects in the film morphology as a consequence of the transfer method. To limit the

number of defects after etching the Cu substrate, Lee et al. reported using the silicone side of a mobile phone screen protector as a substrate for the graphene film.³⁶² This resulted in a better large area of graphene with enhancement to the morphology of the surface. For high temperature growth, the graphene coverage was more than 95 % on the Cu foil surface.^{129, 363} However, the coverage for graphene films grown at low temperature was less than 90 % with an amount of amorphous carbon present on the surface.¹³⁸

Consequently, the growth of continuous graphene films at low growth temperature remains a challenging aim. The growth time of graphene layers on the catalyst can be increased in order to increase the overall percentage coverage of graphene domains. In this work, the cool down rate of graphene growth (~2 hours) was a limiting factor in the growth of large domains of graphene. Additionally, oxygen and water must be avoided under growth condition to obtain high quality and uniform graphene layers. In this work, a reducing mixture of H₂ and Ar carrier gas was used to prevent residual oxidation during the graphene growth. In this way, we could limit the formation of oxidised and amorphous carbon layers that contaminate the graphene layer deposition and result in layer defects. However in our methodology, the wet transfer method for large area graphene onto the PET substrate provided a complication, as shown in Figure 6.4. This figure clearly shows folding of the graphene film due to the transfer onto the PET substrate. An alternative approach to remove contamination is by annealing at a high temperature to remove any residual material from the transfer method.³⁶⁴ However, this approach is unsuitable for flexible substrates due to a high thermal annealing temperature. Han et al. ³⁶⁵ has taken advantage of the high solubility of organic small molecules in the solvent for inserting an organic small molecular buffer layer between the PMMA and graphene layers. This technique is an efficient way to reduce PMMA residual on graphene surface thus improving the graphene morphology.

For better morphology, Liang et al.³⁶⁶ demonstrated that gaps were also formed when the PMMA/graphene/target substrate stack was dried. It was believed for baking the sample before removing the PMMA to evaporate the water in the sandwich graphene then produced a better graphene surface with fewer defects after transfer. In addition, there are clearly defects and wrinkles on the graphene layers as a result of the process. Folding of the graphene and the formation of multilayer films reduces the transmission of the graphene film due to an increase in the number of graphene layers. Nevertheless, large area low temperature graphene have been successfully transferred onto target substrates proving the ability to apply graphene film as a window electrode for larger area OPV.



Figure 6.4: Optical images of large area graphene film transferred onto PET substrate.

6.5 The resistance and optical transmission of large area graphene

In order to be of practical use as a transparent electrode in OPV, both sheet resistance and film transparency are critical properties for the large area graphene films. Sheet resistance of large area graphene films was measured using a home-built four-point probe (see Figure 2.14 in Chapter 2, section 2.4.7). Typical values are given in Figure 6.5 and shown in Table 6-1. The sheet resistance of large area graphene was found to be higher than small area graphene (see Figure 5.5 in chapter 5 section 5.4). The reason for the higher sheet resistance (and therefore lower conductivity) is the reduced uniformity of these large area films and the high-level amount of amorphous carbon that is deposited on and amongst the layers (as demonstrated by the XPS measurements in Chapter 5 (Section 5.8)). Consequently, the transfer of large-scale graphene remains a big challenge in the absence of a polymer support film. Transfer of graphene sheets to 10 cm² resulted in wrinkles and defects such as tears, gaps and cracks in graphene layers. These defects reduce the quality of graphene and therefore the conductivity of films and made procuring suitable electrode materials for subsequent OPV fabrication difficult.

Using a low temperature growth of benzene procedure, Jang et al. reported that the sheet resistance was around ~ 1000 Ω / \Box at 97.6 % transmission for 550 nm wavelength. ¹³⁸ Another work using plasma assisted CVD at low temperature found a sheet resistance ~ 900 Ω / \Box and 92 % of transmittance.³⁶⁷ Using toluene source for growth continuous graphene at low temperature, this graphene films exhibited the sheet resistance of 8.02 k Ω / \Box at 97.33 %

transmission of 550nm wavelength.¹²⁴ For large scale areas using high growth temperature, the graphene film sheet resistance was as low as ~125 Ω/\Box with 97.4 % of transmittance optical.²⁸ Another work at a high growth temperature demonstrated that the sheet resistance of large area ~200 Ω/\Box with a transmittance of 85 % of 500nm wavelength.⁹⁰ Moreover, for increasing the large area of graphene to more than 1 cm² with 1-12 graphene layers at a high growth temperature was shown the sheet resistance ~ 770-1000 Ω/\Box with optical transmittance of 90 % at 500 nm wavelength.⁷⁷ However, fabrication of large area graphene at low growth temperature have exhibited a higher value of sheet resistance due to more amorphous carbon involved in graphene layers and small graphene domains.^{124, 138} Vishwakarma et al. found that the sheet resistance was ~ 1.3 k Ω/\Box sheet resistance at 80 % transmittance for grown a large area of graphene films at low temperature using microwave plasma CVD. ³⁶⁸ Using a roll to roll microwave plasma CVD for growth large area graphene at low growth temperature, this work stabilised the sheet resistance of graphene on PET substrate ~ 0.9- 3 k Ω/\Box with transmission of 89 % wavelength.³⁶⁹



Figure 6.5: UV-vis transmission and sheet resistance of large area graphene films transferred onto PET substrate.

Table 6-1: Figure of merit for several large area graphene films (~4 to 10 cm²) based on UVvis transmission with sheet resistance.

Graphene area film (cm ²) ~	T (%) at 500 nm	R (kΩ⁄□)	FoM
4×2	44.6	0.98	0.045
6×4	54.8	1.35	0.04
8×4.5	79.9	1.89	0.042
10×5	90.7	2.1	0.043
	Aver	0.042	
	Standard o	0.002	

Optical transmission of the large area graphene was also measured. When combined sheet resistance and optical transmission are the two properties used to identify the best electrode for large production of OPV. The film transmission is directly influenced by the number of layers of graphene and reduces as the film thickness increases. By contrast, the sheet resistance is reduced with increasing layers of graphene. Using the ratio between these two parameters, a figure of merit was created to determine the best films to act as transparent electrodes (see the values in Figure 6.5). The best figure merit was around 0.045 for a sheet resistance of ~ 980 Ω/\Box . Each monolayer of graphene reduces film transmission in the visible range by 3 %.¹⁴ We can see that the transmission of the large area graphene films grown at low temperature varies across regions of the one film. This observation shows that there are different number of graphene layers across the substrate and this is not a uniform film. One large area (~ 5 cm×4 cm) was successfully transferred with a sheet resistance ~ 1.25 k Ω/\Box and a transparency ~87.1% at 500 nm wavelength (Figure 6.6). The transmission value suggests that this film has an average of ~ 4 layers of graphene across its entirety.



Figure 6.6: UV-vis transmission spectrum of large area graphene film on PET substrate.

The deposited graphene films have a high transmittance for a wide range of wavelengths (300-2000 nm). By comparison, ITO shows strong absorption in the region of near (0.8-1.4 μ m) and short-wavelength infrared (1.4-2 μ m);³⁷⁰ the prepared graphene films remain transparent in these regions. Again, the transmission of the graphene film is dependent on the number layers of carbon, which determines the film thickness ¹⁴. The electrical measurements of the graphene films carried out by the four point-probe analysis showed a high sheet resistance. However, one film with the transmission of ~67.2 % at 500 nm wavelength had a sheet resistance of ~4400/□ (see Figure 6.7). This finding shows that large area graphene films with a low sheet resistance suitable for electrode materials in OPVs could be obtained.



Figure 6.7: UV-vis transmission spectrum and sheet resistance of large area graphene film on PET.

6.6 The quality of large area graphene

Raman spectroscopy is used to determine the quality of large area graphene using spectra produced from the in-plane optical vibration (degenerate zone centre E_{2g} mode) and second-order zone boundary phonons.³⁷¹ The Raman spectrum of graphene includes the G peak located at ~1580 cm⁻¹ and 2D peak at ~2700 cm⁻¹ and can be used to determine the number layers of n-layer graphene by the ratio between them. ³⁷² In addition the D peak located at ~1300 cm⁻¹ gives an indication of sp³ hybridised carbon present, which is generally regarded to be an indicator of amorphous, aliphatic impurities. In our characterisation, graphene film at large production scale sizes of up to 5 cm² can be seen to have multilayers of graphene on the PET substrate, as shown in Figure 6.8. The G/2D intensity ratio in this spectrum is of 2.97 that is around ~31 of n GL ²³³ with FWHM (25.12 cm⁻¹, 81.98 cm⁻¹) for G and 2D, respectively. The Raman spectra laser power was reduced when measuring graphene on PET due to potential damage to the PET substrate, as compared to when measured on the glass.



Figure 6.8: Raman spectra of large area of graphene film transferred onto flexible PET substrate via the direct transfer method.

A region of a large area film was transferred onto a glass substrate for further analysis (Figure 6.9), where Raman spectra we recorded at different regions across the graphene film as selected by optical microscopy. The film can be seen to contain a varying number of graphene layers at different regions due to lack of uniformity of growth layers and the transfer method. Consequently, the quality of graphene was not consistent from one area to other based solely on the number of layers of carbon. This result again demonstrates the range of graphene quality

resulting from large area film growth. Moreover, the large G peaks reveal defects in the graphene film due to the transfer method. The small domains of graphene at low temperature growth means that continuous layers of graphene are of only limited area, affecting the quality and properties of the large area graphene. In addition, the coverage of the graphene layers can be only a low percentage on the surface of catalyst before the transferring of the film. Figure 6.9 shows variation in the D peak in the graphene spectrum from region to region, indicating that the amorphous carbon between the small graphene domains also varies. Analysis of area 1 in this Figure shows a ratio of I_G/I_{2D} (0.99) indicating ~ 8 graphene layers. ²³³



Figure 6.9: (a) Raman spectra of large area graphene on a glass substrate, and (b) optical micrograph of the graphene film for determination of the Raman analysis regions.

Mapping of I_G/I_{2D} was recorded for large area graphene on a Cu foil ~ 100µm, as shown in Figure 6.10. This image provides a clear view of the graphene layers on the foil. The mapping demonstrates that there are small graphene domains with surrounding amorphous carbon as seen in the I_G/I_{2D} ratio (see Figure 6.10a). This plot is strong evidence for the quality of large area graphene and could provide more information for each peak of the Raman spectrum in the large-scale film. This analysis also provides a more detailed understanding of the quality and defects in graphene films. Figure 6.10b shows the 2D peak map for the graphene film, identifying the quality and layers of graphene. Graphene layers are seen to be overlapping with each other without continuous deposition due to the non-uniformity of the growth mechanism. As a result, the intensity of the G peak is increased in Raman spectra for large area graphene. This measurement shows a high intensity for amorphous carbon across most of the graphene film.


Figure 6.10: (a) I_G/I_{2D} and (b) I_{2D} of large area graphene grown on Cu foil at low temperature growth of 600 °C.

6.7 The performance of large area OPV based on a graphene electrode

The optimisation of the low growth temperature procedure presented in this chapter and earlier has been conducted to produce large area, low temperature graphene as an alternative transparent electrode for OPVs. The results of the optical transmittance and sheet resistance of the large area graphene suggest that it could be used as a transparent window electrode, all be it with high resistance. Multi-layers of graphene have been transferred onto PET and glass substrates for electrode applications. The values obtained for the transmittance of the graphene films (see Figure 6.7) indicated that the average film is of multi-layer graphene. The Raman spectra of the graphene films also give evidence that the graphene films are composed of different numbers of stacked layers carbon. These results explain the fundamental properties of the large graphene films in terms of resistance and transmission.

The first stage of introducing the graphene film into OPV devices was to apply the graphene, retaining the ITO as a contact point for electrical connection, as shown in Figure 6.11a. A simple schematic of the OPV based on graphene electrodes using the ITO contact is illustrated in Figure 6.11b.



Figure 6.11: (a) Optical image of the contact between graphene electrode and ITO for I-V characterisation, and (b) the structure of the OPV based on graphene electrode using ITO contact for measurement.

The fabrication of organic solar cells based on a graphene electrode used P3HT and the fullerene derivative PCBM as a blend active layer. A thin spin coated layer of the conducting polymer PEDOT:PSS was deposited on the graphene electrode at 4000 rpm for 1 minute giving a thickness of around 10 nm. The average thickness of the graphene electrode was around 1nm to 2 nm (a monolayer to two layer graphene film), which is the thinnest layer in the OPV fabrication (see Figure 6.12). After drying at 140 °C for 20 min, the substrate had the polymer active layer P3HT:PCBM (1:0.8) spin-coated from a solution in chlorobenzene at 950 rpm for 1 min to give a thickness of ~ 200 nm. This deposition was followed by thermal annealing at 140 °C for 4 min under a N₂ atmosphere. Finally Ca and Al were deposited by thermal evaporation to give a thickness of 30 nm and 120 nm, respectively. For comparing device performance, standard OPVs were fabricated on an ITO electrode with the same device structure. Current density-voltage (J-V) of OPVs was measured using a Keithley 2400 source meter under a nitrogen (N₂) atmosphere and illuminated with AM 1.5 simulated solar radiation.



Figure 6.12: AFM image of graphene electrode transferred onto Si substrate for thickness measurement.

6.8 OPVs based on graphene films as a transparent electrode

Large area multi-layer graphene films produced at low temperature were used as a replacement electrode for ITO in OPVs. To transfer the graphene electrode a wet transfer method was used to deposit the graphene after the wet etching step onto the desired OPV substrate. The power conversion PCE of OPVs based on this new graphene electrode were not as high as standard OPVs using ITO electrodes and with the same architecture, in the comparison study. However, there is an increasing requirement for alternative transparent electrodes in electronic applications and this technique continues to be an interesting way to fabricate an environmentally friendly, low cost electrode for industrial applications. It remains a significant challenge to realise the promising future of graphene electrodes in the electronic application.

6.8.1 The J-V characterisation of OPVs

Large area graphene films with reasonable sheet resistance (~300 to 800 Ω/\Box) were utilised as window electrodes in OPVs. These graphene electrodes act as flexible electrodes and are lightweight and prepared by low cost fabrication at low temperature CVD growth. It is important to ensure that the electrode window is clean and low in defects. The graphene films were chosen as candidates as alternative OPV electrodes based on the analysis of graphene films conducted in Chapter 5. Graphene electrodes were applied onto glass OPV substrates at room temperature. All current density-voltage (J-V) curves of OPV devices were measured at room temperature of 25°C under a N₂ atmosphere with a masked active area of 3.8 cm². The intensity of AM 1.5 simulated solar illumination was calibrated with a silicon photodiode at $\sim 42 \text{ mW/cm}^2$ and was regularly calibrated stage during OPV measurement.

PEDOT:PSS (thickness 10 nm) was deposited onto the graphene film coated glass substrate having a transparency of 94 to 97 % at 550 nm wavelength and a sheet resistance of 700 Ω/\Box to 1.3 k Ω / \Box . OPV devices were fabricated with architecture graphene/PEDOT:PSS/P3HT: PCBM/Ca/Al and devices with identical layer structure on ITO electrodes were also fabricated. The J-V characterisation of the device with graphene electrode shows a J-V under dark conditions, as shown in Figure 6.13a. The linear, off-zero plot shows that the device is not acting as a diode but instead behaves like a resistor, suggesting that the graphene electrode is introducing a high resistance contact into the device. Under solar illumination, the OPV based on the graphene electrode in my study produced an open circuit voltage (Voc), short circuit current density (J_{sc}), fill factor (FF) and PCE of 0.36 V, 4.28 mA/cm², 0.27 and 0.42 %, respectively. In comparison, Park et al. reported that the use of CVD-graphene grown at a high temperature (1000 °C) as a window electrode was successfully achieved on organic photovoltaic (OPV) devices with a PCE of 0.85%.²⁴⁹ Moreover, CVD-graphene films grown at 1000 °C were utilised as transparent anode electrode for OPVs with sheet resistance around 80 Ω/\Box and transmittance 90 %. The OPV structure was quartz/graphene/MoO₃ + PEDOT:PSS/P3HT:PCBM/LiF/A1 and the outcome of PCE was \sim 2.5 %. 185 These results indicated further improvement of the low temperature growth of graphene as a new transparent electrode for replacing the traditional ITO electrode is needed. By contrast, the ITO based device behaves as expected like a diode and has a much higher efficiency (Figure 6.13b). It is clear that device performance with the graphene transparent electrode was worse than that of the OPV based on ITO. It has a sheet resistance of ~30 Ω/\Box , consequently the higher sheet resistance of the graphene electrode results in the J_{SC} and FF of the device on graphene being significantly reduced compared to the device based on ITO and this led to observed decrease in the efficiency. The V_{oc} of the graphene based device is also lower that its ITO version and this may reflect also the different of work functions of graphene and ITO.



Figure 6.13: Current density – voltage (J-V) characteristics of OPV cells made from P3HT: PC₆₁BM blend films, based on (a) graphene and (b) ITO.

The J-V characteristics of OPV devices based on graphene are presented in Table 6-2 The PCE is lower with the graphene film (0.42 %) compared to that of devices with ITO (3.51 %) as explained above. The PCE of standard devices which are based on ITO electrodes is considered a reasonable result comparing with previous work.³⁷³⁻³⁷⁴ In addition, the hydrophobic nature of graphene makes uniform coating of the PEDOT:PSS layer difficult and this may add to the issue.²⁸³ Defects in the graphene electrode may also result in high recombination rate in active layer, reducing the observed current density of the device. Standard OPV has higher Jsc (10 mA/cm^2) and V_{oc} (0.54 V) values than graphene film based device. A high temperature CVD graphene was also applied as the transparent conductive anode for OPV with structure graphene/poly (3,4-ethylene dioxythiophene):poly (styrene sulfonate) (PEDOT:PSS)/copper phthalocyanine (CuPc)/C 60 /bathocuproine (BCP)/Al. The sheet resistance (Rsheet) of graphene electrode was 3.5 k Ω / \Box at transmittance around 89 % and achieved the PCE ~ 1.18 %. ¹⁶⁴ Devices based on graphene films as an anode electrode for OPV were fabricated by Xu et al. They prepared a structure of quartz/graphene/ PEDOT:PSS/P3HT:PCBM/LiF/Al and obtained a PCE of ~0.13 % using large area production of graphene by spin coating method using graphene solutions.³⁷⁵ In this work, by comparison, using ITO as the electrode for OPV and delivered a PCE of 3.59 %.375 In cathode electrode environment, multilayers of graphene (MLG) film at a high growth temperature have been used in OPVs based on MLG/WPF-6-oxy-F/P3HT:PCBM/PEDOT:PSS/A1. The PCE of these devices achieved about 1.23 %.376 For

more enhancement, multilayers of graphene film as a cathode electrode in an OPV structure consisting of glass/ITO/ZnO/P3HT:PCBM/MLG provided the PCE of 2.5 %.³⁷⁷ For single layers of graphene (SLG) as electrode, an OPV sandwich of ITO/PEDOT/CuPC:C60: TPBi/SLG prepared. However, this architecture resulted in a PCE of around ~ 0.22 %.³⁷⁸

Table 6-2: J-V characterisation of OPVs made from P3HT: PCBM blend films as active layer, based on electrode of ITO and graphene film.

Device Type	PCE (%)	Voc (V)	Isc (A)	FF	Cell Area (mm ²)	J _{sc} (mA/cm ²)
OPV/G	0.428	0.36	1.63E-04	0.27	3.80	4.28
OPV/ITO	3.517	0.55	3.80E-04	0.64	3.80	10.0

The electrical and optical properties of the OPV device with a graphene electrode are degraded due to the transfer method and this could lead to reduction in its quality. Furthermore, one of most common challenges for the integration of graphene electrodes into OPV devices is the incompatibility between the graphene electrode and the PEDOT:PSS hole transport layer (HTL) that results in an increase in the device failure rate.²⁹⁴ Preparing a visually uniform PEDOT:PSS layer on the surface of graphene electrode was a difficult achievement and Figure 6.14 shows the patchiness of the resultant film. The hydrophilic PEDOT:PSS was spin-coated onto graphene electrode, but a conformal and uniform coating could not be achieved because of the hydrophobic nature of the graphene surface.

Another reason of low J-V characterisation in OPV based on graphene, can be the wrinkles and cracks which form in the graphene films due to the wet film transfer. This issue could result in discontinuities in charge transportation channels on the local scale of graphene domains in the electrode and would consequently reduce the efficiency of charge collection at the graphene electrode. Accordingly, the low level of performance in OPV based on graphene electrodes is concluded to be due to the high sheet resistance of the graphene electrode and morphological issues. In addition, this poor performance of devices can be related to a low shunt resistance (R_{sh}) which causes an increasing of the current density in the reverse bias for the dark and under illumination condition analysis. However, this result acts as a successful proof of concept for the use of graphene multi-layers as window electrodes in OPV devices.



Figure 6.14: Optical micrograph of PEDOT: PSS (Al 4083) spin-coated on the graphene electrode.

6.8.2 The external quantum efficiency of OPVs

External quantum efficiency (EQE) is the ratio of the number of charge carriers collected by an OPV device per unit time to the number of photons of a given energy incident on the OPV per unit time at given wavelength and gives an indication of how efficiently the OPV is functioning. So the EQE tells you about the fraction of incident photons that are being converted into electrons in the device. To maximise EQE, it is essential that any graphene window electrode have a transmission as high as possible. EQE allows a study of the contribution of photons of differing energies to photocurrent and thereby allows the researcher to identify wavelengths of light where the device performs poorly. Thus, using EQE analysis provided an enhanced understanding of the behaviour of graphene electrode based OPVs to different wavelengths of light. A tungsten halogen lamp passed through an Oriel Cornerstone 130 monochromator was used to measure EQE.

To illustrate how the ratio of the number of charge carriers collected by OPV based on CVD graphene compared to OPV based on ITO, we have examined the EQE of OPVs based on both electrode materials. Figure 6.15 shows the EQE spectra for graphene and ITO electrode-based OPV devices. From this figure, it can be concluded that the number of photons which are converted to charge carriers in active layer are decreased in OPV-graphene, at least in part because of low transparency (~65 %) of graphene electrode. This measurement supports the

hypothesis that graphene grown at low temperature and wet transferred onto a substrate does not result in a uniform film and its morphology has been affected by transfer process as shown in Chapter 5. These issues can lead to an increase in the reflection of the graphene electrode and also cause a high sheet resistance with surface defects which create a leakage current and short circuit between the electrode and active layer through the PEDOT:PSS layer (see Figure 6.13).



Figure 6.15: EQE spectra of OPV cells using graphene and ITO as transparent electrode. This is for four devices of OPV/G comparing with control standard device of OPV/ITO.

The device with an ITO transparent electrode has higher EQE across the entire wavelength range compared to the five devices based on graphene film as a window electrode. One factor contributing to a high EQE is the optical absorption of the transparent electrode, but here this value is approaching 100 %, similar to the ITO. Consequently, the difference in EQE must be due to the efficiencies of charge collection and charge transfer at the graphene window electrode. EQE can be improved via reducing the number of graphene layers and obtaining a smoother surface (to prevent reflection and scattering of light), a challenge for transferred graphene films utilising the wet transfer method. In this analysis, we considered the poor performance of the graphene electrode could be mainly due to reduced light transmission through a poor graphene electrode that will influence EQE. This is due to a combination of many parameters, such as cracking or contamination from the wet transfer method and an overall low quality

(small flake size, multilayer and amorphous carbon) of the graphene films related to low growth temperature.

To further probe OPVs based on graphene electrode, the internal quantum efficiency (IQE) was calculated and plotted. IQE is the ratio of the number of charge carriers actually collected by the OPV to the number of photons of a given energy that shine on the OPV and are absorbed by the cell (see Figure 6.16). A low IQE indicates that the active layer of the solar cell is unable to make good use of the photons. IQE is considered an inherent property of OPVs and is related to the light trapping into OPV system. EQE gives a comprehensive indicator of both phases of collection and the exciton dissociation in OPVs.



Figure 6.16: EQE and IQE spectra of OPV made from P3HT: PCBM blend films, based on a graphene electrode.

In a device with perfect light trapping, the EQE should be equal to the IQE. ³⁷⁹ Figure 6.16 shows EQE and IQE of the proposed OPV based on the graphene electrode. It is apparent that the device has higher IQE than EQE in the same device showing that all the excitons generated in the device are not collected at the electrodes. The charge collection could be increased with improving the morphology and resistance of the graphene electrode. Improving the quality of graphene electrode, with lower number layers of carbon would lead to an increase in the fraction of the light trapped in the active layer structure.

6.8.3 The resistance of OPV electrodes

Resistance is simply defined as the opposition to the flow of electric current in the circuit. Impedance is opposition to the flow of AC current because of any resistive, inductive or capacitive components in the circuit. It is a combination of both resistance and reactance in a circuit. It is measured in the same units as resistance. The resistance is experimentally considered as the impedance with zero phase angle when the current is not alternating. ³⁸⁰ However, in the majority of situations the phase angle cannot be zero especially with capacitive or inductive influences in the circuit. LCR meter (Keysight E4980A) within the frequency range of 20-106 Hz under dark was analysed this measurement.

To further elucidate the effect of the graphene electrodes, the dark Nyquist plots of devices based on both ITO and prepared graphene electrodes are presented in Figure 6.17a and b. These plots give a complex plane representation of the imaginary part, Z'' of the impedance response versus its real part, Z'. These measurements are applied out at different DC voltage for covering the entire area where is a working operation of OPV (at range 0 V to 0.6 V). It noted for increasing of applied voltage is responded for connected to the recombination kinetics that occurred in ITO device. Moreover, the low voltage region is contributed to dominate through the shunt resistance of device as a result of unavoidable leakage current which realise in graphene device.³⁸¹ The overall impedance response includes a resistance connected in series R_o that is ascribed to the ITO/Graphene sheet and connecting wire contributions, and the results are practically frequency-independent. ³⁸²⁻³⁸³ It is shown that by considering the equivalent AC circuit illustrate in Figure 6.17c, R_o is higher for the graphene-based device and its value does not vary too much, whereas its value for the ITO- based device is less and increases continuously before dropping suddenly above 0.5 V. Ro is represented by a series resistance which can be attributed to the substrate and contacts of the device.³⁸⁴ The equivalent circuit in the low frequency region includes a recombination resistance (R_{rec}) and a relaxation time being the mobile carrier lifetime of the OPV (R_1, C_1) .³⁸⁴ The capacitance (C_1) from this device is associated with chemical capacitance Cµ. This capacitance could be increased via charge and carrier density with a change in the Fermi-level.³⁸⁴⁻³⁸⁵ These results imply an Ohmic contact of graphene (meaning that it acts as a resistor and poorly collects charge) and a more rectifying behaviour, as expected, for ITO substrate.



Figure 6.17: Nyquist plots of OPV devices based on (a) graphene and (b) ITO as transparent electrode, (c) the equivalent AC circuit of OPV.

Detailed analysis for the two electrodes (graphene and ITO) is presented in Figure 6.18a, where the frequency responses of the real part of the OPV impedance is presented on a linear scale. The voltage bias for this analysis was applied from 0.1 to 0.4 V and the real part of the impedance was plotted versus the frequency. At the higher frequency range, the resistance part of the impedance showed similar dropping values for both devices. Figure 6.18b shows the device resistance as a function of bias voltage. It is clear that the real resistance of the OPV based on graphene electrode is higher (~260 Ω) compared with the ITO electrode (~50-70 Ω). The analysis viewed the changing of real part resistance as narrow and width region vs frequency of ITO and graphene devices. The higher sheet resistance of the graphene electrode is therefore directly reflected in the overall resistance of devices, reducing the device performance. The real part of the resistance was reduced constantly via increasing the bias voltage that is related to a reduced value of resistance with a higher voltage at low region of frequency. These results are also reflected in the dark J-V curves, where a linear J vs V plot give a constant resistance for graphene-based device, but a non-ohmic contact is observed for ITO-based OPV device.



Figure 6.18: (a) Dispersion of total real part resistance of impedance versus frequency for OPVs based on graphene and ITO as window electrodes, and (b) the linear J variations vs V for Graphene-based device, and ITO-based OPV device.

6.9 Assessment of OPVs based on graphene and PEDOT:PSS as window electrodes

One question which needs to be answered is whether the device performance seen in the graphene electrode devices actually reflects the graphene as an electrode or, rather, is actually due to the PEDOT:PSS hole transport layer acting as the electrode. The polymer PEDOT:PSS is considered to be an inherently flexible and conducting polymer.³⁸⁶ This polymer material is commonly used in applications of organic devices as electronic blocking layers or, when a specific high conductivity is used, as a polymer electrode. ³⁸⁷⁻³⁸⁸ As such, it is not unreasonable that the PEDOT:PSS may be acting as the electrode in these devices, with the graphene merely relegated to a resistive element.

PEDOT:PSS is identified as a polyelectrolyte complex, intermixed on the molecular scale. The inherently nonconductive PSS part plays several roles. It is a necessary part of overall

conductivity via serving as a counter-ion to stabilise charge carriers produced by primary doping. It also thereby creates a water soluble complex of polyelectrolyte in solutions (water, alcohols and acetone) suitable for environmentally friendly deposition. For high solubility in water, the percentage of PSS in the compound structure is much higher than that of the PEDOT.³⁸⁹ However, the excess of PSS could degrade the primary devices performance. The insulating excess PSS surrounds the conducting PEDOT crystallites and can lead to hindering the charge carriers traveling along the film.³⁹⁰ The PSS can also act as an insulating layer on top of the film that has the ability to decrease the charge carriers moving to an adjoining transport or active layer, essentially acting as a charge barrier.³⁹¹

To determine if device performance was based on graphene or PEDOT:PSS acting as the transparent electrode in these devices and if PEDOT:PSS is actually hindering charge transport to the electrode, we fabricated OPVs based on both graphene and PEDOT:PSS alone as thin film window electrodes. In this way, we could compare the character of graphene electrodes with the polymer electrode. Table 6-3 shows J-V characterisations for both devices based on graphene and PEDOT:PSS electrodes. PEDOT: PSS (Al 4083) electrodes were spin-coated at speed 5000 rpm for 1 min giving a thickness of 10 nm.

Table 6-3: J-V characterisation of OPVs based on graphene and PEDOT:PSS as transparent electrodes.

Device Type	PCE (%)	V _{oc} (V)	I _{sc} (A)	FF	Cell Area (mm ²)	J _{sc} (mA/cm ²)
OPV/PEDOT:PSS/G	1.130	0.53	3.29E-04	0.32	5.0	6.57
Masked OPV/ PEDOT:PSS/G	0.280	0.40	1.31E-04	0.26	3.8	2.62
OPV/ PEDOT:PSS	0.097	0.53	3.59E-05	0.25	5.0	0.71
Masked OPV/ PEDOT:PSS	0.089	0.53	3.31E-05	0.25	3.8	0.66

J-V curves of both sets of OPVs under AM 1.5 illumination are shown in Figure 6.19. The results show that the graphene electrode with better performance at area devices 5 mm² (see Figure 6.19a). In this experiment a device PCE of 1.13 % was obtained – the best obtained for any graphene based device produced in this work. The dark current for the graphene devices exhibits non-diode behaviour so there is clearly a leakage current in the devices. Figure 6.19b shows the J-V plots of OPV based on PEDOT:PSS as an electrode. The devices act as

photoactive resistors with a resistance higher than that observed in the graphene devices, reflecting the low conductivity of the grade of PEDOT:PSS used. Masking the devices to a 3.8 mm² window does not affect the PEDOT:PSS device dramatically but does reduce the apparent performance of the graphene device. Nevertheless, OPVs based on the graphene electrode still out perform that with the PEDOT:PSS electrode device by a factor of ~3, as shown in Table 6-3. Consequently we can be confident that the device performances reported here are a result of the graphene electrode and not simply due to the PEDOT:PSS blocking layer. The dramatically reduction of PCE from 1.13 % to 0.28 % after masking indicates a non-uniform sheet resistance of the graphene film and resulting in charge trapped within and not being able to transfer to the electrodes.



Figure 6.19: J-V characterisation of OPVs based on electrodes of (a) graphene and (b) PEDOT: PSS.

6.10 The effect of masked electrode area on the performance of graphene electrodes

To investigate the practicality of large area graphene as window electrodes in high performance OPV devices, large area graphene devices were fabricated and illuminated under masks of varying sizes. This experiment was undertaken to determine the viability of low temperature graphene electrodes for electronic applications. Initially in this study, devices with an active area of 30 mm² were prepared and their performance was characterised under full illumination

and the standard mask area of 3.8 mm^2 . Typical J-V curves are shown in Figure 6.20. This figure shows an obvious effect of changing the illuminated the area of the graphene electrode on the performance of the OPV. For full area illumination of the device, an open-circuit voltage (V_{oc}) of 0.5 V, a short-circuit current density (J_{sc}) of 8.48 mA/cm², a FF of 29 % and an efficiency (PCE) of 1.27 % are observed. This is the highest efficiency observed for these devices. However, upon applying a mask to the device the performance of the device drops. Under the 3.8 mm² mask, the device achieved lower values in V_{oc}, J_{sc}, FF and PCE of 0.37 V, 3.91 mA/cm², 27 % and 0.39 %, respectively. The reduction in J_{sc} is to be expected but the reductions in V_{oc}, FF and especially PCE are surprising and counter to what might be expected.



Figure 6.20: J-V characterisation of OPV based on graphene electrode at full area and mask area of the device.

The reduction in the OPVs performance with illuminated area could be related to an increase in the density of contamination on the graphene surface. To further probe the influence of scale area electrodes on the performance of OPVs based on graphene films, the graphene area electrode was optimized at areas of full device illumination, 30mm^2 , and with mask areas of 9, 4, 3.8, 3 and 2.5 mm². There is a steady and systematic improvement in device performance as the area of the device increases from 2.5 to 30 mm² (Figure 6.21 and Figure 6.22). The devices improve from ~0.2% with the 2.5 mm² mask to >1 % for the 30 mm² device. This improvement is a function of both the J_{SC} and V_{OC} of the device, both of which also systematically improve, whilst FF remains constant (Table 6-4). This observed improvement in device performance with device area is counter to what might be expected and can only be explained in terms of charge trap states in the graphene electrode.³⁹²

Figure 6.21 shows the series resistance (Rs) of the device as a function of device area. The Rs shows an inverse relationship to the PCE of the devices, systematically decreasing as the area of illumination increases, as shown in Figure 6.21. Increasing the area of illumination on the graphene electrode OPV appears to improve the conductivity of the electrode. This could be a result of two factors. The distance between average site of exciton generation in the active layer and the contact point on the substrate is reduced with by increasing the illuminated area, effectively reducing the average charge pathway through the graphene.



Figure 6.21: Diagram relationship between PCE and Rs of OPVs based on graphene electrodes and scale areas devices.

However, we have also established that the conductivity of the graphene electrode is reduced by defects and contamination. These defects result in charge trapping and lower the conductivity, reducing device performance. When the device is illuminated these charge traps are initially filled. Once this has happened subsequent charges are free to travel through the graphene, resulting in increased photoconductivity of the graphene in contact with the active layer. As the illuminated region is increased in size, the overall conductivity of the graphene electrode is increased and the device performance increase. Voc also increases since, when the traps are filled, recombination due to these traps is eliminated. Thus, counterintuitively, increasing the mask area results in a direct and systematic increase in device efficiency. This is a result which interestingly suggests that large area graphene electrode based OPVs are maybe more viable that small area devices. Overall, these results are promising for the future of low temperature graphene as electrodes in OPV devices.

Device Type	PCE (%)	V _{oc} (V)	I _{sc} (A)	FF	Cell Area (mm ²)	J _{sc} (mA/cm ²)	Rs (Ω)	Rsh (Ω)
OPV/ G	0.21	0.27	1.52E-04	0.26	2.5	3.04	1.58E+03	1.92E+03
OPV/ G	0.19	0.28	1.31E-04	0.26	3	2.61	2.04E+03	2.33E+03
OPV/ G	0.25	0.27	1.32E-04	0.27	3.8	3.49	1.72E+03	2.33E+03
OPV/ G	0.3	0.30	1.91E-04	0.26	4	3.82	1.35E+03	1.70E+03
OPV/ G	0.88	0.42	3.87E-04	0.27	9	7.75	9.08E+02	1.26E+03
OPV/ G	1.14	0.53	3.29E-04	0.32	30	6.58	6.90E+02	2.42E+03

Table 6-4: J-V analysis of OPV based on graphene electrode at different scale area.



Figure 6.22: J-V characterisation of OPV based on graphene film as a transparent electrode at different scale area.

6.11 The fabrication of inverted OPV based on graphene electrode

Typical OPVs are constructed of polymer layers sandwiched between two electrodes, the anode and cathode, and are generally prepared on a glass substrate. For all OPV architectures, one of the electrodes must be optically transparent to allow light to be absorbed in the active layer in OPVs. Typically, the transparent electrode is the anode of the device as shown previously in the ITO, graphene, PEDOT:PSS and G-SNW devices. OPVs designed in an inverted structure are also possible where the cathode becomes the transparent electrode and these often use a zinc oxide (ZnO) transparent film as the electron transport layer.³⁹³

An inverted structure involving a modified graphene cathode as the window electrode was proposed and assessed. Figure 6.23 shows a schematic of the inverted structure OPV based on graphene film as an alternative transparent electrode with G/ZnO/P3HT:PCBM/MoO₃/Ag layer structure. Devices of the structure ZnO/P3HT:PCBM/MoO₃/Ag are common in the literature and generally achieve good efficiencies whilst avoiding the use of problematic materials like ITO (which is rigid and expensive) and PEDOT:PSS (the acidity of which can lead to device degradation).³⁹⁴ In this investigation, an inverted structure OPV based on a ZnO coated graphene electrode was fabricated and assessed, to attempt to improve the stability and performance of devices. Here we produce a device with graphene film as the cathode electrode covered by ZnO as an electron transporting layer (ETL) and molybdenum oxide (MoO₃) replacing PEDOT:PSS as the hole transport layer (HTL).³⁹⁵ This design should exhibit improved device stability with ZnO inserted between the cathode electrode and the active layer for selective collection of the electrons. Additionally, the top anode layer of the OPV should be more air stable with a high work function metal (silver (Ag)) which is used as anode electrode for hole collection, rather than low work function aluminium (Al).³⁴⁶



Figure 6.23: Device architecture of inverted OPV based on graphene film as a transparent electrode.

In this work, ZnO was dispersed in acetone solvent with a concentration of 38 mg/mL. This dispersion was spin-coated at a coating speed of 5000 rpm for 1 min on top of the graphene electrodes to give a ZnO ETL film with a thickness of 10 nm. Devices were then fabricated with P3HT:PCBM as the active layer under the conditions used for conventional OPVs. A MoO₃ layer was then deposited by thermal evaporation to a thickness of 10 nm. MoO₃ is commonly used as an additional electron blocking layer (hole transport layer) in inverted OPV devices. This layer prevents charge recombination occurring at the polymer blend interface.³⁹⁶ In addition, the work function of Ag has been demonstrated to be 4.3 eV and MoO₃ shifts this upon exposure to oxygen to give better band alignment for the metal/polymer interface layers.³⁹⁷ For comparison, standard inverted devices were also fabricated with a structure of ITO/ZnO/P3HT:PCBM/MoO₃/Ag. Characterisation parameters for the inverted OPV based on graphene as a cathode as well as ITO are presented in Figure 6.24, which presents the J-V performance of the prepared inverted OPV devices. It is clear that there is a short current in OPV circuit based on graphene. The PCE of the inverted device based on a graphene electrode is about 0.15 % by comparison with the standard device at 2.29 % (Table 6-5).

Device Type	PCE (%)	V _{oc} (V)	I _{sc} (A)	FF	Cell Area (mm ²)	J _{sc} (mA/cm ²)	Rs (Ω)	Rsh (Ω)
OPV/ITO- ZnO	2.29	0.55	3.59E- 04	0.47	3.8	9.02	3.46E+02	6.73E+03
OPV/G- ZnO	0.15	0.22	1.08E- 04	0.25	3.8	2.74	1.97E+03	2.04E+03

Table 6-5 J-V characterisation of inverted OPVs based on electrodes of ITO and graphene.

Again we observe a lower performance of devices based on graphene electrodes. We observe a low fill factor (FF) of OPV based on graphene film of 0.25, suggesting again, that the high series resistance of the graphene electrode overrides the diode behaviour of the photoactive materials. The standard device displays normal diode behaviour and reasonable short circuit current density of J_{sc} 9.02 mA/cm² (Figure 6.24a). However, the J_{sc} for the OPV with the graphene anode is much lower at 2.74 mA/cm² reflecting the high sheet resistance of the graphene electrode. In addition the V_{oc} of the OPV drops down to ~0.22 V when the graphene electrode is used, as shown in Figure 6.24b. There is Ohmic contact rather than diode behaviour in this device and clearly it is this ohmic contact between the graphene and the active layer in these OPV devices which is limiting their performance.



Figure 6.24: J-V characterisation of inverted OPVs based on transparent electrodes of (a) ITO, and (b) graphene.

6.12 The performance of silver nanowire with the graphene electrode

Transparent electrodes for OPVs are typically optically transparent to visible light with a high electrical conductivity. It is clear from the previous sections that the conductivity of the graphene electrode is too low to support a high performing OPV. One way of improving the conductivity of the graphene electrode without influence on the transmission of the window electrode could be using a layer of silver nanowires (SNW). Films of SNWs have strong inplane conductivity and good optical transparency.³⁹⁸ They can be used as transparent electrodes for anodes or cathodes with a low sheet resistance to complete the OPV circuit and allowing visible light to pass into active layers and thus generate charge carriers. In this work, to see if the performance of graphene based OPVs could be improved, we have prepared SNW films on graphene electrode on large scale, as depicted in Figure 6.25. SNW solution of 5 ml in water was filtered by centrifuge then dissolved in 2 ml from 95 % ethanol and 5 % ethylene glycol. The film was deposited at 4000 rpm for 1 min and the average of thickness around ~ 20 to 30 nm.



Figure 6.25: Schematic of the OPV structure of P3HT: PCBM active layer based on a graphene/SNW window electrode.

The potential benefit of a SNW covered graphene film is that the silver can form a nanonetwork overcoming the effect of cracks or wrinkles on the electrode resulting from the transfer method. To determine the morphology of the SNW film covered graphene electrode was transferred onto a Si substrate for SEM analysis. Figure 6.26a shows SEM of the SNW coated graphene film, revealing that nanowires do, indeed, cover the surface and provide a continuous network across the film. This architecture should significantly enhance the conductivity of the graphene electrode when film formation with a high uniformity is achieved over the graphene surface. The average length of SNW on the graphene surface is around ~57 nm. Indeed, SNW are a 1D nanomaterial specifically constructed for thin network films which has been shown to exhibit high performance as a transparent conductive film.³⁹⁸ However, many issues such as limited conductive direction, low oxidation resistance and poor adhesion with the substrate can restrict the high performance of SNW networks applied the surface of an electrode.³⁹⁹⁻⁴⁰⁰ Consequently, the complex processing of SNW applied as nano-networks has promoted an entire new field of transparent electrodes for a commercial application.

Energy dispersive X-ray spectroscopy (EDS) was used to compositionally analyse the graphene/Ag as illustrated in Figure 6.26b. The spectrum shows a clearly peaks present due to the carbon of the graphene film and silver from the nanowires. Since the SNW do not provide a complete coverage and the graphene layer is only 1-2 nm in thickness, a strong peak for the silicon substrate is also observed.



Figure 6.26: (a) SEM micrograph, and (b) EDS of G-SNW deposited onto the surface of graphene electrode then transferred onto Si substrate, respectively.

UV-vis transmission spectra and sheet resistance values for the graphene electrode before and after SNW deposition are shown in Figure 6.27a. It shows that electric properties of the graphene electrode are improved after applied the SNW network. The sheet resistance electrode has reduced from 735 Ω/\Box to 511 Ω/\Box ; a reduction of ~30 %. The thickness of SNW was less than 5 nm in order to avoid reducing the light transmission. However, the light transmission still decreased from 65.5 to 55.4 % at 500 nm wavelength; about a 15 % reduction in the transmitted light.

Table 6-6 shows the device parameters for devices with a graphene only electrode (G) and one with the new SNW modified electrode (G-SNW). An increase in the PCE of the devices from 0.39 % for the graphene device to 0.48 % for the G-SNW device are observed; a 23 % increase in efficiency, midway between the observed decreases in resistance and transmission for the electrode, and the best efficiency obtained in this work of a 3.8 mm² device. Again, substantial leakage current is observed in the dark J-V curve of the device (see Figure 6.27b and c). Obviously the challenges to performance of OPVs based on graphene electrodes prepared at low growth temperature still existed in this device, but this approach can be considered a successful stepping stone towards creating a commercial and flexible electrode for future industry applications.

Table	6-6:	J-V	characterisation	of OPV	's bas	ed on	graphene	and	graphene	with	SNW	as
windo	w ele	ctroc	les.									

Device Type	PCE (%)	V _{oc} (V)	I _{sc} (A)	FF	Cell Area (mm ²)	J _{sc} (mA/cm ²)	Rs (Ω)	Rsh (Ω)
OPV/G	0.39	0.39	- 1.43E- 04	0.27	3.8	-3.75	2.15E+03	3.08E+03
OPV/G- SNW	0.48	0.47	- 1.37E- 04	0.29	3.8	-3.60	1.90E+03	3.61E+03



Figure 6.27: (a) UV-Vis light transmission spectra and sheet resistance of G-SNW film in before and after deposited of SNW network layer, (b) current density – voltage (J-V) characteristics of OPV cell made from P3HT: PCBM blend films, based on G-SNW electrode, and (c) based on graphene electrode.

6.13 Conclusion

In conclusion, we have developed a procedure for the fabrication of large area OPV devices based on CVD graphene grown at low temperature. The large area graphene has been successfully transferred into the target substrates by a wet method. This methods allowed for the etching of the Cu catalyst and large areas of graphene could be transferred for electrode applications. The morphology, structural, chemical, and optical properties of graphene films were characterised using AFM, optical microscopy, SEM, XPS and Raman spectroscopy and it was found that multilayer graphene was formed with amorphous carbon present, and that the transfer technique resulted in tears, folding and wrinkles in the graphene electrode. Devices were prepared with the deposited graphene as both as the anode and cathode electrodes. The studies of J-V data for these OPV devices based on graphene have demonstrated that the small graphene flakes produced by low temperature growth and the morphological defects resulting from the transfer method limit device performance. We tried to limit the influence of these parameters to improve the properties of graphene electrode by optimising the process and modifying the graphene surface (with SNW, PEDOT:PSS and ZnO). A large area hero device of 1.14 % efficiency was achieved and methodology for preparing optically transparent, large area, low temperature graphene electrodes presented. This work provides the basis for a promising procedure for applying graphene grown at low temperature to industry applications.

7. Chapter seven: Conclusion and future work

7.1 CVD growth of multi-layer graphene at low temperature

This work has shown that chlorobenzene effusing from a PMMA matrix functions as a carbon source for CVD graphene grown at low process temperatures. The graphene deposited is in the form of multi-layered graphene sheets and flecks of single-layer graphene. The range of graphene layers produced starts from a single carbon atom thickness layer to multi-layered carbon deposited as a mixture of small graphene domains and amorphous carbon. It was demonstrated that the amount of H_2 gas flow could optimise the quality of graphene film produced during the growth phase. The flow affected the number of layers of carbon deposited on the Cu catalyst surface, with regions of single-layer graphene found on the Cu foil surface.

In Chapter three, single-layer graphene was grown on the surface of a Cu foil catalyst within the crystal domains of the catalyst, which had been cleaned by electrochemical-polishing and thermal annealing. The smooth catalyst surface, free of the superficial native copper oxide layer, allowed graphene layers to be deposited from a liquid carbon source on the Cu foil substrate via CVD at 600 °C under different H₂ flow rates. PMMA-chlorobenzene was heated to 180 °C to evaporate and transport carbon atoms into the 600 °C catalysis zone. The H₂ provided a reducing atmosphere to form the graphene layer which was monitored and characterised by Raman spectroscopy. The Raman spectrum features gave a clear indication of film variance with H₂ gas flow rate during growth. AFM imaging provided corroborating evidence for single-layer graphene formed in the low temperature growth regime.

7.2 Using residual organic solvents in a PMMA matrix as the carbon source for low temperature growth

In Chapter four, the formation of continuous graphene layers using different carbon sources on the CVD system was investigated. It was found that the number of layers of graphene deposited was influenced by changing the organic solvent within the PMMA matrix with the range of solvents examined including; p-xylene, toluene, o-xylene, chlorobenzene, dichlorobenzene, dichloromethane, chloroform and acetone. Other carbon sources, pyridine and methanol, were reviewed to probe for any dependencies on benzene ring molecular structures in the source and the effect of heteroatoms in the carbon source. The graphene films produced from different carbon sources were initially identified using Raman spectroscopy and TEM. The analyses showed that graphene films could be fabricated from all of the identified liquid sources. However, these films were of differing sheet resistances and transmissions based on the carbon source.

Generally, the sheet resistance and optical transmission of single and low layer number graphene films from each carbon source were at approximately similar levels. Any low transparency was correlated with the Raman spectrum of the graphene film showing atomic thickness commensurate with multi-layers of carbon and the presence of amorphous carbon.

The domain size of graphene is still small for the low temperature CVD growth process as determined via TEM. Different sizes of graphene domain and multi-layer films were deposited on the catalyst surface because of the low temperature growth conditions and the residual liquid carbon sources from the polymer matrix. As a result, we established a new carbon procedure for the growth of graphene layers by the CVD method at low temperature which could be a new path for improving the method of graphene growth for electronic applications.

7.3 The performance of graphene electrodes applied to OPV cells

The attraction of graphene as a future, low-cost, large-area and the transparent electrode has driven this work. Graphene remains a promising window electrode, and the fabrication process of graphene electrodes for small and large area electrodes in OPV devices has been developed in this work. The architecture of OPVs was successfully amended to incorporate graphene electrodes. There were several challenges in the transfer and cleaning of the large-scale graphene electrode swhen applied to OPV substrates. The process created contamination and defects on the electrode surface causing poor performance. Additional cleaning processes could be useful to reduce the influence of the wet transfer method used in this work. However, it is a complicated process by which to achieve a high purity electrode.

The properties of graphene electrodes were determined to give a comparison to the OPV electrode study. The replacement of ITO electrodes is the end goal of this research, and the measurements in this work have laid a foundation upon which future projects may improve outcomes of low-temperature CVD grown graphene. Specifically:

- The sheet resistance and UV-vis transmission of graphene electrodes were measured by a four-point probe and UV-vis spectroscopy, respectively.
- The work function of the graphene electrode was obtained ~ 4.98 and 5.02 eV for graphene films transferred into Si and ITO substrates, respectively.

The characterisation of work function is promising for the potential of graphene films as window electrodes in OPVs instead of ITO electrodes.

The quality and morphology of graphene electrodes were analysed by Raman spectroscopy after the transfer method to determine the influence of the transfer procedure for large area electrodes. Graphene films were transferred to Si substrates for morphology characterisation by SEM, and this method revealed the contamination and defects left from the transfer method.

XPS and EDS were used to determine details of carbon elemental bonding in the deposited carbon on the surface, differentiating amorphous carbon and oxidised carbon from the graphene. This study was done to assess the quality of deposited graphene achieved for use as a graphene electrode within OPVs, and mainly, as ITO electrodes are the current standard for transparent electrodes, to identify areas of opportunity and drawback for OPV fabrication.

7.4 CVD graphene grown at low temperature as alternative window electrodes on OPVs

The project also demonstrated graphene films as working alternative electrodes on OPVs, where the graphene electrodes were fabricated for small and large area OPV devices. The small devices were continuous active OPV cells with areas ~2mm² up to 5 mm² incorporating low temperature CVD grown graphene electrodes from the chlorobenzene-PMMA carbon source. A comparable performance between graphene and ITO window electrodes was achieved using P3HT:PCBM bulk heterojunction devices, particularly with the J-V characterisation of the OPV cell output from working devices. However, there were pathways for current leakage in the graphene electrode devices caused by the recombination of charges in the active layer. These relate to defects in the electrode arising from the wet graphene transfer process; limiting the efficiency of the graphene electrode OPV compared to an OPV with an ITO electrode. This work identified areas for improvement before moving to large-area graphene electrode OPV fabrication.

Large areas of graphene have been successfully grown and transferred into flexible PET and glass substrates, with the first achievement being a graphene film of more than 10 cm² in area deposited on the Cu foil substrate. There was clear evidence of residual defects, arising from the transfer process, affecting the quality of large-area graphene, as shown in optical transparency and sheet resistance analyses. Never the less, graphene electrode large area P3HT:PCBM OPV devices with efficiencies of greater than 1 % were achieved, proving the potential of graphene as a transparent electrode in these devices.

7.5 Future work

Several planned activities build upon the findings of this project. The optimization of CVD graphene at low temperature involved an H₂ gas parameter study of the influence on the number of layers of films. The impact of growth temperature on the quality of graphene has also been investigated based on chlorobenzene-PMMA as a carbon source. These factors should be incorporated into the growth model. Furthermore, the catalyst has a significant impact on graphene growth under low temperature conditions. Using another catalyst for graphene growth such as Ni, Co and Au and utilising organic solvent-PMMA as carbon source would be an interesting follow-up study. This extension could provide an exciting pathway for further mechanistic understanding and to improve the quality of graphene at these conditions. Additionally, mechanical growth modelling at the current growth conditions should be undertaken to understand the growth process and to explain the interactions inside the CVD tube during graphene layer formation.

The carbon bonds of CVD sources and their importance during the growth process require a more chemistry orientated investigation model. The bond dissociation energy of the carbon source is critical at low growth temperatures, and further investigation of the influence of this factor on graphene growth and quality is required.

The graphene electrodes investigated here contain many defects which result in charge trapping and reduce the device efficiency. Light soaking led to the saturation of these trap states and increased device efficiency above 1 %, as demonstrated in Chapter 6. The nature and degree of these trap sites should be further investigated, as minimising or eliminating these sites could dramatically improve the performance of these devices. The proposed mechanisms presented in this thesis can be compared with the well-known high temperature (>900 °C) graphene growth mechanism where C atoms firstly are dissolved into catalyst's bulk atomic matrix and then diffuse to surface at the cooling stage to form a single layer graphene. By contrast, the low temperature (<800 °C) graphene growth mechanism, in particular the single-layer graphene formation, is ill-understood. How surface catalyst atoms promote the C-H or C-Cl bond breaking and C-C bond formation is not discussed in the literature. Most likely, it involves a surface-mediated catalytic reaction pathway, which should be of interest in future work to elucidate the surface-mediated catalytic mechanism.

Upon understanding the lower temperature growth mechanism, the second step is to create a surface catalyst by depositing an optically transparent, thin layer of catalyst material onto an ideal substrate that is suitable for organic solar cell fabrication. By doing so, there would be no need to etch off the catalyst layer, which would eliminate the problematic transfer step. This modification would provide an advantage for large-area production and would be compatible with roll-to-roll (R2R) printing OPV production.

Furthermore, it is essential to look for a combination of carbon source and catalyst that can grow good quality graphene layers with an acceptable level of transparency and sheet conductance under 300 °C, which is the highest heat tolerance that plastic material can sustain. The flexible plastic substrate is an essential criterion for successful (R2R) OPV production.

Overall, this work is a significant advance in the preparation of a large area flexible of OPV based on a graphene electrode. The recent progress of this project demonstrates the potential for improving and applying graphene at large area production with low growth temperatures and low cost in industrial applications. In addition, further work on the life time of those devices and a cost comparison to the existing PV can be done to justify the importance of my studies using graphene as the electrode.

Appendix: Conferences and awards





This is to Certify that

ALAA YOUSIF ALI

Presented in the Inaugural postgraduate Art in MAPS exhibition held on the 23rd of May 2017 and

WON SECOND PRIZE

of a \$200 Westfield Voucher

Dr Michael Gladys School of Mathematical and Physical Sciences The University of Newcastle

CERTIFICATE



CERTIFICATE OF ATTAINMENT

BEST STUDENT PRESENTATION - POSTER

THIS IS TO CERTIFY THAT

ALAA YOUSIF ALI

WAS AWARDED THE PRIZE OF \$1,000 FOR HAVING PRESENTED THE BEST POSTER BY A STUDENT AT THE SMART FUTURE CITIES 2015 CONFERENCE, NEWCASTLE.

> Professor Tim Roberts Conference Organiser and Director Tom Farrell Institute for the Environment The University of Newcastle. 7th October 2015.

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