THE GROWTH OF GRAPHENE/GRAPHITE
THIN FILM ALLOTROPES ON COPPER
SUBSTRATES

by
Kasman, S.Si., M.Si.

Thesis submitted for the degree of Doctoral of Philosophy (Physics)
The University of Newcastle
17 February 2014
DECLARATION

This thesis contains no material which has been accepted 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 in the text. I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying subject to the provisions of the Copyright Act 1968.

Callaghan, 17 February 2014

..................................................

Kasman, S.Si, M.Si
ACKNOWLEDGEMENT

First and foremost, I praise and acknowledge Allah SWT, for giving me the blessing, strength, health and knowledge to finish this thesis. Salawat and salam also propose to the Prophet Muhammad (peace be upon him), the Uswatun Hasanah for all moslems.

I acknowledge the Indonesian Directorate General of Higher Education (DIKTI) for financing and giving me the opportunity to achieve my PhD degree at the University of Newcastle. I also give thanks to the University of Newcastle for awarding me the tuition fee and completion scholarship.

I am heartily thankful to my supervisors, Prof. Dr. Paul Dastoor, for his excellent guidance and providing me with an excellent atmosphere for doing research, Dr. Warwick Belcher who always appreciates and supports to my works, and Dr. Xiaojing Zhou who gives valuable suggestions to find the best recipe for the graphene growth and shares a deep scientific knowledge about my work.

I would like to thank the members of the Centre for Organic Electronics for their assistance, cooperation, guidance and friendship. In particular, Dr. Glenn Bryant, for always being available whenever I needed help with equipment and explaining how the equipment works. Dr. Chhinder S. Bilen for discussing the polymer-based carbon source. Dr. Ben Vaughan and Elisa Sesa, for discussing the structure of graphene-based device. Dr. Daniel Elkington, for correcting my thesis writing. My fellow PhD students – Darmawati, Syahrul, Azzul, Nic, Natalie, Mitchel, Dr. Bofei, Clara and everyone else – thanks for being so easy to get on with and so friendly. Without their co-operation I could not have completed my PhD.

Finally, and most importantly, I would like to thank to my wife, Rinawaty Kato, and my lovely son, Alam Surahman Cakmar, for their quiet patience, continuous support and prayer. Without them, I would never have made it as far as I did.
“This thesis is dedicated to H. Sulaiman, Rinawati Kato and Alam Surahman Cakmar, and to all my extended family”.
Graphene, a monolayer of graphite, has drawn a great deal of attention for organic electronic applications. Excellent optical transmittance combined with its extraordinary electrical properties makes it an attractive material for using as a transparent, conductive electrode in the fabrication of organic solar cells (OSCs). To bring graphene to mass production, synthesis methods are required for its growth as a large-area film. Chemical vapour deposition (CVD) is a novel technique proposed to produce high quality, large-area graphene films. Recently, the use of copper as a catalyst for graphene growth has been more popular compared with other metals since the carbon solubility in copper is much lower, allowing better control over the number of graphene layers. Here, we report optimisation of graphene growth on two different copper substrates - copper foil and thin copper film - at low temperatures (below 500 °C) using poly(methyl methacrylate) (PMMA) as a carbon source. It was found that the 140 °C heated precursor promotes the growth of a mono-layer graphene, while the 400 °C heated precursor results in multi-layer graphene. For optimisation, three different temperature parameters, including the annealing temperature of the copper substrates (T_{anneal}), precursor temperature (T_{precursor}) and growth temperature (T_{growth}), have been identified and independently studied. Firstly, the optimal T_{anneal} of the copper substrates prior to graphene deposition was required to be sufficiently high (> 900 °C) to cause the recrystallisation of large Cu grains in the substrate surface. Secondly, T_{precursor} needs to be high enough to produce volatile precursor fragments which subsequently decompose on the catalyst surface. In the case of PMMA, this requires T_{precursor} > 140 °C. Finally, T_{growth} has to be sufficiently high to activate carbon diffusion and rearrangement on the catalyst surface. Particularly, this temperature needs to be at least 450 °C for a Cu foil catalyst. By working at the T_{anneal} of 900 °C, it was also found that the Cu foil substrate annealed for 10 minutes under hydrogen flow rate of 100 sccm and the thin Cu film substrate annealed for 1 hour under hydrogen flow rate of 50 sccm were the optimal annealing conditions. A pre-thermal annealing study of the copper substrates was undertaken to examine the change of structural and morphological properties. In this study, it was found that the substrates have a good nanocrystalline cubic structure,
dominated by (100) with the crystallize size of ~ 200 nm and (111) planes with the crystallite size of ~ 100 nm for the Cu foil and the thin Cu film, respectively. This treatment also showed that the hydrogen reducing gas effectively removes the copper oxide impurities. Moreover, the samples annealed beyond 900 °C have a smooth surface morphology with uniform coverage and grain sizes ~ 1.3 and ~ 88 µm for thin Cu film and Cu foil, respectively. The annealed copper substrates were further used as catalysts for growing graphene. By working at a growth temperature of 450 °C, the graphene growth time on the Cu foil catalyst and the thickness of thin Cu film catalyst were also optimised, and were found to be 1 minute and 500 nm, respectively. The transmittance of graphene films resulting from the growth on both of the substrates was above 85%. However, their electrical properties were significantly different; the lowest sheet resistances obtained were 1.2 and 14.0 kΩ/□ for the graphene growth on the Cu foil and thin Cu film catalysts, respectively. These results are much higher compared to the best reported R_{sheet} for single-layer graphene (ca.350 kΩ/□) [1-3]. For the processed graphene/graphite films used as a transparent, conductive electrode for fabricating OSC devices, they demonstrated working devices with PCEs of between 0.07 - 0.36 %. The low PCEs of the fabricated devices were due to the high sheet resistance (a few kΩ/sq) of these device electrodes.
Identifying the key thermally activated process at low temperature growth of thin graphitic films on thick copper substrates. Journal of Physical Chemistry C.

Optimizing thin copper film catalysts for the low temperature growth of thin graphene/graphite films. Thin solid Film
# TABLE OF CONTENTS

ACKNOWLEDGEMENT

ABSTRACT

PAPERS IN PREPARATION.

TABLE OF CONTENTS

LIST OF FIGURES.

LIST OF TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

---

1. Introduction and Motivation

   1.1 Motivation

   1.2 Research Objectives

   1.3 Transparent Electrodes

   1.4 Conductive Carbon

      1.4.1 Amorphous Carbon

      1.4.2 Graphite

   1.5 CVD Graphene/Graphite Growth

   1.6 Low Temperature Graphene/Graphite Growth

   1.7 Organic Electronics Application (Study Case: Organic Solar Cells)

      1.7.1 Organic Solar Cell (OSC) Design and Operation Principles

      1.7.2 Characterization of OSCs

   1.8 Thesis Outline

2. Experimental Procedure

   2.1 Preparation

      2.1.1 Carbon Source

      2.1.2 Copper Catalyst

---

viii

v

vii

viii

xii

xviii

xx

1

3

5

6

6

7

14

15

16

16

16

18

22

24

24

24

26
2.2 Graphene Fabrication ........................................................................................................29
2.3 Transfer Process .............................................................................................................30
2.4 OSC device Fabrication ..................................................................................................33
2.5 Characterisation .............................................................................................................34
   2.5.1 Scanning Electron Microscopy (SEM) .................................................................34
   2.5.2 UV-vis Spectroscopy ............................................................................................35
   2.5.3 Transmission Electron Microscopy (TEM) ..........................................................38
   2.5.4 Profilometer ..........................................................................................................40
   2.5.5 Four-point probe conductivity ..............................................................................41
   2.5.6 Atomic Force Microscopy (AFM) ........................................................................44
   2.5.7 Thermogravimetric Analysis (TGA) ....................................................................45
   2.5.8 X-ray Diffraction ....................................................................................................46
   2.5.9 Raman Spectroscopy .........................................................................................48
   2.5.10 OSC device I-V characterization ........................................................................50

3. A Comparative Study of the Effect of Thermal Annealing on the Morphology of
   Copper Foils and Thin Copper Films as Catalysts for Graphene Growth ......................54
   3.1 Introduction ................................................................................................................55
   3.2 Experimental Setup ....................................................................................................58
   3.3 Results and Discussion ...............................................................................................60
      3.3.1 Effect of Annealing Temperature ......................................................................62
      3.3.2 Effect of Annealing Time .................................................................................67
      3.3.3 Effect of Hydrogen Flow Rate ..........................................................................72
      3.3.4 Crystallite and Grain Sizes ................................................................................78
   3.4 Conclusion ..................................................................................................................85

4. Low-Temperature Growth of Graphene on Copper Foil Using PMMA-Derived
   Carbon Source ................................................................................................................86
   4.1 Introduction ................................................................................................................86
   4.2 Experimental Setup .....................................................................................................88
      4.2.1 Sample Preparation ..........................................................................................88
## TABLE OF CONTENTS

4.2.2 Graphene Growth .......................................................... 90
4.2.3 Graphene Transfer .......................................................... 92
4.2.4 Characterisation ............................................................ 94

4.3 Results and Discussion .......................................................... 99
4.3.1 Different annealing temperatures of copper foil for graphene growth ....... 100
4.3.2 Comparison of graphene growth on different temperatures ....................... 101
4.3.3 The influence of the precursor temperature on Graphene growth ............... 106
4.3.4 The variation of graphene growth time ...................................... 111

4.4 Conclusion ............................................................................ 117

5. Low-Temperature Growth of Graphene/Graphite on Evaporated Thin Copper with Direct Transfer on Target Substrate 118
5.1 Introduction ........................................................................... 118
5.2 Experimental Details ............................................................. 121
5.3 Results and Discussion ............................................................ 123
5.3.1 Effect of Copper Catalyst Film Annealing Temperature ......................... 123
5.3.2 Effect of Copper Catalyst Film Thickness ............................................ 126
5.3.3 Effect of Lower Precursor Temperature ............................................. 131
5.3.4 Effect of Lower Copper Catalyst Annealing Temperature ...................... 137

5.4 Conclusion ............................................................................ 142

6. Organic Solar Cell Fabrication with Graphene/Graphite-Based Carbon Electrode 144
6.1 Introduction ........................................................................... 144
6.2 Experimental Setup ............................................................... 147
6.2.1 Structure of OSC devices ....................................................... 147
6.2.2 Preparation of target substrate ................................................. 148
6.2.3 Anode Deposition ............................................................... 150
6.2.4 PEDOT:PSS deposition ....................................................... 152
6.2.5 Active layer deposition ........................................................ 154
6.2.6 Cathode evaporation ........................................................... 155
6.3 Results and Discussion...........................................................................................................157
  6.3.1 Preparation and characterisation.....................................................................................157
  6.3.2 Organic solar cell performance.......................................................................................159
  6.4 Conclusion ........................................................................................................................163

7. Conclusion and Future Work ..............................................................................................164
  7.1 Conclusion ........................................................................................................................164
  7.2 Future Work.......................................................................................................................167

References .................................................................................................................................xxiii
LIST OF FIGURES

Figure 1.1 The development of the annual average price of indium [24]......................... 3
Figure 1.2 The three bond hybridisations found in carbon: sp\(^3\), sp\(^2\) and sp\(^1\) [43]........... 7
Figure 1.3 The crystal structure of graphite. The primitive unit cell is hexagonal, with .......... 8
Figure 1.4 (a) Graphene structure of single 2D-hexagonal sheet of carbon atom, ............... 10
Figure 1.5 (a) Optical image of a graphene film with different thickness, (b) Raman image plotted by the intensity of G band, and (c) Raman spectra as a function of number of layers [64]. .................................................................................. 13
Figure 1.6 High-magnification TEM images of different graphene layers [2]..................... 13
Figure 1.7 A typical five-layer structure of bulk heterojunction (BHJ) OSC devices........... 17
Figure 1.8 Operation principle of BHJ solar cell from charge generation to charge collection. ......................................................................................................................... 18
Figure 1.9 Graph of current versus voltage for OSC devices showing how the device characteristics change upon illumination and indicating the key points on the graph [87]. ................................................................................................................. 19
Figure 1.10 A typical circuit diagram used to model OSC devices ...................................... 22
Figure 2.1 Chemical structure of PMMA ................................................................................. 25
Figure 2.2 SEM images of the uncleaned (left) and cleaned (right) copper foils. (scale bar : 100 µm) ................................................................................................................................. 26
Figure 2.3 The Atomate CVD system ...................................................................................... 27
Figure 2.4 SEM images of (a) thin Cu film and (b) Cu foil before treatment. (scale bar : 200 nm) ................................................................................................................................. 28
Figure 2.5 Schematic diagram of graphene growth in the CVD system............................... 29
Figure 2.6 Schematic diagram of the transfer process of Cu foil-grown graphene film ......... 31
Figure 2.7 Schematic of the etching of thin Cu film ................................................................. 32
Figure 2.8 (a) Graphene substrate with marked active area of 4 mm\(^2\), (b) The device structure of graphene/PEDOT:PSS/P3HT:PCBM/Ca/Al. .................................................. 34
Figure 2.9 (a) Zeiss Sigma VP SEM of the University of Newcastle and (b) Schematic diagram of the SEM [100]. ................................................................. 35
Figure 2.10 UV-vis spectrophotometer .......................................................... 36
Figure 2.11 Optical diagram of spectrophotometer .......................................... 37
Figure 2.12 Photograph (left) [108] and schematic (right) of TEM system .......... 39
Figure 2.13 A photograph of 200 mesh holey carbon TEM grid used as the sample support ................................................................. 40
Figure 2.14 (a) KLA-Tencor Alpha step 500 profilometer, (b) Schematic set-up of the profilometer measurement system ........................................ 41
Figure 2.15 (a) four-point probe resistance measurement, (b) schematic of four-point probe configuration for thin rectangular slide sample ...................... 42
Figure 2.16 (a) Schematic of AFM system, (b) AFM system used in the characterisation of samples ........................................................................ 45
Figure 2.17 Perkin-Elmer Diamond TG/DTA used in characterising the thermal degradation of PMMA [116] ................................................................. 46
Figure 2.18 Schematic illustration of the diffracted beams .................................. 47
Figure 2.19 Philips X’Pert MPD XRD used in characterising the samples ............ 48
Figure 2.20 Schematic diagram of the Raman system (top) [122, 123], photograph of UNSW Renishaw inVia Raman microscope system (bottom) .......... 49
Figure 2.21 The zenith angle of the sun (top) and the solar radiation spectra of AM0 & AM1.5[125-127] ........................................................................... 51
Figure 2.22 Newport AM1.5 solar simulator with a sample holder used in testing the OSC devices ................................................................. 52
Figure 2.23 Experimental setup of device I-V characterisation .......................... 53
Figure 3.1 Schematic of the effects of annealing treatment: (a) recovery, (b) recrystallisation, and (c) grain growth ......................................................... 57
Figure 3.2 Schematic of the Atomate CVD furnace used for annealing the copper .... 60
Figure 3.3 XRD spectra of the as-received Cu foil (top) and the as-evaporated Cu thin film (bottom) ................................................................. 61
Figure 3.4 XRD profiles measured at room temperature of the as-received and annealed copper foils ................................................................. 62
Figure 3.5 SEM images of the copper foils annealed for 10 minutes at 700, 800, 900 and 950 °C (scale bar: 100 µm) ................................................................. 64
Figure 3.6 XRD patterns of the as-evaporated and annealed thin copper film samples. ........ 65
Figure 3.7 SEM images of thin copper films annealed at different temperatures for 10 minutes. .................................................................................................................................................. 66
Figure 3.8 XRD patterns of the copper foil samples annealed for 10, 30, 60 and 90 minutes at 900 °C ......................................................................................................................... 68
Figure 3.9 SEM images of copper foil annealed at 900°C for 10, 30, 60 and 90 minutes. (scale bar: 100 µm) ................................................................................................................ 69
Figure 3.10 XRD patterns of the thin copper films annealed at 450 °C for different times of 2, 5 and 20 hours .................................................................................................................................. 70
Figure 3.11 SEM images of thin copper film annealed at 450 °C for 0, 1, 3, 5, 10 and 20 hours. ......................................................................................................................................... 71
Figure 3.12 SEM images of copper foils annealed at 900 °C for 10 minutes under different flow rates of hydrogen gas ................................................................. 74
Figure 3.13 SEM images of thin copper film at 450 °C for 1 hour under different flow rates of hydrogen gas (scale bar: 1 µm) ................................................................................ 75
Figure 3.14 EDS analysis of the sample annealed at 450 °C under the hydrogen-free atmosphere by applying two different energies of 2 and 10 keV ............. 76
Figure 3.15 XRD profile of the thin copper film annealed at 450 °C under the hydrogen-free atmosphere ................................................................................................................ 77
Figure 3.16 Illustration for measuring the FWHM of a diffraction peak ................................ 79
Figure 3.17 SEM image of 800 °C-annealed copper foil with high brightness and contrast. ...... 81
Figure 3.18 Crystallite and grain sizes on Cu foil (above) and thin Cu film as a function of annealing temperature ...................................................................................... 83
Figure 4.1 Furnace temperature versus time graph for the annealing process, with the corresponding argon and hydrogen flows ....................................................... 89
Figure 4.2 Photograph of as-received (left) and as-annealed (right) copper foil. .............. 89
Figure 4.3 Schematic of the graphene growth from PMMA-derived carbon source on Cu foils ....................................................................................................................................... 91
Figure 4.4 Schematic mechanism of graphene growth involving the decomposition of PMMA ......................................................................................................................... 92
Figure 4.5 Schematic diagram of the process of transferring a Cu foil-grown graphene film. ................................................................. 94
Figure 4.6 SEM image of graphene grown on copper foil................................. 95
Figure 4.7 Comparative Raman spectra of a graphene film grown on copper foil (top) and a blank copper foil (bottom). Regions scanned are indicated with dashed circle in optical microscopy images. ........................................ 96
Figure 4.8 Optical image of graphene film on quartz substrate.......................... 97
Figure 4.9 SEM images of a graphene film after transferring onto the ITO-coated glass substrate.................................................................................. 97
Figure 4.10 UV-vis absorption spectroscopy of the transferred graphene on a quartz substrate (growth temperature at 450 °C)........................................... 98
Figure 4.11 TEM images of graphene film transferred on TEM grid with low magnification (a) for imaging and high magnification (b) for calculating the number of the layers. (scale bar : 20 nm) ........................................... 99
Figure 4.12 Raman spectra of the films grown on copper foil annealed at temperatures of 600, 700, 800 and 900 °C. .................................................... 100
Figure 4.13 Comparative SEM images of the samples grown at temperatures of 350 °C (top) and 450 °C (bottom) on copper catalyst................................. 102
Figure 4.14 Comparative SEM images of the samples grown at 350 °C (top) and 450 °C (bottom) on copper catalyst after transferred onto the ITO-coated glass. .... 103
Figure 4.15 UV absorption spectra of the samples grown at 350 and 450 °C.................. 104
Figure 4.16 Raman spectra obtained from the samples grown at 350 and 450 °C............. 105
Figure 4.17 TEM images of the samples grown at 350 °C (top) and 450 °C (bottom). .......... 106
Figure 5.1 Schematic diagram of graphene growth in the CVD system......................... 122
Figure 5.2 UV-vis absorption spectra of films grown at 450 °C for 1 minute using thin copper films annealed at four different temperatures of 600, 700, 800 and 900 °C for 1 hour................................................................. 124
Figure 5.3 Raman spectra of samples grown at 450 °C for 1 minute using thin copper films annealed at four different temperatures of 600, 700, 800 and 900 °C for 1 hour................................................................. 125
Figure 5.4 The FWHM of 2D peak on sample S4. ................................................. 125
Figure 5.5 Electrical conductivity of the film samples grown from the evaporated thin copper with different annealing temperatures of 600, 700, 800 and 900 °C. .... 126
Figure 5.6  The SEM images with two different magnifications of 5,000x (left) and 100,000x (right) on the 200 nm copper film thickness after annealing at 900 °C for 1 hour with the scale bars of 10 µm and 200 nm, respectively.................... 128

Figure 5.7  The SEM images with two different magnifications of 50,000x (left) and 100,000x (right) on the 500 nm copper film thickness after annealing at 900°C for 1 hour with the scale bars of 1 µm and 200 nm, respectively.......................... 128

Figure 5.8  The corresponding Raman spectra recorded from the areas marked with dashed circles in optical micrographs on the copper samples (a), the two different areas (bright and dark) of sample S5 (b) and sample S6 (c).......................... 130

Figure 5.9  Optical images of the as-evaporated thin copper (a), the annealed thin copper (b), the graphene-grown thin copper (c) and the graphene film on quartz substrate (d). ........................................................................................................ 132

Figure 6.1  The structures of fabricated OSC devices. ................................................................. 148

Figure 6.2  The scheme of preparation for making a patterned ITO-coated glass substrate..... 149

Figure 6.3  ITO substrate OSC devices............................................................................................ 150

Figure 6.4  Quartz substrate OSC device......................................................................................... 151

Figure 6.5  The Laurell spin coater used for depositing the thin layers..................................... 152

Figure 6.6  The process of removing PEDOT:PSS from the ITO finger and common contacts of the ITO (top) and graphene (bottom) substrates................................................. 153

Figure 6.7  The visible transmission spectra for the PEDOT:PSS and ITO.................................. 154

Figure 6.8  Photograph of the (a)sample holder for evaporation and (b) evaporation system................................................................................................................................. 155

Figure 6.9  The masks used for evaporating the Ca/Al on the OSC devices: (a) the ITO-based OSC device with the design A, (b) the graphene/graphite/PEDOT:PSS-based OSC device with the design A, and (c) the graphene-based OSC device with the design B. .................................................................................... 156

Figure 6.10  The active cell areas of fabricated OSC devices using the different evaporation masks. ............................................................................................................................................... 156

Figure 6.11  AFM images for graphene A (a), graphene B (b), graphene C (c), ITO (d) and PEDOT:PSS (e) (scan size : 5µm x 5µm). ....................................................................................... 159

Figure 6.12  Current density-voltage (J-V) curves of the structure A-based OSC devices with graphene A, graphene B, graphite and ITO as the transparent electrodes, respectively........................................................................... 161
Figure 6.13 Current density-voltage (J-V) curves of the structure B-OSC devices with graphene C and PEDOT:PSS coating as the transparent electrodes, respectively................................................................. 161
Table 2.1 A typical recipe used in annealing copper catalyst. .................................................. 28

Table 2.2 A specific recipe used in growing graphene film. .................................................. 30

Table 2.3 Correction factor \( C\left( \frac{b}{s}, \frac{a}{b} \right) \) for the measurement of sheet resistance with the four-point Probe. ................................................................. 43

Table 3.1 The variation of experiment conditions for studying the effects of thermal annealing on the microstructure of copper foil and thin copper films. ......................... 59

Table 3.2 Average crystallite size of the as-received and annealed copper foil at various temperatures. ............................................................................................................. 81

Table 3.3 Average crystallite size of the copper foil annealed at 900 °C for various times. ..... 82

Table 3.4 Average crystallite size of the as-evaporated and annealed thin copper film .......... 82

Table 3.5 Average crystallite size of the thin copper film annealed at 450 °C for various times. .......................................................................................................................... 82

Table 4.1 A particular recipe used in growing graphene films ................................................. 91

Table 4.2 Sheet resistance and transparency of graphene films grown on the 900 °C-annealed Cu foil substrates. .................................................................................................. 101

Table 4.3 The values of \( I_{2D}/I_G \) ratio obtained from bright and dark areas on the samples grown for different exposure times. ................................................................. 115

Table 4.4 Sheet resistance and transparency of graphene films grown on the 900 °C-annealed Cu foil substrate with the optimal growth conditions. .............................. 116

Table 5.1 The \( I_{2D}/I_G \) intensity ratio and the FWHM of 2D peak of graphene on the glass. ...... 131

Table 5.2 Sheet resistance and transparency of the samples grown on the thin Cu film for different times. ............................................................................................................. 139

Table 6.1 Summary of the properties of OSC devices employing graphene as a transparent electrode ........................................................................................................... 146

Table 6.2 The transparency and sheet resistance of the bottom electrodes prepared for building OSC devices. ................................................................. 158

Table 6.3 Performance details of OSC devices ........................................................................ 162
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Length of sample</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>AM1.5</td>
<td>Air Mass 1.5: Reference Solar Spectrum for OSC characterisation</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>a-C</td>
<td>Amorphous carbon</td>
</tr>
<tr>
<td>b</td>
<td>Width of sample</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Heterojunction</td>
</tr>
<tr>
<td>DLC:H</td>
<td>Hydrogenated diamond-like a-C</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>G</td>
<td>Graphene</td>
</tr>
<tr>
<td>GE</td>
<td>Graphene electrode</td>
</tr>
<tr>
<td>GLC</td>
<td>Graphitic-like a-C</td>
</tr>
<tr>
<td>G(s,t)</td>
<td>Proportionality constant depending upon the geometry of sample</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>I</td>
<td>Electrical Current</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage Characterisation</td>
</tr>
<tr>
<td>LG</td>
<td>Large-area graphene</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>MPP</td>
<td>Maximum Power Point</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>OSC</td>
<td>Organic Solar Cell</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PCBM</td>
<td>Phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>PEDOT</td>
<td>poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PLC:H</td>
<td>Hydrogenated polymeric-like a-C</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PSS</td>
<td>poly(styrenesulfonate)</td>
</tr>
<tr>
<td>( P_{\text{max}} )</td>
<td>Maximum Power Point of I-V Curve</td>
</tr>
<tr>
<td>QHE</td>
<td>Half-integer quantum Hall effect</td>
</tr>
<tr>
<td>( R )</td>
<td>Resistance</td>
</tr>
<tr>
<td>( R_q )</td>
<td>Root mean surface roughness</td>
</tr>
<tr>
<td>( R_s )</td>
<td>Series Resistance</td>
</tr>
<tr>
<td>( R_{\text{sh}} )</td>
<td>Shunt Resistance</td>
</tr>
<tr>
<td>( R_{\text{sheet}} )</td>
<td>Sheet Resistance</td>
</tr>
<tr>
<td>( s )</td>
<td>Distance between two neighboring tungsten pins (2 mm)</td>
</tr>
<tr>
<td>( \text{scmm} )</td>
<td>Standard cubic centimeter per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>( t )</td>
<td>Thickness of sample (mm)</td>
</tr>
<tr>
<td>TAC</td>
<td>Tetrahedral a-C</td>
</tr>
<tr>
<td>( T_{\text{ANNEAL}} )</td>
<td>Annealing temperature of copper catalyst</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>( T_{\text{GROWTH}} )</td>
<td>Growth temperature</td>
</tr>
<tr>
<td>( T_{\text{PRECURSOR}} )</td>
<td>Precursor temperature</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>( V_{\text{max}} )</td>
<td>Voltage at MPP</td>
</tr>
<tr>
<td>( V_{\text{oc}} )</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Conductivity (S/cm)</td>
</tr>
<tr>
<td>$C\left(\frac{b}{s}, \frac{a}{b}\right)$</td>
<td>Additional dimensionless correction factor</td>
</tr>
</tbody>
</table>
Introduction and Motivation

The main focus of this thesis was to grow thin films of graphene/graphite allotropes at low temperatures and to assess their suitability for use as an alternative transparent electrode in organic solar cells (OSCs). This chapter will briefly introduce the motivation and research objectives and also provide some relevant information on subjects including transparent electrodes, conductive carbon, graphene growth and OSC fabrication.

1.1 Motivation

Graphene, a monolayer of graphite, as an alternative transparent electrode material has drawn a great deal of attention in organic electronic research fields. Many applications in electronic technologies have been reported in the recent literature including light-emitting diodes [4], field-effect transistors [5], transparent conducting electrodes [6, 7], organic memory devices [8], sensor [9] and solar cells [10-13]. A key graphene application is as a transparent, conductive electrode in the fabrication of OSCs due to its extraordinary electrical and optical properties [14-18]. Indeed, graphene has been proposed as one of the most promising organic materials for the commercial fabrication of OSCs [19].
Currently, transparent electrodes in solar cell technologies are dominated by metal oxide films. Indium tin oxide (ITO) is one of the most widely used metal oxide electrodes as it has a low sheet resistance coupled with a high optical transmittance. For typical high-quality ITO electrodes, the sheet resistance is below 36 Ω/sq with a transmittance of over 80% [20-22]. However, limited indium resources and an increasing demand from the rapidly expanding display market have increased the cost of ITO significantly, which presents a serious risk to the realisation of low cost and large scale OSC fabrication. In 2010, the price increased to up to $640/kg [23]. The cost increase is also shown on the graph of indium price development, after decreasing sharply in 2009 (Figure 1.1) [24]. In addition to the high prices, the deposition of ITO onto substrates is typically through a sputtering process, which requires high vacuum conditions thereby increasing fabrication costs as well as the energy payback time. Other drawbacks of ITO appear to be mainly due to (1) the occurrence of ion diffusion from ITO in to the active layer, (2) the poor transparency in the near-infrared region, (3) the instability of ITO towards acids or bases, and (4) the limited application for flexible devices due to the brittle nature of indium [25-29]. Hence, alternative electrode materials for ITO that are sustainable and economically viable, as well as having high transparency, excellent conductivity, chemically good stability and flexibility are urgently needed for the future development of organic solar technology. With the discovery of graphene for use as a transparent electrode in organic solar cells, this development becomes possible.
1. Introduction and motivation

In this thesis, the possibility of graphene growth by heating a solid carbon source in a chemical vapour deposition (CVD) system, is explored using a number of fabrication approaches, with a focus on growing graphene at a relatively low temperature (\(<500\) °C). The mechanism of film formation is studied and preliminary transparent conducting electrodes for OSC devices are produced and characterised.

1.2. Research Objectives

The research objectives of this work are to synthesize scalable graphene films using CVD at temperatures below 500 °C and to use these new materials as the transparent electrode for organic solar cells replacing ITO. The technical objectives are as follows:

1. Investigation of thermal effects on copper catalyst

In this study, copper has been chosen as catalyst for graphene synthesis due to its low carbon solubility (\(<0.001\) atomic%) \(\text{[30]}\) at elevated temperatures allowing greater control over the number of graphene layers. The unannealed Cu foil has a
much smaller grain size with a vast number of grain boundaries which allow multilayer graphene growth. The boundary effect can be reduced by forming a larger Cu grain size via annealing, since it facilitates the growth of larger graphene flakes [27]. Therefore, it is necessary to study the thermal effect on copper substrates by annealing at different temperatures, for different annealing times and under different hydrogen flow rate. The annealed copper substrates are characterised by using scanning electron microscopy (SEM), X-ray diffraction (XRD) energy dispersive X-ray spectroscopy (EDS) analysis. The changes in properties such as crystallinity and surface morphology on the Cu catalyst due to the pre-thermal treatment are reported.

(2) Low-temperature graphene growth on copper foil

In this work, CVD is selected due to being the most promising technique to produce scalable graphene films, as reported by the present literature [1, 31-33]. Using CVD, the graphene grown on annealed Cu foils is conducted at temperatures below 500 °C by using a poly (methyl methacrylate) (PMMA) precursor deposited on glass slides. The resulting graphene films are characterised by various techniques including ultraviolet-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM), SEM, profilometer, four-point probe resistivity measurement and Raman spectroscopy to evaluate the influence of the annealing temperature of Cu foil, growth temperature, precursor temperature and growth time. These techniques allow for optimisation of the conditions for growing graphene at low temperatures.

(3) Low-temperature graphene growth on evaporated thin copper film

By maintaining the synthesis temperatures and carbon source from the previous stage, a more efficient way to produce a graphene-based carbon electrode is developed. The electrode is directly grown on the thermally deposited Cu substrate. The resulting graphene films are characterised by various techniques such as UV-vis spectroscopy, SEM, atomic force microscopy (AFM), profilometer, four-point probe resistivity measurement and Raman spectroscopy to evaluate the influence of the annealing temperature of thin Cu film, catalyst thickness, growth time, lower
1. Introduction and motivation

precursor temperature and the lower annealing temperature of the substrate. Using this technique, there is reduced damage to the film because all transfer processes have been eliminated.

(4) Organic solar cell fabrication with graphene-based carbon electrode

As reported in the existing literature [10, 12, 13, 34-36], the efficiency of graphene-based OSCs is not yet comparable to that of their ITO-based counterparts. Therefore, a study on the surface quality of graphene layer is of great interest and importance to understand graphene based OSCs. In this work, studies using graphene anodes which are produced by different methods are conducted.

1.3 Transparent Electrodes

Many alternative transparent electrode materials have been developed in order to replace ITO, such as metal grids [28, 37], metallic nanowires [38], conductive polymers like poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) [29, 39], and carbon nanotubes (CNTs) [30, 40]. Amongst them, CNT films show high transparency across the visible light spectrum and the individual CNTs have high conductivity. However, the junctions between CNTs have a high resistance resulting in a limitation to conductive pathways within the films. Additionally, the high surface roughness of such films and the high energy consumption of the preparation process limit its further application. Thus, CNTs films are currently not competitive with ITO as transparent electrodes for practical applications [41, 42].

Currently, graphene that has high transparency with excellent conductivity is becoming a promising electrode material for fabricating OSC devices. The OSC devices have shown reasonable performance – approaching that of ITO-based OSC devices [35, 36]. Although this research is still in its early stages, graphene has already offered some high potential advantages over traditional transparent electrode materials.
1. Introduction and motivation

1.4 Conductive Carbon

Carbon bonding can adopt three distinct hybridisations: sp, sp$^2$ and sp$^3$. Consequently, carbon can form a variety of different allotropes, which can appear in both crystalline and non-crystalline forms. The crystalline form occurs if carbon consists of only one type of bonding hybridisation, while the non-crystalline form is produced if it contains a mixture of bonding hybridisations. In this section, a non-crystalline form (amorphous carbon) and a crystalline form (graphite) of carbon, as well as the single layer form of graphite (graphene) will be reviewed in more detail.

1.4.1 Amorphous Carbon

Amorphous carbon (a-C) is a non-crystalline form of carbon that contains a short-arrayed network of highly disordered mixtures of sp$^3$, sp$^2$ and sp$^1$ atoms (Figure 1.2). In the sp$^3$ configuration, four valence electrons of a carbon atom are each assigned to a tetrahedrally directed sp$^3$ orbital forming a strong $\sigma$ bond to an adjacent atom. In the sp$^2$ configuration, three of them enter trigonally directed sp$^2$ orbitals forming $\sigma$ bonds in a plane, while the remaining electron lies in a $\pi$ orbital lying normal to the $\sigma$ bonding plane. In the case of the sp orbital, two electrons occupy $\sigma$ orbitals, each forming $\sigma$ bond directed along $\pm x$-axis, while the remaining two electrons occupy $\pi$ orbitals in the y and z directions [43]. The term a-C is also used to refer to the hydrogenated and doped forms of non-crystalline carbon. The mixture of any these bonds with other carbon atoms or dopants can result in some advantageous variations in material properties such as tetrahedral a-C (TAC), hydrogenated diamond-like a-C (DLC:H), hydrogenated polymeric-like a-C (PLC:H) and graphitic-like a-C (GLC). The properties of an a-C film are strongly dependent on the fraction of sp$^2$ and sp$^3$ atoms, particularly the optical band gaps. For example, TAC film with more than 65% of sp$^3$ atoms have a band gap of 1.6-2.6 eV compared to GLC film with less than 30% of sp$^3$ atoms which have a band gap of 0-0.6 eV [44]. In fact, the band gap values directly correspond to the electrical conductivity of the a-C films; the lower band gap the higher electrical conductivity.
1. Introduction and motivation

Figure 1.2 The three bond hybridisations found in carbon: sp$^3$, sp$^2$ and sp$^1$ [43].

In recent years many efforts have experimentally been conducted by both academic and industrial researchers to increase the conductivity of a-C films. Highly conductivity pathways could be useful to the electronics industry for making intricate connections between devices [45]. Certain a-C films have also been found to be semiconducting. Such films show increased conductivity by depositing at a growth temperature above 550 °C [46] by doping with moderate sulphur concentration [47] and by carbonizing in a H$_2$ atmosphere [48].

1.4.2 Graphite

Graphite is one of two main allotropic forms of carbon consisting of three-fold coordinated planar layers of sp$^2$ bond hybridizations, in AB stacking sequence (Figure 1.3). The sp$^2$ hybridisation links carbon atoms in a two dimensional (2D) layer of hexagons. In the plane layer of graphite, each carbon atom contributes three electrons to the formation of σ-bonding and one remaining electron in the p$_z$ orbitals to form a delocalised orbital of π symmetry. This delocalisation allows the fourth valence electron (π-electron) in carbon atoms to move freely in the plane, and, as such, the π-electrons
play a dominant role in the electronic properties of graphite. As a result, graphite is anisotropic; that is the electrical and thermal conductor is good within the layers due to the in-plane metallic bonding and is poor perpendicular to the layers due to the weak van der Waals forces between the layers.

Figure 1.3 The crystal structure of graphite. The primitive unit cell is hexagonal, with dimensions $a = 2.46$ Å and $c = 6.71$ Å. The in-plane bond length is $1.42$ Å.

The anisotropy of graphite allows other chemical elements to reside between the layers resulting in intercalation compounds [49]. The graphite intercalation compound (GIC) is generally more electrically conductive than graphite, since there is charge transfer between the intercalate and graphite. Such GICs can be exfoliated upon heating. The exfoliated graphite flakes are compressed without a binder resulting in mechanical interlocking. Consequently, a flexible and resilient sheet is formed – known as flexible graphite [50].

Distinguishing between graphite and multi layer graphene (MLG) films, it depends on the electrical and thermal context of the measurement. Electrically, a film is referred to as a MLG as long as it is thin enough to have its carrier density tuned via electrostatic gating. While, in the thermal context, the film is reasonably considered as a MLG as long as its Raman spectrum is distinctively different from that of graphite; reached at 7–10 graphene layers [51-54]. Thus, the film is considered to be MLG when its lattice dynamic–phonon properties are different from those of graphite ($\leq 10$ layers $\approx 3.5$ nm).
1.4.3 Graphene

Graphene is a mono-layer structure of two-dimensional graphite with the hexagonal packed structure, as shown in Figure 1.4a [55]. The carbon bonds are sp² hybridized, consisting of the in-plane σ and the out-of-plane π bonds (Figure 1.4b). The σ bond is a strong interaction that acts as the rigid backbone of the structure, while the π bond is a weak interaction correlating to a delocalised network of electrons and provides the interaction among graphene layers or between graphene and substrate. With these unique structural characteristics, graphene has shown outstanding thermal, mechanical, optical and electrical properties [56].

1.4.3.1 Properties of Graphene

One of the most remarkable properties of graphene is that its charge carriers behave as massless relativistic particles or Dirac fermions, and electrons losing their rest mass (m₀) can freely move with only little scattering under ambient conditions [16, 57]. Due to this behaviour, some extraordinary properties of graphene have been investigated by researchers. Firstly, graphene is a zero-bandgap 2D semi-metal showing band-overlap at the two conical points (K and K’) in the Brillouin zone (Figure 1.4c), where the energy bands obey a linear dispersion relationship [55]. Secondly, it exhibits a strong ambipolar electric field effect, i.e., the charge carriers can be alternated between holes and electrons depending upon the nature of the gate voltage. The measured values of charge carrier concentrations and room-temperature mobilities are up to 10¹³ cm⁻² and ~10⁴ cm²/V.s, respectively [15]. Thirdly, both charge carriers in graphene have an unusual half-integer quantum Hall effect (QHE) as observed by adjusting the chemical potential using the electric field effect. In addition to its exceptional properties, the optical transmittance of a graphene single layer is equal to ~97.7 % of incident light, and its absorbance spectrum is almost flat in the visible range; despite being only one atom thick, graphene absorbs a significant fraction of incident white light equal to ~2.3 %, which is visible even to a simple optical microscope observation. The fine structure constant, α = e²/2ε₀hc (where e is the unit electromagnetic charge, ε₀ is the permittivity constant, h is Plank’s constant, and c is the speed of light) is the parameter that describes coupling between light and relativistic electrons and that is traditionally
associated with quantum electrodynamics [58]. The optical absorption of graphene saturates when the input optical intensity is above a threshold value. This behaviour, called nonlinear optical saturable absorption, is due to the zero band gap. Moreover, the measured thermal conductivity value of single-layer graphene at room temperature is \( \sim 5000 \text{ W mK}^{-1} \). Graphene also possesses excellent mechanical strength. The intrinsic mechanical properties of free-standing monolayer graphene membranes were measured by nano-indentation in an AFM. The breaking strength is 42 Nm\(^{-1}\) and the Young's modulus is 1.0 TPa, indicating it is one of the strongest materials ever measured [57].

Figure 1.4 (a) Graphene structure of single 2D-hexagonal sheet of carbon atom, (b) schematic of the in-plane bonds and the \( \pi \) orbitals perpendicular to the plane of graphene, and (c) electronic band structure of single-layer graphene [55].

To produce graphene with the remarkable properties as mentioned above, a consistent, reliable, simple and inexpensive method of growing high-quality, uniform, continuous, single layer graphene films is a prerequisite. The following subsection will briefly review the historical development of methods for producing graphene thin films.
1. Introduction and motivation

1.4.3.2 Fabrication Techniques of Graphene

Since the discovery of graphene was reported by Geim’s group in 2004, it has attracted much intensive attention of researchers keen to further its development. Various methods have been developed for the fabrication of graphene and its derivatives using several different approaches. The original mechanical exfoliation method from platelets of highly oriented pyrolytic graphite (HOPG) results in small amounts of graphene with high structural and electronic quality and consistent optical properties [15]. Currently, mechanical exfoliation is the simplest technique to prepare micron-size graphene flakes for fundamental research purposes and for proof-of-concept devices in the foreseeable future [57]. Though this method gives the good electrical and mechanical properties, it cannot be scaled up for mass production of graphene due to non-configuration. To produce a large number of graphene films, one method used is chemical cleavage from graphite [59]. Although the resulting graphene films are variable in thickness, the optical properties are consistent, similar to films produced using the mechanical cleavage method. As such, both mechanical methods produce films on a small scale, in the tens of microns, so that they are obviously not suitable for large-scale preparation.

One proposed method to produce large area sheets of graphene is graphitisation of silicon carbide (SiC). By this approach, graphene is epitaxially grown via vacuum graphitisation on insulating SiC surfaces. The graphitisation of carbon can take place when this material is heated around to 1400 °C [60]. The shortcomings of this technique are the high initial cost of the SiC wafer, the large number of defects in the layers and the difficulty to transfer to other substrates, such as silicon, for integration with Si based devices [61]. Another approach is the chemical exfoliation from graphite, graphite oxide (GO), and graphite intercalation compounds, to produce scalable graphene. The graphene films result from the colloidal suspension of these materials through simple chemical reactions or electrochemical methods.

So far, the exfoliation of GO has attracted the majority of attention by researchers as the strongly hydrophilic nature of its layers allows an easily aqueous intercalation. As a direct consequence, single-layer GO sheets can be completely exfoliated by sonication. Unfortunately, GO is an insulating material that has to be reduced in order to produce
1. Introduction and motivation

Graphene. This reduction step often leaves defects in the graphene crystal structures which disrupt the electronic properties [62]. The latest method, which is very promising for synthesis scalable, high-quality graphene film, is chemical vapour deposition (CVD). Graphene growth by this technique will be discussed in more detail in Section 1.5.

1.4.3.3 Characterisation of graphene

Some of the used characterisation techniques for graphene films are optical microscopy [63, 64], SEM [65, 66], AFM [67, 68], TEM [2], and Raman spectroscopy [64, 69]. Among these, optical and Raman microscopy are widely used since they are the most convenient and reliable. Optical microscopy and Raman techniques can be used to identify different layers of graphene via color contrast. Ni’s group compared the characterisation results of both methods by comparing out the film visible in Raman but invisible in optical microscope. In comparison, the optical and Raman images of graphene film in Figure 1.5a & b show that the contrast in the Raman image is clearer. The number of graphene layers was confirmed by using Raman spectroscopy (Figure 1.5c). Additionally, AFM is an effective way to characterise the morphological features of graphene film, but it is not accurate for measuring the number of graphene layers. A method that can accurately count the number of graphene layers is TEM, as seen in Figure 1.6. Furthermore, TEM can also provide the electron diffraction pattern, which can reveal the hexagonal pattern of the graphene crystal structure.
1. Introduction and motivation

Figure 1.5 (a) Optical image of a graphene film with different thickness, (b) Raman image plotted by the intensity of G band, and (c) Raman spectra as a function of number of layers [64].

Figure 1.6 High-magnification TEM images of different graphene layers [2].

A quick and effective way to identify the structure and quality of graphene is Raman spectroscopy. The spectrum of graphene samples present three main features: (1) D band at 1350 cm\(^{-1}\) associated with the existence of defects: the lower intensity, the fewer defects of the graphene layer, (2) G band at 1580 cm\(^{-1}\) as E\(_{2g}\) mode of graphite, which is due to the sp\(^2\)-bonded carbon atoms in a 2D hexagonal graphite layer, and (3) G’ or 2D band at 2700 cm\(^{-1}\) involving the scattering of two phonons with opposite momentum around the high symmetry K point in the first Brillouin zone of graphene. The latter feature can also be used to clearly distinguish the number of stacked graphene
layers by characterising the position and shape: the thinner graphene layer, the sharper and more symmetric, as above shown in Figure 1.5c.

1.5 CVD Graphene/Graphite Growth

The essence of this technique is that precursors in the vapor phase react with the catalyst’s surface at elevated temperatures under low or atmospheric pressure. This reaction results in the deposition of a thin film. In the case of graphene synthesis, precursors are usually carbon-containing materials, such as methane, PMMA, polystyrene, alcohol, and benzene. To grow graphene with high quality, several factors must be well understood such as the growth kinetics, the interaction with the underlying catalyst, and the required optimal gas ratio, growth time and growth temperature. In particular, the solubility of carbon in the transition metal along with the CVD conditions play an important role in determining the growth mechanism and ultimately controls the number of graphene layers.

Ferrary et al. (2006) first reported successful graphene deposition via CVD using nickel (Ni) metal as catalyst. The resulting graphene films were non-uniform in thickness and had folds (approaching 35 graphene layers) all over the catalyst’s surface. By varying the thickness of this catalyst, O’Brien et al. found that increased nickel thickness led to a greater surface coverage as well as increasing the number of layers in many areas [70]. Moreover, Reina et al. (2009) successfully synthesised a large fraction of single- and bi-layer graphene in regions up to ~20 μm in lateral size. Lee et al. optimised the synthesis conditions by investigating the effects of synthesis temperature and cooling rate in the ranges of 850-1,000 °C and 2-8 °C/min, respectively. They found that a cooling rate of 4 °C/min after 1,000 °C synthesis is the most effective condition for producing monolayers of graphene, with the best obtained sheet resistance being 1,540 Ω/sq (87 % transparent) [71]. Another synthesis condition investigated was the catalytic metal type. Sukhdea (2009) demonstrated that using cobalt catalyst instead of nickel in growing graphene virtually eliminates the thickest, most undesirable regions. However, thicker
patches are still present throughout, probably due to the polycrystalline nature of the original cobalt surface [72].

To address the above limitations, researchers have selected copper as a catalyst for growing graphene for few reasons: (1) the Cu/C binary phase diagram shows a low carbon solubility (<0.001 atomic%) which limits the amount of segregated C and precludes the growth of additional graphene layers from the bottom which can lead to better control of graphene film growth over a reasonable temperature range (800-1000 °C), (2) the absence of a copper carbide line compound, and (3) wet etchant selectivity to graphene. Moreover, the resulting graphene is primarily a monolayer and continuous with numerous boundaries and large areas. Furthermore, the graphene films grown on a Cu substrate can be transferred onto other substrates of interest under ambient conditions.

Recently, graphene growth on copper (Cu) catalyst has shown promising results that may serve as an alternative route towards scalable growth of graphene with higher monolayer coverage [3, 32, 73]. The solubility of carbon in Cu is negligible (of the order of ppm even at 1000 °C) so the carbon precursor forms graphene directly on copper surface during the growth step [57, 73]. Additionally, higher synthesis temperatures result in a faster growth rate with generally higher quality graphene coverage and the growth mechanism is based on surface adsorption [74].

Economically, all of the above approaches are not desirable, since they require high temperature in growing graphene (> 800 °C). Therefore, a low-temperature growth method allowing the production of large-scale graphene films is necessary, since it is more convenient, economical, environmentally friendly and readily applicable for scalable electronic devices.

1.6 Low Temperature Graphene/Graphite Growth

Much research has been focused on developing CVD growth methods by using gaseous raw materials, such as methane and ethylene, for obtaining large sheets of monolayer or
bilayer graphene. However, using these materials requires a high temperature to decompose them to carbon atoms [1, 32, 75]. As a direct consequence, they are limited for wider application in technologies.

Solid carbon sources such as PMMA, sucrose and fluorene, have also been reported by Sun et al. to produce monolayers of graphene [76]. A minimum growth temperature of 800 °C has been used to eliminate defect formation in the graphene film. For mass production of conductive transparent electrodes, the lower the temperature required to produce high-quality graphene, the better in the effective-cost management and the less challenges in the device process. Recently, using liquid sources such as benzene or pyridine, Li et al. [77] and Xue et al. [78] reported that a single layer of graphene can be fabricated at temperatures as low as 300 °C. However, it is not clear what the electrical properties are of these low temperature grown films after transfer and whether it is possible to produce large area graphene sheets.

In this work, graphene films are grown on both copper foils and evaporated thin copper films at low temperatures below 500 °C in a CVD furnace by using a PMMA coating as the solid carbon source. The precursor was annealed at the desired growth temperatures by introducing a mixture of hydrogen (H₂) and argon (Ar) gases for different times.

### 1.7 Organic Electronics Application (Study Case: Organic Solar Cells)

#### 1.7.1 Organic Solar Cell (OSC) Design and Operation Principles

Generally, OSCs are designed in a five-layer device structure as shown in Figure 1.7. The first layer is a substrate which is made of transparent materials such as glass, polyester, quartz, etc. On top of the substrate, an ITO coating is used as a transparent conductive electrode. On top of the ITO electrode, a PEDOT:PSS layer is deposited to form the third layer. This layer functions to perform hole transporting, exciton-blocking
and smoothing and also prevents the diffusion of oxygen from ITO [79-82] to active layer (the fourth layer), which is a donor/acceptor-blend material. The top layer is usually deposited with a metallic cathodic conducting material such as aluminum, gold, silver, and calcium.

Figure 1.7 A typical five-layer structure of bulk heterojunction (BHJ) OSC devices.

The operation of a typical OSC cell, e.g. BHJ solar cell, can be schematically described in Fig.1.8 by the following four steps [83]. Firstly, the incident photons propagate through the transparent substrate until they reach the active layer. Then, these photons are absorbed to generate excitons, which are strongly bound electron-hole pairs [84]. For a typical organic semiconductor, the exciton diffusion length is around 10-20 nm [85]. Secondly, the generated excitons produce electron-hole pairs that are split at the donor-acceptor interface due to the offset of the HOMO and LUMO states of the donor and the acceptor [86]. Thirdly, these separated charges are transported to the respective electrodes. During the transport of charges, they can recombine and the absorbed energy can be dissipated without generating photocurrent. Also, interaction with atoms or other charges may lower the charge mobility and thereby limit the generated photocurrent. Finally, the electrons transferred to the acceptor material are extracted at a metal
electrode with a relatively low work function (e.g. Al, Ca), while the holes traveling through the donor layer are collected at a transparent electrode (ITO). The collected charges on the electrodes are subsequently delivered into the outer circuit.

Figure 1.8 Operation principle of BHJ solar cell from charge generation to charge collection.

1.7.2 Characterization of OSCs

The current density-voltage (J-V) curve is the most significant characteristic of OSC performance. This characterisation is used to determine the power conversion performance in order to know how effective the device converts photon energy into electrical energy. Figure 1.9a shows the typical shape and the key points of the plot for the performance of an OSC device. In the dark, the graph passes through the origin.
because there is no current at the short current \((J_{sc})\) condition. While, the graph shifts downward under illumination because the incident photon generates current and the offset current density in the 4\(^{\text{th}}\) quadrant of J-V curve indicates this photogenerated current.

Figure 1.9  Graph of current versus voltage for OSC devices showing how the device characteristics change upon illumination and indicating the key points on the graph [87].

To quantitatively analyse the performance a solar cell, the following terms, (including some items denoted on the graph) are frequently used as follows:

1) **Short-Circuit Current \((I_{sc})\)**
   
   This is the current flowing through an illuminated solar cell when the electrodes are short-circuited. The \(I_{sc}\) is the maximum current that can be achieved by a solar cell. The solar cell current depends on the incident photon flux density and the active area. The dependence of the \(I_{sc}\) on the area can be removed by using the short-circuit current density \((J_{sc})\), that describes the maximum current delivered by a solar cell.
2) Open-Circuit Voltage ($V_{oc}$)
This is the maximum possible voltage across a solar cell when no current is flowing. The $V_{oc}$ corresponds to the forward bias voltage, at which the dark current compensates the photo-current, and depends on the photo-generated current density ($J_{ph}$).

3) Maximum Power Point (MPP)
The point ($V_{mpp}$, $J_{mpp}$) on the J–V curve is where the maximum power ($P_{max}$) is produced as above illustrated in Figure 1.9. The rectangle area is formed between a point on the graph and the axes. The $P_{max}$ point is the point on the graph where the product of $J_{mpp}$ and $V_{mpp}$ is obtained.

4) Fill Factor (FF)
The ratio of a solar cell’s actual maximum power output to its theoretical power output if both current and voltage are at their maxima, $I_{sc}$ and $V_{oc}$, respectively. This term is a key quantity used to measure cell performance that is a function of the ‘squareness’ of the I-V graph. The value of this fill factor is always less than one; the closer to one, the better the quality of the cell. In terms of the above quantities, it is defined as:

$$FF = \frac{I_{mpp} \times V_{mpp}}{I_{sc} \times V_{oc}}$$

(1.1)

5) Power Conversion Efficiency ($\eta_e$)
This term is the ratio of power output ($P_{out}$) to power input ($P_{in}$). In other words, the $\eta_e$ measures the amount of power produced by a solar cell relative to the power available in the incident solar radiation. In the photovoltaic cell measurement using solar simulators, $P_{in}$ is the sum over all wavelengths and is generally fixed at 100 W/cm². This is the most general way to define efficiency. In terms of above defined quantities, the formula for $\eta_e$ is:

$$\eta_e = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}}$$

(1.2)
1.7.3 Equivalent circuit

Parameters such as Jsc, Voc, FF, ηe are used to quantitatively analyse the performance of a solar cell. By considering the externally observable characteristics, when an ideal solar cell is activated, the expression of dark current (Id) is exactly the same as that for the current flowing in a p-n junction of ideal diode:

\[
I_d = I_0 \left\{ \exp \left( \frac{qV}{nkT} \right) - 1 \right\}
\]

(1.3)

Where \( I_0 \) is the reverse saturation current, \( q \) is the electron charge, \( V \) is the applied voltage, \( n \) is the diode factor representing deviation from ideal diode characteristics, \( k \) is Boltzmann’s constant, and \( T \) is the absolute temperature. On the other hand, when photons illuminate a cell, a photo-generated current \( I_{ph} \) flows as an anode reverse current. \( I_{ph} \) is linearly proportional to the intensity of illumination. Therefore, taking current flow in positive direction, the current/voltage relationship becomes:

\[
I = -I_{ph} + I_0 \left\{ \exp \left( \frac{qV}{nkT} \right) - 1 \right\}
\]

(1.4)

If a load resistance, \( R \), is connected to the solar cell, the voltage \( V_R \) across, and the current \( I_R \) through the load are given by the point at which the IV characteristic of the solar cell intersects the straight line represented by \( V = -IR \). At this point, the output power in the load, \( P_{out} \), is equal to \( I_R^2 \cdot R \) and it is clear that a light electrical energy conversion is occurring. When the terminals of the solar cell are disconnected or shorted, the solar cell output power = 0. By adjusting the value of the load resistance, an optimum operating point can be found at which output power is a maximum.

The magnitude of FF is dependent on resistances within the solar device, namely shunt (\( R_{sh} \)) and series (\( R_s \)) resistances, as modelled in Figure 1.10. \( R_{sh} \) allows current to bypass another point in the circuit. Large \( R_{sh} \) can result in a high FF as it prevents the current from leaking. On the other hand, \( R_{sh} \) can decrease as result of active layer
defects and charge trapping sites. \( R_s \) describes the contact and bulk resistances within the cell and tends to be a property of the active layer material. To improve charge transport a higher mobility material is used which decreases the series resistance. The FF can therefore be thought to represent the competition between recombination and transport within the active layer of the device [34].

![A typical circuit diagram used to model OSC devices.](image)

**Figure 1.10** A typical circuit diagram used to model OSC devices.

### 1.8 Thesis Outline

The thesis is arranged into seven chapters. Chapter 1 covers general information about transparent electrodes, conductive carbon, low-temperature graphene fabrication, and applications of graphene in OSC devices as well as the outline of thesis. Chapter 2 explains the experimental techniques applied to this work starting from the preparation of copper catalysts to the characterisation of OSCs and the equipment used. The purpose of this chapter is to provide a full understanding to readers about the applied methods in obtaining experiment results and the relevant equipment for characterising the samples in the remaining chapters. Chapter 3 systematically presents the study of thermal effects on copper catalysts. This experiment is crucial since the annealing induces the formation of large copper grains and consequently drives the formation of graphene flakes. Chapter 4 focuses on graphene growth at temperatures below 500 °C on copper foil using CVD with PMMA as the carbon source. Chapter 5 develops the
graphene growth using evaporated Cu thin film as the catalyst. The resulting graphene films are used to serve for fabricating OSC devices. In Chapter 6, we demonstrate preliminary studies showing that low-temperature grown graphene films can serve as transparent conductive anodes for OSC devices. The graphene electrodes were grown on copper catalysts by annealing the PMMA carbon source coated on glass slide, followed by etching away the copper. After etching, only a graphene film remains on the substrate. The conclusions, and suggestions and recommendations for further research are provided in Chapter 7.
Experimental Procedure

This chapter includes details of all experimental techniques used in this work including sample preparation, graphene growth, the transfer process, characterisation and fabrication of OSC devices.

2.1 Preparation

2.1.1 Carbon Source

In this work, the solid-state method was used for growing graphene films since it is cheap and safe compared with the explosive, gaseous raw carbon sources used in a gaseous CVD process. Herein, poly(methyl methacrylate) (PMMA) (Figure 2.1) was used as a carbon source due to its low thermal decomposition temperature. Studies of PMMA degradation at low temperatures have been carried out as previously reported [88-93]. Kashiwagi et al. [92] first showed that PMMA weight loss was initiated by scissions of head-to-head linkages (H-H) around 165 °C. Later, Manring et al. [93] reported that the weak head-to-head bonds first reduce the polymer degradation temperature by promoting facile homolytic scission of the chain around 270-300 °C.
Moreover, Lomakin et al. [94] demonstrated that free-radical polymerized PMMA decomposes around 272 °C, with initiation occurring at double bonds at chain ends. Indeed, when PMMA is heated above 300 °C, its chemical bonds tend to decompose. For use as a carbon precursor, this polymer was diluted with chlorobenzene to a concentration of 100 mg/mL and then deposited on glass by drop casting. A crucial requirement in graphene formation is that the molecular backbone of the PMMA source should be completely composed of carbon atoms. These atoms can then become the main source of sp² hybridized carbon bonds in the graphene sheets [95]. By considering this requirement, the growth temperature of graphene on copper catalysts was experimentally conducted at temperatures above 300 °C, namely 350 and 450 °C. While for decomposition of the precursor, the PMMA was heated at two different temperatures, 140 and 400 °C, respectively.

Figure 2.1 Chemical structure of PMMA
2. Experimental Procedure

2.1.2 Copper Catalyst

Copper foil (Sigma-Aldrich, code: 1001328641, cut into 2x1 cm² in size, 99.98% in purity, 25-µm-thick) and thin copper film (99.99+% in purity, 500-nm-thick) thermally vapour deposited on to glass/quartz substrates were used as catalysts for growing graphene in a CVD furnace system.

Unlike the thermally-deposited thin Cu films, the cut copper foils were first cleaned of any unwanted contaminations such as grease and thin layer or organic impurities (see Figure 2.2). These contaminants can lead to the deposition of amorphous carbon at high temperatures and serve as multilayer graphene nucleation sites [96]. The cleaning process was conducted by washing with acetone in order to remove these contaminants, followed by an isopropanol (IPA) washing to remove any acetone residue left over on the foil. Afterwards, the foils were put into de-ionized (DI) water and sonicated to remove remaining organic solvents. After drying, the foils were kept as flat as possible by pressing them between two clean glass slides.

Figure 2.2 SEM images of the uncleaned (left) and cleaned (right) copper foils. (scale bar : 100 µm)

Both copper substrates may contain a thin layer of native copper oxide (due to exposure to air) before they are loaded into the 2-inch diameter quartz tube furnace of CVD system (Figure 2.3). This oxidation is highly undesirable for graphene growth. A
2. Experimental Procedure

technique used to remove the oxidation is thermal annealing under an argon and hydrogen atmosphere. The argon is introduced to replace oxygen (O\textsubscript{2}) which has oxidised the copper, while the hydrogen is used to reduce the native copper oxide layer and increase the grain size of the copper [97, 98].

![The Atomate CVD system](image)

Figure 2.3 The Atomate CVD system.

In addition to the removal of copper oxides, the annealing treatment is also used to form larger copper grain sizes, since both of the substrates initially have much smaller grain size with a large number of grain boundaries (Figure 2.4). The formation of large grains allows growth of high-quality graphene film [99]. The thermal annealing was conducted in the CVD system by varying the experimental parameters of temperature, time, and hydrogen flow rate. A typical thermal annealing recipe is summarised in Table 2.1. Copper catalyst was loaded into the quartz tube and then flushed with argon (100 sccm) for 2 minutes in order to replace the oxygen-rich atmosphere. Afterward, the temperature was ramped up to 900 °C for 12 minutes under a hydrogen (50 sccm) and argon (100 sccm) atmosphere. During the elevation of temperature, hydrogen was used to reduce oxidation of copper. After reaching the annealing temperature, the flow rates of the gases were left unchanged and annealing was performed for 90 minutes. After the annealing step, the temperature was decreased and the furnace was allowed to cool.
down naturally under hydrogen (50 sccm) and argon (100 sccm) atmosphere. The copper catalyst was then unloaded from the quartz tube at room temperature.

![Figure 2.4 SEM images of (a) thin Cu film and (b) Cu foil before treatment. (scale bar : 200 nm)]

Table 2.1 A typical recipe used in annealing copper catalyst.

<table>
<thead>
<tr>
<th>Duration (h:m:s)</th>
<th>Temperature (°C)</th>
<th>H$_2$ (sccm)</th>
<th>Ar (sccm)</th>
<th>Pressure (mTorr)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:02:00</td>
<td>100</td>
<td>100</td>
<td>500</td>
<td>500</td>
<td>Flush</td>
</tr>
<tr>
<td>00:12:00</td>
<td>900</td>
<td>100</td>
<td>500</td>
<td>500</td>
<td>Ramp up</td>
</tr>
<tr>
<td>01:00:00</td>
<td>900</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>Anneal</td>
</tr>
<tr>
<td>01:00:00</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>Cool down</td>
</tr>
<tr>
<td>00:05:00</td>
<td>25</td>
<td>100</td>
<td>500</td>
<td></td>
<td>Flush</td>
</tr>
</tbody>
</table>
2.2 Graphene Fabrication

The as-annealed copper foil and thin deposited copper film were used as the catalyst for growing graphene films at low temperatures of 350 and 450 °C in a 2-inch diameter quartz tube furnace of the CVD system, into which PMMA-coated glass and the copper catalysts were loaded. The positions of these materials in the tube furnace through which hydrogen and argon gases can be flowed are shown schematically in Figure 2.5. The CVD system (Atomate Corporation) provides three heating coil zones with a neighbouring distance of 8 inches and uses a standard coil heater element of NiCr that can reach up to 1100 °C. The system is fully computer controlled and has several recipes already available, including for the growth of carbon nanotubes (CNTs), metal and metal oxide nanowires, graphene and ZnO films.

![Figure 2.5 Schematic diagram of graphene growth in the CVD system.](image)

Figure 2.5 Schematic diagram of graphene growth in the CVD system.
A typical graphene growth recipe is summarised in Table 2.2. In the beginning of the growth process, the tube was evacuated to 100 mTorr using a mechanical pump. Once this pressure was achieved, the tube was back filled with argon gas (100 sccm) maintaining the temperature at 100 °C for 2 min, and flushing the unwanted gases. Afterwards, the catalyst temperature was ramped up to 450 °C for 5 minutes, while the precursor temperature was kept at 100 °C. During the elevated temperature, hydrogen gas (50 sccm) was introduced to prevent oxidation. Once the growth temperature was achieved, the precursor acting as the carbon source was heated at 140 °C for 1 minute under a H₂/Ar (50 and 100 sccm, respectively) atmosphere. After the synthesis phase, the furnace was promptly cooled to room temperature over a time of 30 min without changing the H₂/Ar atmosphere. At the end of the process, the flow rate of Ar gas was maintained for 5 min before the sample was removed. The system pressure was maintained at 500 mTorr throughout.

Table 2.2 A specific recipe used in growing graphene film.

<table>
<thead>
<tr>
<th>Duration (h:m:s)</th>
<th>Precursor Temperature (°C)</th>
<th>Catalyst Temperature (°C)</th>
<th>H₂ (sccm)</th>
<th>Ar (sccm)</th>
<th>Pressure (mTorr)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:02:00</td>
<td>100</td>
<td>100</td>
<td></td>
<td>100</td>
<td>500</td>
<td>Flush</td>
</tr>
<tr>
<td>00:10:00</td>
<td>100</td>
<td>450</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>Ramp up</td>
</tr>
<tr>
<td>00:01:00</td>
<td>140</td>
<td>450</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>Anneal</td>
</tr>
<tr>
<td>00:30:00</td>
<td>25</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>Cool down</td>
</tr>
<tr>
<td>00:05:00</td>
<td>25</td>
<td>25</td>
<td></td>
<td>100</td>
<td>500</td>
<td>Flush</td>
</tr>
</tbody>
</table>

2.3 Transfer Process

The as-grown graphene on Cu foil needs to be transferred to a target substrate, as shown schematically in Figure 2.6. In the beginning of the transfer process, the Cu/graphene stack was spin-coated (75 µL, 5000 rpm for 1 min) with PMMA (dissolved in chlorobenzene at a concentration of 50 mg/mL), which was then cured on a hot plate at
180 °C for 1 min. The graphene film was separated from the Cu foil by etching away the foil in an aqueous iron nitrate solution (0.05 mg/mL). Typically, the time needed to completely etch a copper foil of 2cm x 1cm in size was about 48 hours, resulting in a floating PMMA/graphene stack. The floating stack was picked up by a clean glass substrate and transferred to a petri dish containing DI water for 30 min. The washed stack was subsequently transferred onto the target substrate. After drying in air for ~30 minutes, the dried stack was spin coated (75 µL, 5000 rpm for 1 min) with a 10 mg/mL dissolved PMMA solution in order to dissolve the pre-coated PMMA. The new PMMA film was slowly cured at room temperature for ~30 min and then removed by rising in acetone and IPA 3 times, each. The remaining graphene film was dried by a stream of N₂ gas. Finally, the graphene film was dried in a vacuum oven at 70 °C for 2 h.

Figure 2.6 Schematic diagram of the transfer process of Cu foil-grown graphene film.
Unlike the copper foil-grown graphene, for graphene grown on thin copper film it is not necessary to transfer the graphene from the film to target substrate. This is because the film, on which graphene is synthesized, is evaporated directly onto the target substrate. Figure 2.7 shows a scheme of the etching of thin copper film. The film was dissolved with the same etchant solution for dissolving the copper foil. In comparison, the etching time on a size of $2\times1\text{cm}^2$ for completely dissolving the 500 nm-thin copper film was much faster (~30 minutes) than that of the 25-µm Cu foil (~48 hours). The graphene film settles directly onto the underlying substrates. The remaining graphene film on substrate was washed by dipping in DI water three times and then naturally dried in air atmosphere for ~30 minutes. The last drying step was by heating in a vacuum oven at 70 °C for 2 h.

Figure 2.7 Schematic of the etching of thin Cu film.
2.4 OSC device Fabrication

The as-produced graphene substrates were studied for use as transparent conductive electrodes in OSC devices (Figure 2.8a). In this study, the device structure used was graphene/poly(3,4-ethylenedioxythiophene-poly(styrenesulfonate) (PEDOT:PSS)/poly(3-hexylthiophene-2,5-diyl):(Phenyl-C61-butyric acid methyl ester) (P3HT:PCBM)/Ca/Al (Figure 2.8b), while a standard ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al device was used as a reference. Both devices were fabricated using a similar process. A thin PEDOT:PSS layer of ~50 nm was deposited onto the substrate by spin-coating. This PEDOT:PSS is commercially available as an aqueous dispersion (Clevious P VP Al 4083), and before use is filtered by a Whatman Puradisc 0.45µm PES filter. The PEDOT:PSS spun films were then baked on a hot plate at 140 °C for 30 min to remove water. The annealed substrates were immediately transferred into a nitrogen atmosphere glovebox system. The subsequent fabrication steps were all carried out in the nitrogen atmosphere. A blend of P3HT (Rieke) and PCBM (Solenne) at 1:0.8 mass ratio was prepared via dissolution of 18 mg/mL in 1,2-dichlorobenzene and sonicated for 1 h. This P3HT:PCBM blend used was then spun onto the top of PEDOT:PSS layers at 2000 rpm for 60 seconds followed by drying on a hot plate at 50 °C for 4 min. Afterward, on top of the dried active layer a buffer layer of calcium (20 nm) and a metal cathode of aluminium (100 nm) were thermally vapour deposited in vacuum using an Angstrom Engineering evaporator under a pressure of ca. 1x10⁻⁶ Torr. Finally, the devices were thermally annealed in on a hot plate at 140 °C for 4 min.
2.5 Characterisation

The graphene films are characterised by SEM, UV-vis spectroscopy, TEM, profilometry, four-point probe conductivity measurement, AFM and Raman spectroscopy. Other instruments used in this work are thermogravimetric analysis (TGA) and XRD for characterising the precursor and the catalyst, respectively. Details on the each of these techniques are provided in the following sections.

2.5.1 Scanning Electron Microscopy (SEM)

The SEM is an instrument that uses a fine electron beam for observation of a sample surface. In this work, the Zeiss Sigma VP SEM of the University of Newcastle was used (Figure 2.9a) for characterising the topography of the sample surface. Manually, this instrument has resolutions of 1.3, 1.5 and 2.8 nm at operating voltages of 20, 15 and 1 kV, respectively. Typically, the electron beam energy used was 3 kV and the

Figure 2.8 (a) Graphene substrate with marked active area of 4 mm², (b) The device structure of graphene/PEDOT:PSS/P3HT:PCBM/Ca/Al.
magnification of images was set to 150,000 times. Schematically, the SEM is shown in Figure 2.9b. The beam is produced by an electron gun located at the top of the microscope. Under vacuum, the beam travels through a scanning coil and magnetic lenses, which focus it down toward the sample. The beam hitting the sample results in the backscattered and secondary electrons. These electrons are collected by detectors and then converted into a signal that is sent to a TV scanner to form the 2-D image [100, 101]. The result is a topographical image with a resolution of 2.6 nm.

Figure 2.9 (a) Zeiss Sigma VP SEM of the University of Newcastle and (b) Schematic diagram of the SEM [100].

2.5.2 UV-vis Spectroscopy

UV-vis spectroscopy uses photons in the ultraviolet and visible regions of the electromagnetic spectrum to probe the electronic properties of organic materials, since they absorb light in this part of the spectrum. The degree of absorption is a function of the wavelength of light. Absorption occurs when an incident photon’s energy is equal to the energy requirement for an electronic transition within the molecule. Absorption is generally the result of the excitation of electrons to non-bonding or \( \pi^* \) orbitals and thus
the resulting absorption characteristics can give a lot of information about the electronic structure [102]. The absorbance (A) of the energy of incident light (wavelength) is described by Beers law:

$$A = -\log\left(\frac{I}{I_0}\right)$$  

(2-1)

While the ratio of the intensity of transmitted light to the intensity of incident light (I/I₀) is described as transmittance [103, 104].

In this work, the ultraviolet region of spectrum used was limited to 200-330 nm in wavelength and the visible region of spectrum from 330-700 nm. When determining the absorption of graphene samples, the selected spectrum is UV region, while for determining samples’ transmission, the visible region is selected at a wavelength of 550 nm. All of the UV-vis spectra were collected on a Varian Cary 6000i UV-vis-NIR spectrophotometer (Figure 2.10). The measurement of all samples were conducted after scanning a baseline reference using a buffer blank in order to remove artefacts introduced by spectrophotometer [105].

Figure 2.10 UV-vis spectrophotometer.
This spectrophotometer consists of two sources used to scan the entire UV-vis band. One is a deuterium lamp covering the UV spectrum (200-330 nm) and another one is tungsten lamp covering the visible spectrum (330-700 nm). The optical schematic of the spectrophotometer is shown in Figure 2.11. The lamps illuminate the entire band of UV-visible light. This radiation is converted to narrow bands by the monochromator (grating, prism) to be further sent to the beam splitters. The beam splitter sends a separate band to a cell containing a sample and a reference. The detector measures the difference between the transmitted light through the sample (I) vs. the incident light (I₀) and sends this information to the recorder. The data is typically plotted as a function of wavelength (see inset), where the y-axis of the spectrum is in absorbance (A).

\[ A = \log\left(\frac{I_0}{I}\right) \]
2.5.3 Transmission Electron Microscopy (TEM)

TEM was used as a method of imaging and identifying the number of graphene layers present. A Jeol JEM-2100 LaB6 TEM equipped with digital imaging (Figure 2.12a) was used for characterising the sample. This equipment operates at an accelerating voltage of 200 kV. Figure 2.12b schematically shows the TEM components, the working principle of which is similar to SEM. An electron beam is generated by an electron gun located at the top of the microscope and accelerated to the required high energy. This beam travels down to the sample through the microscope column which contains magnetic lenses and apertures. In imaging of the sample, the objective lens is the most important because it generates the first intermediate image which determines the resolution of final image. The beam then hits the sample and results in the backscattered and secondary electrons. These electrons are collected by detectors which convert them into a signal that is sent to a TV scanner to form the 2-D image. TEM gives a much better image than SEM, since it has high contrast and high resolution with magnification of up to 800,00 and 1,500,000 times, respectively [106, 107].
A 200 mesh holey carbon TEM grid (ProSciTech) (see Figure 2.13) was used as a support to hold a fragment of sample for imaging. In the sample preparation, a graphene fragment floating on DI water was picked up using the TEM grid and naturally dried in air.
2.5.4 Profilometer

A profilometer is a stylus-based instrument used to accurately measure the topography of a sample and features such as surface roughness and step heights. In this work, the Alpha Step 500 (KLA-Tencor) (Figure 2.14a) was used to measure thin film thicknesses. Schematically, the measurement setup of the profilometry system is shown in Figure 2.14b. This instrument is able to measure thicknesses of less than 10 nm up to 0.3 mm as result of the deflection of the stylus when it is gently dragged over the film surface. The stylus is a key component in the profilometer because it forms the interface between the surface being scanned and the data acquisition system. Moreover, the profilometer enables scans of up to 10 mm with vertical resolution on the order of 5 angstroms and speeds in the range of 2-200 µm/sec [109].
2. Experimental Procedure

2.5.5 Four-point probe conductivity

The four-point probe is a method used to measure the resistivity of a material by contact with its surface. This technique has widely been applied both in research and manufacturing [110, 111]. Figure 2.15 shows a photograph of the four-point probe and a schematic of the four-point probe configuration. This instrument comprises four tungsten pins with 2 mm spacing (s) and 100 µm radii. Each metal tip is held by springs in order to minimise sample destruction during probing. During the measurement, an auto-mechanical stage of four metal tips travels up and down. The outer two probes are supplied with current (I) from a high impedance current source, while the voltage (V) is measured across the inner two probes. When measuring a sample with low resistivity, high current is needed in the outer probes to obtain a good voltage reading.

Figure 2.14 (a) KLA-Tencor Alpha step 500 profilometer, (b) Schematic set-up of the profilometer measurement system.
2. Experimental Procedure

Figure 2.15 (a) four-point probe resistance measurement, (b) schematic of four-point probe configuration for thin rectangular slide sample.

In this work, the four-point probe measurement was used to measure the resistivity of samples. Since the measured samples had a thickness (t) of less than half the probe spacing (t < s/2) with a finite area of length(a) \times width(b) as configurated in Figure 2.14b, the calculation of electrical conductivity (\(\sigma\)) is given by:

\[
\sigma = \frac{1}{\rho}
\]

(2.2)

\[
\rho = R_{\text{sheet}} \times t
\]

(2.3)

\[
R_{\text{sheet}} = R \times G
\]

(2.4)

\[
R = \frac{V}{I}
\]

(2.5)

\[
G = \frac{\pi}{\ln 2} \cdot t \cdot C\left(\frac{b}{s}, \frac{a}{b}\right)
\]

(2.6)
2. Experimental Procedure

Where,

\[ s = \text{Distance between two neighboring tungsten pins (2 mm)} \]
\[ a = \text{Length of sample (mm)} \]
\[ b = \text{Width of sample (mm)} \]
\[ t = \text{Thickness of sample (mm)} \]
\[ \sigma = \text{conductivity (S/cm)} \]
\[ R_{\text{sheet}} = \text{sheet resistance (ohm/square)} \]
\[ R = \text{resistance (ohm)} \]

\[ G(s,t) \] is the proportionality constant depending upon the geometry of sample.

\[
\frac{\pi}{\ln 2} \cdot t = 4.5324 \cdot t
\]

is the geometric factor for an infinitely large slice of thickness \( t < s \).

\[ C\left(\frac{b}{s}, \frac{a}{b}\right) \] is the additional dimensionless correction factor since the measured sample has a finite, rectangular shape. Based on \( a, b \) and \( s \) values, the value of this factor is tabulated in Table 2.3 [112].

<table>
<thead>
<tr>
<th>b/s</th>
<th>a/b = 1</th>
<th>a/b = 2</th>
<th>a/b = 3</th>
<th>a/b ≥ 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td></td>
<td></td>
<td>0.9998</td>
<td>0.9994</td>
</tr>
<tr>
<td>1.25</td>
<td></td>
<td></td>
<td>1.2407</td>
<td>1.2248</td>
</tr>
<tr>
<td>1.50</td>
<td></td>
<td>1.4788</td>
<td>1.4893</td>
<td>1.4893</td>
</tr>
<tr>
<td>1.75</td>
<td></td>
<td>1.7198</td>
<td>1.7238</td>
<td>1.7238</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td>1.9454</td>
<td>1.9476</td>
<td>1.9476</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td>2.3532</td>
<td>2.3541</td>
<td>2.3541</td>
</tr>
<tr>
<td>3.0</td>
<td>2.4575</td>
<td>2.7000</td>
<td>2.7005</td>
<td>2.7005</td>
</tr>
<tr>
<td>4.0</td>
<td>3.1137</td>
<td>3.2246</td>
<td>3.2248</td>
<td>3.2348</td>
</tr>
<tr>
<td>5.0</td>
<td>3.5098</td>
<td>3.5749</td>
<td>3.6750</td>
<td>3.6750</td>
</tr>
<tr>
<td>7.5</td>
<td>4.0095</td>
<td>4.0361</td>
<td>4.0362</td>
<td>4.0362</td>
</tr>
<tr>
<td>10.0</td>
<td>4.2209</td>
<td>4.2357</td>
<td>4.2357</td>
<td>4.2357</td>
</tr>
<tr>
<td>15.0</td>
<td>4.3882</td>
<td>4.3947</td>
<td>4.3947</td>
<td>4.3947</td>
</tr>
<tr>
<td>20.0</td>
<td>4.4516</td>
<td>4.4553</td>
<td>4.4553</td>
<td>4.4553</td>
</tr>
<tr>
<td>40.0</td>
<td>4.5120</td>
<td>4.5129</td>
<td>4.5129</td>
<td>4.5129</td>
</tr>
<tr>
<td>∞</td>
<td>4.5324</td>
<td>4.5324</td>
<td>4.5324</td>
<td>4.5324</td>
</tr>
</tbody>
</table>
2.5.6 Atomic Force Microscopy (AFM)

The Cypher AFM instrument produced by Asylum Research (see Figure 2.16a) was used in this work for investigating the surface morphology of graphene film. This instrument provides high resolution topographical images of materials. It has a spatial resolution of less than 1 nm and relies on the forces between the AFM tip and the sample to produce images. The sharpness of the AFM tip directly affects the image resolution and typically has a radius of curvature from a few to tens of nanometres. Schematically, the AFM system is shown in Figure 2.16b. When the tip is brought within close proximity of the sample surface, the forces between the tip and sample cause the cantilever to deflect. Changes in the surface topography and material result in changes in the cantilever deflection which is measured by reflecting a laser beam onto a photodetector. A piezoelectric scanner rasteres the sample underneath the tip, providing surface topography in the x, y and z-directions. Since large changes in surface height could result in the collision of the tip and the sample surface, the AFM relies on a feedback loop and the piezoelectric scanner to maintain a constant force on the cantilever [113, 114].
2.5.7 Thermogravimetric Analysis (TGA)

TGA is a simultaneous thermoanalytical technique for measuring the mass loss/gain of a sample on which the mass is monitored as a function of temperature or time as the sample is subjected to a controlled temperature program in a controlled atmosphere. Due to the mass change, this instrument can quantify loss of water, loss of solvent, loss of plasticizer, decarboxylation, pyrolysis, oxidation, decomposition, weight % filter, and weight % of ash. A TGA (Figure 1.17) consists of a sample pan that is supported by a precision balance. This pan resided in a furnace is heated or cooled during the experiment. A sample purge gas which may be inert or a reactive gas controls the sample environment. The heating rate is programmable from 0.01 to 100 °C/min and can operate with various purge gasses and flow rates [115].
In this work, the Perkin-Elmer Diamond TG/DTA was used for investigating the degradation of PMMA as a function of temperature. This polymer was heated up 550 °C with the heating rate of 10 °C/min under a nitrogen flow of 200 ml/min.

Figure 2.17 Perkin-Elmer Diamond TG/DTA used in characterising the thermal degradation of PMMA [116].

2.5.8 X-ray Diffraction

X-ray diffraction (XRD) is a non-destructive technique used to identify the chemical composition, determine the degree of crystallinity and analyse the atomic level structure of a material. In XRD, an X-ray beam hits a sample and the diffracted beams emerging from it are detected. The intensity of diffraction is dependent on the interaction of the beam with the sample. Schematically, the principle of the technique is illustrated as shown in Figure 2.17.
2. Experimental Procedure

![Diagram of diffracted beams](image)

Figure 2.18 Schematic illustration of the diffracted beams.

The diffraction pattern was first described by Max von Laue (1912) and then William Lawrence Bragg and William Henry Bragg (1913) postulated Bragg’s law to explain the patterns [117-119].

\[
n\lambda = 2d\sin\theta
\]  

(2.7)

where \(n\) is the order of the diffraction beam, \(\lambda\) is the wavelength of the incident wave, \(d\) is the spacing between the adjacent planes of the atoms and \(\theta\) is the incidence of X-ray beam. The diffraction pattern is a plot of intensity vs. the scattering angle, \(2\theta\).

In this work, a Philips X’Pert MPD XRD (Figure 2.18) was used for investigating the thermal effects on crystallinity and domain size of both Cu foil and thin Cu film (see Chapter 3). The intensity and peak of samples resulted were observed with the diffraction spectrum. The intensity of the investigated samples is associated with the orientation of different crystallographic planes. The peak width of the samples corresponds to the average crystallite size. In fact, a sharp peak indicates a sample with large crystallite size, while the broad peak is due to a decrease of crystallite size. The broadening of the XRD peak can also result from variation in d-spacing caused by microstrain.
2. Experimental Procedure

2.5.9 Raman Spectroscopy

Raman spectroscopy is a powerful technique for characterising sp\(^2\) and sp\(^3\) hybridised carbon atoms, including those in graphite and graphene \([52, 120-122]\). This spectroscopic technique is based on inelastic scattering of monochromatic light by using a laser usually with a power of up to 2 watts. For power in milliwatts, the analysed sample does not suffer damage. Using a large sample spot also significantly reduces the risk of sample damage. Schematically, the Raman instrumentation is shown in Figure 2.19a. The laser power, which is controlled by an optic attenuator is directed to the sample by a microscope objective, which leads to an excitation of sample. The excited sample causes Rayleigh and Raman scattering. Rayleigh scattering is filtered out, while Raman scattering is collected by a lens and then sent through interference filter (wavelength selector) to obtain the Raman spectrum. The spectrum gives information about the rotational and vibrational modes and low frequency transitions of the sample. The shifted frequency is due to an energy gain or loss associated with the vibrational energy of sample.

Figure 2.19 Philips X’Pert MPD XRD used in characterising the samples.
Figure 2.20 Schematic diagram of the Raman system (top) [122, 123], photograph of UNSW Renishaw inVia Raman microscope system (bottom).
In this work, a Renishaw inVia Raman microscope (Figure 2.19b) based at the University of New South Wales (UNSW) was used to characterise the number of graphene layers and identify the quality of the structure of the graphene. The Raman spectrum visibly assigns three prominent peaks: $D$, $G$ and $2D$ at $\sim 1350 \text{ cm}^{-1}$, $\sim 1582 \text{ cm}^{-1}$ and $\sim 2685 \text{ cm}^{-1}$. The $D$ peak relates the disordered structure of graphene - the absence of $D$ peak in Raman spectra indicates that graphene has a perfect structure. The $G$ peak corresponds to the planar configuration $sp^2$ bonded carbon that constitutes graphene - the shifting of peak position gives information about the graphene layer thickness. The $2D$ peak is the spectrum of graphene - the intensity and shape of $2D$ peak indicates the number of graphene layers [122, 124].

2.5.10 OSC device I-V characterization

The current-voltage (I-V) curve for an OSC device can give information as to how effective the device is performing. In testing the device, a standard condition used is under Air Mass 1.5 (AM1.5). AM1.5 describes the spectrum of solar radiation that consists of wavelengths ranging from the far infrared to the near ultraviolet. This typical value of AM represents an optical path which is 1.5 times the thickness of atmosphere, which is achieved when the sun is at an angle of $48.2^\circ$ above the horizon, as seen in Figure 2.21 [87].
Experimental Procedure

Figure 2.21 The zenith angle of the sun (top) and the solar radiation spectra of AM0 & AM1.5[125-127].

In this work, a Newport Class A solar simulator (Figure 2.22), which approximates a standard reference solar spectrum and intensity, was used for illuminating the tested devices. This simulator contains a xenon incandescent lamp and an AM1.5 filter. The xenon lamp has a very flat spectrum within the range of 300-1000 nm leading to an ideal light source for generating the AM1.5 illumination condition, while the AM1.5 filter provides a spectrum close to the AM1.5 spectrum. The simulator intensity was set to 1 sun (100 W/cm²) using neutral density filters and measured with a calibrated silicon photodiode (PV Measurement Inc.) with a KG-5 filter.
Figure 2.22 Newport AM1.5 solar simulator with a sample holder used in testing the OSC devices.

For characterising the OSC device I-V curve under either dark or illumination conditions, a computer-controlled Keithley 2400 Source-Meter unit was used. The sourcemeter systematically sweeps the potential between the two electrodes of the device, while concurrently recording the output current produced by the device under test. All devices were tested in a sample holder and under an N\textsubscript{2} atmosphere. The experimental setup is shown in Figure 2.23. Schematically, the workings of the simulator are shown in Figure 2.24 and consist of a Xenon lamp and associated optics.
Figure 2.23 Experimental setup of device I-V characterisation.

Figure 2.24 The schematic of the simulator [128].
This chapter outlines a comparative study of the effect of thermal annealing on the morphology of two different copper substrates including commercial copper foil and thin copper film. The thermal treatment on these copper will be carried out by varying the annealing temperature, annealing time and hydrogen flow rate. The aim of this study is to find an optimum condition for preparing the copper foil and thin copper film substrates for graphene growth.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

3.1 Introduction

There are a few options for catalysts to be used for graphene growth, such as, Ni, Pd, Ru, Ir and Cu, which have been reported in the literature [129]. The most well studied and promising catalysts are nickel and copper due to their ready availability, and they have attracted extensive interest in the last three years since the report of large-area graphene thin films for conductive and transparent electrodes by Kim et al. [1, 130, 131]. In particular, copper foils and copper thin films have been widely employed.

As discussed in Chapter 1, the preference for copper catalysts is due to a few reasons. Firstly, the Cu/C binary phase diagram shows a low carbon solubility [132, 133] which limits the amount of segregated C on the catalyst surface and hence precludes the growth of additional graphene layers from the bottom growth interface [73]. Secondly, the absence of a copper carbide line compound [73]; and, thirdly, wet etchant selectivity to graphene [134]. The quality of the resulting graphene is greatly influenced by the morphological and crystallite properties of the catalyst which can be refined by thermal annealing. To ensure high quality graphene deposition, this treatment serves two main functions. Firstly, the catalytic activity of copper can be increased by removing the native oxides, i.e. tenorite (CuO) and cuprite (Cu₂O) [135], which may cover the as-received Cu surface. To remove the oxides, the as-received copper must be annealed by introducing hydrogen as a reducing gas [98]. Secondly, by increasing the Cu grain size and rearranging the surface morphology the growth of large graphene flakes can be facilitated [136].

There are some practical complications involved when using copper foils as the catalyst. For example, it takes quite a number of hours to etch away the copper foil as the thickness of a copper foil is generally in the range of tens micrometres. The etching of different Cu catalyst thicknesses (12.5, 25 and 50 µm) was conducted by Xuesong Li, et al. [3] showing that the etching time was a function of thickness. Furthermore, it normally requires a transfer step which uses PMMA as the transfer agent, which is very hard to wash off completely once the graphene film is transferred to a substrate and can lead to contamination to some degree.
To eliminate the transfer step, much thinner (hundreds of nanometres) copper thin films are more desirable. These copper thin films can be easily deposited to selected substrates and be etched away quickly without the need for a transfer step. Annealed copper foils preferentially form as a Cu(100) crystalline face [137], while thermally grown copper thin films lead to prefer in the Cu(111) crystalline orientation. These different crystalline structures lead to different graphene growth which has been reported by Ruoff etc. Further work by Pasupathy [138] also reported that a single crystal Cu(111) face is superior to a Cu(100) face to grow more uniform graphene sheets. However, thermally grown copper thin films form small nanodomains and require an annealing step to form large domains which in turn, determine the dimensions of the graphene sheet and electrical properties of the graphene films. Therefore, it is especially important to understand the exact crystal structure evolution of copper thin films during the pre-treatment before the graphene growth.

To understand the formation of large grain sizes within the copper surface, the growth mechanism of the new texture needs to be considered, particularly the recrystallisation kinetics. The recrystallisation of copper can be influenced by many factors including deformation degree, deformation rate, annealing temperature, annealing time, starting grain size, existing impurities and others. Among them, the annealing parameters play a crucial role in forming the desired texture [139]. The annealing process is distinguished by three different stages, as schemed in Figure 3.1 [140, 141]:

1. **Recovery**
   In this process, the rearrangement of dislocations and the annihilation of point defects occurs within the existing grains, but no change in the grain structure takes place. The results of this process are the formation of subgrains and subgrain boundaries. Usually, this stage takes place at low temperatures (\(< 300 ^{\circ}C\)) [142-144].

2. **Recrystallisation**
   This stage is a process of nucleation and growth of strain-free grains in the deformed matrix occurs due to thermal activation. This thermal activation increases with increasing temperature. The growth of new grains leads to the elimination of
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Dislocations at the boundaries of the newly-formed grains. The lowest temperature at which these are no appearance of stress-free grains in the structure of a previously plastically deformed material is called the recrystallisation temperature.

3. Grain growth

This process is a grain growth of recrystallised material such that its grains become larger. The occurrence of larger grain growth results from further annealing at the same temperature or at a higher temperature. Boundaries between the annealed grains migrate to form a larger grain size.

![Figure 3.1 Schematic of the effects of annealing treatment: (a) recovery, (b) recrystallisation, and (c) grain growth.](image)

The formed copper substrate grain boundaries, on the other hand, induced by the thermal annealing process result in defects in the crystal structure of CVD grown graphene film. The occurrence of defects is due to the bonding of the carbon atoms along those lines not following the simple Bravais lattice from a repetition of the unit cell. This acts as a barrier for charge transport resulting in the degradation of the electrical properties of the deposited film. Moreover, these boundaries can significantly degrade the superlative mechanical property of graphene. Therefore, it is desirable to maximise the size of domains to limit the frequency of domain boundaries.

This chapter outlines a detailed study of the grain size, crystallinity and surface morphology as a function of thermal processing. The goal of this chapter is to provide
insights into effects of thermal annealing on copper on which graphene is grown at high temperatures. The thermal annealing of copper by varying the annealing temperature, annealing time and hydrogen flow rate were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy disersive X-ray spectroscopy (EDS) analysis.

### 3.2 Experimental Setup

To prepare a catalyst with high quality for growing graphene, two kinds of copper, i.e. commercial copper foil (99.98 % purity; 25 µm thick) and thin copper film (99.99+ % purity; 500 nm thick), were employed for studying the effects of thermal annealing on their microstructure, as listed in Table 3.1. All these experiments were conducted in an Atomate CVD furnace (Figure 3.2) by introducing a mixture of H$_2$/Ar (50 and 100 sccm, respectively) gas under a pressure of 500 mTorr, except for the study of the variation of hydrogen flow rate. The introduction of hydrogen gas is desired to reduce copper oxides which may occur on the surface, while argon gas is applied to remove H$_2$O steam as reaction products or unwanted gases. Properties of the studied samples were characterised by using XRD for the crystal structure and SEM for the morphological surface, while EDS analysis was used to confirm the presence of copper oxide on the hydrogen-free flowed sample.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Table 3.1 The variation of experiment conditions for studying the effects of thermal annealing on the microstructure of copper foil and thin copper films.

<table>
<thead>
<tr>
<th>Copper kind</th>
<th>Annealing temperature (°C)</th>
<th>Annealing time (min.)</th>
<th>Hydrogen flow rate (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial copper foil</td>
<td>700</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>Thin copper film</td>
<td>450</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

### 3.3 Results and Discussion

In order to study the effect of annealing on the microstructure of both types of annealed copper substrates, in particular the crystal structure of the samples, X-ray diffraction measurements were used. In this technique, a CuKα radiation source ($\lambda = 1.54056$ Å) was employed and the diffraction patterns were recorded by varying diffraction angle (20) in the range 30° to 80°. XRD patterns of the as-received copper foils and the as-evaporated thin copper films are shown in Figure 3.3. Three major peaks at 20 (degrees) values of 43.4°, 50.6° and 74.2° are well defined. These peaks respectively correspond to reflections from the (111), (100) and (110) planes. A much more preferential orientation in the [100] and [111] directions as observed from the samples of copper foil and thin copper film, respectively. All the diffraction peaks measured in the 20 range
correspond to the face-centered cubic (FCC) structure of copper with lattice constant $a = 3.615 \, \text{Å}$ and is in good agreement with the standard data card (JCPDS Card No. 85-1326) value [145]. The sharpness of the diffraction peaks suggests that the as-received copper foil and the as-evaporated thin copper film are well crystallized. Moreover, the absence of copper oxide (i.e. CuO, Cu$_2$O) peaks indicates the high quality of prepared samples.

Figure 3.3  XRD spectra of the as-received Cu foil (top) and the as-evaporated Cu thin film (bottom).
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

3.3.1 Effect of Annealing Temperature

To understand the effect of annealing temperature on the microstructure of the two types of copper substrate, two sets of annealing were employed in this study. One was a copper foil annealed at temperatures of 700, 800, 900 and 950 °C for 10 minutes. The other was thin copper film annealed at temperatures of 450, 600, 700, 800 and 900 °C for 1 hour. These samples were characterised by using XRD and SEM.

![XRD profiles](image)

Figure 3.4 XRD profiles measured at room temperature of the as-received and annealed copper foils.

Figure 3.4 shows XRD profiles of the as-received and annealed copper foils. Within the 2θ range revealed in this figure, three major reflections from (111), (100), and (110) planes at the angle of 43.4°, 50.6° and 74.2°, respectively, are identified on the as-received sample relating to the diffraction peaks of pure copper, and an extra peak on all annealed samples resulting from an impurity material. Comparing with the intensities of (111) and (110) peaks in the annealed samples, those of the (100) peak are very strong.
This significant difference indicates that the film is preferentially aligned in the [100] direction. In the (100) plane, the peaks on the samples annealed at 800 and 900 °C are stronger than those of the samples annealed at 700 and 950 °C. This observation is due to a re-crystallisation of the (100) plane in which some sub-grains coalesce to form a new grain, as clearly seen in Figure 3.5 on the 800 °C annealed sample. In this sample, the coalesced sub-grains are clearly observed with a size of around 100 µm. Moreover, the (100) peak of the sample annealed at 950 °C is slightly weaker than that of the samples annealed at 800 and 900 °C. This decrease is due to the completion of new grain formation which the shape of grain structure is more regularly oriented. In addition to these peaks, a low peak at 2θ value of 45.4° is detected indicating the presence of an impurity on it.

In addition to the XRD study of the crystal structure of the copper foil samples, the surface morphological features of the all samples were recorded by SEM with magnification 50,000x as shown in Figures 3.5. From the micrographs, it is seen that the samples annealed at 700 °C do not have an observable grain size. However, as the annealing temperature increases, the grain size grows significantly. In fact, at temperatures of 800 and 900 °C, grain structures with uniform coverage of the surface are well defined but with randomly oriented morphology. A grain shape with regular orientation is observed at 950 °C and the grain dimension is around 80 µm.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Figure 3.5 SEM images of the copper foils annealed for 10 minutes at 700, 800, 900 and 950 °C (scale bar: 100 µm).

Similarly, the microstructure of thin copper films annealed at temperatures of 450, 600, 700, 800 and 900 °C was also studied by using XRD and SEM techniques as revealed in Figure 3.6 and Figure 3.7, respectively. From Figure 3.6, it is found that the diffraction peak of (111) plane on the samples is more intense than that of (100) and (110) planes. This observation indicates that the crystal structure with a (111) plane is more favourable than the others. However, the intensity of this plane increases after annealing, indicating the formation of larger grain structures, consistent with the previous report by Vinci et al. [146]. A very strong (111) intensity is detectable when
the sample is annealed at 900 °C. This peak increase is due to further re-crystallisation with a much larger grain size. On the other hand, the peak of the (110) plane exhibits no significant change indicating that the thermal annealing treatment does not cause a formation of other grain textures.

![XRD patterns of the as-evaporated and annealed thin copper film samples.](image)

Figure 3.6 XRD patterns of the as-evaporated and annealed thin copper film samples.

To confirm the change of (111) diffraction peaks on the thin copper film, observations were made in the SEM images of the films. Figure 3.7 shows that a noticeable grain growth on the thin copper films is clearly observed after annealing at temperatures above 700 °C. In fact, at 800 °C, grain structures clearly appear with a dominant size of around 0.6 µm. A much larger grain size of around 1.3 µm occurs at 900 °C. This observation confirms that it is the large grain size that is strongly associated with the high intensity diffraction peak, shown in Figure 3.6.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Figure 3.7 SEM images of thin copper films annealed at different temperatures for 10 minutes.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Thus, it is clear that annealing temperature is a critical factor affecting the structure of the copper films due to grain-boundary diffusion at high temperatures [147]. Our observation of the evolution of thin copper film morphology from 450 to 900 °C indicates that higher annealing temperatures lead to larger grain size as shown in Figure 3.7.

3.3.2 Effect of Annealing Time

In order to study the effect of annealing time on the microstructure of copper catalysts, the copper foil was further studied by annealing for various annealing times (10, 30, 60 and 90 minutes) at a selected annealing temperature of 900 °C. The thin copper film evaporated on glass substrate was annealed for times of 1, 5, 10, and 20 hours at a fixed temperature of 450 °C. One of the applications of the graphene electrodes is to replace indium tin oxide (ITO) as the transparent electrode for flexible organic photovoltaics (OPV) which require a low temperature process, therefore, a relative low temperature at 450 °C annealing temperature was also been selected for an extended period of annealing time and compared to the high temperature (> 600 °C) annealed counterparts.

Figure 3.8 shows that the diffraction peaks of the (111) and (110) planes are very weak, while the diffraction peak of (100) plane is significantly stronger. The weakness of the peaks indicates that the film content of these planes is much less than that of (100) plane, as discussed previously. Additionally, the (100) diffraction peak of the 90-min annealed sample is slightly weaker than that of the other annealing times. The decrease of this intensity results from the completion of recrystallization.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Figure 3.8 XRD patterns of the copper foil samples annealed for 10, 30, 60 and 90 minutes at 900 °C.

To observe the morphological surface of the above four samples, SEM was used with a magnification of 50,000x, as shown in Figure 3.9. From these observations, there is no significant difference on the grain size of 900 °C annealed copper foils for the different times. However, there is a slight morphological difference which is observable. For 10 and 30 minutes, the surfaces appear rough and some grain sizes are not well-defined. Whereas, for 60 and 90 minutes the surfaces appear quite smooth and all grain sizes are well defined.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

![SEM images of copper foil annealed at 900°C for 10, 30, 60 and 90 minutes.](image)

Figure 3.9  SEM images of copper foil annealed at 900°C for 10, 30, 60 and 90 minutes. (scale bar : 100 µm)

Similarly, another study of thin copper films to further understand the grain formation was conducted by annealing for various times of 0, 1, 3, 5, 10 and 20 hours at the fixed temperature and hydrogen flow rate of 450 °C and 50 sccm. The main reason behind the selection of the low annealing temperature was that the film was evaporated on a glass substrate. Figure 3.10 shows XRD patterns of the samples annealed for three different times of 2, 5 and 20 hours. In this figure, it appears that the intensity of (111) diffraction peak systematically increases with increasing annealing time. This is an indicator that increased recrystalisation occurs on the samples annealed for longer times. Figure 3.11
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

shows a series of SEM images with magnification of 250000x indicating the morphology at different reaction stages corresponding to the different annealing times. From the micrographs in Figure 3.11, it appears that the grain size develops with increasing annealing times. The increase of grain dimension is about 8 to 18 times the original size with the largest grain size of ~680 nm, seen on the 20 hour annealed sample.

Figure 3.10  XRD patterns of the thin copper films annealed at 450 °C for different times of 2, 5 and 20 hours.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Figure 3.11  SEM images of thin copper film annealed at 450 °C for 0, 1, 3, 5, 10 and 20 hours.
3.3.3 Effect of Hydrogen Flow Rate

Hydrogen is a reducing gas which plays a crucial role in forming the surface morphology of the copper catalyst. When hydrogen is introduced, a number of the gas molecules are absorbed by the catalyst. The absorbed hydrogen interacts with impurities in the microstructure to form an insoluble, generally gaseous phase such as $\text{H}_2\text{O}$. The hydrogen in the bulk copper is very mobile and begins to accumulate at pores and micropores related to grain boundary inclusions or other microstructural defects. The diffusivity and solubility of hydrogen in copper is very low, thus achieving equilibrium of hydrogen saturation in copper takes exceptionally long times. Consequently, the permeability of hydrogen through copper is also very low due to the combination of low diffusivity for hydrogen and low solubility of hydrogen.

Copper alloys are susceptible to hydrogen attack because hydrogen can reduce copper oxide, producing copper and water through reaction,

$$\text{Cu}_2\text{O} + \text{H}_2 \rightarrow 2\text{Cu} + \text{H}_2\text{O}$$

When the reaction takes place at temperatures above the critical temperature of water, the copper oxide inclusion is replaced with vapour phase water which is virtually insoluble in copper.

To determine the influence of hydrogen gas on the formation of morphological structure on copper’s surface, both kinds of copper substrate were studied by annealing under various flow rates. The goal of this study is to find an optimal hydrogen flow rate for resulting in a smooth surface of the substrates. Considering the crucial role of hydrogen gas in forming the surface morphology of the substrates, a shorter annealing time is preferred since the grain formation on the substrates occurs. From the previous study of different annealing times on both the substrates as shown in Figure 3.9 and 3.11, the grains were formed on copper foil and thin copper film when annealed for 10 minutes and 1 hour, respectively. Consequently, in this study, the copper foil was introduced to flow rates of 0, 5, 25, 50, 100 and 200 sccm with a fixed annealing temperature and
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Figure 3.12 reveals SEM images of copper foils annealed by introducing different hydrogen flow rates at a fixed temperature and time of 900 °C and 10 minutes, respectively. Rises in the hydrogen flow rate leads to the structure of the surface changing such that the structure enlarges and also coalesces resulting in a smoother surface, excepting the 200 sccm-treated foil. The foils introduced with 0 sccm and 5 sccm show a structure with slightly similar shape and size, but with more contaminants on the foil treated in the hydrogen-free atmosphere. By increasing the hydrogen flux to 25 sccm, some structures coalesce with increase in size. When the flux is increased further, it is clear that a smooth surface appears due to the completion of structure coalescence. However, the 200 sccm-treated copper foil shows a growth of new structures with various shapes and sizes resulting in a rough surface. This observation indicates that the optimal condition to prepare the copper foil as catalyst for graphene growth is by annealing at the temperature of 900 °C for 10 minutes under the hydrogen flow rate of 100 sccm.

Figure 3.13 shows that no significant development of the grain size is observed with increasing the flux of hydrogen gas. However, the grains are well-defined with irregular shapes and sizes when introducing a hydrogen flow rate above 10 sccm. The grains are not clearly observable on the samples introduced with 5 sccm and without hydrogen gas, and the hydrogen-free treated film surface is much rougher than that of the 5 sccm-treated surface. This roughness may be caused by the presence of a thin oxide layer. This study shows that the 1 hour-treated hydrogen flow rates do not form a larger grain, meanwhile, the large grain size can facilitate the growth of large graphene flakes [136]. In comparison, the grain size of the 20 hours-annealed thin Cu film with the fixed hydrogen flow rate of 50 sccm (see Figure 3.11) was much larger than that of the 1 hour-annealed thin Cu film with the varied hydrogen flow rates (see Figure 3.13). This reveals that the best condition to prepare the thin copper film as catalyst for graphene
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

growth is by annealing at the temperature of 450 °C for 20 hours under the hydrogen flow rate of 50 sccm.

Figure 3.12 SEM images of copper foils annealed at 900 °C for 10 minutes under different flow rates of hydrogen gas.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Figure 3.13 SEM images of thin copper film at 450 °C for 1 hour under different flow rates of hydrogen gas (scale bar: 1 µm).
Apart from the SEM observation, another characterisation used in this study was EDS analysis. This method was applied to confirm the presence of a thin oxide layer on the hydrogen-free flowed thin Cu film (see Figure 3.13). In EDS analysis, two different energies of 2 and 10 keV were applied in order to identify the element contents in different depths on the copper bulk, with the higher energy electron beam probing deeper into the bulk of the material [148, 149]. By applying the 10 keV energy, the presence of carbon, oxygen and copper elements is detected as shown in Figure 3.14. Interestingly, when applying the 2 keV energy, the content of carbon and oxygen elements increases, while the copper content decreases. This change is due to the formation of both elements on the copper surface, indicative of a thin copper oxide layer and amorphous carbon layer being formed on the surface. To identify the kind of copper oxide, XRD was used. In this XRD experiment, two low extra peaks are found at 36.4° and 60.0° indicative of resulting from the copper oxides of Cu₂O [111] and Cu₂O [220], respectively, as seen in Figure 3.15 [150].

![Figure 3.14](image)

Figure 3.14  EDS analysis of the sample annealed at 450 °C under the hydrogen-free atmosphere by applying two different energies of 2 and 10 keV.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Figure 3.15  XRD profile of the thin copper film annealed at 450 °C under the hydrogen-free atmosphere.

Considering the SEM observations on the hydrogen-treated substrates, it can be summarised that the 900 °C-annealed Cu foils show an enhanced grain growth in increased H₂ flow rate due to removal of impurities that “pin” the grain boundary diffusion. Another summary is that the 450 °C-annealed thin Cu films are no change in grain size as result of the insufficient energy for recrystallisation. However, the smoothing of the surface occurs as impurities are removed and rearrangement of Cu atoms within the grains is enabled.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

3.3.4 Crystallite and Grain Sizes

3.3.4.1 Crystallite Size

To get a deeper insight into the influence of annealing on the copper microstructure, the crystallite size of the grains in both kinds of copper substrates were calculated. Crystallites are crystal units in a material that diffract in phase. When related to metallic films, the term ‘crystallite’ is also used to represent the crystal units in metallic films. In principle, the analysis of the crystallite size in XRD patterns is performed by measuring the broadening of a particular peak in a diffraction pattern associated with a particular planar reflection from within the crystal unit cell. The crystallite size \( D \) of the copper can be deduced using the Debye-Scherrer formula as follows [151]:

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

(3.3)

where, \( \lambda \) is the wavelength of the incident X-rays (0.154056 nm for Cu K\( \alpha_1 \)), \( \beta \) the half width of diffraction peak measured in radians, and \( \theta \) the diffraction angle. From Equation 3.3, the crystallite size is inversely related to the full width half maximum (FWHM) of the diffraction peak. The more narrow the diffraction peak, the larger the crystallite size. The calculation of crystallite size from XRD is a quantitative approach which is widely accepted and used in scientific community.

The K\( \alpha_1 \) and K\( \alpha_2 \) radiations cannot be separated by the XRD monochromator resulting in two different closely neighbouring peaks with the K\( \alpha_2 \) peak on the right. The intensity of the K\( \alpha_2 \) line is about half of the corresponding K\( \alpha_1 \) line. The two peaks are more clearly separated with increasing diffraction angle [152]. By considering this statement, the FWHM of diffraction peak can determined by measuring the peak width at the intensity value of K\( \alpha_2 \) peak, as illustrated in Figure 3.16.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

In this study, the calculation of crystallite sizes was carried out on the greatest preferential orientation of each copper kind. From the above XRD patterns in Figures 3.3, 3.5, 3.7 and 3.9, the greatest degrees of crystallographic orientation are the (100) and (111) planes for the copper foil and the thin copper film, respectively. The average crystallite sizes calculated are tabulated in Table 3.2, 3.3, 3.4 and 3.5.

3.3.4.2 Grain size

Copper is a polycrystalline material composed of aggregates of many small, different types of crystals joined at boundaries. The aggregations of individual crystals are called “grains” and the boundaries between them are “the grain boundaries”. Grain size and the corresponding spatial distribution of grain boundaries have an important impact on the morphology of copper surface. When annealing, the morphology can change to be smooth with much better uniformity in grain and even the grain size becomes bigger [153].
In order to estimate the planar grain size, an efficient and unbiased technique used was the standard intercept count method of ASTM E112 [154], which is based on the number of grain boundary intersections per unit length, \( P_L \). This unit is a random test line that produces on statistically representative sections [155]. Mathematically, it is defined as:

\[
P_L = \frac{P_i}{L_T/M}
\]

(3.4)

where \( P_i \) is the number of grain boundary intersections counted on the test line, \( L_T \) is the total test length and \( M \) is the magnification.

The reciprocal of \( P_L \) is the mean lineal intercept length, \( L_\varepsilon \), that is the average length of a line segment crossing a sufficiently large number of grains. It is proportional to the equivalent diameter of a spherical grain.

\[
L_\varepsilon = \frac{L_T}{P_i \times M}
\]

(3.5)

In this study, the determination of grain sizes on both of the copper substrates was obtained by using the standard intercept count method of ASTM E112. Figure 3.17 shows a SEM micrograph of a copper foil sample that has been increased the brightness and contrast to clearly differ the boundaries between grains. To calculate the number of grain boundary intersections, a test circle with eight straight-line segments is placed on this image. The number of these points are determinated by counting 1 for each intercept, 1 for each tangential intersection, 0.5 when the end of test line ends exactly on a grain boundary and 1.5 when the intersection occurs at a triple point. By recalling Equation 3.5, the grain size of the sample can be determined. The average grain sizes on samples as shown in Figure 3.5, 3.7, 3.9 and 3.11 are tabulated in Tables 3.2, 3.3, 3.4 and 3.5.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Figure 3.17 SEM image of 800°C-annealed copper foil with high brightness and contrast.

Table 3.2 Average crystallite size of the as-received and annealed copper foil at various temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Crystallite size</th>
<th>Grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T_{\text{ann}})</td>
<td>(D) (nm)</td>
</tr>
<tr>
<td>Unannealed</td>
<td></td>
<td>125.0</td>
</tr>
<tr>
<td>700</td>
<td></td>
<td>208.3</td>
</tr>
<tr>
<td>800</td>
<td></td>
<td>208.2</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td>178.2</td>
</tr>
<tr>
<td>950</td>
<td></td>
<td>178.4</td>
</tr>
</tbody>
</table>
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

Table 3.3  Average crystallite size of the copper foil annealed at 900 °C for various times.

<table>
<thead>
<tr>
<th>Annealing time $t_{\text{ann}}$ (min)</th>
<th>Crystallite size $D$ (nm)</th>
<th>Grain size $L_\varepsilon$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>178.2</td>
<td>87</td>
</tr>
<tr>
<td>30</td>
<td>207.8</td>
<td>88</td>
</tr>
<tr>
<td>60</td>
<td>201.1</td>
<td>82</td>
</tr>
<tr>
<td>90</td>
<td>131.5</td>
<td>78</td>
</tr>
</tbody>
</table>

Table 3.4  Average crystallite size of the as-evaporated and annealed thin copper film

<table>
<thead>
<tr>
<th>Annealing temperature $T_{\text{ann}}$ (°C)</th>
<th>Crystallite size $D$ (nm)</th>
<th>Grain size $L_\varepsilon$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td>43.7</td>
<td>0.05</td>
</tr>
<tr>
<td>450</td>
<td>91.1</td>
<td>0.08</td>
</tr>
<tr>
<td>600</td>
<td>91.9</td>
<td>0.66</td>
</tr>
<tr>
<td>700</td>
<td>109.3</td>
<td>0.67</td>
</tr>
<tr>
<td>800</td>
<td>110.2</td>
<td>0.66</td>
</tr>
<tr>
<td>900</td>
<td>121.4</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Table 3.5  Average crystallite size of the thin copper film annealed at 450 °C for various times.

<table>
<thead>
<tr>
<th>Annealing time $t_{\text{ann}}$ (hour)</th>
<th>Crystallite size $D$ (nm)</th>
<th>Grain size $L_\varepsilon$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td>43.7</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>84.1</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>91.1</td>
<td>0.38</td>
</tr>
<tr>
<td>20</td>
<td>91.1</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Particularly, the results of above tabulated-crystallite and grain sizes as a function of annealing temperature are plotted in Figure 3.18. It is clearly seen that the crystallite sizes of both catalysts increase significantly after annealing. While, the significant increase of grain sizes occurs after annealing beyond 800 °C and 450 °C for Cu foil and thin Cu film, respectively.

Figure 3.18 Crystallite and grain sizes on Cu foil (above) and thin Cu film as a function of annealing temperature.
Based on the crystallite and grain sizes as tabulated above, the crystallite size of the (100) plane is bigger than that of (111) plane. In fact, the crystallite size of the Cu foil is ~ 1.5-2 times than that of the thin Cu film. More significantly, the grain size of Cu foil (~ 80 µm) is much bigger than that of the thin Cu film (~1 µm). The average crystallite size of both copper kinds slightly increases after annealing compared with their original size. For thin copper films, the crystallite size gradually grows bigger with increasing annealing temperature, but there is no significant change for various times. By contrast, the copper foil does not show an increase of crystallite size when annealed above 800 °C and a significant decrease of crystallite size when annealed for the longer time of 90 minutes. These results show that annealing provides larger crystallites compared to the original size. In addition to the crystallite sizes, the grains of Cu foil are well defined after annealing above 700 °C. The formed grain sizes do not show a significant change by increasing the annealing temperatures and times. On the other hand, the grains of the unannealed thin Cu film are observed to be ~ 0.05 µm in size. An increase of grain size occurs when annealed beyond 600 °C and more significantly increases when annealed at 900 °C with ~ 1.3 µm in size. Moreover, a slight increase of grain size is observable by increasing the annealing times.

By studying the effect of the annealing temperature, annealing time and hydrogen flow rate on copper foil in forming a grain structure, an annealing temperature at 900 °C for 10 minutes under hydrogen flow rate of 100 sccm was selected at the optimum conditions. These experimental parameters were employed when annealing copper foil catalysts prepared for growing graphene, as discussed in Chapter 4. While, the combination of parameters for thin copper was selected to be an annealing temperature at 450 °C for 20 hours under hydrogen flow rate of 25 sccm. The choice of this low temperature is due to the use of glass as a substrate in evaporating thin copper film. Glass undergoes mechanical changes, such as bending, when annealed above 450 °C and even melts when annealed above 550 °C. The chosen experimental parameters were employed in providing the catalyst for growing graphene, as discussed in Chapter 5.
3. A comparative study of the effect of thermal annealing on the morphology of copper foils and thin copper films as catalyst for graphene growth

3.4 Conclusion

As-received copper foil and as-evaporated thin copper film were annealed with various temperatures, times, hydrogen flow rate for studying the change of structural and morphological properties. The foil was annealed: initially at 700-950 °C for a fixed time and hydrogen flow rate of 10 minutes and 50 sccm, respectively, then for 10 to 90 minutes at the selected temperature 900 °C and a fixed hydrogen flow rate of 50 sccm, and finally under various hydrogen flow rates of 0, 5, 25, 50, 100 and 200 sccm by selecting the temperature and time of 900 °C and 10 minutes. In contrast, the thin Cu film was annealed firstly at 450 to 900°C for a time and hydrogen flow rate of 1 hour and 50 sccm, respectively, then for 1 to 20 hours at the fixed temperature and hydrogen flow rate of 450 °C and 50 sccm, and lastly under hydrogen flow rates of 0, 5, 10, 25, 50 and 100 sccm by selecting the temperature and time of 450 °C and 1 hour. Structural properties were studied by means of XRD, SEM and EDS analysis. The XRD results revealed that both of the copper substrate types have a good nanocrystalline cubic structure, dominated by (100) and (111) planes for the copper foil and the thin copper film, respectively. Moreover, the absence of copper oxide peaks on the annealed copper under hydrogen atmosphere indicates that the reducing gas effectively removes the copper oxide impurities. The SEM results show that the samples annealed at beyond 900 °C have a smooth surface morphology with uniform coverage and large grain size around 1.3 and 80 µm for thin copper film and copper foil, respectively. An optimal hydrogen flow rate of 100 sccm for smoothing the copper foil surface was determined.
4

Low-Temperature Growth of Graphene on Copper Foil Using PMMA-Derived Carbon Source

4.1 Introduction

For the mass production of conductive transparent electrodes, a growth technique is required which can produce high-quality graphene in a cost-effective manner. In this context, chemical vapour deposition (CVD) using metal catalysts is a promising method which has the potential to achieve high quality graphene growth across large area [1, 32, 156]. The formation of graphene by CVD using gaseous hydrocarbon carbon sources has been investigated by employing metal catalysts including ruthenium, nickel, iridium, copper cobalt, platinium, molybdenum [2, 3, 33, 61, 72, 156-161]. Of these
metals, nickel and copper are the two most used catalysts when forming graphene films due to the modest cost and availability [162]. Thin nickel film was used as a catalyst for growing a CVD large-area graphene films [2, 163], but the high carbon solubility and small grain size of this metal seem to limit the single layer defect-free growth. Moreover, the high absorption of this metal results in an overabundance of carbon which crystallises into discrete graphite domains and often produces inhomogeneous films. Therefore, nickel is not favoured for use as a catalyst to produce a uniform, large-area, single-layer graphene. On the contrary, copper attracts less carbon (onto its surface only rather than absorbing it into its bulk), since weak bonds hold the carbon atoms to copper’s surface. These bonds can only be formed with open bonding sites at the surface of the lattice. Additionally, copper allows a self-limited growth resulting in monolayer graphene. Therefore, copper is the most favoured catalyst which can facilitate the growth of large-area, highly conductive and transparent graphene films with uniform single-layer thickness [32, 164].

In addition to the use of metal catalysts in growing graphene, various kinds of carbon sources have also drawn attention from researchers. Methane gas is one of most used carbon sources in the formation of single layer or multiple layer graphene by CVD [32, 75, 99, 132, 165]. The number of graphene layers obtained highly depends on the CVD growth conditions including temperature [74], methane flow rate and partial pressure [32, 75, 99, 132]. However, this precursor requires a high growth temperature, typically 1035 °C [99]. A low temperature growth technique is more desirable, since it is more convenient, economical, environmentally-friendly, and suitable for industrial application. Recently, Sun et al. reported graphene growth at low temperatures using solid carbon sources such as poly(methyl methacrylates) (PMMA), sucrose and fluorene [76]. The lowest temperature applied for growing graphene was 400 °C. However, graphene films with free defect formation were only obtained by growing at a minimum temperature of 800 °C [76]. More recently, using liquid carbon sources such as benzene or pyridine, Li et al. [77] and Liu [166] et al. reported that a single layer of graphene can be fabricated at a temperature as low as 300 °C. However, these reports did not detail the electrical properties of these low-temperature grown graphene films after transfer, and whether or not it is possible to produce graphene on a large scale.
In this work, graphene growth on Cu foil (99.98% purity; 25 µm thick) at relatively low temperatures (below 500 °C) under a low pressure of 500 mTorr is demonstrated using PMMA as the carbon source. The CVD method used features a much lower growth temperature than previously reported \([1, 32, 71, 75]\). In this method, some important experimental parameters including precursor temperature, growth time and temperature were varied to investigate their effects on resulting graphene film. The as-grown graphene film on the foil was transferred onto target substrates using a sacrificial PMMA layer. The surface morphology and electrical conductivity of the fabricated film were characterised.

### 4.2 Experimental Setup

#### 4.2.1 Sample Preparation

As-purchased copper foil (Sigma-Aldrich, code: 1001328641, 25 µm in thickness, 99.98% trace metals basis, cut into 2x1 cm\(^2\) in size) was prepared for using as a catalyst in the CVD process. The cut copper foil was cleaned up, as mentioned in Subsection 2.1.2, in order to remove any unwanted contaminants. Afterwards, the cleaned foil was annealed at 900 °C for 10 min whilst under a flow of a H\(_2\)/Ar mixture (100 and 100 sccm, respectively) under a total pressure of 500 mTorr, as schematically shown in Figure 4.1. These annealing parameters were selected based on the results of previous experiments as discussed in Chapter 3. By thermal annealing, copper crystallites can be formed on the surface which gives an indication to the subsequent graphene growth. Figure 4.2 shows a comparative photograph of as-received and as-annealed copper foils. The surface of annealed foil appears much smoother and shinier than that of the as-received foil.
Figure 4.1  Furnace temperature versus time graph for the annealing process, with the corresponding argon and hydrogen flows.

Figure 4.2 Photograph of as-received (left) and as-annealed (right) copper foil.
4. Low-temperature growth of graphene on copper foil using PMMA-derived carbon source

4.2.2 Graphene Growth

The as-annealed copper foils were used as a catalyst for growing graphene film at low temperatures in a 2 inch diameter quartz tube furnace in the CVD system, into which PMMA-coated glass and the Cu foils are loaded. In this work, two different temperatures of 350 and 450 °C were employed for heating the catalyst on which the graphene film was grown. The carbon source of PMMA which was placed at a distance of 8 inches away from the catalyst and was heated at temperatures of 140 and 400 °C for various times. The carbon source was carried by argon and hydrogen gases toward the heated catalyst for growing graphene film. Figure 4.3 shows the scheme used for graphene growth on copper catalyst. The PMMA-coated glass and the cut copper catalysts were put on two different quartz boats. After adjusting the distance between both boats to 8 inches, they were loaded into the CVD tube. In the beginning of the growth process (Table 1), the tube was evacuated to 100 mTorr by using a mechanical pump. Once the pressure was achieved, the tube was back filled with argon gas (100 sccm) with the temperature maintained at 100 °C for 2 min. This gas is introduced to flush out the unwanted gases. Afterward, the temperature of the Cu foils was increased to the synthesis temperature of 450 °C for 5 minutes. Maintaining the catalyst temperature, the precursor was heated at the temperature of 140 °C for 1 minute. After the synthesis phase, the furnace was promptly cooled to room temperature for 30 min. At the end of the process, the cooled furnace was maintained at the same flow rate of argon gas for 5 min before the sample was removed. From the elevation to cooling-down process, the sample was exposed to a hydrogen flow rate of 50 sccm, while the system pressure and the flow rate of argon gas were maintained at 500 mTorr and 100 sccm, respectively.
4. Low-temperature growth of graphene on copper foil using PMMA-derived carbon source

Figure 4.3 Schematic of the graphene growth from PMMA-derived carbon source on Cu foils.

Table 4.1 A particular recipe used in growing graphene films

<table>
<thead>
<tr>
<th>Duration (h:m:s)</th>
<th>Precursor Temp. (°C)</th>
<th>Catalyst Temp. (°C)</th>
<th>H$_2$ (sccm)</th>
<th>Ar (sccm)</th>
<th>Pressure (mTorr)</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:02:00</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>500</td>
<td>Flush</td>
</tr>
<tr>
<td>00:05:00</td>
<td>100</td>
<td>450</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>Ramp up</td>
</tr>
<tr>
<td>00:01:00</td>
<td>140</td>
<td>450</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>Synthesis</td>
</tr>
<tr>
<td>00:30:00</td>
<td>25</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>Cool down</td>
</tr>
<tr>
<td>00:05:00</td>
<td>25</td>
<td>25</td>
<td>100</td>
<td>500</td>
<td></td>
<td>Flush</td>
</tr>
</tbody>
</table>

Generally, the mechanism of graphene growth on copper surfaces consists of nucleation sites, a subsequent expansion of the nuclei into domains, followed by the domains developing into a continuous covalently bonded film [167]. Figure 4.4 shows schematically the mechanism of graphene growth that corresponds to the decomposition of the PMMA molecule. The products of decomposition such as carbon radicals or gas molecules are transported toward the annealed copper by carrier gases (i.e. hydrogen and argon). The copper catalyst can accelerate the decomposition for forming graphene on the copper surface. In other words, the products coming closer to the copper catalyst are further decomposed resulting in metastable carbon atoms and molecules. The carbon
atoms are deposited on the copper surface on which a nucleation site with sp² structure is formed. The following carbon atoms are epaxially deposited onto the existing monolayer graphene film [168]. However, in reality, the formation of multilayer graphene flakes can still be occasionally obtained. This formation is due to the complicated kinetic procedures of the CVD growth process.

![Schematic mechanism of graphene growth involving the decomposition of PMMA.](image)

Figure 4.4 Schematic mechanism of graphene growth involving the decomposition of PMMA.

### 4.2.3 Graphene Transfer

In order to transfer a graphene film onto the desired substrate, the unloaded sample from the CVD furnace is first covered with a thin polymer film. This film serves as mechanical support for graphene film during subsequent processing steps. Next, the
copper is removed using an etchant, leaving the graphene attached only to the polymer. After transferring the graphene/polymer film onto the desired substrate, the graphene film can be isolated by dissolving the polymer using a solvent [1, 169].

In this work, PMMA was chosen as a supporting layer since it can provide a rather smooth and flat surface and prevent folding or tearing of the graphene film. Iron (III) nitrate nanohydrate [Fe(NO$_3$)$_3$.9H$_2$O] was selected as the etchant solution due to the absence of resulting gaseous products which can damage the graphene structure [2, 3]. The time taken for complete removal of the foil depends on the etchant concentration, the area, and thickness of the foil. Typically, a 1 cm$^2$ by 25 µm thick Cu foil can be completely dissolved by the aqueous iron nitrate solution of concentration 0.05 g/mL overnight [3]. Schematically, the transfer process of a Cu foil-grown graphene film is shown in Figure 4.5. Before the etching process, 75 µL of PMMA (dissolved in chlorobenzene with a concentration of 50 mg/mL) was spin-coated at 5000 rpm for 1 min on the graphene film on the Cu foil. Then, the PMMA-supported film was cured on a hot plate at 180 °C for 1 min. After annealing, the graphene/PMMA stack was removed from the Cu foil by etching away the foil in the solution for ~48 hours, resulting in the floating PMMA/graphene film. The floating PMMA/graphene film was picked up by a clean glass substrate and transferred to a petri dish containing deionized (DI) water for 30 min. The clean film was subsequently transferred onto a substrate and dried for ~1 hour in air. The dried PMMA film was re-dissolved by spin coating a 10 mg/mL PMMA solution (75 µL, 5000 rpm for 1 min). The new PMMA film was slowly cured at room temperature for ~30 min and then removed by the slow flow of acetone and IPA 3 times, respectively, leaving the graphene film on the substrate. The graphene film was dried with a stream of N$_2$ gas. The remaining water in graphene film can be removed by drying in a vacuum oven at 70 °C for 2 hours.
4. Low-temperature growth of graphene on copper foil using PMMA-derived carbon source

Figure 4.5 Schematic diagram of the process of transferring a Cu foil-grown graphene film.

4.2.4 Characterisation

In this work, characterisation of graphene was conducted both before and after transferring onto the target substrate. The graphene film grown on copper foil was characterised using two different methods. The first is through the use of SEM imaging, which was used to identify the nucleation sites and domain boundaries that formed...
when graphene grows on the copper substrate, as shown in Figure 4.6. This method is certainly not fool proof, but effective for the beginning of characterisation.

![SEM image of graphene grown on copper foil.](image)

Figure 4.6 SEM image of graphene grown on copper foil.

Another simple characterisation method for identifying and determining the number of graphene layers on the copper foil is through the use of Raman spectroscopy. A typical Raman spectrum of graphene presents three dominant features: the G-band (~1582 cm\(^{-1}\)), D-band (~1350 cm\(^{-1}\)), and 2D-band (~2690 cm\(^{-1}\)). Thus, if an intense peak is present at 2700 cm\(^{-1}\) (I\(_{2D}\)), then it is an indication that graphene is present on the sample. In addition, the ratio of the I\(_{2D}\) and I\(_G\) (~1600 cm\(^{-1}\)) peaks can be used to determine the number of graphene layers [1, 53, 170, 171]. Figure 4.7 shows Raman spectra of the grown graphene on copper foil and blank copper foil. The graph of graphene-coated copper foil shows evidence of graphene on the sample with the appearance of 2D Peak, while the blank copper control sample has no Raman peaks.
4. Low-temperature growth of graphene on copper foil using PMMA-derived carbon source

Figure 4.7 Comparative Raman spectra of a graphene film grown on copper foil (top) and a blank copper foil (bottom). Regions scanned are indicated with dashed circle in optical microscopy images.

Aside from the graphene characterisation on copper foil, the identification of graphene film transferred on a target substrate was carried out by using optical microscopy, SEM, ultraviolet absorption microscopy and TEM. The optical microscopy method was used to distinguish graphene film from the substrate. Figure 4.8 shows an optical microscopy image of graphene film transferred on SiO₂ substrate. This figure shows a folded and wrinkled sheet which could be a large graphene segment. At the edge of folded sheet, a visual distinction between the graphene film and the substrate can be observed. In fact, the color of graphene film appears darker than that of the substrate. In this case, it indicates that graphene layer ripped and folded at some points during the transfer.
4. Low-temperature growth of graphene on copper foil using PMMA-derived carbon source

Figure 4.8 Optical image of graphene film on quartz substrate.

SEM can also be used to identify graphene film after transferring onto a target substrate. Figure 4.9 shows a graphene film transferred onto a ITO-coated glass substrate. In this figure, two different colors with high contrast are observed indicating that the darker area is a top layer of graphene film settling on the underneath layer. The folded film is also observed at the edges of the top layer. Moreover, the straight striations of graphene film occur because it follows the striations of the underlying copper catalyst, as observed in the optical microscopy image shown in Figure 4.7.

Figure 4.9 SEM images of a graphene film after transferring onto the ITO-coated glass substrate.
The absorption properties of graphene can also be identified by using UV-vis linear absorption spectroscopy. Sun et al. characterised graphene films and found a strong absorption band at about 270 nm. The absorption peak near 270 nm is an indication of graphene formation [76]. Figure 4.10 shows an absorption spectrum of a film after transferring onto a quartz substrate. The identified film has a maximum absorption peak at about 270 nm. The occurrence of the absorption relates to $\pi-\pi^*$ transition, from aromatic C-C bonds, indicating that graphene is on the sample.

![UV-vis absorption spectroscopy of the transferred graphene on a quartz substrate (growth temperature at 450 °C).](image)

To complete the characterisation of graphene, TEM was used for imaging the graphene film and also for calculating the number of graphene layers, as shown in Figure 4.11. In this figure, a folded sheet of graphene film lying on TEM grid can clearly be seen and the graphene film with four layers can also be observed.
4. Low-temperature growth of graphene on copper foil using PMMA-derived carbon source

Figure 4.11 TEM images of graphene film transferred on TEM grid with low magnification (a) for imaging and high magnification (b) for calculating the number of the layers. (scale bar : 20 nm)

4.3 Results and Discussion

CVD was used for graphene growth on a copper catalyst in this work. Copper foil with (100) dominant index facet was used as the catalyst for graphene growth. This copper was prepared by annealing at 900 °C for 10 minutes under a H₂/Ar mixture (100 and 100 sccm, respectively) in order to provide a catalyst with smooth surface morphology and large domain size, as mentioned in Chapter 3. Under these catalyst conditions, high quality graphene films were realised. PMMA was used as a solid precursor, while hydrogen and argon were used as carrier gases. The precursor was heated at two different temperatures: 140 and 400 °C. One is below and one is above the PMMA fully decomposed temperature of 300 °C [88]. In this work, four different experimental parameters including annealing temperature of copper foil, growth temperature, precursor temperature and growth time, were varied. The resulting films were characterised by using optical microscopy, SEM, Raman spectroscopy, UV-vis spectroscopy, four-point probe, AFM and TEM.
4. Low-temperature growth of graphene on copper foil using PMMA-derived carbon source

4.3.1 Different annealing temperatures of copper foil for graphene growth

In the first investigation, a PMMA precursor temperature of 400 °C was used. Copper foil was annealed at four different temperatures of 600, 700, 800 and 900 °C for 10 minutes and used as a catalyst for the graphene growth. Graphene growth on the annealed copper foils was conducted under the same conditions: a growth temperature of 450 °C, a growth time of 1 hour, and a H₂/Ar gas mixture of 50 and 100 sccm, respectively. This study was aimed at determining the correlation between the annealing temperature of the copper foil and graphene formation. Figure 4.12 shows the Raman spectra of the obtained films after growing on the copper surfaces. In this figure, it is observed that the 2D peak appears for the samples annealed at 800 and 900 °C only. The presence of this peak is indicative that graphene can be formed on copper foil annealed beyond 800 °C. To determine the number of graphene layers of the samples, the ratio of the I₂D and I₆G peaks is a good measure since this ratio is strongly affected by the number of layers [75]. From the calculation, the 800 °C annealed sample gave an I₂D/I₆G ratio of 1.22 whereas the 900 °C annealed sample gave an I₂D/I₆G ratio of 1.38 indicating that the scanned regions of both samples have more than two graphene layers [75, 172]. By comparing the values of the I₂D/I₆G ratio, this also confirms that the catalyst prepared by annealing at 900 °C can grow a graphene film with better quality than that annealed at 800 °C. This study indicates that the quality of the graphene is related to the underlying catalyst, as discussed in Chapter 3 where the 900 °C annealed catalyst was observed to have a larger grain Cu size than the 800 °C annealed catalyst. In fact, the former has a Cu grain size of ~ 87 µm, while the latter has a Cu grain size of ~ 63 µm. For all further studies, copper catalysts prepared for graphene growth were annealed at 900 °C.

For growing graphene films on the 900 °C-annealed Cu foil substrates, ten graphene samples were characterised using four-point probe and UV-vis spectroscopy in order to measure their sheet resistance (R_sheet) and transparency, respectively. The results of these measurements (Table 4.2) revealed that the average R_sheet and transparency of these samples were 8.4 ± 3.2 kΩ/□ and 90.9 ± 3.2 %, respectively. This measurement indicates that the transparency of resulted graphene film is comparable to the transparency of ITO (80%) [20] indicating its suitability as a transparent electrode for
OSC devices. However, the $R_{\text{sheet}}$ is much higher than that of ITO (36 Ω/$\Omega$) [20] causing a challenge to get a comparable performance to ITO when is applied it as a graphene electrode in OSC device. Therefore, it is necessary to further investigate the graphene growth to upgrade its electrical property.

Figure 4.12  Raman spectra of the films grown on copper foil annealed at temperatures of 600, 700, 800 and 900 °C.
4. Low-temperature growth of graphene on copper foil using PMMA-derived Carbon source

Table 4.2 Sheet resistance and transparency of graphene films grown on the 900 °C-annealed Cu foil substrates.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$R_{\text{sheet}}, \text{k}\Omega/\square$</th>
<th>T (%) @ $\lambda = 550 \text{ nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>15.6</td>
<td>90.3</td>
</tr>
<tr>
<td>G2</td>
<td>6.1</td>
<td>93.2</td>
</tr>
<tr>
<td>G3</td>
<td>5.6</td>
<td>90.8</td>
</tr>
<tr>
<td>G4</td>
<td>5.0</td>
<td>84.7</td>
</tr>
<tr>
<td>G5</td>
<td>7.7</td>
<td>87.9</td>
</tr>
<tr>
<td>G6</td>
<td>8.4</td>
<td>91.5</td>
</tr>
<tr>
<td>G7</td>
<td>8.4</td>
<td>93.8</td>
</tr>
<tr>
<td>G8</td>
<td>10.1</td>
<td>95.2</td>
</tr>
</tbody>
</table>

4.3.2 Comparison of graphene growth on different temperatures

To study the growth and characterisation of graphene, two different growth temperatures of 350 and 450 °C were compared for growing graphene on copper catalysts while the copper annealing temperature of 900 °C and the growth time of 1 hour were kept constant. The main reason behind the low growth temperatures is that the PMMA precursor decomposes at 300 °C [88], so at temperatures above 300 °C, the carbon source completely decomposes into carbon atoms. Figure 4.13 shows comparative SEM images of the samples grown at temperatures of 350 and 450 °C. At low magnification, there is no significant difference on the surface of the samples. On both samples, copper domain boundaries are clearly visible as patches of varying shape. However, a difference can be clearly observed at high magnification. In fact, the sample grown at 350 °C appears to have a rough surface with a lot of dark lines remaining on the surface. Possibly, the dark lines are tears in the graphene due to the difference of thermal expansion between graphene and copper. The sample grown at 450 °C appears to have a smooth surface with the islands of graphene growth. This difference is indicative that the growth at 450 °C allows the formation of a better quality graphene film.
4. Low-temperature growth of graphene on copper foil using PMMA-derived Carbon source

Figure 4.13 Comparative SEM images of the samples grown at temperatures of 350 °C (top) and 450 °C (bottom) on copper catalyst.

For further comparison, the graphene films grown on copper foil were transferred onto quartz substrates after etching the foils. The graphene films were then characterised by SEM using two different detectors: In-lens and secondary electron (SE). Using the In-lens detector (Figures 4.14a and 4.14b), a clear edge effect with good imaging of surface structures is visible in which striations on both the samples can clearly be observed as a result of the underlying copper striations. Moreover, the upper layers are clearly visible. The other detector (Figures 4.14c and 4.14d), SE, gives little information of surface morphology of both the samples. However, the amorphous carbon (as dark
spots in the image) settling on the surfaces can be observed more clearly and also the folding of the edge of graphene films can be detected. The 350 °C-grown sample appears to have a lot of amorphous carbon on the surface, while the 450 °C-grown sample has less amorphous carbon. In addition, the surface of the 350 °C-grown sample appears much rougher with a lot more folding compared to the 450 °C-grown sample. This comparison shows that samples grown at 450 °C produce a better quality graphene film compared to samples grown at 350 °C.

Figure 4.14 Comparative SEM images of the samples grown at 350 °C (top) and 450 °C (bottom) on copper catalyst after transferred onto the ITO-coated glass.
Another characterisation technique used to compare the performance of both samples was UV absorption spectroscopy. On both samples absorption peaks around 270 nm are detected indicating that graphene is present on the samples [76]. However, the peak of the 450 °C-grown sample is much higher than that of the 350 °C-grown sample. In addition to the optical properties, the electrical properties of both samples were also measured by four-point probe. The results obtained were sheet resistances of 10.4 kΩ/sq for the 350 °C-grown sample and 4.2 kΩ/sq for the 450 °C-grown sample. This difference confirms that the 450 °C grown sample leads to a high quality graphene film.

![UV absorption spectra of the samples grown at 350 and 450 °C.](image)

To confirm the presence of graphene and determine the number of graphene layers on both samples, Raman spectroscopy was used. The main features of Raman spectroscopy attributable to graphene (D, G and 2D peaks) were found on both samples as shown in Figure 4.16. The appearance of the 2D peak confirms the presence of graphene on the samples. The values of $I_{2D}/I_G$ ratio obtained were 0.58 and 0.73 for the samples grown at 350 and 450 °C, respectively. These values indicate that the number of graphene layers on both samples is more than 2 [1].
In order to determine the exact number of layers in the graphene films, high resolution transmission electron microscopy (HR-TEM) was used. In a graphite crystal, layers of carbon atoms are arranged in a hexagonal lattice forming graphite c-planes with a distance between these planes of around 0.34 nm. [173, 174] When a graphene flake is folded, those planes are parallel to the electron beam and visible as dark lines with 0.34 nm spacing between them. By counting those lines in HR-TEM, the thickness of the flake can be determined quite exactly. Figure 4.17 shows HR-TEM images of the samples grown at 350 and 450 °C with layers of 5 and 4 layers, respectively.

Figure 4.16 Raman spectra obtained from the samples grown at 350 and 450 °C.
4. Low-temperature growth of graphene on copper foil using PMMA-derived Carbon source

4.3.3 The influence of the precursor temperature on Graphene growth

Having considered the annealing temperature of Cu foil substrate and the growth temperature, the heating temperature of precursor was also varied. Figure 4.18 shows the TGA mass plot of PMMA drop cast from a chlorobenzene solution. Two plateau regions are clearly indicated at: (a) around 140 °C (correspondently to the loss of ~30% of the mass) and then (b) at > 400 °C (corresponding to total mass loss). Two different heating temperatures of 140 and 400 °C were applied to evaporate the PMMA precursor. In order to investigate these two precursor temperature regimes, the
evaporated PMMA molecules were carried to the surface of Cu catalyst using a H₂/Ar mixture (50 and 100 sccm, respectively) and then pyrolysed at 450 °C to form a carbon structure of graphene.

The graphene growth using the precursor heated at the two different temperatures was characterised by Raman spectroscopy. Figure 4.19 shows the Raman spectroscopy of the graphene film grown at temperature of 450 °C by heating the precursor at 400 °C. In this figure, it is observed that the intensity ratio of I_2D/I_G is less than 2 suggesting the presence of a few graphene layers in the studied region [75]. This value is consistent with the TEM measurement. While, the Raman spectroscopy of the grown graphene film on Cu foil catalyst by heating the precursor at the temperature of 140 °C is shown in Figure 4.20. In this figure, two different spots were characterised by scanning the light and dark regions. In the light region, it is observable that the intensity ratio of I_2D/I_G is less than 2 indicating that this region has a few graphene layers. While, in the dark region, the intensity ratio of I_2D/I_G is more than 2 indicating that this region has monolayer graphene. The difference of graphene layers on these scanned regions indicates that the resulted graphene film is not uniform.
Figure 4.19 Raman spectroscopy of the graphene film grown at 450 °C by the precursor at 400 °C.
Figure 4.20 Raman spectroscopy of the grown graphene film on copper foil by annealing the precursor temperature at 140 °C for both light region (upper) and dark region (lower).
Comparing the two precursor temperatures of 400 and 140 °C shown above, growth at a precursor temperature of 140 °C results in the formation of monolayer graphene film whereas heating the precursor at 400 °C results in the growth of a few graphene layers. However, the 140 °C-heated precursor results in a graphene film with a lower defect density since it has a much lower D-peak than that of the 400°C-heated precursor.

It is clear that the formation of these thin graphene films is very different when the precursor is held at 140 °C compared to 400 °C. Typically, PMMA only decomposed above 300 °C [88], whereas here we see the loss of ~ 30 % of the precursor at temperature of 140 °C. It seems reasonable to hypothesise two possible origins for this mass loss: (a) low molecule weight PMMA fragment, (b) entrenched solvent. However, in this case it seems unlikely that entrenched solvent is the main source of the mass loss at 140 °C since 30% of the mass is lost, which seems too high for entrenched solvent. Furthermore, if the PMMA is held at 140 °C for 15 minutes, in excess of 80 % of the total mass is lost (Figure 4.21). Thus, we speculate that the better graphene observed at a 140 °C heating of the precursor is the result of a lower flux of carbon atoms to the Cu surface, resulting in the formation of less amorphous carbon.

Figure 4.22 Mass remaining of precursor vs time
4. Low-temperature growth of graphene on copper foil using PMMA-derived Carbon source

4.3.4 The variation of graphene growth time

In order to determine how to grow graphene more efficiently, another study was conducted by growing graphene for various times. In this study, two different precursor temperatures (i.e. 140 and 400 °C) were applied, while the temperature of graphene growth was kept at 450 °C. Initially, the growth time was varied for five different times of 1, 30, 60, 180 and 300 s while keeping the precursor temperature of 400 °C. The SEM images of graphene growth stages are shown in Figure 4.23. For a growth time of 1 s, it appears some islands of graphene growth of various sizes are present, while the white dots are contaminants which possibly result from PMMA precursor fragments. After annealing for longer times, the copper surface is fully covered by graphene films on which new growth domains with lobed shapes are formed. The size of the new growth domains increases with increasing annealing times due to the occurrence of domain coalescence, but does not completely cover the copper surface. This result indicates that the graphene growth for 300 s can result in the smoothest surface, with little of the precursor fragments remaining.

Figure 4.23 SEM images of graphene growth on copper foil by annealing the precursor at 400 °C for 1 s, (b) 30 s, (c) 60 s, (e) 180 s, and (f) 300 s with scale bars of 1 µm, 100 nm, 200 nm, 200 nm and 200 nm, respectively.
Another experiment in this study was to vary the exposure time. Exposure times of 1, 10, 30, 60, 300 and 3600 s with a precursor temperature of 140 °C were used. Figure 4.24 shows a series of SEM images of graphene growth stages on a copper foil catalyst by growing at a temperature of 450 °C. In these images, graphene appears dark since the emission of secondary electrons for copper is significantly higher than that for graphene. On the other hand, the appearance of white dots in the images is due to the presence of contaminants. After an exposure time of 1 s, (figure 4.24a) a few growth domains about 30 nm in size appear. Between an exposure time of 10 s and 30 s, the domain size increases as a result of additional carbon atoms being adsorbed on the edges of the growth sites. This increase continues until the domains start to coalesce and then form larger islands. The coalesced graphene islands fully cover the surface of the copper foil after synthesising for exposure times longer than 30 s, as seen in Figure 4.24e-f.

Figure 4.24  SEM images of graphene growth on copper foil by annealing the precursor at 140 for  (a) 1 s, (b) 10 s, (c) 30 s, (d) 1 min, (e) 5 min, and (f) 1 hour. (scale bar : 1 µm)
To confirm the presence of graphene on the copper surface and estimate the number of graphene layers, Raman spectroscopy was used for characterising the samples by scanning at two different spots. The scan spots were conducted on bright and dark regions marked with black and red dashed circles, respectively, as seen on optical microscopy images (Figure 4.25). Figure 4.26 shows the corresponding Raman spectra of the samples characterised on dark and bright regions. All Raman spectra obtained from the areas circled on the samples are indicative of a few graphene layers, since the 2D-band to G-band intensity ratio ($I_{2D}/I_G$) is less than 2 [52, 75]. However, the sample grown for 1 s has better quality of graphene film because both of the scanned regions have the ($I_{2D}/I_G$) ratio of $>1$, as tabulated in Table 4.3.

Figure 4.25 Optical microscopy images of the as-grown graphene films on copper catalyst with the precursor temperature of 140 °C. (The characterised regions are marked with dashed circle)
Figure 4.26 Raman spectra of the samples grown on copper foil catalyst for different exposure times at bright (top) and dark (bottom) regions.
4. Low-temperature growth of graphene on copper foil using PMMA-derived Carbon source

Table 4.3 The values of $I_{2D}/I_G$ ratio obtained from bright and dark areas on the samples grown for different exposure times.

| Growth Time (s) | Bright region | | | Dark region | | |
|-----------------|---------------|------|----|-----------------|------|
|                 | $I_G$ | $I_{2D}$ | $I_{2D}/I_G$ | $I_G$ | $I_{2D}$ | $I_{2D}/I_G$ |
| 1               | 450   | 525   | 1.17 | 4200  | 5600  | 1.33   |
| 10              | 600   | 475   | 0.79 | 2500  | 1250  | 0.50   |
| 30              | 725   | 550   | 0.76 | 3000  | 3900  | 1.30   |
| 60              | 600   | 500   | 0.83 | 3900  | 3400  | 0.87   |
| 300             | 1425  | 1000  | 0.7  | 2250  | 1900  | 0.84   |
| 3600            | 1025  | 574   | 0.56 | 2500  | 2100  | 0.84   |

The surface coverage by annealing the precursor at 400 °C is quicker than that by annealing the precursor of 140 °C, since the high temperature causes a fast evaporation on the precursor. Consequently, the high flux precursor fragments are carried toward the heating zone, where the fragments are decomposed into carbon atoms. Then, the abundant carbon atoms are quickly absorbed by copper surface.

Based on the conditions of graphene growth above, a recipe selected was by annealing the Cu foil at 900 °C for 10 minutes, growing graphene at 450 °C for 1 minute and heating the precursor at 140 °C. This recipe was used to grow graphene films with a 2 mm x 1 mm – sized area and graphene electrodes for fabricating OSC devices. For the characterisation of electrical and optical properties, all samples were transferred onto a target substrate. The large-area graphene films (LG) were transferred onto a glass substrate, while the graphene electrodes (GE) were transferred onto a patterned ITO-coated glass substrate. The values of its $R_{\text{sheet}}$ and transparency were tabulated in Table 4.4. These results show that the $R_{\text{sheet}}$ and transparency of all samples were ~ 3.0 kΩ/□ and ~ 91 %, respectively. The two graphene electrodes were used for fabricating OSC devices as shown in Chapter 6.
4. Low-temperature growth of graphene on copper foil using PMMA-derived Carbon source

Table 4.4 Sheet resistance and transparency of graphene films grown on the 900 °C-annealed Cu foil substrate with the optimal growth conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$R_{\text{sheet}}, \text{k}\Omega/\square$</th>
<th>$T$ (%) @ $\lambda = 550 \text{ nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LG-1</td>
<td>2.4</td>
<td>95.5</td>
</tr>
<tr>
<td>LG-2</td>
<td>1.6</td>
<td>96.5</td>
</tr>
<tr>
<td>LG-3</td>
<td>2.0</td>
<td>97.5</td>
</tr>
<tr>
<td>LG-4</td>
<td>1.2</td>
<td>88.8</td>
</tr>
<tr>
<td>LG-5</td>
<td>1.5</td>
<td>89.0</td>
</tr>
<tr>
<td>LG-6</td>
<td>2.8</td>
<td>87.5</td>
</tr>
<tr>
<td>GE-1</td>
<td>9.8</td>
<td>86.1</td>
</tr>
<tr>
<td>GE-2</td>
<td>2.4</td>
<td>92.4</td>
</tr>
</tbody>
</table>

Previous studies of graphene growth on copper substrates have shown that the quality of graphene growth is dependent upon growth temperature [74]. Indeed, for deposition of graphene from gas phase precursor (such as methane), temperatures of around 1000 °C are typically used. Much recent effort has focussed on reducing graphene growth temperature by changing to different precursors and by optimising the CVD growth parameter. The results presented in this chapter reveal that rather than a single growth temperature, there are actually three critical temperature parameters that need to be optimised independently. Firstly, there is the annealing temperature ($T_{\text{ANNEAL}}$) of the Cu foil prior to graphene deposition, which needs to be sufficiently high ( > 900 °C) to cause the recrystallisation of large Cu grains in the substrate surface. Secondly, there is the precursor temperature ($T_{\text{PRECURSOR}}$), which needs to be high enough to produce volatile precursor fragments which subsequently decompose on the catalyst surface. In the case of PMMA, this requires $T_{\text{PRECURSOR}} > 140$ °C. Finally, there is the Cu foil growth temperature ($T_{\text{GROWTH}}$), which has to be sufficiently high to active carbon diffusion and rearrangement on the catalyst surface. For a Cu foil catalyst, this temperature needs to be at least 450 °C.
4.4 Conclusion

A systematic study of graphene growth at the temperatures below 500 °C on (100) dominant indexed copper catalysts using PMMA as the carbon precursor was conducted. For the graphene growth at the temperatures, a minimum temperature of copper annealing was 800 °C. Moreover, a comparative study of growth temperature indicates that the 450 °C-grown samples result in a better quality graphene film compared to the 350 °C-grown samples. This is indicative that at temperatures below 500 °C, graphene can be successfully grown with the assistance of an annealed copper catalyst. Moreover, graphene growth by heating the carbon precursor of 140 °C for less than 60 seconds can result in a bilayer graphene film.
By considering the annealing conditions (Chapter 3) and the growth temperatures (Chapter 4) for copper foil, this chapter outlines a further study of graphene growth using evaporated thin copper film substrate as a catalyst. This study will be carried out to find the effects upon graphene growth by varying the annealing temperature on the substrate, the thickness of thin Cu film catalyst, the heating low temperature of precursor and the growth time of the 450 °C-annealed thin Cu catalyst.

5.1 Introduction

For many technological applications such as transparent conductors [6, 175], sensors [9], memory devices [8], transistors [5], light-emitting diodes [4] and solar devices [11, 12], the growth of large-area, high quality graphene with a relatively low fabrication cost is highly desirable. Currently, growing graphene by chemical vapor deposition (CVD) onto metal substrates is a readily accessible route for fabricating continuous
large area graphene with high quality. The growth of the films is limited by catalyst sizes and the capacity of the CVD furnace used [2, 3, 176]. The main mechanism of graphene growth by this method is governed by surface chemistry and driven by the low solubility of carbon in metals such as nickel or copper at the specific growth temperature (900-1000 °C). Using this technique, large areas of monolayer graphene can be produced with domain sizes comparable to the largest flake size that can be produced by mechanical exfoliation [1, 2]. In particular, copper is a unique catalyst for graphene because it dissolves carbon atoms into its bulk very slowly, and has closed d shells and free-electron-like surface states along with an established catalytic activity to hydrocarbon gases [136]. These unique properties have attracted considerable interest in both academic and industrial communities. Yu et al. observed that the formation of graphene is due to the precipitation of carbon during cooling down [158]. Other research groups have investigated the use of liquid or solid carbon sources for growing graphene [76, 77, 95].

To develop the growth of graphene on the metal to the point where it is a viable route to large-area applications, a reliable method in which the graphene film is able to be subsequently transferred from the metal surface to a more useful substrate, e.g. plastic or glass after etching, is required [1]. A transfer technique was developed by using a polymer coating [e.g. polymethyl methacrylate (PMMA)] as a temporary support layer during the etching of the metal in order to prevent folding or tearing of the graphene film [130, 177]. However, during the transfer process a number of significant problems can occur. Firstly, the complete separation of graphene from the substrate surface can result in mechanical damage of the transferred graphene film such as tearing or cracking [178]. Secondly, the alignment between the graphene film and the target substrate presents additional technical challenges. Thirdly, these transfer procedures are often performed in aqueous solutions and it is difficult to remove the liquid residue trapped within the interfacial space between the graphene and the target substrate [179]. As a result, the quality of the resulting graphene varies from sample to sample, since strong bonding between graphene and the corresponding metal surface substantially alters the charge transport of graphene [178, 180]. Consequently, the main challenge of CVD graphene growth is not only how to grow a high quality large-area graphene layer, but also how to reliably transfer the graphene onto other substrates.
To eliminate the complicated graphene transfer, Ismach et al. [181] and Su et al. [182] recently demonstrated direct graphene deposition onto insulating substrates through surface catalytic decomposition of hydrocarbon precursors on thin copper films. Moreover, Yan et al. investigated the carbon diffusion from solid source precursors through nickel [183]. However, the graphene films were obtained at a high growth temperature of 1000 °C, increasing the cost of fabrication. To minimize the graphene growth temperature, Lee et al. [184] reported that the graphene film with high structural quality could be synthesized at low temperatures (400-800 °C) using ethylene precursor. Similarly, Li et al. [77] demonstrated the graphene growth at the same temperatures using various liquid and solid precursors. In 2009, an fabrication of CVD graphene transistors was demonstrated by Levendorf et al. [176] using the method of transfer-free process. The demonstration of transfer-free graphene device is an attractive step towards production-scale use of CVD graphene for microelectronics.

In this chapter, a simple method is demonstrated for the direct transfer of large-area graphene films (> 1 cm²) grown at temperatures below 500 °C. The catalyst used for growing graphene was an evaporated thin copper film instead of a copper foil. The thin copper was evaporated on to the desired substrate. An advantage of this technique is that the graphene film grown on the catalyst settles on the substrate after etching the underlying metal catalyst away. One of the substrates used was a patterned indium tin oxide (ITO) slide for directly depositing a graphene electrode in order to fabricate organic solar cells (OSCs), as discussed in Chapter 6. The removal of the metal catalyst allows the graphene film to settle onto the substrate on which the catalyst was evaporated. To experimentally demonstrate this method, the evaporation of thin copper on the desired substrate was first conducted. Then, graphene growth on the metal catalyst at temperatures below 500 °C using PMMA as a carbon source was performed. The effect on the surface morphology of catalysts annealed at different temperatures, copper thicknesses, precursor temperatures and growth times were studied.
5.2 Experimental Details

Two substrates, glass and quartz, were used as the substrate for evaporating the thin copper films. The substrates were first cleaned by rinsing three times with acetone to remove any contaminants, followed by an isopropanol wash to remove any acetone residue left over on the substrates. Afterwards, the substrates were submerged in de-ionized water and then sonicated for 30 minutes to remove remaining organic solvents. After drying with a stream of nitrogen gas, the substrates were transferred to the evaporation chamber. Copper shots (99.99+% purity) were thermally vapour deposited onto the substrates using an Angstrom Engineering evaporator under a pressure of ~ 10^{-6} Torr. The evaporation rate of copper was 2 Å/s. Two thicknesses of copper films were evaporated: 200 nm and 500 nm. The copper-covered substrates were unloaded after cooling down for 15 minutes. Next, the substrates were annealed in a CVD furnace to allow the growth of the copper grains. The thin copper film deposited on glass was annealed at 450 °C for 20 hours under a mixed (H₂/Ar = 25/100, sccm) gas. The thin copper film deposited on quartz was annealed at four different temperatures of 600, 700, 800 and 900 °C for 10 minutes under a mixed (H₂/Ar = 100/100, sccm) gas. The selected annealing conditions are based on the results of the study of the effects of thermal annealing on the microstructure of copper catalyst film, as described in Chapter 3.

The CVD furnace was used for graphene growth on the copper catalysts at relatively low temperatures using PMMA as precursor solid. The vapourised precursor was transported to the copper catalyst assisted by carrier gases of hydrogen and argon. Before running an experiment, the PMMA precursor and the annealed thin copper film were loaded and placed at different heating zones separated by a distance of 8 inches, as shown schematically in Figure 5.1. The precursor was heated at two different temperatures of 140 and 400 °C, while the copper catalyst was annealed at three different synthesis temperatures of 350, 400 and 450 °C. In all the experiments, cooling down was carried out by initially opening the furnace lid about 3 cm in height and then completely opening it when it reached 150 °C. The hydrogen flow rate was kept constant during the complete cycle of heating, growing and cooling down on each experiment, while the argon flow rate of 100 sccm and chamber pressure of 500 mTorr.
were also kept constant during the complete cycle of all process steps. Samples were unloaded from the quartz tube only after the sample temperature was below 50 °C.

The evaporated graphene films were characterised by using scanning electron microscopy (SEM), ultraviolet-visible (UV-vis) spectroscopy, profilometry, Raman spectroscopy and atomic force microscopy (AFM). The surface morphology of graphene films was characterized in a Zeiss Sigma VP SEM and a Cypher AFM. The transmission spectrum in the visible region and the absorption peak in the ultraviolet region of the samples were measured by a Varian Cary 6000i UV-Vis-NIR spectrophotometer. The four probe technique, as noted in 2.4.5, was applied for measuring the electrical conductivity of the samples. Characterisation of the number of graphene layers was completed by using a Renishaw InVia Raman spectrometer. The latter equipment was also used for identifying the quality of the graphene films.

![Schematic diagram of graphene growth in the CVD system](image)

Figure 5.1 Schematic diagram of graphene growth in the CVD system
5.3 Results and Discussion

One of the main aims of this work was to fabricate large-area graphene with high quality using a simple process. To improve the quality of graphene, the growth conditions of the copper foil catalyst were optimised, as discussed in Chapter 4. By using evaporated thin copper as a catalyst, the transfer step was eliminated.

5.3.1 Effect of Copper Catalyst Film Annealing Temperature

In the beginning of this study, the evaporated thin copper prepared as a catalyst for growing graphene was first annealed at four different temperatures of 600, 700, 800 and 900 °C for 1 hour, named as samples S1, S2, S3 and S4, respectively. Then, each sample was grown at 450 °C for 1 minute under a mixed (H₂/Ar =1:2) gas. The purpose of this study is to find a correlation between copper grain size (see Subsection 3.3.1) and graphene formation. To characterise graphene formation in the samples, UV-vis absorption spectroscopy was used. The presence of graphene is indicated by a peak at ~270 nm [76]. Figure 5.2 shows UV-vis absorption spectra of the resultant films after growing at 450 °C for 1 hour using evaporated copper thin films annealed at the various temperatures. From the graphs, it can be seen that the samples prepared by annealing at the temperatures of 600 (S1) and 700 °C (S2) show no observable absorption peak, while a graphene peak is detected for samples prepared by annealing at higher temperatures. For the sample prepared by annealing at 800 °C (S3), the peak is observable, but quite broad, while a more distinct peak is observed on the sample prepared by annealing at 900 °C (S4). The results of this study indicate that no graphene formation occurs on samples S1 and S2 because no copper grains on these samples are formed, consistent with the results presented in Figure 3.5. On the other hand, graphene formation occurs on the samples S3 and S4 because copper grains are formed with average sizes of 0.6 and 1.5 µm, respectively. In comparison, the peak of sample S4 is significantly narrower than that of sample S3. Moreover, the relative peak of sample S4 is much higher than that of sample 3. This difference indicates that larger copper grain size results in a better quality graphene film.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.2 UV-vis absorption spectra of films grown at 450 °C for 1 minute using thin copper films annealed at four different temperatures of 600, 700, 800 and 900 °C for 1 hour.

For further characterisation, Raman spectroscopy using a laser excitation wavelength of 520.7 nm was used to detect the presence of graphene in all the samples and estimate the number of graphene layers. The presence of graphene is determined by the appearance of a peak at ~ 2700 cm⁻¹, well-known as the 2D peak. The number of graphene layers can be confirmed by using the intensity ratio of 2D- and G-peaks (I_{2D}/I_G) [3]. Figure 5.3 reveals Raman spectra of all the above samples characterised by UV-vis absorption spectroscopy. For samples S1 and S2, the D- and G-peaks are detected, but there is no observable 2D-peak. This result is indicative of graphite with disorders or defects such as point defects, subdomain boundaries, and edges [121, 185] being formed on the samples, but no graphene formation. As the annealing temperature is increased, a Raman signal for graphene is observed. In fact, for sample S3 a 2D peak is detected which has a I_{2D}/I_G ratio of 0.49 with a FWHM of 75 cm⁻¹ suggesting the presence of graphene of only few layers. A significantly higher intensity of Raman peaks is detected for S4 with the I_{2D}/I_G ratio of 0.81 with the FWHM of 65 cm⁻¹ (see Figure 5.4) indicating that graphene is on the sample with a thickness of three to five layers [3].
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.3 Raman spectra of samples grown at 450 °C for 1 minute using thin copper films annealed at four different temperatures of 600, 700, 800 and 900 °C for 1 hour.

Figure 5.4 The FWHM of 2D peak on sample S4.

In order to determine the electrical conductivity, \( \sigma \), of all the samples, the measurement of sheet resistance (\( R_s \)) and thickness (\( t \)) were conducted using a four-point probe and profilometer, respectively. From the recorded measured data, the conductivity of all the samples can be calculated by recalling the equations in subsection 2.4.3.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

\[ \sigma = \frac{1}{R_s \times t} \]  

(5.1)

The results of calculated conductivity are plotted in Figure 5.5. The low conductivity values of sample S1 and S2 are possibly caused by the presence of many of defects or an abundance of amorphous carbon offering extra resistance to charge transport. On the other hand, the significantly higher conductivities of samples S3 and S4 indicate a better quality of film associated with the presence of graphene. These results clearly demonstrate that the conductivity of samples containing graphene is higher than that of the samples without graphene.

![Figure 5.5](image)

Figure 5.5 Electrical conductivity of the film samples grown from the evaporated thin copper with different annealing temperatures of 600, 700, 800 and 900 °C.

5.3.2 Effect of Copper Catalyst Film Thickness

By considering the above results and selecting the annealing temperature of 900 °C for 1 hour, a study was also carried out to compare PMMA-derived graphene grown on two different thin copper thicknesses of 200 and 500 nm, named as samples S5 and S6, using the same conditions as above. These thicknesses were selected because very thin copper films (e.g. 100 nm) can in fact be discontinuous [181]. Moreover, it has been
shown that a thickness of less than 500 nm for annealing at ≥ 800 °C [136] and ~ 1000 °C [176, 181] can result in a problem with de-wetting. On the other hand, very thick films (e.g. 1000 nm) can cause a large strain on the structure due to the different thermal expansion of the film with the substrates that may lead to cracks and/or film delamination [181]. Moreover, by annealing at 900 °C the evaporation and de-wetting of the copper film can be avoided as observed by Ismach et al. [181].

The main reason behind the temperature selection is that these annealing conditions fabricate a better quality graphene film as seen in Figure 5.3. By considering these arguments, a study of graphene growth was conducted on thin copper films with two different thicknesses of 200 and 500 nm.

The surface morphology of the 200 nm sample was recorded by SEM with two different magnifications of 5,000x and 100,000x, as shown in Figure 5.6. In this image, the quartz substrate appears dark since the emission of secondary electrons for copper is significantly higher than that for quartz. At the low magnification of 5000x, a number of dark spots across the surface are observable. The dark spot marked with a red square can be clearly seen by increasing the magnification to 100,000x. On the spot, a film can be also seen with a wrinkle cross the hole. Interestingly, the 100,000x micrograph shows evidence of a thin film crossing the open hole, consistent with a graphene/graphitic carbon layer. Similarly, the surface morphology of the 500 nm sample was also recorded by SEM with two different magnifications of 50,000x and 100,000x, as shown in Figure 5.7. At the low magnification of 50,000x, there are a lot of tiny clusters with the average size of 20 nm, but no damage (holes) on the copper surface is detectable. To clearly observe the red squared area, the magnification was increased to 100,000x. In this area, the grain boundaries are clearly observed. From the comparison study of different copper thickness, it is found that damage (holes) due to annealing-induced evaporation can occur on the 200 nm copper film when annealed at 900 °C, while no damage on the 500 nm copper film is detectable.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.6 The SEM images with two different magnifications of 5,000x (left) and 100,000x (right) on the 200 nm copper film thickness after annealing at 900 °C for 1 hour with the scale bars of 10 µm and 200 nm, respectively.

Figure 5.7 The SEM images with two different magnifications of 50,000x (left) and 100,000x (right) on the 500 nm copper film thickness after annealing at 900 °C for 1 hour with the scale bars of 1 µm and 200 nm, respectively.

For comparison, Raman spectroscopy was also used for characterising graphene, as it can provide rich structural information, including D-, G- and 2D-peaks at around 1350, 1580 and 2700 cm⁻¹, respectively. The D peak is related to disorder or defects. Figure 5.8a shows the corresponding Raman spectra of the copper-substrate samples recorded from the areas marked with dashed circles in the optical micrographs. The corresponding Raman spectra were collected from sample S5 (Figure 5.8b) and S6 (Figure 5.8c) on two different areas (bright and dark) indicated by dashed circles in
optical micrographs. The $I_{2D}/I_G$ intensity ratio and the FWHM of the 2D-peak of both samples are tabulated in Table 5.1. The shape and position of the 2D peak can be used to clearly distinguish single-layer, bi-layer, and multi-layer graphene [121]. Single-layer graphene usually has a single and sharp 2D peak below 2700 cm$^{-1}$, and bilayer graphene exhibits a broader and upshifted 2D peak located at 2700 cm$^{-1}$. In the case of graphene sheets with more than five layers, they exhibit broad 2D peaks that are upshifted to positions greater than 2700 cm$^{-1}$, similarly with bulk graphite. For this reason, the graphene film obtained in this comparative study is ~ 4-5 layers. These results clearly demonstrate that the use of 500 nm thick copper films can result in high quality graphene, compared to graphene grown on a 200 nm thick copper film. Therefore, the thin copper film thickness selected for the following studies was 500 nm.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.8 The corresponding Raman spectra recorded from the areas marked with dashed circles in optical micrographs on the copper samples (a), the two different areas (bright and dark) of sample S5 (b) and sample S6 (c).
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Table 5.1 The $I_{2D}/I_G$ intensity ratio and the FWHM of 2D peak of graphene on the glass.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Bright area</th>
<th>Dark area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_{2D}/I_G$</td>
<td>FWHM (cm$^{-1}$)</td>
</tr>
<tr>
<td>200</td>
<td>0.55</td>
<td>75</td>
</tr>
<tr>
<td>500</td>
<td>0.85</td>
<td>55</td>
</tr>
</tbody>
</table>

In addition to the Raman spectroscopy characterisation, four-point probe measurement and UV-vis spectroscopy were used to determine the sheet resistance ($R_{\text{sheet}}$) and transparency (%) of the compared samples, respectively. At the as-prepared thin Cu film thickness of 200 nm, the graphene film resulted had a $R_{\text{sheet}}$ of 92.3 kΩ/□ coupled with the transparency of 91.5%. While, at the as-prepared thin Cu film thickness of 500 nm, it had a lower $R_{\text{sheet}}$ of 14.0 kΩ/□ coupled with the transparency of 85.7%. The lower $R_{\text{sheet}}$ value indicates improved electrical properties suggesting that the optimum thickness of prepared thin Cu film for graphene growth is > 500 nm.

5.3.3 Effect of Lower Precursor Temperature

To further improve the quality of graphene, another study was carried out by heating the precursor at a lower temperature than that of previous studies (all the above experiments employed a precursor temperature of 400 °C). In this study, graphene growth was conducted by heating the precursor at 140 °C and maintaining the annealing and growth conditions as above. The main reason for the selection of this precursor temperature was that the mass of chlorobenzene-disolved PMMA lost $\sim$ 30 % when annealed as shown in Figure 4.18 (Chapter 4). This indicates that the PMMA precursor can be evaporated at the temperature and then the vapour phase is carried toward the surface of thin Cu catalyst by introducing a mixture of H$_2$/Ar gases. The PMMA molecules in the CVD zone are further decomposed to be carbon atoms that are deposited onto the catalyst. In the other words, the lost mass can be a carbon source for growing graphene.
Figure 5.9 shows optical images of the evaporated thin copper and the as-grown graphene films. In this figure, contaminants are observed on all the samples. The contaminations possibly occur in the evaporation chamber after evaporating the copper shots onto the surface substrate. The as-prepared thin copper (Figure 5.9a) appears smoother than the annealed thin copper (5.9b). The copper surface might be expected to become much rougher after annealing due to the larger grain formation. After graphene growth (Figure 5.9c) the surface appears much darker, indicating graphene is on the sample. After locally etching the copper, the graphene film settles onto the substrate (see Figure 5.9d). In this figure, a number of wrinkles and contaminants are clearly detected.

Figure 5.9 Optical images of the as-evaporated thin copper (a), the annealed thin copper (b), the graphene-grown thin copper (c) and the graphene film on quartz substrate (d).

Further characterisation of the samples was performed by using the Cypher AFM to characterise the surface morphology of the evaporated thin copper and graphene films. Figure 5.10 shows a series of AFM measurements from preparation to fabrication. In
this measurement, two different scanning sizes of $20 \times 20 \, \mu m^2$ and $5 \times 5 \, \mu m^2$ were used. By this measurement, a distinguishable surface morphology of the samples with different values of roughness is observed. On the as-evaporated thin copper, the grains (see Figure 5.10a) are clearly seen with very tiny sizes, while roughnesses (Ra) of 3.21 nm and 1.98 nm are recorded for the scanning areas of the $20 \times 20 \, \mu m^2$ and $5 \times 5 \, \mu m^2$ imaged areas, respectively. The surface of the sample appears to be much rougher after annealing, since the grain size is bigger (see Figure 5.10b). The increasing roughness is evidenced by the increasing Ra values of 35.3 and 25.5 nm for $20 \times 20 \, \mu m^2$ and $5 \times 5 \, \mu m^2$, respectively. The values slightly decrease to be 28.8 ($20 \times 20 \, \mu m^2$ in scan size) and 21.5 nm ($5 \times 5 \, \mu m^2$ in scan size) after graphene growth (see Figure 5.10c). Moreover, a number of precursor features are clearly observable. After etching the copper, which leaves behind the graphene film on the substrate (see Figure 5.10d), the roughness values of the film significantly decrease to be 4.6 and 4.4 nm for $20 \times 20 \, \mu m^2$ and $5 \times 5 \, \mu m^2$, respectively. In this figure, the growth islands are clearly observable and also a number of tiny precursor fragments are detected on the surface.

In addition to using the AFM for surface characterisation, it can also be utilised to measure the thickness of graphene film. The measurement is usually performed on the edge of a film by scanning along a straight line from one point to another point through both substrate and graphene film, as shown in Figure 5.11. By imaging using a high spatial resolution, the measurement of a partial graphene film was conducted with the obtained thickness of $\sim 1.97 \, \text{nm}$. Given that the spacing between each graphene layer is 0.34 nm [186], the thickness of the graphene film suggests that $\sim 5$ layers of graphene are present, consistent with the obtained Raman results.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.10 AFM images of as-evaporated thin copper (a), the annealed thin copper (b), the graphene-grown thin copper (c) and the graphene film on quartz substrate (d).
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.11 The AFM tapping mode topography image of a partial graphene with the thickness of ~ 1.79 nm in the height profile along red solid line.

In order to characterise the optical properties of the sample, UV-vis spectroscopy was used to measure absorption and transparency within a scanning area of 10x10 mm². Figure 5.12 shows the UV-vis spectroscopy of the sample and quartz slide. In this spectrum, there is an absorption peak at a wavelength of 268 nm indicating there is a graphene on the sample [76]. The sample has a transparency of 89.8% at 550 nm. Since one layer graphene absorbs ~ 2.3% of light corresponding to the transmittance of ~ 97.7% [58], it indicates that the sample has a graphene film with 4-5 layer, again consistent with the previous results.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.12 UV-vis absorption spectroscopy of a sample grown at 450 °C for 1 minute using the 500 nm thin copper as a catalyst. The inset shows the optical transmission of the sample.

The sheet resistance ($R_{\text{sheet}}$) of the sample was measured using the four-point probe at four different areas as shown in Figure 5.13. This measurement was performed after characterising the transmission and absorption of the sample, since this technique can result in damage of the sample. The sheet resistance was found to be $15.3 \pm 1.4$ kΩ per square. By applying the AFM measured thickness ($t = 1.97$ nm), the conductivity of the sample was $335.9 \pm 32.0$ S/cm.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

5.3.4 Effect of Lower Copper Catalyst Annealing Temperature

In addition to the annealing of evaporated thin copper film beyond 500 °C, a trial of annealing the evaporated thin copper at 450 °C for 20 hours and then growing under identical conditions as above was also attempted. This study was mainly aimed at preparing a graphene electrode for building organic solar cells (OSCs). The main reason behind the selection of a lower annealing temperature was because the substrates used for evaporating thin copper films were both blank and patterned ITO-coated glass (see Figure 5.14), and this glass is a temperature-sensitive material. If annealed above 500 °C, its mechanical property significantly changes resulting in bending and even melting. Moreover, the electrical properties of ITO as an electrical contact in OSCs significantly degrade if annealed above 450 °C [187]. The films grown on blank glass were used for characterisation, while films grown on patterned ITO-coated glass were used as a rigid substrate for the fabrication of OSCs (Chapter 6).
For this study the graphene growth was initially conducted using different synthesis times of 5, 15, 30 and 60 minutes and maintaining a fixed precursor temperature of 400 °C and a mixed H₂/Ar (50 and 100 sccm, respectively) gas. The results of this experiment were characterised using UV absorption spectroscopy (see Figure 5.15a) and then Raman spectroscopy (see Figure 5.15b). In Figure 5.15a, an absorption peak at ~ 270 nm is not observable indicating that there is no graphene on the samples. However, a peak at 244 nm appears on the samples annealed for 5 and 15 minutes which may result from amorphous carbon or a fragment of PMMA precursor. To confirm the absence of graphene on the samples, Raman spectroscopy (Figure 5.15b) provides evidence that no graphene formation occurs on the samples due to the appearance of D and G peaks only indicating only graphite formation with some defects.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.15 (a) UV absorption spectra and Raman spectra (b) of the samples grown for four different exposure times of 5, 15, 30 and 60 minutes.

The electrical and optical properties of the samples were determined by measuring the $R_{\text{sheet}}$ and transparency, as shown in Table 5.2. This shows that the graphite films resulted are excellent transparency (> 90%). However, each sample has very high $R_{\text{sheet}}$ (>64 M$\Omega$/□) indicating that it has much poorer electrical characteristics.

Table 5.2 Sheet resistance and transparency of the samples grown on the thin Cu film for different times.

<table>
<thead>
<tr>
<th>Growth time (min)</th>
<th>$R_{\text{sheet}}$ (M$\Omega$/□)</th>
<th>Transparency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>64.8</td>
<td>89.6</td>
</tr>
<tr>
<td>15</td>
<td>79.9</td>
<td>97.4</td>
</tr>
<tr>
<td>30</td>
<td>72.5</td>
<td>91</td>
</tr>
<tr>
<td>60</td>
<td>138.6</td>
<td>96.6</td>
</tr>
</tbody>
</table>

To further study the variation of growth time, an experiment was carried out by annealing the precursor at 140 °C under the same gas mixture (H$_2$/Ar). Figure 5.16 shows the SEM images of the samples obtained for different growth times of 30, 60 and 300 seconds. The evolution of a cluster formation on the surface with increasing exposure time is clearly observed from the SEM images. In Figure 5.16a, the carbon-
absorbing thin copper surface appears darker since the charging of copper is significantly higher than that of carbon. This result indicates that a growth process has started on some grains. However, before completely absorbing carbon over the copper surface, a number of small clusters are deposited on copper’s surface. By increasing the magnification of SEM, clusters with a very tiny size of ca. 12.5 nm can be clearly seen. The deposited clusters possibly result from precursor fragments which are not decomposed completely. The grain boundaries are very clear with very small grain sizes of ~ 400 nm. Figure 5.16b shows the SEM image of the sample exposed for 60 s. In this figure, the number of clusters deposited on the copper surface significantly increases, almost covering the surface. Moreover, the size of cluster evolves to ~ 100 nm. Very significantly, the clusters cover the surface (see Figure 5.16c) and even stack to form a multi-layer film as can clearly be seen on the high magnification SEM images. By 300 s plates of precursor can be seen completely covering the copper surface.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

Figure 5.16 SEM images of the samples synthesised for different exposure times of 30 s (a), 60 s (b) and 300 s (c).

The samples grown at different synthesis times were further characterised using Raman spectroscopy, as shown in Figure 5.17. In this figure, all the samples displayed the D- and G-peaks, but no observable 2D peaks. This result again indicates that there is no graphene on the samples. Interestingly, the intensity of the D peak decreases with increasing exposure time. In particular, the 300 sec-synthesised samples had a low intensity of the D peak indicating low defects of the sample.
5. Low-temperature growth on graphene/graphite on evaporated thin copper with direct transfer on target substrate

5.4 Conclusion

After several trials of different experimental parameters, graphene growth conditions were optimised. It was found that 500 nm thick copper films with an annealing temperature of 900 °C for 1 hour under a mixture of H₂/Ar (50 and 100 sccm, respectively) gas followed by graphene growth with a precursor temperature, synthesis temperature and synthesis time of 140 °C, 450 °C and 1 minute, respectively, is the best recipe so far. Furthermore, in order to prepare electrodes for building OSCs working at temperatures below 500 °C for both annealing and growth conditions, it was found that a thin copper film annealed at 450 °C for 20 hours under a mixture of H₂/Ar (25 and 100 sccm, respectively) gas results in the best film using the same growth recipe of the previous study (see Chapter 4). The lowest sheet resistance (R\text{sheet}) of the resulted films were 14.0 kΩ/□ and 64,000 kΩ/□ for growing films on the 900 °C-annealed and 450 °C-annealed thin Cu substrates, respectively. These results are much higher compared to the graphene film (2.4 kΩ/□) grown on the 900 °C-annealed Cu foil. The electrical property of these films was corresponded to the formation of grain size on copper surface. In fact, the largest grain Cu sizes were ~ 0.7, 1.3, and 88 μm for the 450 °C-
annealed thin Cu (see Table 3.5), the 900 °C-annealed thin Cu (see Table 3.4), the 900 °C-annealed Cu foil (see Table 3.3), respectively.

It is believed that the failure of graphene growth when working at temperatures below 500 °C might be due to the very small grain size of prepared copper catalyst leading to poor electrical properties [188]. Consequently, the precursor fragments deposited on the catalyst are not completely decomposed for arrangement to a graphene film. Optically, the resulting films had high quality with above 85% transparency. However, the electrical properties of the films were poor, which would lead to poor performance if used as an electrode in an OSC.
Organic Solar Cell Fabrication with Graphene/Graphite-Based Carbon Electrode

6.1 Introduction

Electronic and optoelectronic devices which use organic materials as both electrode and active layer materials (such as, organic light-emitting diodes (OLEDs) [4], organic solar cells (OSCs) [10, 12, 13], and as the electrode only for organic field-effect transistors (OFETs) [5, 189], organic memory devices [8] and organic sensors [9]) have recently attracted intensive attention inspired by the promise of low-cost fabrication. In particular, the use of organic electrodes in OSCs has been extensively investigated by both research groups and the industrial community. An important part of this class of optoelectronic device is the transparent conductive electrode through which light couples to the device. In order to realise the goal of a high-performance organic transparent electrode, there are many scientific challenges for fabrication which must be overcome. Currently, transparent electrodes in solar cell technologies are dominated by metal oxide films, such as indium tin oxide (ITO) and fluorine tin oxide (FTO). ITO is
one of the most widely used metal oxide electrodes, but is very expensive [23] and has limited application for flexible devices due to the brittle nature of the oxide [25, 26]. The drawbacks of this material limit its use in many commercial applications where cost and mechanical flexibility are important. Substitutes for ITO with comparable performance but lower cost and greater ease of fabrication are highly desirable. Hence, the search for organic electrode materials that are sustainable, have a low fabrication cost and are flexible, whilst retaining the high conductivity and transparency is necessary for the future development of organic solar technology. Due to its extraordinary electrical and optical properties, graphene is ideally suited for use as a transparent electrode in organic solar cells [15, 16, 55, 57].

Graphene as an alternative electrode material in OSCs has been studied by a number research groups [11, 12]. The best power conversion efficiency (PCE) of devices fabricated using various structures is summarised in Table 6.1. The group of Wang et al. (2008) first implemented the reduction of graphene oxide (rGO) film as the electrode for solid-state dye-sensitized solar cells (DSSCs). The PCE of the device was 0.26 %, while the PCE of a control device using FTO as the electrode was 0.84 % [34]. Since Wang’s group have applied a graphene electrode in DSSCs, many research groups have focused their attention on fabricating a graphene electrode in OSC devices. Wu et al. Group demonstrated a marginally improved PCE of 0.4 % using rGO as the anode and CuPc and C_{60} as photoactive materials. However, the performance of the devices was less than that of the ITO-based device (0.84 %) [13]. In the following year, Wang et al. still fabricated an OSC, using graphene fabricated by CVD as the anode, and a P3HT:PCBM blend as the active layer. The PCEs obtained were 0.21 % before UV treatment, 0.74 % after UV treatment and 1.71 % after UV treatment of the graphene anode modified by self-assembled pyrene butanoic acid succidymidy ester (PBASE). This treatment revealed an improvement of the device performance, but was still much lower than that of an equivalent ITO-based device (3.1 %) [35].

In 2010, the group of Xu et al. adopted Wang’s device structure using a rGO film as the anode. The fabricated device showed poor performance (0.13 % PCE) which was much lower than that of the reference device (3.59 % PCE) which used a ITO as the anode [12]. However, the group of De Arco et al. have reported that the performance of CVD graphene-based OSC devices is comparable to the ITO-based OSC devices with PCEs
of 1.18 % and 1.27 %, respectively. Through characterisation under bending conditions, the CVD graphene-based OSC device was shown to be more flexible compared to the reference (ITO anode) device. In fact, the CVD graphene-based OSC device could operate under bending conditions up to 138°, whereas the reference device displayed cracks and irreversible failure under bending of 60° [190]. Furthermore, Park et al. reported that sheet resistance and graphene surface wetting properties could be improved by AuCl$_3$ doping and obtained a PCE of 1.63 % [36]. The improving performance of these various devices shows that graphene has a realistic chance of being competitive in transparent and flexible technologies.

Table 6.1 Summary of the properties of OSC devices employing graphene as a transparent electrode.

<table>
<thead>
<tr>
<th>Research groups</th>
<th>Graphene</th>
<th>$R_{\text{sheet}}$ (Ω/sq)</th>
<th>T (%)</th>
<th>Device structures</th>
<th>PCE ( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wang et al [34]</td>
<td>rGO</td>
<td>1.8k</td>
<td>70.7</td>
<td>DSSC</td>
<td>0.26</td>
</tr>
<tr>
<td>Wu et al. [13]</td>
<td>rGO</td>
<td>500k</td>
<td>85</td>
<td>G/CuPc/C$_{60}$/BCP/Ag</td>
<td>0.4</td>
</tr>
<tr>
<td>Wang et al. [35]</td>
<td>CVD</td>
<td>1.35k</td>
<td>91</td>
<td>G/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>1.71</td>
</tr>
<tr>
<td>Xu et al. [12]</td>
<td>rGO</td>
<td>17.9k</td>
<td>69</td>
<td>G/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>0.13</td>
</tr>
<tr>
<td>Arco et al. [10]</td>
<td>CVD</td>
<td>230</td>
<td>72</td>
<td>G/PEDOT:PSS/CuPc/C$_{60}$/BCP/Al</td>
<td>1.27</td>
</tr>
<tr>
<td>Park et al. [36]</td>
<td>CVD-AuCl$_3$</td>
<td>300k</td>
<td>91.2</td>
<td>G/PEDOT:PSS/CuPc/C$_{60}$/BCP/Ag</td>
<td>1.63</td>
</tr>
</tbody>
</table>

The graphene electrodes used for fabricating the devices above are typically grown at high temperatures of $>> 500$ °C. This method of graphene growth is not suitable for low-cost fabrication of OSC devices since the high-temperature growth consumes huge energy resulting in the high cost of fabrication. Here, two different methods were used for growing graphene films at 450 °C which were then used as transparent conductive electrodes for fabricating OSC devices. One method was by growing graphene on
copper film and then transferring onto a patterned ITO-coated glass substrate after etching the copper, as discussed in Chapter 4. The other was by directly growing graphene/graphite on the target substrate assisted by evaporated thin copper, as discussed in Chapter 5. In the latter method, graphene was produced by growing it on a 900 °C-annealed thin Cu substrate, while graphite was produced by growing it on a 450 °C-annealed thin Cu substrate.

6.2 Experimental Setup

6.2.1 Structure of OSC devices

Graphene films were studied for use as transparent conductive electrodes in OSC devices. Two types of device structure in this study were utilised as shown in Figure 6.1. The first structure (structure A) was graphene/poly(3,4-ethylenedioxythiophene-poly(styrenesulfonate) (PEDOT:PSS) /poly(3-hexylthiophene-2,5-diyl):(Phenyl-C61-butyric acid methyl ester) (P3HT:PCBM)/Ca/Al. For comparison, a standard device using ITO as the transparent electrode was fabricated. The other structure (structure B) was graphene/P3HT:PCBM/Ca/Al. For comparison, a device using a PEDOT:PSS coating as the transparent anode was also fabricated. The main difference between these structures was the deposition of the transparent electrodes with or without an interface layer of PEDOT:PSS prior to the deposition of active layer. The electrodes employed in the structure A were deposited with the PEDOT:PSS interface layer, while the electrodes employed in the structure B were not deposited with the interface layer. Alternatively, the device with the structure A was deposited with an interface layer prior to further deposit the P3HT:PCBM layer, while the device with the structure B was fabricated without the interface layer. Moreover, for the structure A-based OSC device two different materials (ITO and Al) were applied as contacts to the electrodes, while the structure B-based OSC device used the ITO material as the contact only.
The PEDOT:PSS layer sandwiched between the transparent electrode and P3HT:PCBM layer was used to block electrons and increase the hole transport from the P3HT to the electrode and therefore to minimise the recombination of electrons and holes at the interface. The other thin interface layer used in both the structure types was calcium. This interface layer was sandwiched between the P3HT:PCBM layer and Al electrode. The use of this layer was to block the holes and enhance the electron transport efficiency from the PCBM to the Al electrode.

6.2.2 Preparation of target substrate

In order to prepare a target substrate for placement of placing a transparent electrode, patterned ITO-coated glass (Kintec) with the dimensions of 17.5 mm x 12.5 mm x 0.7 mm, which has six separate fingers with width of 2 mm and one common contact of 3.5 mm in width, was used, as shown in Figure 6.2a. The substrate was obtained via acid etching of the ITO substrate. The middle area of ITO was etched away by an aqueous HCl solution (0.25 M), while the areas used as contacts to the devices were protected by covering with adhesive tape (Figure 6.2b). After etching, the tape was mechanically peeled away resulting in a modified pattern on the glass. The new pattern will be referred
to as the patterned ITO-coated glass substrate (Figure 6.2c). This substrate was further used as a rigid substrate for all graphene-based OSC devices.

![Diagram of substrate preparation](image)

Figure 6.2 The scheme of preparation for making a patterned ITO-coated glass substrate.

In order to remove any contaminants on the substrates, they were first cleaned using the following steps [102]:

1. The substrates were placed in a glass beaker of acetone and sonicated at room temperature for 5 minutes.
2. After sonication, the substrates were rinsed three times with acetone.
3. The substrates were then submerged in isopropanol and again sonicated at room temperature for 5 minutes.
4. After sonication, the substrates were rinsed three times with isopropanol.
5. Another rinse using reverse-osmosis (RO) water was performed three times.
6. Each substrate was then dried under a flow of N₂.
7. For the ITO-based OSC device (standard device), when dry, the substrate was then placed in an ozone treatment box for a minimum of 15 minutes.
6. Organic solar cell fabrication with graphene/graphite-based carbon electrode

6.2.3 Anode Deposition

6.2.3.1 ITO Substrate

In this design, a patterned ITO-coated glass substrate was used as a rigid substrate for OSC devices, as schematically shown in Figure 6.3. To build this device, a graphene film was first positioned on the substrate (6.3a). Two different techniques were conducted for placing the film on the target substrate. One was via a transfer process in which the graphene film grown on a 900 °C-annealed copper foil was transferred onto the substrate after etching away the foil. The other was without a transfer process in which the graphene film was directly grown on a 450 °C-annealed thin Cu substrate and the graphene was then left behind on the film after etching away the copper. The resulting graphene films were patterned by dividing them into three different active cell areas (6.3b). Then the PEDOT:PSS and P3HT:PCBM films were deposited by spin-coating (6.3c). The Ca and Al were thermally vapour deposited on top of the spin-coated films (6.3d).

![Figure 6.3 ITO substrate OSC devices](image-url)
6. Organic solar cell fabrication with graphene/graphite-based carbon electrode

6.2.3.2 Quartz Substrate

In this design, a quartz slide rather than the patterned ITO-coated glass substrate was used as a rigid substrate for OSC devices as shown in Figure 6.4. To place a graphene film on the substrate, the direct transfer technique was conducted as mentioned above. After etching, the resulting graphene film was patterned by dividing into two different areas of common contact and active cells (6.4a). To protect the contact from contaminants during the deposition of PEDOT:PSS and P3HT:PCBM, this area was covered by adhesive tape (6.4c) which was adhered to the multiple layers of plastic tape (6.4b). After depositing these materials, the tape was peeled away. Afterward, a patterned plastic mask was used to form active cell areas and individual contacts onto substrate. The masked substrate was thermally vapour deposited an interfacial layer of calcium and followed by a cathode of aluminium (6.4d). The size of active cell areas was then determined by the area of patterned mask which was applied for testing a graphene-based OSC device.

Figure 6.4 Quartz substrate OSC device
6.2.4 PEDOT:PSS deposition

In this subsection, the deposition of PEDOT:PSS is explained in detail for structure A with ITO contact. A PEDOT:PSS dispersion sourced from Heraeus was used for depositing a hole transporting layer onto the graphene and ITO electrodes in the device structure A (see Figure 6.1a) as well as a transparent electrode in the device structure B (see Figure 6.1b). This PEDOT:PSS is commercially available as an aqueous dispersion (Clevios P VP Al 4083) with a solid content of 1.2%. This dispersion has a viscosity of 60–100 mPa, and forms solid films of conductivity ~ 1 S/cm [191]. Before use, the PEDOT:PSS solution was filtered using a Whatman Puradisc 0.45 μm PES filter in order to produce a PEDOT:PSS dispersion with smaller particle size. Once filtered the PEDOT:PSS was deposited onto the substrate using a Laurell spin coater, as shown in Figure 6.4. In this work, the spin speed for coating a PEDOT:PSS film was set at 4000 rpm for 90 seconds. Before spinning, 75 μL of the solution was dropped onto, and then spread over, the substrate. These parameters result in a coating with the thickness of ~ 50 nm. Before drying, the common contact ITO pad was exposed to allow connection with the PEDOT:PSS film. A cotton bud was used to gently rub away the PEDOT:PSS layer on both the ITO and graphene substrates, as shown in Figure 6.5. Afterward, the substrates were heated on a hot plate at 140 °C for 30 min to remove water. The dried substrates were immediately transferred into a nitrogen atmosphere glovebox system.

Figure 6.5 The Laurell spin coater used for depositing the thin layers.
In this work, the PEDOT:PSS coating layer used had a thickness of \(~ 50 \text{ nm}\) with transparency of 96.1\% (at \(\lambda = 550 \text{ nm}\)). The spectrum of the layer shows a relatively flat transmission across the range of interest in the visible region. This spectrum indicates that \(\approx 4\%\) of available light is lost to absorption in the PEDOT:PSS layer. In particular, the standard device had lost \(\approx 7\%\) of the incident light (ITO loss plus PEDOT:PSS loss) before hitting the active layer, since the transparency of ITO (at \(\lambda = 550 \text{ nm}\)) was 97.0 \% (Figure 6.7).

Figure 6.6 The process of removing PEDOT:PSS from the ITO finger and common contacts of the ITO (top) and graphene (bottom) substrates.
6. Organic solar cell fabrication with graphene/graphite-based carbon electrode

6.2.5 Active layer deposition

In order to deposit an active layer on the top of PEDOT:PSS layer, a blend of P3HT and PCBM at a 1:0.8 mass ratio was used. This P3HT:PCBM blend was prepared via dissolution of 10 mg P3HT and 8 mg PCBM in 1 mL chloroform via sonication for 1 hour. This blend was then spun on top of the PEDOT:PSS layer at 2000 rpm for 60 seconds. After spin coating, the film deposited on the top of the common and individual contact ITO pads were removed using a cotton-tip. Afterward, the substrates were dried on a hot plate at 50 °C for 4 min. This heating gently drives water out from the film, and avoids major changes in the films hydrophilicity [192]. For further layer depositions, the annealed substrates were transferred into a nitrogen-filled glovebox. In this glovebox, the substrates were loaded into a sample holder (see Figure 6.7a) and transferred into the evaporation chamber system (see Figure 6.7b) for evaporation of a calcium interfacial layer followed by a cathode layer of aluminium.
6. Organic solar cell fabrication with graphene/graphite-based carbon electrode

6.2.6 Cathode evaporation

In order to completely fabricate an OSC device, on the top of the dried active layer an interface layer of calcium (20 nm) and a metal cathode of aluminium (100 nm) were subsequently deposited in vacuum using an Angstrom Engineering evaporator at a pressure of ca. 1x10^{-6} Torr. In this study, three different masks (see Figure 6.8) were used for evaporating the Ca and Al layers on different OSC devices. The two masks used for design A had rectangular holes of size of 5.5 mm x 15 mm and 2 mm x 15 mm for the ITO-based OSC device and the graphene/graphite/PEDOT:PSS-based OSC device, respectively. While the remaining mask used for design B had holes sized 3 mm x 3 mm for patterning a common cathode contact and 2 mm x 12.5 mm for patterning the active cell areas and individual anode contacts. The active cell areas obtained (see Figure 6.9) were therefore 5 mm^2 (2 mm x 2.5 mm) and 4 mm^2 (2 mm x 2 mm) for the ITO-based OSC device and the graphene/graphite/PEDOT:PSS-based OSC device, respectively.

Figure 6.8 Photograph of the (a) sample holder for evaporation and (b) evaporation system.
Figure 6.9 The masks used for evaporating the Ca/Al on the OSC devices: (a) the ITO-based OSC device with the design A, (b) the graphene/graphite/PEDOT:PSS-based OSC device with the design A, and (c) the graphene-based OSC device with the design B.

Figure 6.10 The active cell areas of fabricated OSC devices using the different evaporation masks.
6.3 Results and Discussion

In this work, graphene/graphite films used as a transparent electrode for an OSC device are demonstrated. The devices were built using the two different structures (the structures A and B (see Figure 6.1)) discussed earlier. In order to compare the performance of graphene/graphite-based OSC devices to standard devices, devices using ITO (structure A) and PEDOT:PSS (structure B) electrodes were also fabricated and characterised.

6.3.1 Preparation and characterisation

Using structure A, two different substrates were used: ITO (see Figure 6.3) and quartz substrates (see Figure 6.4). To fabricate the ITO substrate-based OSC devices, four different anodes including ITO, PEDOT:PSS, graphene and graphite were used. Commercial ITO with sheet resistance of 15 Ω/sq (97 % transparency) was used as the anode for a standard device. A PEDOT:PSS anode was prepared by spin coating a PEDOT:PSS solution on the ITO substrate and then annealing. The two remaining anodes were produced using different growth methods. Graphene films (Graphene A and C) were grown on copper foil and then transferred onto the ITO substrate, while a graphite anode was derived from direct film growth on a thin copper-deposited ITO substrate and then the film was then obtained after etching the copper. A second class of OSC device was fabricated using quartz substrate. For the quartz substrate-based device, a graphene film (Graphene B) was employed. This anode was produced by growing it on a 900 °C-annealed thin Cu substrate. The difference between both device classes is that the ITO substrate-based device uses the ITO as a common contact, while the quartz substrate-based relies on the aluminium as a common contact.

The transparent electrodes for building the OSC devices were characterised by measuring the sheet resistance and transmittance using a Varian Cary 6000i UV-vis-NIR spectrophotometer and a Fluke 79-III multimeter, respectively. The results of these measurements are tabulated in Table 6.2. All the transparent electrodes have a transmittance above 86 % allowing the bulk of the incident light to reach the active
6. Organic solar cell fabrication with graphene/graphite-based carbon electrode

Layer in the device. The sheet resistance of the carbon-based electrodes are observed to be much higher (> 3 orders of magnitude) than the ITO.

Table 6.2 The transparency and sheet resistance of the bottom electrodes prepared for building OSC devices.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Conditions of growth</th>
<th>Transmission (%)(λ=550 nm)</th>
<th>Sheet resistance, $R_{\text{sheet}}$(Ω/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene A</td>
<td>ITO contact</td>
<td>86.1</td>
<td>9.8k</td>
</tr>
<tr>
<td>Graphene B</td>
<td>no ITO</td>
<td>95.8</td>
<td>32.7k</td>
</tr>
<tr>
<td>Graphene C</td>
<td>ITO contact</td>
<td>92.4</td>
<td>2.4k</td>
</tr>
<tr>
<td>Graphite</td>
<td>ITO contact</td>
<td>92.6</td>
<td>580k</td>
</tr>
<tr>
<td>ITO</td>
<td>ITO electrode</td>
<td>97.0</td>
<td>15.0</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>ITO contact</td>
<td>96.1</td>
<td>1.5M</td>
</tr>
</tbody>
</table>

Another characterisation of the transparent electrodes conducted was surface morphology using a Cyper atomic force microscopy (AFM) with a scan size of 5 µm x 5 µm. The results of AFM scanning are shown in Figure 6.11. The surface of graphene A, B and C (Figures 6.11a, 6.11b and 6.11c) show tiny clusters with the average size of ~ 150, ~ 40 and ~150 nm, respectively, that possibly arise from incomplete decomposition of the PMMA precursor as discussed in section 4.4.3. Moreover, straight striations are observed on graphene A and C but not graphene B since the graphene growth follows the striations of the copper catalyst. In these anodes, the surfaces are free from “spikes” which would result in shorts in the OSC device. Nevertheless to prevent shorts, an interface layer was used in devices with the thickness of ~ 50 nm. The morphology of ITO (Figure 6.11d) and PEDOT:PSS(Figure 6.11e) electrodes were scanned with the same resolution. The AFM image shows that the surface morphology of ITO is much smoother than that of the graphene films, but much rougher than the PEDOT:PSS anode. The root mean squared surface roughnesses ($R_{\text{rms}}$) of graphene A, graphene B, graphene C, ITO and PEDOT:PSS are 4.8, 4.4, 4.37, 2.4 and 0.75 nm, respectively.
6. Organic solar cell fabrication with graphene/graphite-based carbon electrode

6.3.2 Organic solar cell performance

In order to demonstrate how the graphene/graphite/PEDOT:PSS films and ITO performed as transparent electrodes, full OSC devices with two different structures (A and B) were characterised. The electrodes of graphene A, graphene B, graphite and ITO were used for the structure A, while the electrodes of graphene C and PEDOT:PSS were used for the structure B. The transmittance and sheet resistance of these electrodes are tabulated in Table 6.2. All devices were fabricated under identical conditions, in a nitrogen atmosphere glovebox system. The current density-voltage (J-V) curves were measured at room temperature under 100 mW/cm² AM1.5G simulated solar illumination. The illumination intensity was measured using a calibrated silicon photodiode.
For structure A, the J-V characteristics of typical organic solar cells obtained using anodes of graphene A, graphene B and graphite and a standard cell fabricated with an ITO anode are shown in Figure 6.12. The structure A-based OSC devices were distinguished by using two different contact materials, i.e. ITO and Al. The ITO contact was used to give a connection on the electrode of graphene A and graphite, while the Al contact was used to give a connection on graphene B. An overall power conversion efficiency (PCE) of 0.36 % was achieved using graphene A as transparent electrode, while the graphite showed a lower efficiency of 0.16 %, as shown in Table 6.3. Overall performance of the devices with ITO contact was strongly influenced by the sheet resistance of the used transparent electrodes. Indeed, the graphene A with the lower $R_{\text{sheet}}$ of 9.8 kΩ/□ results in the higher PCE of 0.36 %, while the graphite with the higher $R_{\text{sheet}}$ of 580 kΩ/sq results in the lower PCE of 0.16 %. Furthermore, when a commercial ITO, with much lower $R_{\text{sheet}}$ of 15 Ω/sq, was used as the anode for the standard device, a PCE of 2.41 %, much higher than that of the graphene A/graphite-based OSC device, is obtained. The lower efficiency of the devices based on graphene/graphite anode is, therefore, mainly due to their higher sheet resistance. Interestingly, the graphene A-based OSC device prepared showed a Voc (~ 0.6 V) comparable to the reference device with an ITO anode, suggesting similar recombination behaviour in both devices. Moreover, performance of the anodes (graphene A and graphite) with contact ITO was compared to the performance of graphene B with Al contact. This comparison shows that the anodes with ITO contact have a better performance than that of the graphene B. This difference in the device performance indicates that, as expected, the connection of ITO to the graphene film is much better than the aluminium as a contact material.
Figure 6.12 Current density-voltage (J-V) curves of the structure A-based OSC devices with graphene A, graphene B, graphite and ITO as the transparent electrodes, respectively.

Figure 6.13 Current density-voltage (J-V) curves of the structure B-OSC devices with graphene C and PEDOT:PSS coating as the transparent electrodes, respectively.
Table 6.3 Performance details of OSC devices

<table>
<thead>
<tr>
<th>Anode</th>
<th>Conditions of growth</th>
<th>J_{sc} (mA/cm(^2))</th>
<th>V_{oc} (mV)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene (A)</td>
<td>ITO contact</td>
<td>1.43</td>
<td>610</td>
<td>0.41</td>
<td>0.36</td>
</tr>
<tr>
<td>Graphene (B)</td>
<td>no contact</td>
<td>0.60</td>
<td>530</td>
<td>0.30</td>
<td>0.09</td>
</tr>
<tr>
<td>Graphene (C) only</td>
<td>ITO contact</td>
<td>3.09</td>
<td>87</td>
<td>0.25</td>
<td>0.07</td>
</tr>
<tr>
<td>Graphite</td>
<td>ITO contact</td>
<td>0.75</td>
<td>535</td>
<td>0.33</td>
<td>0.16</td>
</tr>
<tr>
<td>ITO</td>
<td>ITO electrode</td>
<td>8.57</td>
<td>598</td>
<td>0.47</td>
<td>2.41</td>
</tr>
<tr>
<td>PEDOT:PSS only</td>
<td>ITO contact</td>
<td>0.18</td>
<td>520</td>
<td>0.32</td>
<td>0.04</td>
</tr>
</tbody>
</table>

In addition to the structure A-based OSC device, graphene C and PEDOT:PSS were employed as electrodes for fabricating the structure B-based OSC devices and also compared. In this case, PEDOT:PSS was used as the anode rather than the interface layer in fabricating this structure. The measured J-V curves of the fabricated two OSC devices are shown in Figure 6.13. The photovoltaic performance of these devices has been tabulated in Table 6.3, as shown above. Both devices show poor performance. Although the graphene employed as the anode has a lower R_{sheet} (2.4 kΩ/sq), the performance is still poor (PCE =0.07 %) due to the absence of PEDOT:PSS as the hole transporting layer in this structure. Consequently, the high value of the roughness of surface morphology (R_{rms} = 4.37 nm) may cause a short current or leakage leading to a linear J-V curve. On the other hand, the PEDOT:PSS coating with a much higher R_{sheet} (1.5 MΩ/sq) shows slightly lower performance with a PCE of 0.04%. This comparison shows that the results observed for graphene A and graphite are not solely due to the PEDOT:PSS interface layer.
6.4 Conclusion

In this work, we demonstrated the fabrication of graphene-based OSC devices with a PCE of 0.36 %. This device is comparable in the literatures: untreated Wang’s device (0.21 %) [35] and Xu’s device (0.13 %). Moreover, the fabricated device showed a Voc (~ 0.6 V) comparable to the standard device with an ITO anode, suggesting similar recombination behaviour in both devices. Furthermore, the device with ITO contact demonstrated better performance compared to that with Al contact. This is indicative that the ITO has better connection to the graphene film than the Al.

We have shown that graphene/graphite prepared at < 500 °C can perform as well (if not better) as an electrode in OSCs, as graphene grown at 900 °C. Clearly, the poor performance of the graphene devices compared to those prepared with ITO is not a result of graphene quality. Rather, we believe, it is an issue of the difficulty in connecting both the active layer and the overall circuit to the graphene electrode. Although this problem may also be due to in part to the natural anisotropy of electrical conduction in graphene. This problem will need to be addressed before graphene is successfully used in OSC devices.
7 Conclusion and Future Work

7.1 Conclusion

Chemical vapour deposition (CVD) using a copper catalyst is a very promising method for the synthesis a scalable, high-quality graphene film, which would be an alternative transparent, conductive electrode in the fabrication of organic solar cells (OSCs). In this work, graphene films are grown on both copper foils and evaporated thin copper films at temperatures below 500 °C in a CVD furnace by using a poly(methyl methacrylate) (PMMA) coating as the solid carbon source. The precursor was annealed at the desired growth temperatures by introducing a mixture of hydrogen (H₂) and argon (Ar) gases for different times. The work presented in this thesis has potential applications in the fabrication of OSC devices with graphene films as the transparent, conductive electrode.

In Chapter 2, all experimental techniques used in this work including sample preparation, graphene growth, the transfer process, characterisation and fabrication of OSC devices are explained. For the carbon source preparation, the PMMA was diluted
with chlorobenzene to a concentration of 100 mg/mL and then deposited on a glass substrate by drop casting. The catalysts were prepared by annealing both copper foil and thin copper film substrates in the CVD system whilst varying the experimental parameters of temperature, time, and hydrogen flow rate. The annealed copper substrates were used as the catalyst for growing graphene films at low temperatures of 350 and 450 °C by heating the precursor at the temperatures of 140 and 400 °C under a hydrogen and argon atmosphere. The graphene films produced were characterised by scanning electron microscopy (SEM), ultraviolet-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM), profilometry, four-point probe conductivity measurement, AFM and Raman spectroscopy. Other characterisations were thermogravimetric analysis (TGA), X-ray diffraction (XRD) and current-voltage (I-V) curve for the precursor, the catalyst and the OSC device, respectively.

In Chapter 3, we outlined a detailed study of the grain size, crystallinity and surface morphology as a function of thermal processing. The goal of this chapter was to provide insights into the effects of thermal annealing on copper on which graphene is grown at high temperatures. The thermal annealing of copper by varying the annealing temperature, annealing time and hydrogen flow rate were investigated by SEM, XRD and energy disersive X-ray spectroscopy (EDS) analysis. We found that both of the copper substrate types have a good nanocrystalline cubic structure, dominated by (100) and (111) planes for the copper foil and the thin copper film, respectively. Moreover, the absence of copper oxide peaks on the annealed copper under hydrogen atmosphere indicates that the reducing gas effectively removes the copper oxide impurities. The SEM results show that the samples annealed at beyond 900 °C have a smooth surface morphology with uniform coverage and grain sizes around 1.3 µm and 88 µm for thin copper film and copper foil, respectively. Furthermore, an optimal hydrogen flow rate of 100 sccm for smoothing the copper foil surface was determined.

In Chapter 4, we conducted a systematic study of graphene growth at the temperatures below 500 °C on (100) dominant indexed copper catalysts using PMMA as the carbon precursor that was heated at two different temperatures: 140 and 400 °C. To provide the catalyst with smooth surface morphology and large domain size, the copper was annealed at 900 °C for 10 minutes under a H₂/Ar mixture (100 and 100 sccm, respectively). Under these catalyst conditions, high quality graphene films were
realised. We found that the 450 °C-grown samples result in a better quality graphene film compared to the 350 °C-grown samples. This is indicative that at temperatures below 500 °C, graphene can be successfully grown with the assistance of an annealed copper catalyst. Moreover, graphene growth by heating the carbon precursor of 140 °C for less than 60 seconds can allow to grow a monolayer graphene film.

In Chapter 5, we demonstrated a simple method for the direct transfer of large-area graphene films (> 1 cm²) by growing at temperatures below 500 °C using PMMA as a carbon source. The catalysts used for growing graphene were evaporated thin copper films annealed at two different temperatures of 450 and 900 °C. The thin copper was evaporated onto the desired substrate. An advantage of this technique is that the graphene film grown on the catalyst settles on the substrate after etching the underlying metal catalyst away. One of the substrates used was a patterned indium tin oxide (ITO) slide for directly depositing graphene electrode in order to fabricate OSCs, as discussed in Chapter 6.

In Chapter 5, we also studied the effect on surface morphology of catalysts annealed at different temperatures, copper thicknesses, precursor temperatures and growth times. After several trials of different experimental parameters, the graphene growth conditions were optimised. It was found that 500 nm thick copper films with an annealing temperature of 900 °C for 1 hour under a mixture H₂/Ar (50 and 100 sccm, respectively) gas followed by growing graphene with the precursor temperature, synthesis temperature and synthesis time of 140 °C, 450 °C and 1 minute, respectively, is the best recipe so far. Using this growth recipe, it was also found that a thin copper film annealed at 450 °C for 20 hours under a mixture of H₂/Ar (25 and 100 sccm, respectively) gas results in the best film (graphite) which is prepared as a transparent conductive electrode for building OSCs. It is believed that the failure of graphene growth in working at temperatures below 500 °C might mainly be due to the very small grain size (~ 0.7 µm) of the copper catalyst leading to poor electrical properties [188]. Consequently, the precursor fragments deposited on the catalyst are not sufficiently decomposed for arranging in to a graphene film. Optically, the resulted films had high quality with above 85% transparency. However, the electrical properties of the films were still poor, which would lead to poor performance if used as an electrode in an OSC.
In Chapter 6, we used two different catalyst preparation methods in order to fabricate transparent conductive electrodes for fabricating OSC devices. One method was by growing graphene on copper foil and then transferring onto a patterned ITO-coated glass substrate after etching the copper, as discussed in Chapter 4. The other was by directly growing graphene/graphite on the target substrate assisted by evaporated thin copper, as discussed in Chapter 5. In this work, four graphene/graphite films prepared by growing at 450 °C on both copper foil and thin copper film were used as transparent electrodes for fabricating OSC devices. We found that despite of the high sheet resistance (a few kΩ/sq) of these electrodes, they demonstrated working devices with PCEs of between 0.07 - 0.36 %. For comparison, the OSC device with a PEC of 0.36 % is much poorer than that of the PBASE-modified Wang’s device (1.71 %) [35], but better than the untreated Wang’s device (0.21 %) [35] and Xu’s device (0.13 %) [12]. Interestingly, the OSC device prepared in this study showed a Voc (~ 0.6 V) comparable to the reference device with an ITO anode, suggesting similar recombination behaviour in both devices.

7.2 Future Work

Graphene growth on a Cu foil catalyst has shown exceptional electrical and optical properties to be used as a transparent, conductive electrode in OSC devices. However, the devices fabricated here still show poorer performance than that of ITO-based OSC devices due to the higher roughness of its surface. It is expected that after the optimisation of graphene growth by working at the temperature below 500 °C to produce the film with desired electrical, optical and morphology properties, graphene may become more attractive than ITO and will realize its potential to be a low cost, economically viable OSC technology.

To produce graphene film more simply, a method has been demonstrated by directly growing it on the target substrate assisted by a thin evaporated Cu catalyst. However, the conductivity of the resulting graphene films is much lower. This is because the annealed thin Cu prepared as the catalyst for growing graphene has small grain sizes. The next stage would be to find an optimal annealing condition for forming large Cu grains on the thin Cu surface.
References


7. Reiter, F., Carbon based nanomaterials as transparent conductive electrodes in George W. Woodruff School of Mechanical Engineering, 2011, Georgia Institute of Technology.


