2D materials with enhanced thermoelectric (TE) properties

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**2D MATERIALS WITH ENHANCED THERMOELECTRIC
(TE) PROPERTIES**

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2019

2D MATERIALS WITH ENHANCED THERMOELECTRIC (TE) PROPERTIES

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

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Chapter 4 is accepted as Li Lynn Shiau, Simon Chun Kiat Goh, Xingli Wang, MinMin Zhu, Mamina Sahoo, Chuan Seng Tan, Chao-Sung Lai, Zheng Liu and Beng Kang Tay. Effects of precursors' purity on graphene quality: synthesis and thermoelectric effect. In AIP Advances (April 2020 issues)

The contributions of the co-authors are as follows:

- I provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Simon, Dr Xingli Wang, Prof Tan Chuan Seng and Prof Tay Beng Kang.
- I co-designed the study with Simon and Mamina Sahoo and performed all the laboratory work at the School of Electrical Electronic and Engineering and the Singapore Synchrotron Light Source. Simon and Xingli analyzed the Raman and XPS data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Prof Chao-Sung Lai and Mamina Sahoo assisted in preparation of pristine graphene sample.
- Prof Zheng Liu and Dr Zhu MinMin assisted in sample fabrication and characterization.

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The contributions of the co-authors are as follows:

- Simon Chun Kiat Goh suggested the materials area and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr Xingli Wang, Prof Tan Chuan Seng and Prof Tay Beng Kang.
- Dr MinMin Zhu performed graphene synthesis. Simon prepared graphene functionalization. I carried out TEM, XPS and raman analysis for data evaluation.
- Prof Zheng Liu assisted in sample characterization and manuscript revision.

4/11/19

Date

Shiau Li Lynn

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Table of Contents

ACKNOWLEDGEMENT	8
LIST OF FIGURES	11
LIST OF TABLES	17
ABSTRACT	18
1 INTRODUCTION.....	20
1.1 MOTIVATION.....	20
1.2 OBJECTIVES.....	25
1.3 MAJOR CONTRIBUTION OF THE THESIS	25
1.4 ORGANIZATION OF THE THESIS.....	26
2 LITERATURE REVIEWS	28
2.1 THERMOELECTRIC OVERVIEW.....	28
2.2 CHALLENGES IN ENHANCING THERMOELECTRIC (TE) PROPERTIES.....	31
2.3 SEEBECK'S EFFECT IN THERMOELECTRIC (TE) INFRARED (IR) SENSORS....	33
2.4 LOW DIMENSIONAL THERMOELECTRIC (TE) MATERIALS	36
2.5 PHYSICAL AND CHEMICAL PROPERTIES OF GRAPHENE AND BEYOND GRAPHENE MATERIALS	42
2.6 GRAPHENE SYNTHESIS	44
2.6.1 <i>Mechanical exfoliation/ cleavage</i>	45
2.6.2 <i>Arc discharge</i>	46
2.6.3 <i>Oxidative exfoliation-reduction</i>	47
2.6.4 <i>Epitaxial growth on silicon carbide (SiC)</i>	49
2.6.5 <i>Substrate-free gas phase (SFGP)</i>	50
2.6.6 <i>Chemical vapor deposition (CVD)</i>	51
3 GRAPHENE SYNTHESIS AND EXPERIMENT SETUP.....	53
3.1 INTRODUCTION.....	53
3.2 GRAPHENE PREPARATION METHODOLOGY	53
3.2.1 <i>Graphene growth using chemical vapour deposition (CVD)</i>	53
3.2.2 <i>Graphene Transfer</i>	54
3.3 CHARACTERIZATION OF AS-GROWN GRAPHENE.....	55
3.3.1 <i>Raman spectroscopy</i>	55
3.4 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS).....	57
3.5 TEST STRUCTURE DESIGN AND SIMULATION	59
3.6 TEST STRUCTURE FABRICATION	62
3.7 THERMOELECTRIC (TE) PROPERTIES CHARACTERIZATION.....	64
3.8 SUMMARY	69
4 DEFECTS ENGINEERING OF GRAPHENE BY GAS SOURCES	70
4.1 PRELUDE	70
4.2 INTRODUCTION.....	70
4.3 DEVICE FABRICATION AND CHARACTERIZATION	71
CHARACTERIZATION	72
4.4 RESULTS AND DISCUSSION.....	72
4.5 SUMMARY	90

5	METAL DECORATED GRAPHENE.....	91
5.1	PRELUDE	91
5.2	INTRODUCTION.....	91
5.3	HYBRIDIZATION OF METAL NPS-DECORATED GRAPHENE	93
5.4	RESULTS AND DISCUSSION	94
5.4.1	<i>Comparative study of Au reduction methods for graphene – Au NPs hybridization</i>	<i>94</i>
5.4.2	<i>Metal NPs-decorated Graphene for thermoelectric power factor enhancement</i>	<i>100</i>
5.5	SUMMARY	110
6	THERMOELECTRIC BEYOND GRAPHENE.....	111
6.1	PRELUDE	111
6.2	INTRODUCTION.....	111
6.3	MOLYBDENUM DISULFIDE (MoS ₂).....	112
6.3.1	<i>Growth and Characterization.....</i>	<i>114</i>
6.3.2	<i>Theoretical Discussion.....</i>	<i>118</i>
6.4	BISMUTH OXYSELENIDE (Bi ₂ O ₂ Se)	121
6.4.1	<i>Growth and Characterization.....</i>	<i>121</i>
6.4.2	<i>Results and Discussion</i>	<i>124</i>
6.4.3	<i>Summary.....</i>	<i>129</i>
7	FUTURE WORKS – GRAPHENE-BASED THERMOPILE WITH HEAT ABSORBER AND F-DOPED GRAPHENE AS LOW THERMAL BUFFER... 131	
7.1	METHODS	133
7.2	CHARACTERIZATION	133
7.3	RESULTS AND DISCUSSION.....	133
7.4	DEVICE FABRICATION OF THERMOCOUPLE WITH ABSORBER	136
7.5	TITANIUM NITRIDE (TiN) THIN-FILM ABSORBER	137
7.6	META-ABSORBER - SIMULATION	139
8	CONCLUSION	142
9	LIST OF PUBLICATIONS	145
	BIBLIOGRAPHY	147

List of Figures

Figure 1 Typically high efficiency TE materials with ZT as a function of temperature. Inset: relation between η , T and ΔT of materials with different ZT. Reproduced with permission [30].	29
Figure 2 Carrier charge flows from hot to cold junction for a TE material for depiction of Seebeck coefficient.	30
Figure 3 The blackbody radiation curves according to Planck's law as a function of wavelength. T=6000K is the temperature of sun with a peak in the visible range. Blue line represents Wien's displacement law. Maximum wavelength of an object shifts as the temperature decreases [43].	34
Figure 4 Seebeck effect generates in (a) thermocouple (b) thermopile [45].	35
Figure 5 Electronic DOS for (a) bulk 3D crystalline semiconductor, (b) 2D quantum well, (c) 1D nanowire/nanotube, and (d) 0D quantum dot. Reproduced with permission [47].	37
Figure 6 (a) ζ_{opt}^* vs B (inset shows variations of $Z_{3D}T$ with ζ^* at fixed B). (b) $Z_{3D}T$ vs B with optimal ζ^* . Reproduced with permission [48].	39
Figure 7 (a) ζ_{opt}^* vs B plot. (b) $Z_{2D}T$ vs B with optimal ζ^* . Reproduced with permission [48].	41
Figure 8 Layered 2D materials family. Materials highlighted in blue, green and orange are stable in ambient, potentially stable in ambient condition and stable only in inert condition, respectively. Materials highlighted in grey are materials in which the 3D compounds have been exfoliated into monolayers but not widely studied yet [53].	43
Figure 9 (a) Crystal structure of (a) MoS ₂ and (b) Bi ₂ O ₂ Se [58].	44
Figure 10 Synthesis methods of graphene. Reproduced with permission [59].	45

Figure 11 Two directional routes of mechanical exfoliation. Reproduced with permission [61].	46
Figure 12 (a) Graphene synthesized from an arc discharge system. (b) shutter used to control exposure time of substrate to carbon flux from arc medium. Reproduced with permission [65].	47
Figure 13 Synthesis of GO-based on improved Hummers method. Reproduced with permission [66].	49
Figure 14 Graphene epitaxial growth on SiC. Yellow and grey dots represent Si and C atoms, respectively. Sublimating of Si at high temperature (arrow) leaving a carbon-rich surface that forms graphene sheet. Reproduced with permission [70].	50
Figure 15 (a) Graphene synthesis through the SFGP method. (b) Dispersed graphene sheet in methanol. (c) Typical TEM of freely suspended graphene on a lacey carbon TEM grid. Arrows indicate region of monolayer graphene. Scale bar: 100nm. Reproduced with permission [71].	51
Figure 16 (a) experimental setup of remote radio frequency PECVD system for CVD graphene synthesis. (b) Schematic illustration of c-PECVD growth. (c) AFM images of a peel-off graphene film (right) before and (left) after c-PECVD. (d) Experimental plots of temperature vs H ₂ content at 48, 90 and 300mTorr. (e) AFM images of peel-off graphene flakes after activation of the edges with H ₂ plasma (250 mTorr, 500 °C) for 20 min (left), followed by CH ₄ + H ₂ plasma CVD (30% H ₂ , 300 mTorr, 550 °C) for 80 min (right). (f) AFM images of CH ₄ + H ₂ plasma CVD (20% H ₂ , 300 mTorr, 600 °C) for 40 min (right). The height profile is shown below the AFM image. Scale bar (c, e, f): 500nm. Reproduced with permission [75].	52
Figure 17 Monolayer CVD growth of graphene.	54

Figure 18 Raman Spectroscopy of as-grown CVD graphene.....	57
Figure 19 XPS wide scan spectra of CVD growth monolayer graphene.	58
Figure 20 XPS C 1s spectra of as-grown CVD monolayer graphene.....	59
Figure 21 Planar test structure design for relative temperature measurement and thermoelectric voltage measurement.	61
Figure 22 Simulated temperature profile on Si/SiO ₂ substrate.	62
Figure 23 Fabrication process flow chart.	63
Figure 24 (a) Patterned graphene (b) 1 st EBL exposure of alignment mark, shown in purple color (c) Fabricated test structure with heater and thermometer lines, additional test pads at the center of the structure are for four-point probe measurement.	64
Figure 25 Experimental setup for TE properties measurement.	65
Figure 26 Temperature gradient generated by the heater line at three different locations.	66
Figure 27 Measured temperature difference at three different locations from the heater.	67
Figure 28 Seebeck voltage versus temperature difference across the three graphene samples at zero gate voltage.	68
Figure 29 Deconvoluted XPS spectra of C1s for (A) PG, (B) 99-5G and (C) 99- 0G.	75
Figure 30 Deconvoluted XPS spectra of O1s for (A) PG, (B) 99-5G and (C) 99- 0G.	76
Figure 31 XPS spectra of C1s for PMMA.....	76
Figure 32 AFM performed in tapping mode for measurement area of 50 um x 50 um at 1 Hz for A) PG, B) 99-5G and C) 99-0G.....	78

Figure 33 Acquired Raman spectra for PG, 99-5G and 99-0G. G peak is observed to red-shift from 1953cm ⁻¹ (PG) to 1585cm ⁻¹ (99-5G) to 1583cm ⁻¹ (99-0G).....	79
Figure 34 Measured voltage difference as a function of temperature difference between hot and cold junctions. Inset shows the illustration of the fabricated graphene TE device.....	82
Figure 35 Cycling stability test for ON/OFF the PG sample.....	84
Figure 36 Experimentally extracted sheet resistance using van der Pauw's structure.....	85
Figure 37 Comparison of PG operation in vacuum versus in air.....	86
Figure 38 The nature of transient rise time as simulated by Lumerical DEVICE.	87
Figure 39 Surface of CVD graphene.....	95
Figure 40 Size distribution of Au NPs when reduced by various reduction methods on CVD graphene. A) Spontaneous reduction via charge transfer, B) Photoreduction using UV, C) in NaBH ₄ and D) Spin dropped Au solution prior to UV reduction. The red arrows indicate the presence of 10 nm size Au NPs.	96
Figure 41 XPS spectra of Au 4f from the Au NPs fabricated using various reduction methods.....	98
Figure 42 C1s XPS spectra of UV reduced Au-decorated graphene compare to Pristine graphene.	99
Figure 43 O1s XPS spectra of UV reduced Au-decorated graphene compare to Pristine graphene.	99
Figure 44 TEM images of graphene-metal NPs (A,B: Au; C,D: Ag; E,F: Pt)....	102
Figure 45 XPS spectra of functionalized graphene with A) Au, B) Ag and C) Pt.	103

Figure 46 Raman spectra for Graphene-Au (A-C), Graphene-Ag (D-F) and Graphene-Pt (G-I). (A,D,G), (B, E, H) and (C, F, I) are the corresponding sequential D, G and 2D peaks for Graphene-Au, Graphene-Ag, and Graphene-Pt, respectively. Guidelines and arrows have been inserted into selected figures to indicate red shifting of G and 2D peaks.	106
Figure 47 Customized cold wall CVD system.....	114
Figure 48 Schematic plot of cold wall CVD for large scale MoS ₂ growth.....	115
Figure 49 Visual inspection of large scale, uniform MoS ₂ growth on 6-inch sapphire substrate.....	116
Figure 50 (A) Raman and (B) PL spectrum of as-grown MoS ₂ taken at different positions. Position 1 denotes the center of the 6-inch substrate and position 5 denotes the edge of the substrate.....	117
Figure 51 (A) AFM image of as-grown MoS ₂ film and (B) measured height profile using a customized cold wall CVD system.	118
Figure 52 (A) Schematic of simulating temperature gradient using COMSOL Multiphysics, (B) Time to reach steady-state, (C) Temperature distribution graph.	120
Figure 53 (A) Schematic diagram of Bi ₂ O ₂ Se using the CVD method. (B) As a grown optical image of Bi ₂ O ₂ Se, crystal size ~ 50 μ m. (C) Raman spectrum of Bi ₂ O ₂ Se showing the characteristic A _{1g} peak at 159.1cm ⁻¹ . (D) AFM measurement of the thickness of the as-grown Bi ₂ O ₂ Se crystal, measured thickness around 12nm.	123
Figure 54 Temperature- and laser power-dependent Raman spectra of 12nm thick suspended Bi ₂ O ₂ Se. (A) Temperature-dependent (C) Laser power-dependent. Linear fitting of the A _{1g} peak frequency as a function on (B) laser power and (D) temperature, respectively.	125

Figure 55 (A)Seebeck coefficient of n-type $\text{Bi}_2\text{O}_2\text{Se}$ measured at 300K. (B)	
Seebeck coefficient of $\text{Bi}_2\text{O}_2\text{Se}$ at 275K and 300K.....	128
Figure 56 Results of fluorination process using XPS.	135
Figure 57 Raman spectroscopy of FG.....	136
Figure 58 FTIR spectrum of fabrication TiN absorber.....	138
Figure 59 Process flow of integrating TiN absorber onto graphene TE device.	
.....	139
Figure 60 Simulation results of the proposed meta-absorber.....	141

List of Tables

Table 1 Principles, formulae, applications of Seebeck, Peltier and Thomson effects.....	21
Table 2 High performance TE materials developed over the last few years.	30
Table 3 Comparison of different types of IR detectors.....	35
Table 4 Density of states for semiconductor with 3, 2, 1, 0 degrees of freedom for propagation of electrons. The dispersion relations are assumed to be parabolic.	37
Table 5 Summary of recently reported Seebeck coefficient of various 2D materials at room temperature.	68
Table 6 Precursors gas major and minor constituents and their amount present	72
Table 7 Comparison of different reduction methods.....	97
<i>Table 8 Compiled Seebeck coefficient, resistance and PF ratio. SD = standard deviation.....</i>	<i>107</i>
Table 9 Compiled sheet resistance and the SD of pristine, Au-decorated Graphene, Ag-decorated Graphene, and Pt-decorated Graphene, respectively.	109
Table 10 Materials' properties used in simulation.....	120

Abstract

Graphene, one of the most well-studied two-dimensional (2D) materials, has been identified as a prospective thermoelectric (TE) material. Computational studies have shown that graphene can possibly achieve extraordinary TE effect even though it has yet to be showcased experimentally. Lower than expected TE effect is caused by the presence of random defects and grain boundaries introduced during growth. These defects can influence the electrical properties of the monolayer carbon network negatively. As such, there are limited development in the area of graphene TE device research.

To overcome the ill effects of poor control exercised during graphene growth, a methodology concerning defect density manipulation is discussed. The presence of oxygen molecules in the methane precursor has been identified as the main source of contaminant. Oxygen could oxidize methane to become methanol and formaldehyde. During graphene growth, these molecules are incorporated into the graphene superlattice. The amount of defects commensurate with the amount of oxygen present.

While low defect graphene is generally favoured for most applications, highly defective graphene can realize structures with different properties. Examples are when defective graphene is functionalized with ultraviolet photoreduced metal nanoparticles to form p-type graphene-Au, graphene-Ag and graphene-Pt, the associated sheet resistances improved by a factor of 5.26, 1.43 and 1.33, respectively. In particular, an 80% decrease in sheet resistance was reported in

Au-graphene system. It translates to a more than three times increase in thermoelectric power factor.

Besides graphene, n-type materials, MoS₂ and Bi₂O₂Se devices are fabricated. In this case, they are grown via cold wall and hot wall CVD methods, respectively. The materials demonstrated a large Seebeck coefficient of 300 $\mu\text{V/K}$ and 555 $\mu\text{V/K}$ at room temperature, respectively. Finally, both n- and p- type will be paired up to form a working thermocouple. With a suitable absorber, the formation of a thermopile could be used for thermal detection purpose.

This thesis paves ways for the development of 2D material based thermal detection system with performance far exceeding that of current systems. The final setup will showcase a nano-sized detector system. The system can be incorporated at relatively low cost, onto platforms that enable remote sensing with minimal human intervention.

1 Introduction

1.1 Motivation

Semiconductors based thermoelectric materials was first studied by Professor Abram Loffe and his co-workers [1] in the early 1960s. This work has led to active thermoelectric research, with the discovering and investigating of many new thermoelectric materials, such as Bi_2Te_2 , Bi_2Se_3 , Sb_2Te_3 as well as their alloys [2]. Since their discovery, bismuth and telluride based semiconducting materials are considered the gold standard as thermoelectric materials. This has been the case for the past thirty years. Despite the introduction of many advanced fabrication techniques, only incremental improvement in performance has been observed over the years. The breakthrough came in the early 90's, Hicks and Dresselhaus demonstrated an enhancement in the thermoelectric figure of merit conferred by two-dimensional (2D) PbTe quantum well over that of its three-dimensional (3D) counterpart [3]. That pioneering work rekindled much interest in thermoelectric research ever since.

Seebeck effect, Peltier effect and Thomson effect are closely related to their principles shown in Table 1. Seebeck and Peltier effects are the same physical process but with different manifestations of outputs. On the contrary, the Thomson effect is an extension of the Seebeck-Peltier effect. In all, these effects are demonstrated by the use of thermoelectric active materials. As such, these materials have found wide uses in a multitude of industries and applications.

Table 1 Principles, formulae, applications of Seebeck, Peltier and Thomson effects.

	Seebeck effect	Peltier effect	Thomson effect
Principles	The emf produced in a circuit when the two junctions of two different materials are maintained at different temperatures	When the current passes through the circuit of two dissimilar materials, heat is either absorbed or released at the junction of the materials depending on the current direction	Heat is absorbed or released when the current flow in the material with a certain temperature gradient. The heat is proportional to both the electric current and the temperature gradient
Equation	$\Delta V = S \cdot \Delta T$	$Q = (\Pi_A - \Pi_B) \cdot I$	$q = -KJ \cdot \nabla T$
Applications	Thermopile, thermoelectric generators	Peltier heat pumps, refrigerators	Thermoelectric generators/thermoelectric heat pump combined devices

This thesis emphasizes the study of thermoelectric properties of 2D materials for the generation of the Seebeck effect. Their potentials to be used as thermal infrared (IR) detectors will be investigated. IR detectors are typically constructed

by an array of thermopiles. Thermopile is a popular choice for IR detectors due to its “always on” characteristics, broad absorption range as well as the associated manufacturing costs. It is formed by connecting a series of p- and n-type thermocouples. While in the early days, it has been explored as a possible detector for use in low-cost spectrometers and gas sensors.

Theoretical calculation has shown strong evidence of improvement in the thermoelectric performance of bulk materials when organized into a 2D multi-quantum-well superlattice [4-7]. In principle, the enhancement of thermoelectric properties in a 2D quantum well structure lies in the increase in the number of density of states (DOS) at each electronic sub-band. The increase in the vibrational scattering at the boundary between the quantum well and the adjacent barrier of superlattice further enhance the thermoelectric effect. A common expression of the performance of a thermoelectric material is the dimensionless figure of merit, ZT as shown in equation (1) [8]:

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (1)$$

where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. These three terms describe the thermoelectric properties of a given material. T is the working temperature expressed in Kelvin (K).

An enhancement in ZT can be achieved by reducing the material dimension. The improvement in performance is due to (1) enhancement of DOS near Fermi level that leads to an improvement in Seebeck coefficient, (2) increment of carrier mobility at a given carrier concentration when the quantum confinement

conditions are met and (3) increment of boundary scattering of phonons at the barrier-well interfaces that lower the thermal conductivity. Here, 2D materials which are confined by their ultrathin physical dimensions leads to improvement in thermoelectric properties. Typical examples of 2D materials with potentially good thermoelectric properties are graphene [9, 10], MoS₂ [11, 12] and black phosphorus (BP) [13, 14].

Ultimately, this thesis aims to construct and investigate 2D materials thermoelectric thermal detector. The fundamental unit of a thermal detector is a thermocouple. A thermopile consists of numerous pairs of thermocouple. A thermocouple comprises p- and n-type materials. Suitable novel p- and n-type materials will be investigated. The Seebeck coefficient and electrical conductivity studies are carried out systematically.

Specifically, the realization of a graphene-based detector could address the limitations experienced by current thermoelectric (TE) thermal detector systems. Presently, those detectors suffer from poor resolution and detectivity due to the low Seebeck coefficient as well as a poor figure of merit (ZT). On the contrary, 2D materials, due to quantum confinement effect, have showcased giant thermoelectric ZT phenomenon. With proper characterization and selection of different 2D materials, excellent next-generation TE detectors can be realized.

Graphene is considered to be one of the most well-studied 2D materials. Due to the influence of oxygen atoms present in the sp³ network, it is a predominantly p-type material. Thus far, it has been identified as a prospective TE material. While computational studies have shown that graphene can achieve $ZT > 1$, it has yet

to be demonstrated experimentally. This is largely fuelled by the presence of random defects and grain boundaries. These defects negatively influence the electrical properties of the monolayer carbon network. Because of the underlying issues associated with graphene growth control, there is limited development in the area of graphene TE device research.

To overcome the ill effects of poor control exercised during graphene growth, a methodology concerning defect growth manipulation will be discussed. By controlling the amount of oxygen present in the CVD tube furnace, defects density can be controlled. Thus, graphene of varying quality can be obtained at will, depending on needs.

Defect sites and grain boundaries are deemed undesirable in many cases. If their presence can be controlled, these high energy sites can enable the graphene superlattice to be modified for different end applications. The trade-off would bring about an increase in sheet resistance which decreases electrical performance. To address that, metal nanoparticles functionalized graphene are reported for the possible decrease in sheet resistance which could improve the overall thermoelectric power.

Unlike conventional silicon-based thermopile, suspension of monolayer 2D materials requires delicate process handling and extended labour hours with low throughput [15, 16]. Furthermore, modulation of charge carrier density is difficult to achieve due to very weak capacitive coupling between 2D materials and gate through the air or vacuum gap. Thus, an exploration to seek a suitable physical support with low in-plane and cross-plane thermal conductivity is warranted.

Amongst those low dimension 2D insulator materials, fluorinated graphene is deemed to be highly suited due to its lattice constant matching that of graphene. Therefore, its thermal and electrical insulating properties will be characterized and the preliminary results reported. Finally, the integration of graphene and beyond graphene materials on fluorinated graphene as thermocouple pair will be discussed. The process flow to realize a thermopile with a suitable meta-surface absorber will be described.

1.2 Objectives

The main objectives of this PhD study are to explore and enhance the thermoelectric properties of 2D materials and to characterize their feasibility to be used as thermal IR detectors.

The goals are listed as follow:

- Manipulation of CVD growth graphene by controlling the amount of oxygen present.
- Functionalizing graphene with different metal nanoparticles to improve overall thermoelectric power factor.
- Development of 2D n-type thermoelectric materials beyond graphene.

1.3 Major contribution of the Thesis

The main contributions of this thesis are summarized as follow:

- 1) It was found out that the defects density in graphene could be altered by the presence of a minute amount of oxygen in the precursors. It provides a glimpse into the urgent need to standardize carbon precursors for

graphene growth. It explains the reasoning behind varying quality of graphene is obtained from different CVD growth system. This work has been demonstrated and explained in chapter 4.

- 2) For the first time, the application of UV-assisted reduction of metal nanoparticles decorated graphene for thermoelectric demonstration has been highlighted. Physiosorbed metal nanoparticles introduced strain onto the graphene lattice. However, it does not change the Seebeck coefficient of graphene.
- 3) New n-type materials such as MoS_2 and $\text{Bi}_2\text{O}_2\text{Se}$ are investigated as the potential thermoelectric materials. This work involves materials growth and the thermoelectric parameters characterization. Simulation and experimental results are portrayed in chapter 6.

1.4 Organization of the thesis

This thesis is organized in the following chapters:

Chapter 1 introduces the motivations, objectives, major contributions and organization of this thesis.

Chapter 2 provides a review of the background of 2D TE materials and understanding the physics on graphene in particular with an emphasis on graphene and its associated physical and chemical properties. In addition, graphene synthesis and characterization are reported as well.

In chapter 3, general graphene growth parameters are described and discussed. Graphene device fabrication process flow is described as well. Characterization tools, specifically Raman spectroscopy, will be mentioned in greater detail.

In chapter 4, graphene synthesized using precursors with different amounts of O₂ residual gas is evaluated. The fabricated graphene devices are characterized. A mechanistic insight into the formation of defects is described in the final segment.

In chapter 5, graphene decorated with metal nanoparticles is showcased. Later, different characterization tools are used to study the properties of the hybridized graphene. The significance of the results will be explained.

In chapter 6, the synthesis of n-type non-graphene 2D materials is evaluated, electrically and thermally. Their properties are then discussed for possible incorporation to form graphene-based TE devices

In chapter 7, fluorinated graphene are proposed as possible thermal insulating layer for graphene and non-graphene TE materials. Proposals on the construction of a possible graphene TE thermal detector is explained

2 Literature reviews

2.1 Thermoelectric Overview

Thermoelectricity is a phenomenon where heat energy is converted into electrical energy and vice versa. The phenomenon of thermoelectric effect was discovered by Thomas Seebeck in 1821. He found out that the generation of a potential gradient when a conductor was subjected to a temperature gradient. In this case, thermal energy is converted to electrical energy.

Many electrical devices in our everyday lives are powered by TE effect. Such devices have been used in the fields of solid-state power generation and refrigeration, thermal management and energy harvesting [17-19]. The reasons why TE devices are popular are as follows: simple to operate, do not produce undesirable noise and vibration and long operating life. Given the advantages of TE devices, thermoelectric based detectors are worthy to be explored further. As such, developed TE devices can possibly be used for the perpetual harvesting of heat energy. This topic has generated much attention lately. However, many proposed TE devices suffer from poor responses. This is due to the poor energy conversion [20, 21]. To overcome the current situation, many efforts have been focused on exploring and developing high efficiency TE materials.

TE effect is dependent on the intrinsic properties of a material. An important consideration is a material specific Figure-of-merit (ZT) as mentioned in equation (1). ZT is a dimensionless property that evaluates the energy conversion efficiency of a thermoelectric material based on the TE properties. The heat-to-electrical energy conversion efficiency of a power generation device is given by equation (2) [22]:

$$\eta = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + T_c/T_h} \quad (2)$$

where $ZT = S^2\sigma T/\kappa$, $\bar{T}$ is the average temperature between the hot and cold junctions of a TE materials. The ZT value of a material is proportional to its TE efficiency. Figure 1 shows the different types of TE materials with ZT values higher than 1. Moreover, ZT is temperature dependent. The inset further shows that when $ZT = 1$, the conversion efficiency is approximately 5% as compared to a theoretical maximum of 25 % at 400K. Measured efficiencies of selected state-of-the-art materials, shown in Table 2 are as such, $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice [23], [24], SnSe [25], Cu_2Se [26], $\text{Cu}_2\text{CdSnSe}_4$ [27], BiCuSeO [28] and lead-free SnTe [29].

Figure 1 Typically high efficiency TE materials with ZT as a function of temperature. Inset: relation between η , T and ΔT of materials with different ZT . Reproduced with permission [30].

As a comparison, ZT of the commercially available TE materials is around 1..

Table 2 High performance TE materials developed over the last few years.

Materials	Carrier type	ZT	T (K)
SnSe single crystal [31]	P	2.6	923
PbTe-SrTe [32]	P	2.2	915
Bi _{0.5} Sb _{1.5} Te ₃ [33]	P	1.86	320
Cu ₂ Se [34]	P	1.8	1000
PbTe/PbS nanoparticles [35]	n	1.85	623
Mg _{3.2} Sb _{1.5} Bi _{0.49} Te _{0.01} [36]	n	1.51	716

Figure 2 shows the generation of electromotive force from the diffusion of charge carriers and the phonon drag between the hot and cold junction. The system is in semi-equilibrium where the chemical potential (μ) of the carrier concentration is balanced by the intrinsic electrostatic potential, known as Seebeck voltage [37]. Here, the Seebeck coefficient is defined in equation (3),

$$S = \frac{1}{e} \frac{\partial_x \mu}{\partial T} \quad (3)$$

Figure 2 Carrier charge flows from hot to cold junction for a TE material for depiction of Seebeck coefficient.

In a TE material, the major carriers such as electrons and holes contribute to electrical conductivity (σ) and electronic thermal conductivity (κ_e) while the

phonons contribute to the lattice thermal conductivity (κ_l). It can be written in equation (4) [8]:

$$ZT = \frac{S^2 \sigma}{\kappa} T = \frac{S^2 \sigma}{\kappa_e + \kappa_l} T \quad (4)$$

2.2 Challenges in enhancing thermoelectric (TE) properties

The interdependency of the TE properties is summarized as the function of scattering factor (r), carrier effective mass (m^*) and carrier mobility (μ). From the kinetic definition of the Seebeck coefficient (S), it is the energy difference between the average energy of charge carrier and Fermi energy [38]. In metal and degenerate semiconductors, the Seebeck coefficient can be expressed as equation (8) [39],

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (8)$$

From the electrical transport coefficient theory [38], an increase in carrier concentration (n) will increase the Fermi energy as well as the average energy. On the other hand, when the increase in Fermi energy exceeds the average energy, it decreases S . It is common for most homogeneous TE materials, to possess high n , which positively influence its electrical conductivity (σ) but at the expense of a lowers S . m^* is the effective mass in which large effective mass will lead to high S but suffers in term of σ , as lower μ is related to heavier carriers. Moreover, the relationship between effective mass and the material carrier mobility highly depends on the electronic structure, scattering mechanism and anisotropy of the materials. In general, high effective mass and low mobility

materials are called polaron conductors. These materials include, ionic compounds, oxides and chalcogenides [40]. On the contrary, low effective mass and high mobility materials which comprise a mixtures of elements with small electronegativity differences (SiGe, GaAs) [41].

On the other hand, low carrier concentration (n) will lead to low electrical conductivity as shown in equation (9) where n is related to σ through carrier mobility (μ).

$$\sigma = ne\mu \quad (9)$$

Thermal conductivity of a thermoelectric material is a function of κ_e and κ_l as shown in equation (4) and (10). Wiedemann-Franz law states that electronic thermal conductivity is related to the electrical conductivity by

$$\frac{\kappa_e}{\sigma} = LT \quad (10)$$

where L is the Lorenz factor which is $2.4 \times 10^{-8} J^2 K^{-2} C^{-2}$ for free electrons and it varies with carrier concentration. From equation (9) & (10), the electronic thermal conductivity can be rewritten to

$$\kappa_e = \sigma LT = \mu neLT \quad (11)$$

Therefore, equation 11 expresses that any attempt to increase electrical conductivity (σ) will in turn, increase the electronic thermal conductivity (κ_e). This case, thermal conductivity (κ) increases as a whole. To overcome the increase

in κ_e , various methods have been developed to decrease κ_l . One of the ways is to increase phonon scattering by introducing defects. However, this will lead to a decrease in carrier mobility as well as electrical conductivity which continues to pose a challenge to the improvement of ZT in bulk TE materials.

2.3 Seebeck's effect in thermoelectric (TE) infrared (IR) sensors

All materials above absolute zero (0 K) will emit infrared (IR) radiation. The emitted frequency ranges from $3 \times 10^{11} - 4 \times 10^{14}$ Hz which corresponds to $0.75 - 1000 \mu\text{m}$ in wavelength. A blackbody is an ideal object that absorbs and emits all radiation. At thermal equilibrium, the relationship between IR radiation and temperature is often expressed using Planck's law (Figure 3). Depending on the temperature of the object, Planck radiation has a maximum intensity at a particular wavelength which can be approximated by the Wien's displacement law in equation (5) [42].

$$\lambda_{max} = \frac{b}{T} \quad (5)$$

Figure 3 The blackbody radiation curves according to Planck's law as a function of wavelength. $T=6000\text{K}$ is the temperature of sun with a peak in the visible range. Blue line represents Wien's displacement law. Maximum wavelength of an object shifts as the temperature decreases [43].

An IR detector is a device that is capable of detecting an external IR radiation. A thermocouple pair consists of a n-type and p-type materials. It utilizes the working principle of thermoelectric (TE) effect, is one type of thermal IR detectors. Seebeck effect of a TE IR sensor allows the sensing of a temperature change with readout in terms of voltage output. Figure 4a shows the generation of a potential difference via a change in temperature between the hot and cold junctions in a TE material [44] as shown in equation 6. The Seebeck coefficient is then determined by the slope of the $\Delta V / \Delta T$. Thermopiles (Figure 4b) can be fabricated by connecting a number of thermocouples serially.

$$\text{Thermocouple} \quad V_{AB} = S_{AB} \cdot \Delta T \quad (6)$$

$$\text{Thermopile} \quad V_{out} = N \cdot V_{AB} \quad (7)$$

where V_{AB} is the voltage difference between the two dissimilar materials induced by temperature difference at the hot and cold junctions of the thermocouple. S_{AB} is the Seebeck coefficient which describes the output voltage per degree of temperature difference. The sensitivity of the thermopile increases as the number of thermocouples increases. Therefore, V_{out} is proportional to the number of thermocouple pairs used as shown in equation (7).

Figure 4 Seebeck effect generates in (a) thermocouple (b) thermopile [45].

Thermopile based thermal detectors have merits over that of photodetectors. Most photodetectors require active cooling to reduce signal to noise ratio. With proper isolation of temperatures at the junctions, TE IR detectors do not require active cooling for a reasonable readout signal. That explains why TE IR detectors are widely used in the industry for IR detection. Furthermore, these detectors provide large working (sensing) temperature range, spectral response characteristics that are not wavelength dependent. Lastly, TE detectors work in an “always on” mode, reducing the need for optical chopping.

Table 3 Comparison of different types of IR detectors

Detector Type		Advantages	Disadvantages
Thermal	Thermopile	DC & AC response No biasing Low cost Active device	Low responsivity Medium response time
	Bolometers	Passive device High electrical sensitivity Fast response time	Vacuum operation Constant need for heat regulation

	Pyroelectric	High responsivity High SNR	Vibration responsive
Photon	Intrinsic (HgCdTe)	Easy bandgap tailoring Well-developed theory and experiments Multicolour detectors	Non-uniformity over large area High cost in growth and processing Surface instability
	Extrinsic (Si:Ga, Si:As)	Very long wavelength operation Relatively simple technology	High thermal generation Extremely low temperature operation
	Free Carriers (PtSi, IrSi)	Low-cost, high yields Large and close packed 2D arrays	Low quantum efficiency Low temperature operation
	Quantum wells (GaAs/AlGaAs)	Matured material growth Good uniformity over large area Multicolor detectors	High thermal generation Complicated design and growth

2.4 Low dimensional thermoelectric (TE) materials

It has been proposed that an alternate way to improve one's TE performance is to reduce the material dimensionality. The theoretical justification will be shown below. Thus far, ZT greater than 1 has been reported in low dimensional materials [23, 46]. A decrease in the dimensionality of a material allows a new variable of length scale for the control of material's intrinsic properties. As the size of the material approaches the nanometer scale, a drastic change in the electronic density of states occurs (Figure 5). Such discovery opens up many opportunities. These measures include the variation S , σ and κ quasi-independently. As the DOS discretizes, This gives rise to quantum confinement effects as the number of atoms in any direction becomes small ($< 10^2$).

In this thesis, the discussion on low dimensional TE materials are centred on two-dimensional materials. As such, all calculations, experiments, and discussions in subsequent chapters are focused on two-dimensional materials.

Figure 5 Electronic DOS for (a) bulk 3D crystalline semiconductor, (b) 2D quantum well, (c) 1D nanowire/nanotube, and (d) 0D quantum dot. Reproduced with permission [47].

Table 4 Density of states for semiconductor with 3, 2, 1, 0 degrees of freedom for propagation of electrons. The dispersion relations are assumed to be parabolic.

Degrees of freedom	Dispersion (Kinetic energy)	Density of states	Effective density of states
3 (bulk)	$E = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2 + k_z^2)$	$\rho_{DOS}^{3D} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E - E_C}$	$N_C^{3D} = \frac{1}{\sqrt{2}} \left(\frac{m^* kT}{\pi \hbar^2} \right)^{\frac{3}{2}}$
2 (quantum well)	$E = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2)$	$\rho_{DOS}^{2D} = \frac{m^*}{\pi \hbar^2} \sigma(E - E_C)$	$N_C^{2D} = \frac{m^*}{\pi \hbar^2} kT$
1 (quantum wire)	$E = \frac{\hbar^2}{2m^*} (k_x^2)$	$\rho_{DOS}^{1D} = \frac{m^*}{\pi \hbar} \sqrt{\frac{m^*}{2(E - E_C)}}$	$N_C^{1D} = \sqrt{\frac{m^* kT}{2\pi \hbar^2}}$

0 (quantum dot)	-	$\rho_{DOS}^{0D} = 2\delta(E - E_C)$	$N_C^{0D} = 2$
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Theoretical calculations have justified the positive effect of quantum-well structures (2D) on the thermoelectric ZT . The expressions are as shown [48].

ZT for 3D material

$$\text{Electronic dispersion relation} \quad \varepsilon(k_x, k_y, k_z) = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 k_z^2}{2m_z} \quad (12)$$

To consider conduction along the x-direction only,

$$\sigma = \frac{1}{2\pi^2} \left(\frac{2k_B T}{\hbar^2} \right)^{3/2} (m_x m_y m_z)^{1/2} F_{1/2} e \mu_x \quad (13)$$

$$S = -\frac{k_B}{e} \left(\frac{5F_{3/2}}{3F_{1/2}} - \zeta^* \right) \quad (14)$$

$$\kappa_e = \frac{\tau \hbar^2}{6\pi^2} \left(\frac{2k_B T}{\hbar^2} \right)^{5/2} \left(\frac{m_y m_z}{m_x} \right)^{1/2} \times k_B \left(\frac{7}{2} F_{5/2} - \frac{25}{6} F_{3/2} \right) \quad (15)$$

where F_i is the Fermi-Dirac function given by

$$F_i = F_i(\zeta^*) = \int_0^\infty \frac{x^i dx}{e^{(x-\zeta^*)} + 1} \quad (16)$$

ζ^* is the reduced chemical function (relative to the edge of the conduction band) and it can be varied through doping. τ is the relaxation time; m_x , m_y , m_z are the effective mass components, μ_x is the mobility in x-direction and κ_e is the electronic thermal conductivity. By substituting the above parameters into equation 4, the following expression can be obtained

$$Z_{3D}T = \frac{\frac{3}{2} \left(\frac{5F_{3/2}}{3F_{1/2}} - \zeta^* \right)^2 F_{1/2}}{\frac{1}{B} + \frac{7}{2} F_{5/2} - \frac{25F_{3/2}^2}{6F_{1/2}}} \quad (17)$$

where

$$B = \frac{1}{3\pi^2} \left(\frac{2k_B T}{\hbar^2} \right)^{3/2} (m_x m_y m_z)^{1/2} \frac{k_B^2 T \mu_x}{e \kappa_l} \quad (18)$$

Here, B is determined by the intrinsic properties of the given material. Both B and ζ^* are crucial in maximizing $Z_{3D}T$ of a material. One can obtain the optimal value of ζ^* from figure 6a by calculating B and by adjusting the value of ζ^* to match that of an optimal ζ^* modulated by doping with suitable impurities. It is shown in figure 6b that $Z_{3D}T$ increases as B increases. Thus it is possible to maximize $Z_{3D}T$ by choosing the current to flow in the direction with the highest mobility μ_x .

Figure 6 (a) ζ_{opt}^* vs B (inset shows variations of $Z_{3D}T$ with ζ^* at fixed B). (b) $Z_{3D}T$ vs B with optimal ζ^* . Reproduced with permission [48].

ZT for 2D material

In addition, the expressions for S , σ , κ and ZT are also derived for quantum-well structure. The expressions demonstrate the superiority of TE properties exhibited in low dimensional materials. It is assumed that electrons only occupy the lowest

sub-band (n=1) of the quantum well. It is further assumed that the tunneling effect through a wide-gap semiconductor is negligible.

$$\text{Electronic dispersion relation} \quad \varepsilon(k_x, k_y) = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 \pi^2}{2m_z a^2} \quad (19)$$

The equation above indicates the free-electron like motion in the x-y plane and a bound state in the z-direction (for an infinite potential barrier). The results are:

$$\sigma = \frac{1}{2\pi a} \left(\frac{2k_B T}{\hbar^2} \right) (m_x m_y)^{1/2} F_0 e \mu_x \quad (20)$$

$$S = -\frac{k_B}{e} \left(\frac{2F_1}{F_0} - \zeta^* \right) \quad (21)$$

$$\kappa_e = \frac{\tau \hbar^2}{4\pi a} \left(\frac{2k_B T}{\hbar^2} \right)^2 \left(\frac{m_y}{m_x} \right)^{1/2} k_B \left(3F_2 - \frac{4F_1^2}{F_0} \right) \quad (22)$$

F_i is defined in equation 16 and a is the width of the quantum well,

$$\zeta^* = \left(\zeta - \frac{\hbar^2 \pi^2}{2m_z a^2} \right) / k_B T \quad (23)$$

Thus, ZT for a 2D material is:

$$Z_{2D} T = \frac{\left(\frac{2F_1}{F_0} - \zeta^* \right)^2 F_0}{\frac{1}{B'} + 3F_2 - \frac{4F_1^2}{F_0}} \quad (24)$$

$$\text{where} \quad B' = \frac{1}{2\pi a} \left(\frac{2k_B T}{\hbar^2} \right) (m_x m_y)^{1/2} \frac{k_B^2 T \mu_x}{e \kappa_l} \quad (25)$$

The maximum of $Z_{2D} T$ occurs when $\zeta^* = \zeta_{\text{opt}}^*$ which is similar to the case for 3D material. Figure 7 shows the plot of ζ_{opt}^* and $Z_{2D} T$ vs B' . However for the case

of 2D quantum well, the expression of ζ^* is different from that of 3D. Thus, ζ^* can be varied by either doping or by changing the layer thickness a . This additional degree of freedom allows the improvement of $Z_{2D}T$ above that of the 3D bulk materials. In this case, 2D materials are demonstrated to be suitable candidates for use as TE materials.

Figure 7 (a) ζ_{opt}^* vs B plot. (b) $Z_{2D}T$ vs B with optimal ζ^* . Reproduced with permission [48].

In most cases, 2D, 1D, and 0D nanomaterials are capable of reducing their thermal conductivity. Examples include Si nanowires ($ZT_{200K}=1$) [49], quantum nanodot alloys ($ZT_{800K}=2.2$) [46], $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice ($ZT_{300K}=2.4$) [23] and layered structure of 2D crystalline sheets ($ZT_{900K}=3$) [50]. These class of materials has been shown to suppress the reduction in electrical conductivity. Reduced dimensional materials' electrical conductivity was proven to be larger than their bulk counterparts [51]. Furthermore, 2D TE materials have shown great potential in thermal management and TE energy generation. However, in this work, 1D and 0D nanomaterials are not discussed. This is because these materials are difficult to scale up in a standard CMOS foundry.

2.5 Physical and chemical properties of graphene and beyond graphene materials

Carbon, the building block of graphene, is the fourth most abundant element in the universe by mass. Arguably, this means that graphene precursors can be harvested at low cost for a multitude of end uses [52].

One of the most widely studied 2D materials is graphene. Graphene is made up of a monolayer network of hexagonal graphitic honeycomb. The interplanar spacing of graphene is 0.335 nm while the sp² C-C interatomic bond length is 0.142 nm. The interlayer of graphene is held by van der Waals forces which can be easily broken using various exfoliation techniques. A number of unique electrical, chemical and mechanical properties of graphene have been investigated since it was first isolated via mechanical exfoliation. Graphene has been exhibited to be 100 times stronger than steel in proportion to the thickness (tensile strength to be 130 GPa). From electrical and thermal measurements, graphene has been shown to possess very high electron mobility (200000 cm²·V⁻¹·s⁻¹) and thermal conductivity (4.84-5.3 x 10³ W·m⁻¹·K⁻¹). Moreover, it has been experimentally concluded that it is optically transparent. As an excellent research material, graphene has demonstrated excellence in the following areas. These include, high frequency electronics, bio/chemical sensors, wide bandwidth photodetectors, energy generation, and storage.

While monolayer graphene has shown to outshine many other materials in different applications, it is still challenging to make graphene IR detector. This is attributed to shortcomings of graphene: high κ which leads to a small S . To

overcome that, it is imperative to lower its dimensions as well as the need for nanostructuring. Various ways have been proposed to tune thermal conduction in graphene, boundary scattering, defect engineering as well as introducing weakly coupled interfaces. These techniques have shown the possibility to decrease κ .

Graphene Family	Graphene		hBN "White graphene"	BCN	Fluorogra- phene	Graphene oxide
2D Transition Metal Dichalcogenides (TMDC)/ Metal Dichalcogenides	MoS ₂ , WS ₂ , MoSe ₂ , WSe ₂		Semiconducting dichalcogenides: MoTe ₂ , WTe ₂ , ZrS ₂ , ZrSe ₂		Metallic dichalcogenides: NbSe ₂ , NbS ₂ , TaS ₂ , TiS ₂ , NiSe ₂	
					Layered semiconductors: GaSe, GaTe, InSe, Bi ₂ Se ₃	
2D Oxides	Micas, BSCCO	MoO ₃ , WO ₃	Perovskite-type: LaNb ₂ O ₇ , (Ca,Sr) ₂ Nb ₃ O ₁₀ , Bi ₄ Ti ₃ O ₁₂ , Ca ₂ Ta ₂ TiO ₁₀		Hydroxides: Ni(OH) ₂ , Eu(OH) ₂	
	Layered Cu oxides, Bi ₂ O ₂ Se	TiO ₂ , MnO ₂ , V ₂ O ₅ , TaO ₃ , RuO ₂			others	

Figure 8 Layered 2D materials family. Materials highlighted in blue, green and orange are stable in ambient, potentially stable in ambient condition and stable only in inert condition, respectively. Materials highlighted in grey are materials in which the 3D compounds have been exfoliated into monolayers but not widely studied yet [53].

Besides graphene, there is an increase in research on 2D transition metal dichalcogenides (TMDCs). Examples of such semiconducting TMDCs are MX₂ (M = Mo, W; X = S, Se, Te) [54, 55] as shown in figure 8. These 2D TMDCs are made up of hexagonal M plane sandwiched between two hexagonal X planes. Each MX₂ plane is held by strong ionic covalent bond. On the other hand, the inter planes are bounded by weak Van der Waal forces. Figure 9a shows the structure of layered MoS₂ stack with interlayer Van der Waals interactions. Amongst these MX₂, MoS₂ and WSe₂ are the most well-known and studied of all. The thermal conductivity (κ) of MoS₂ and that of disordered layered WSe₂ were

experimentally measured to be 34.5 W/mK [56] and 0.05 W/mK [57], respectively. The disordered layered WSe_2 is due to the random stacking of the well-crystallized WSe_2 . The results indicated that these materials exhibit generally low κ . Thus, such property may potentially improve the ZT of the TE materials.

Besides MX_2 , 2D oxides are popular choices for TE. A new material, $\text{Bi}_2\text{O}_2\text{Se}$, as shown in Fig 9B, is a potential candidate for TE material. It will be discussed in chapter 6.

Figure 9 (a) Crystal structure of (a) MoS_2 and (b) $\text{Bi}_2\text{O}_2\text{Se}$ [58].

2.6 Graphene synthesis

Graphene can be synthesized by a number of methods. These methods can be broadly classified into two categories: top-down techniques (destructive) and bottom-up techniques (constructive). Figure 10 shows a non-exhaustive presentation of synthesis techniques. Amongst the techniques, well-known graphene synthesis methods that will be reviewed in the following sections are mechanical exfoliation/ cleavage, arc discharge, oxidative exfoliation and reduction, chemical vapor deposition (CVD), epitaxial growth on SiC and

substrate-free gas-phase synthesis. Special emphasis on the CVD growth method will be presented.

Figure 10 Synthesis methods of graphene. Reproduced with permission [59].

2.6.1 Mechanical exfoliation/ cleavage

The normal force synthesis route is represented by the peeling of graphite using advanced machinery. It is carried out by an ultra-sharp single diamond wedge which eliminates the need for manual operation [60]. The shear force synthesis route involves ball milling and fluid dynamic methods. This method utilizes grinding media in the form of balls to exfoliate graphite into graphene flakes of nanometer thickness [61]. The quality of the milled graphene is controlled by the grinding media, process time, milling speed, matrix and initial size of the precursor [62]. However, this is a time-consuming process and is not suitable for large scale production. Figure 11 shows two directional routes of mechanical exfoliation such as the normal force and the shear force routes.

Figure 11 Two directional routes of mechanical exfoliation. Reproduced with permission [61].

2.6.2 Arc discharge

Arc discharge is commonly used in fullerene and CNT synthesis. The method can be adapted for graphene synthesis. The reaction chamber of the arc discharge process as shown in figure 12. An anode (carbon precursor) and a cathode (graphite rod) are submerged in a gas/ liquid medium to improve the process stability. With the application of an electrical current through the medium, a high temperature plasma (3727 – 5727 °C) is generated from the dissociation of the medium. The plasma is sufficiently hot to sublime the precursor [63]. The medium used in most arc discharge chamber is usually H₂/ He. While it is effective, the uses of vacuum equipment and high precision air pressure render this method expensive and unfavorable for large scale production. To lower the manufacturing cost, air has been used in place of H₂/ He. Moreover, in recent times, graphene has been successfully synthesized from petroleum asphalt in water arc discharge system [64].

Figure 12 (a) Graphene synthesized from an arc discharge system. (b) shutter used to control exposure time of substrate to carbon flux from arc medium. Reproduced with permission [65].

2.6.3 Oxidative exfoliation-reduction

Graphene oxides (GO) are mostly synthesized by the oxidative exfoliation of graphite crystal. It is then followed by a reduction step to form a graphene sheet or reduced graphene oxides (rGO). GO synthesis technique have been refined over time as reported. From Brodie to Staudenmaier, then Hofmann and finally Hummers method, GO synthesis has been gradually optimized (figure 13). As reported in the early methods, reaction temperatures occur below 100 °C. Low production temperature is generally preferred to maintain a low production cost. However, toxic gases such as NO_2 and N_2O_4 are generated during the production process. [66] This then calls for alternative synthesis methods. As such, the Hummers method is widely adopted for GO synthesis due to its fast and safe process. Modified Hummers method introduces an even greener approach by eliminating the use of NaNO_3 . The proposed method further decreases the production cost while keeping environmental protection cost low.

The oxidation process increases the distance between the graphite layers from 0.335 to 0.625 nm. Some processes also introduce graphite intercalation compounds [67]. These molecules or atoms weaken the interlayer Van der Waals force. This leads to carbon sheet displacement. Exfoliation is then carried out by sonication in an appropriate solvent to further weaken the Van der Waals forces holding the carbon sheets to produce highly dispersed single-, bi-, and few-layer GO. The newly formed products are generally highly defective. Therefore, reduction methods through chemical, thermal and electrochemical processes are used to restore the honeycomb structure of the highly disrupted sp^2 bonds in GO. In principle, the reduction method aims to remove the oxygen-containing functional groups such as carbonyl, hydroxyl and carboxylic in GO. Thus, high quality rGO (low defect density) can be obtained via this reduction method.

Figure 13 Synthesis of GO-based on improved Hummers method. Reproduced with permission [66].

2.6.4 Epitaxial growth on silicon carbide (SiC)

SiC epitaxial growth involves sublimating Si at a high temperature which enables excessive C atoms to aggregate and form a sp^2 hybridized network that induces the formation of graphene. Figure 14 shows the thermal evaporation ($1200 - 1600^\circ C$) of graphene on a hexagonal SiC substrate under vacuum/ inert condition [68]. Non-homogeneity in the grown graphene [69] could be caused by the presence of different polar faces such as Si-face or C-face graphene. More studies are required to provide a deeper understanding of the growth mechanisms as well as the interfacial interaction between graphene and the SiC substrate. This energy intensive process is costly to operate. Therefore, it might not be a scalable process for mass production.

Figure 14 Graphene epitaxial growth on SiC. Yellow and grey dots represent Si and C atoms, respectively. Sublimating of Si at high temperature (arrow) leaving a carbon-rich surface that forms graphene sheet. Reproduced with permission [70].

2.6.5 Substrate-free gas phase (SFGP)

Graphene can be synthesized in gas phase reaction in the absence of a substrate [71] (Figure 15). Under atmospheric conditions, an aerosol mixture of liquid ethanol and argon gas is placed in a microwave-generated plasma. Ethanol droplets are vaporized and dissociated in the plasma region over a period of 1 s and thus forming graphene. It had been shown that ethanol with a volumetric flow rate of 164 mg/min is capable of producing approximately 2 mg/min of graphene. So far, the effects of different carbon precursors on graphene production have been investigated. Further studies on morphological characterization and the removal of unwanted amorphous byproducts are required [71]. This method is promising for the future commercial production of graphene. This is due in part to the technical ability in forming clean and high-quality graphene.

Figure 15 (a) Graphene synthesis through the SFGP method. (b) Dispersed graphene sheet in methanol. (c) Typical TEM of freely suspended graphene on a lacey carbon TEM grid. Arrows indicate region of monolayer graphene. Scale bar: 100nm. Reproduced with permission [71].

2.6.6 Chemical vapor deposition (CVD)

CVD method shown in figure 16 has been the most scalable process that is capable to produce high quality and large surface area graphene to date. As such, this method of graphene synthesis is adopted in this thesis. the process will be described in greater detail in the following chapter. Briefly, CVD grown graphene involves the decomposition of hydrocarbon precursors (CH_4 , C_2H_2 , C_2H_4 , and C_6H_{14}) to form graphene on metallic catalysts at high temperature [72, 73]. The process starts with the carbon precursor dissociating into free C and H atoms on the hot metal catalyst surface. Then, C atoms diffuse through the surface of the bulk metal catalyst. When the density of carbon exceeds that of its solubility limits, carbon precipitates to form graphene. Different substrates such as glass, silicon, quartz, sapphire, and boron nitride have been developed to improve the CVD process and was reported by Chen *et al.* previously [74].

While the production of high quality graphene with highly interconnected structure has been reported, contamination issues have been reported as well. Contaminants arising from improper removal of catalyst residues and polymeric residue introduced during the transfer step possibly contributed to the presence of contaminants adsorbed onto the graphene surface. Often they bring about catastrophic consequences to the fabricated graphene devices. Therefore, investigation and mitigation works to overcome the problem have to be promptly carried out.

Figure 16 (a) experimental setup of remote radio frequency PECVD system for CVD graphene synthesis. (b) Schematic illustration of c-PECVD growth. (c) AFM images of a peel-off graphene film (right) before and (left) after c-PECVD. (d) Experimental plots of temperature vs H₂ content at 48, 90 and 300mTorr. (e) AFM images of peel-off graphene flakes after activation of the edges with H₂ plasma (250 mTorr, 500 °C) for 20 min (left), followed by CH₄ + H₂ plasma CVD (30% H₂, 300 mTorr, 550 °C) for 80 min (right). (f) AFM images of CH₄ + H₂ plasma CVD (20% H₂, 300 mTorr, 600 °C) for 40 min (right). The height profile is shown below the AFM image. Scale bar (c, e, f): 500nm. Reproduced with permission [75].

3 Graphene Synthesis and Experiment Setup

3.1 Introduction

In this chapter, the main experimental techniques that have been utilized in this work will be discussed in detail. In particular, the process of graphene growth using chemical vapour deposition (CVD), transfer of graphene from the growth substrate onto a desired working substrate will be discussed. The fabricated device is then subjected to various characterization tools such as Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Finally, the simulation and actual experimental results will be presented and compared.

Thereafter, the discussed graphene synthesis and device fabrication and characterization methodologies will be adopted to the rest of this thesis.

3.2 Graphene preparation methodology

3.2.1 Graphene growth using chemical vapour deposition (CVD)

Graphene used in this work is grown via chemical vapour deposition (CVD) method and is shown in figure 17. The two fundamental processes of CVD growth graphene are the pyrolysis of carbonaceous precursor material for carbon forming and the formation of hexagonal carbon (graphene) by the disassociated carbon atoms. Commercially available copper (Cu) foil of 25 μm thick is used as the growth substrate as well as metal catalyst for monolayer graphene. Metal catalyst is used to reduce the activation energy barrier from 2500 to around 1000 $^{\circ}\text{C}$ during pyrolytic decomposition and formation of graphene structure. Firstly, Cu foil was placed in the center of the 1-inch diameter quartz tube. The tube was allowed to heat up to 1035 $^{\circ}\text{C}$ with a constant flow of H_2 (20 sccm). The ramp

rate is 25 °C/min. Thereafter, Cu foils were annealed for thirty minutes under a constant flowing stream of H₂ to remove surface oxides. Then, 40 sccm of CH₄ and 10 sccm of H₂ was continuously charged into the reaction chamber for graphene growth for a duration of 30 minutes. Then, the furnace was allowed to air cool to about 600 °C. At this point, CH₄ and H₂ gas supply were cut. The furnace as allowed to cool down further under Ar purging. Finally, the graphene on Cu was carefully removed from the furnace.

Figure 17 Monolayer CVD growth of graphene.

3.2.2 Graphene Transfer

CVD grown graphene requires the transfer from the Cu substrate to a different substrate. It is noted that the presented methodology enables the growth of monolayer graphene on both sides of the copper substrate. Subsequent removal of the Cu underlayer can be achieved by spin coating a layer of polymer onto the grown graphene to form a transfer layer. The two most popular graphene transfer techniques are using thermal release tape or Poly-methyl methacrylate (PMMA). Here, graphene is transferred using PMMA. PMMA is used as the sacrificial transfer layer is because it is able to preserve continuous graphene sheet which is important for device fabrication. The graphene transfer steps using PMMA are as follow:

Step 1: Spin coat PMMA (3000 rpm, 30 s) onto one side of the Cu foil and cure at 180 °C for 2 minutes.

Step 2: Flip to the side with no PMMA coverage and apply oxygen plasma to etch away the graphene on this side of Cu foil.

Step 3: Dissolve the Cu foil using Ammonia Persulfate (APS) of 0.15 % volume concentration overnight.

Step 4: Submerge the PMMA/Graphene film into deionized (DI) water to remove the APS solution. Repeat twice.

Step 5: Transfer the PMMA/Graphene film to the targeted substrate (Si/SiO₂) for further device fabrication

Step 6: Dissolve the PMMA in acetone to complete the graphene transfer.

3.3 Characterization of as-grown graphene

3.3.1 Raman spectroscopy

Raman spectrometer UHTS300 (WITec) was used to characterize the quality of the as-grown CVD graphene. Raman signals were recorded from 1200-3000 cm⁻¹ spectral range using 532 nm excitation laser with 600 grooves per mm grating, 100x microscope objective for the focusing and collection of Raman scattered light in a spectrum. Each spectrum was analyzed using the WITec software.

The G, and 2D bands as shown in the figure are the predominant peaks in the graphene spectrum generated by the Stokes phonon energy shift due to laser excitation. The G band (1588 cm^{-1}) is an in-plane vibrational mode and the position is highly sensitive to the thickness of the sample. As the layer number increases, the position of the G band shifts towards the lower energy, indicating the softening of the bonds in the graphene layer. The intensity of the G band follows a linear relation to the layer thickness as it grows larger from single to multilayer graphene.

The 2D band (2677 cm^{-1}) is the second-order of D band, a result of two phonon lattice vibrational process. It is generally a strong signal in graphene. It does not require the presence of defects on the graphene surface to be activated. This explains why it can be seen in all graphene Raman spectra. This band can also be used to determine the graphene layer thickness by analyzing the band position and band shape. Single peak is observed in single layer graphene with full width half maximum (FWHM) of around 30 cm^{-1} . Additional layers of graphene will broaden the 2D band, causing it to split into several overlapping modes with lower intensity. It is also possible to identify single layer graphene by the peak intensity ratio of the 2D and G band. In this work, the I_{2D}/I_G is found out to be 2.5 and it corresponds to single layer graphene.

The D band (1345 cm^{-1}), also known as disorder band, activated by a graphene edge or defect, is typically weak or non-existent in high quality graphene. The intensity of the D band is proportional to the number of defects in the material. The D band exhibits dispersive behaviour due to its resonant nature and the mode is dependent on the type of excitation laser used. Thus, the position and

shape of this band vary with the used of different excitation laser frequencies. Therefore the characterization of D band in different samples has to be based on the same excitation laser frequency. Here, the intensity of the D band is low due to the high quality of as-grown CVD graphene.

Figure 18 Raman Spectroscopy of as-grown CVD graphene.

3.4 X-ray photoelectron spectroscopy (XPS)

Synchrotron XPS was performed using the Surface, Interface and Nanostructure Science (SINS) beamline located at the Singapore Synchrotron Light Source (SSLS). XPS characterization was performed on CVD grown and PMMA transferred graphene as shown in figure 19 and figure 20. The graphene samples were annealed at 300 °C under Ar/H₂ environment for 2 hours prior to XPS

measurement to ensure that the sample surface is free from defects. Photoemission spectra were recorded using Omicron EA 125 hemisphere energy analyzer equipped with monochromatized Mg-K α -X-ray source. The wide scan of the transferred graphene is shown in figure 19. The absence of Cu suggests that the majority of the Cu substrate had been etched away during the PMMA transfer.

In figure 20, the deconvoluted C 1s peaks reveal the presence of various states of carbon. The major peak at 284.8 eV can be assigned to the pristine six-member sp² carbon ring (C=C) in a typical graphitic setup [76]. The spectra confirm that most of the C atoms reside in the honeycomb configuration. The spectrum further discloses the presence of sp³ C (C-C) and C-O with peaks assigned to 285.3 eV and 286.5 eV respectively [77].

Figure 19 XPS wide scan spectra of CVD growth monolayer graphene.

Figure 20 XPS C 1s spectra of as-grown CVD monolayer graphene

3.5 Test Structure Design and Simulation

A test structure is fabricated to study the thermoelectric properties of the as-grown graphene. The proposed planar test structure in this project was simulated using COMSOL Multiphysics to obtain the temperature flow profile from the heater to the thermometers at the hot and cold junction. The planar test structure was benchmarked using SiO₂ as the thermal insulating layer material. The criteria of the thermal insulating layer material is to have thermal conductivity as close to air as possible. Comparing the thermal conductivity between air and SiO₂, the thermal conductivity of air is 0.024 W/mK whereas that of SiO₂ is between 1.3 to 1.5 W/mK . SiO₂ base layer, given its ease of fabrication, is commonly reported in the literature. However, it is well known that SiO₂ is not a good thermal

insulating material. Therefore, for the setup of a non-suspended TE device, materials with good electrical conductivity and poor thermal conductivity should be sought. Figure 21 shows the design of the planar test structure lithographically patterned on wet thermal oxide grown 300 nm thick SiO_2 on top of Si substrate.

The fabricated test structure serves two main purposes. Firstly, it is used to measure the relative temperature difference (ΔT) between the thermometer at the hot and cold junction. Equation (26) shows the related parameters in the test.

$$R = R_{ref} [1 + \alpha(T - T_{ref})] \quad (26)$$

R_{ref} and T_{ref} are the resistance and temperature at $25\text{ }^\circ\text{C}$. Temperature difference is measured using the four-wired method with a resolution finer than 0.01 K by recording the resistance changed at the hot and cold junction as the current is passed through the heater.

Secondly, this test structure allows the measurement of thermoelectric voltage (ΔV) between the hot and cold junction. A current is passed through the heater to generate a temperature gradient ΔT along the length of the sample. The Seebeck coefficient, S , is then obtained through equation (27):

$$S = -\frac{\Delta V}{\Delta T} \quad (27)$$

$\Delta T \ll T$ is required to allow the measurement lies in the linear response region. A large S is desired in a TE material as it will give a higher ZT value.

Figure 21 Planar test structure design for relative temperature measurement and thermoelectric voltage measurement.

The dimension of the fabricated graphene device, as shown in figure 21, is $16\ \mu\text{m} \times 64\ \mu\text{m}$ (breadth x length). The distance between the heater and the hot junction thermometer is $4\ \mu\text{m}$. The width of the heater and both thermometers lines are fixed at $4\ \mu\text{m}$.

The simulated temperature profile was obtained using COMSOL Multiphysics as shown in figure 22. The simulation was conducted on a SiO_2/Si substrate. For easy visualization, the heater and the graphene structure were represented by two rectangles perpendicular to each other. From the steady-state study, heat was generated by the heater, to a set temperature of $301\ \text{K}$ through current joule heating. The heat was allowed to radiate from the source. From the simulation results, the temperatures at both hot and cold junctions on the graphene strip were measured to be $1.3\ \text{K}$. The simulated temperature difference in this structure is similar to that of experimentally gathered data. Experimental results will be mentioned in detail in the following sections.

Figure 22 Simulated temperature profile on Si/SiO₂ substrate.

3.6 Test Structure Fabrication

Fabrication of the test structure is done in the Centre of Advanced 2D Material (CA2DM) using Electron Beam Lithography (EBL) technique. Details of the process are elaborated in the flow chart shown in figure 23:

Figure 23 Fabrication process flow chart.

EBL is a maskless lithography process and in order to make a precise structure on the graphene sample, two separate EBL exposures are needed. After the CVD growth and transfer of graphene processes, graphene was first patterned using a standard UV lithography (Figure 24a) process. Subsequently, the pattern was subjected to O₂ plasma to reveal the needed pattern. Then the patterned graphene was coated with PMMA resist and was patterned using a FEI NanoSem 230 EBL system to create the alignment marks. The distance from the center of the graphene to the bottom left-hand corner of a mark was measured. It was done in order to locate the position of the writing of test structure in the second exposure. After the second exposure and development, Ti/Au (10 nm/80 nm) was then evaporated onto the substrate using an AJA electron beam evaporator to form the heater and thermometer lines (Figure 24c). Finally, the lift-off process was carried out in acetone.

Figure 24 (a) Patterned graphene (b) 1st EBL exposure of alignment mark, shown in purple color (c) Fabricated test structure with heater and thermometer lines, additional test pads at the center of the structure are for four-point probe measurement.

3.7 Thermoelectric (TE) Properties Characterization

Here, we demonstrated the preliminary gate voltage-less study of the thermoelectric properties of CVD graphene in a non-vacuum environment. The TE properties of CVD graphene existed without the need for gate tuning and all

measurements were done under room temperature and pressure. In this section, the test setup and test results of the TE properties will be discussed. Figure 25 shows a probe station equipped with Keithley 4200-SCS for TE properties measurement. The probe station also comes with a temperature controllable heating plate.

Figure 25 Experimental setup for TE properties measurement.

To determine the temperature gradient of the experiment setup, an additional test was run to measure the temperature at three locations upon applying the current through the heater as shown in figure 25. The dimensions of the heater and thermometers are the same as discussed above. Thermometers 1,2 and 3 are located $4\ \mu m$, $32\ \mu m$ and $64\ \mu m$ away from the heater respectively as shown in figure 26. Thermometers 1 and 3 represent that of the hot and cold junctions of the test structure.

Figure 26 Temperature gradient generated by the heater line at three different locations.

Figure 27 shows the temperature generated at three different locations upon applying the current from 15 mA to 55 mA stepwise. The results show that the temperature increment is proportional to the heater input. A total of 55 mA is needed to achieve the required 1.3 K difference between the hot and the cold junctions.

Figure 27 Measured temperature difference at three different locations from the heater.

To measure the thermally induced voltage ΔV as shown in figure 24, a controlled temperature difference ΔT is applied to the heater by probing the top two Au/Ti pads. Measurement is collected by probing the hot and cold junctions. Separately, temperature variations are obtained through the two thermometers with four Au/Ti pads each. The resulting Seebeck coefficient measured at room temperature as by the slopes of the linear curves. As shown in figure 28, the calculated Seebeck coefficient of the three graphene samples, samples 1, 2 and 3, are 168, 156 and 153 $\mu V/K$, respectively. In this case, a large Seebeck coefficient is obtained without the need to vary gate voltage. The experimentally measured Seebeck coefficient is among the highest as reported in the literature.

Figure 28 Seebeck voltage versus temperature difference across the three graphene samples at zero gate voltage.

Table 5 shows the summary of the Seebeck coefficient obtained from various 2D materials on SiO₂ substrate in the recent literatures. Here, this work shows promising results as the Seebeck coefficient is better than gate voltage controlled graphene samples and is comparable to that of monolayer MoS₂.

Table 5 Summary of recently reported Seebeck coefficient of various 2D materials at room temperature.

Sample	Seebeck coefficient ($\mu V/K$)	Source
G/SiO ₂ - 1L	168	This work
G/SiO ₂ - 1L	109	[78]
G/SiO ₂ - 2L	~100	[79]
WSe ₂ - 3L	89	[80]

MoS₂ - 1L	~200	[81]
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3.8 Summary

The chapter highlights the methods and parameters used for the growth of monolayer graphene and the characterization, followed by the fabrication of test structure and testing. It is confirmed that the synthesized graphene is monolayer in nature. The presence of defects in the graphene honeycomb structure has decreased the thermal conductivity of graphene. Despite that, the graphene exhibited excellent electrical conductivity which renders it a suitable TE material. The design of the test structure and the fabrication process were discussed and described in detail. Simulation of the temperature profile generated by the heater was done using COMSOL Multiphysics to understand the insulating property of the SiO₂ layer as the supporting structure in place of air. The temperature difference between the hot and cold junction was verified experimentally to be around 1.3 K which corresponded to the simulated result.

Finally, the testing demonstrated that the Seebeck coefficient measurement of gate voltage-less CVD graphene in a non-vacuum environment. The calculated Seebeck coefficient of the monolayer CVD graphene in this work is $168\mu\text{V/K}$. Non-vacuum test environment allows convenient and fast study of TE properties of the material and easy transition for investigation of the TE properties other 2D materials. More importantly, it reveals the fact that graphene is highly stable in air.

4 Defects engineering of graphene by gas sources

4.1 Prelude

CVD is a promising method to grow graphene. It enables the production of high quality and large crystal size graphene. Possibly, it can be scaled up for mass production of graphene. Leading up to that, CVD grown graphene is crippled by inconsistencies in batch production, presence of uncontrolled defects that affect the excellent physical and electrical properties of graphene and such. Thus, it is important to identify and address the root cause of lower than expected graphene quality. and to use it for defects control that can benefit different applications.

4.2 Introduction

To begin with, graphene was characterized using the mechanical exfoliation method, however, many techniques have been developed to obtain a larger area graphene sheet [61] with improving film quality. These techniques have been discussed in chapter 2. One major disadvantage of these techniques is the synthesis of defective graphene. Generally, defective graphene film shows point defects such as single vacancy, double vacancy, adatom, Stone-Wales, adatom-single vacancy, and inverse Stone-Wales defects [82, 83]. Thus, many research works have been devoted to reduce defects on CVD graphene previously. Developments in this area include temperature control, minimizing hydrocarbons contamination, metal to carbon solubility selection as growth media and underlying metal crystallinity [84]. Recently, Lin *et al* demonstrated that contamination in the formation of amorphous C sp^3 can be minimized by stacking Cu foil with Cu foil during the CVD growth of graphene [85].

So far, defect engineering techniques have been demonstrated to explore the possibilities to manipulate the physical and chemical properties of graphene [86]. To be more specific, defects are purposely introduced onto the graphene surface by physical and chemical ways in order to change its intrinsic characteristics. Ar irradiation, laser ablation, use of different substrate [87] are characterized under physical alteration. They are generally applied onto small graphene samples in order to understand the effect of defects on the overall performance of the graphene device. Separately, B, N and O elements have been shown to introduce defects on graphene [86] via chemical doping. Thus, defects can be induced during synthesis via physical and chemical ways on the entire graphene substrate. Yuki et al presented a detailed study that defects can be generated on graphene samples which were subjected to O₂ plasma, depending on plasma intensity and time [88].

In this chapter, graphene defect density is shown to vary during CVD synthesis when subjected to CH₄ precursors of different amounts of elemental contaminants. A mechanism involving in situ doping would be discussed and the graphene TE properties would be characterized.

4.3 Device fabrication and characterization

Fabrication

The general graphene synthesis and device fabrication have been discussed in chapter 3. Here, CH₄ precursors containing different amounts of CH₄ were ordered. The gas composition was analyzed by the supplier to ensure consistency. The gas composition and their major constituents are shown in

Table 6. The purchased gases were used as-is without further purification during the growth process.

Table 6 Precursors gas major and minor constituents and their amount present

Gas mixture constituent and concentration (V/V) %			
Name	CH ₄	O ₂	N ₂
PG	99.999	0.001	0.0035
99-5G	99.5	0.005	0.025
99-0G	98.9	~0.005	0.85-1.15

Samples growth in the presence of 99.999%, 99.5% and 99.0% CH₄ gases are named as PG, 99-5G and 99-0G, respectively thereafter.

Characterization

Raman spectroscopy was used to characterize the as-grown three graphene variations using a 532 nm laser and a 100x focusing lens. The thermoelectric properties of the fabricated device were performed on a probe station with a B1500A semiconductor characterization system in a vacuum environment. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were also carried out to investigate the quality of the as-grown graphene samples.

4.4 Results and Discussion

Here, the characterization of as-grown graphene via XPS is discussed. As the electron charging effect will result in elemental peak shift, graphene C1s peak

position was compared to that of adventitious carbon and compensated accordingly. Figure 29 shows the details of the deconvoluted peaks of graphene C1s. Several peaks existed and were corresponded to that of C=C, C-C, C-O, O=C-O at 284.8, 285.3, 286.6 and 288.9 eV, respectively [89]. After comparison with the peak ratio of sp² (C=C) and sp³ (C-C) was compared, it is observed that the ratio of sp³ / sp² increases in the following sequence: 99-0G > 99-5G > PG. The presence of more sp² than sp³ indicates a lower concentration of defects as sp² bonds are generally found in pristine graphene. On the other hand, the existence of the sp³ bond suggests the presence of a defective and imperfect graphene layer. Thus, the increase in the sp³ / sp² ratio represents the increase in lattice defects.

XPS spectra of deconvoluted O1s peaks for PG, 99-5G, and 99-0G are shown in figure 30. The deconvoluted peaks were assigned to C-O, Si-O, and O=C-O at 532.6, 533.4 and 533.8 eV, respectively. It is observed that the intensity of C-O and O=C-O peaks were in good agreement with the amount of oxygen present during graphene synthesis. The XPS results gathered clearly revealed the possible incorporation of oxygen containing carbon species in the graphene superlattice. Although there is a possibility that atmospheric oxygen can be captured by graphene, it was shown previously that such p-doping is negligible [90].

The route to realizing graphene device is long. Thus, there are many possible points for the introduction of contaminants. A well-documented example is the transfer of contaminants from PMMA, which as illustrated by the process flow, is necessary to release graphene from the Cu foil. As such, methodologies have

been concocted to resolve the issue. To date, methodologies such as scrubbing and cleaning using harsh chemicals and electron beam have been explored [91-94]. Most of the presented techniques are non-scalable, time consuming and costly at the present moment. Therefore, in my opinion, the use of commonly available chemicals should be approached. Wang *et al* proposed that PMMA is mostly removed from graphene washed in acetone bath for three hours and longer [93]. Following this methodology, a longer cleaning time in acetone was devised. Samples were soaked in acetone for 72 hours. Subsequently, the samples were triply cleaned with liberal amounts of acetone, isopropanol, and water. To ensure surface cleanliness, XPS analysis was carried out. The spectra (cleaned graphene / SiO₂ / Si) were referenced to PMMA coated SiO₂ / Si wafer. As shown in figure 31, peaks assigned to C-H, C-O, and O=C-O are found at 285, 287 and 289 eV, respectively [95]. Due to the equal presence of both O=C-O and C-O in the polymer, these two peaks should be presented with roughly similar XPS intensity. These features are not observed in all the cleaned graphene as shown in figure 29. Possibly, even when present, it could be below that of the detection limit of the XPS equipment. At this juncture, it can be inferred that acetone cleaning is sufficiently effective in removing PMMA from the graphene surface. Given that the PMMA layer has the propensity to interfere with the end uses, alternative materials could be explored for graphene wet transfer in the future. One possible material is paraffin wax which has a lower affinity to graphene [96]. This likely allows easier paraffin removal post-transfer.

Figure 29 Deconvoluted XPS spectra of C1s for (A) PG, (B) 99-5G and (C) 99-0G.

Figure 30 Deconvoluted XPS spectra of O1s for (A) PG, (B) 99-5G and (C) 99-0G.

Figure 31 XPS spectra of C1s for PMMA.

The surface morphology of processed graphene samples were studied using AFM in tapping mode. In total, 512 lines were taken in an area of $50\ \mu\text{m} \times 50\ \mu\text{m}$.

In addition, AFM was carried out at a low frequency for heightened sensitivity. The surface profiles of samples PG, 99-5G and 99-0G could be observed in figure 32. The root mean square (R_q) for the surfaces are arranged in the following sequence: (high) PG > 99-5G > 99-0G (low). The relationship between surface roughness and the amount of oxygen present in graphene can be explained as follows. In the case that more oxygen containing molecules are incorporated into the graphene network during synthesis, the network has a higher sp^3 to sp^2 ratio. At the same time, the graphene assumes a more tetrahedral than planar configuration. Moreover, O=C-O and C-O are more electronegative and therefore could interact better with the underlying SiO_2 layer. Due to Van der Waal forces [90], the graphene film is drawn towards the substrate. It has to be noted that all interaction between graphene and SiO_2 layer is largely a physical process [97]. By this argument, the graphene film assumes the surface profile of the SiO_2 layer. It is then purported that when more C-O and O=C-O are incorporated into graphene, it will lead to the formation of an amorphous carbon network with even better contact with the substrate. In view of the worsening performance of such devices with an increase in defects density, such study was not carried out in this work.

Figure 32 AFM performed in tapping mode for measurement area of 50 μm x 50 μm at 1 Hz for A) PG, B) 99-5G and C) 99-0G.

In the following section, Raman spectroscopy was carried out to gain a deeper understanding of the fabricated graphene samples under different reaction conditions. Prior to measurement, the following steps were executed. Firstly, all samples were measured at once to eliminate the introduction of defects such as humidity variations, temperature fluctuation, and varying equipment condition, etc. Thereafter, a high power objective lens (100X) was used to focus on the graphene surface. The laser source (He-Ne, 532 nm) was switched on throughout. Then, the focal length was adjusted vertically until the highest intensity was obtained. To ensure consistency, tests were performed at the graphene surface of three locations – at the center, top and bottom of the graphene samples. The above steps were repeated for all samples. The results of the Raman spectra for PG, 99-5G, and 99-0G were shown in figure 33.

Figure 33 Acquired Raman spectra for PG, 99-5G and 99-0G. G peak is observed to red-shift from 1953cm^{-1} (PG) to 1585cm^{-1} (99-5G) to 1583cm^{-1} (99-0G).

As shown in figure 33, the defect peak (D) presents at around 1350 cm^{-1} is associated with the A_{1g} breathing mode at boundary $\mathbf{K}$ of the Brillouin zone [98]. Although some work reported the presence of a D' peak that is typically visible at 1620 cm^{-1} , it was absent in all the samples fabricated. Generally, the D' peak, due to an intravalley process interaction, appears for higher defect density as well as shorter inter-defect distance. Using the fact presented by Cancado et al, associated the D' peak intensity to defect density and purported distance between defects, it could be taken that inter-defect distance in PG, 99-5G and 99-0G exceeds 7 nm [99]. Separately, the G peak which appears at 1590 cm^{-1} is associated with the E_{2g} phonon from the Brillouin zone.

Raman peaks are used to determine the state of bonding. There are many earlier works that discussed the significance of G and 2D peak shifts. Such phenomena could be an effect of local/global strain as well as the presence of dopants. With reference to figure 33, G peak red-shifted from 1593 cm^{-1} (PG) to 1583 cm^{-1} (99-0G). Since the 2D peak for all three samples is fixed at 2677 cm^{-1} , it can be inferred that the shift is due to doping. It has been documented that the n-doping of graphene would result in red shifting of G peak and blue shifting of the 2D peak. In the case of p-doping, both G and 2D peaks will blue shift. In the absence of a noticeable 2D peak shift in all 3 cases, n- or p- doping can be ruled out.

This fact further concretizes that O atoms are incorporated into the graphene structure during the synthesis process. Being electronegative in nature, the distortion in the structure network is caused by both C-O and O-C=O bonds, in which shorter bond length is expected. A pulling (tensile) force is exerted by the presence of O atoms at the defect sites to the surrounding bonds. This resulted in overall bond length shortening throughout the structure. Thus, the effects of lattice distortion is known to correlate to the number of defect sites on graphene. The argument supports the experimental observation that the blue shift in the G peak of 99-0G is more than that of 99-5G from the PG peak position.

The presence of more C-O and O=C-O molecules enables 99-0G to interact with the SiO_2 underlayer thin film more than 99-5G and PG. However, the grainy appearance, as revealed by AFM and shown in figure 32, could be a result of stress. At high stress points in the graphene network, the graphene layer may have detached from the substrate and buckled up. Such bulging allows the graphene to relieve excessive stress experienced at/near defect sites.

Seebeck coefficient of the three graphene variations were measured using equation (27).

$$S = -\frac{\Delta V}{\Delta T} \quad (27)$$

Higher Seebeck coefficient is preferred in order to have higher TE performance. In this work, a single material “thermocouple” device was fabricated for the measurement. It was undertaken to understand how graphene responds to external stimuli. In this case, heat is generated by a microheater line located approximately $4 \mu m$ from the graphene. The graphene edge close to the microheater is denoted as the hot junction (T_1) with reference to figure 34 (graphical inset). The other end of the graphene, which is away from the heat source, is denoted as the cold junction (T_2). For the microheater, the heat generation profile can be calculated by the following between resistance and temperature.

$$R_1 - R_2 = \alpha(T_1 - T_2) \quad (28)$$

Where ($R_1 - R_2$) is the change in resistance between the set temperature (T_1) and the reference temperature (T_2). α is the temperature coefficient of resistance (TCR) for deposited conductive material for which in this case is, Au. The change in resistance could be used to quantified the temperature of the hot junction, T_1 .

To alter the microheater output, the output from a calibrated power supply was modulated by the modulation of input voltage and/or current. The obtained ΔV

measured by a semiconductor characterization system (Agilent) was plotted against the calculated change in temperature as shown in figure 34. The Seebeck coefficient can be calculated by the slope.

Figure 34 Measured voltage difference as a function of temperature difference between hot and cold junctions. Inset shows the illustration of the fabricated graphene TE device.

From figure 34, it can be observed that PG samples affords the highest response amongst the three samples. The calculated Seebeck coefficient is as follows: PG ($105.1 \mu\text{V/K}$) > 99-5G ($89.4 \mu\text{V/K}$) > 99-0G ($69.6 \mu\text{V/K}$). This is attributed to the defect density present in the sample where higher defect density results in a lower Seebeck coefficient.

The simplified representation of the Seebeck in equation (27) could be expanded to explain on entropic carrier transport (numerator) and the carrier's charge

transport (denominator) [100]. Furthermore, the numerator is determined by electron-electron interaction while the denominator is decided by purely electron-phonon interaction. The phenomenon of electron-phonon influencing the Seebeck coefficient has been reported, albeit in low-temperature experiments [98]. At higher temperatures, electron-electron interaction supersedes that of electron-phonon. Often, the presence of defect sites could influence the electron donating and withdrawing effect within the graphene network. As such, the overall electronic properties of the material could change [101]. It explains the fact that alteration in defect density, to a certain degree, affects the overall charge transport. The difference in the Seebeck coefficient is reflected in figure 34.

To understand that further, a four-point probe sheet resistance measurement study was carried out. The results of the Van der Pauw sheet resistance were shown in figure 35. It can be seen that the introduction of oxygen during synthesis contributes to a higher defect density resulting in an increase in sheet resistance [102].

As PG shows the highest Seebeck coefficient amongst the samples, it is further characterized for operation stability at 80% of the maximum tested value.

In figure 35, it can be observed that when graphene is subjected to on/off cyclical operation, no noticeable change to measured output response. Small fluctuations in the range of 2-4 μV can be attributed to the limitation of the measurement tool. Furthermore, the time response for the device is measured to be approximately

Figure 35 Cycling stability test for ON/OFF the PG sample.

As shown in figure 36, sheet resistances based on a 4-point Van der Pauw's structure were measured. Sheet resistances corroborate with the increase in defects as revealed by Raman spectroscopy in figure 33.

Figure 36 Experimentally extracted sheet resistance using van der Pauw's structure.

Separately, the PG graphene sample was probed in air. To maintain consistency, the sample was placed firmly on the temperature controlled bottom plate which had been set to 25 °C. The comparative results are shown in figure 37. It can be seen that an approximate 20 % dropped in Seebeck coefficient. This is caused by additional factors such as convection airflow which promotes channels of heat loss. On the flip side, the dropped in the Seebeck coefficient could be compensated by minimum packaging. The vacuum packaging reliability issues could be eliminated.

Figure 37 Comparison of PG operation in vacuum versus in air.

Using the Lumerical DEVICE as observed in figure 38, we attempt to elucidate the nature of the transient rise time as shown in figure 35. In the simulation, graphene was simulated to be on a SiO_2 block where the thickness $T_{\text{Oxide}} \gg T_{\text{Graphene}}$. The graphene acts as a perfect conductor to illustrate 1) graphene excellent thermal conductivity and 2) as a guide for better visualization of heat flow profile in underlying thermal oxide. Heat impulse was introduced into the structure at $t = 0$. The cross-sectional of heat flow was measured up to $200 \mu\text{s}$. Tracking heat flow with time, it can be inferred that a total time of $150 \mu\text{s}$ is needed to establish a steady-state heat gradient in the oxide layer. Moreover, the steady-state thermal profile is established almost instantly ($< 1 \mu\text{s}$) in the top graphene layer. During the actual experiment, the total time needed to establish steady-state comprises joule

heating in the microheater line (Slow), delayed thermal response in SiO₂ (Slow) and graphene thermal response (Fast). To improve the response time, it is essential to keep the microheater “always ON”. In addition, a mechanically controlled shutter can be included for precise control of heat input.

Figure 38 The nature of transient rise time as simulated by Lumerical DEVICE.

Although not shown, a similar output response is gathered after months of storage post-fabrication. Samples were intentionally left in air. This suggests that the system is highly stable. The authors propose to perform reliability studies on such a graphene thermoelectric device in future.

Although the effect of strain on thermal conductivity is not carried out in this work, it is noteworthy to report a work investigated by Wei *et al.* The work showcased

that tensile strained graphene has lowered the thermal conductivity by slowing down the phonon group velocity [103]. This could result in a higher figure of merit (ZT).

In-Situ doping mechanistic insight

CVD grown graphene have been widely reported for a number of years [104]. However, many authors reported varying degrees of success in obtaining pristine graphene via the pyrolysis of carbon-containing precursors. That is, a spectrum of graphene has been synthesized and reported [105]. Therefore, it is clear that one of the key issues is a lack of control over precursors' quality with regards to the presence of impurities or contaminants.

As described previously, CH_4 undergoes pyrolysis at elevated temperatures to yield hydrogen and carbon. Subsequently, carbon atoms undergo segregation to form graphene sp^2 superlattice in the presence of a transition metal catalyst such as Cu or Ni [106]. The classical reaction is often carried out in the absence of oxygen molecules. In this case, a typical pyrolytic chemical reaction of methane is as follows

Although environmental O_2 can be purged with inert gases for an extended period of time or evacuated under vacuum, it is not always simple to exclude O_2 entirely. One probable source of O_2 contaminant is a constituent of the residual gas in the methane gas cylinder. However, it is difficult

to eradicate the presence of oxygen which could influence the quality of the eventual graphene sample. To shed light on the effect of oxygen atoms on graphene and defect formation, CH₄ precursors with different O₂ content were used to synthesize graphene. From the analytical data presented in this work, we would like to propose the following insight. A side reaction involving rapid formation of CH₃OH and CH₂O could occur in the reaction chamber in the presence of quartz tube at elevated temperature [107] such as equations (29) and (30).

It was shown that the rate of reaction of CH₃OH pyrolysis increased in the presence of H₂ [108]. Separately, in the presence of O₂, methane combustion could produce formaldehyde [109, 110]. Subsequently, Cu metal might catalyse the carbonylation of (-C-O) and (-C=O) where it could be incorporated with C atoms for graphene synthesis. The methanol and formaldehyde formed during pyrolysis (fast reaction), could be incorporated as C=O and C-O into the expanding graphene superlattice as defects [111]. Plausibly, graphene and the existence of defect sites could drive the oxidation of methane to methanol and/or formaldehyde, propelling the reaction forward. Other probable by-products for methane combustion is CO₂ and CO which are unlikely to be incorporated into the graphene network.

4.5 Summary

CVD is a well-known process that is capable of producing large graphene films. Today, many efforts are still on-going in order to understand the growth conditions that could affect the graphene quality. It has been shown that the quality of graphene could be affected by the residual constituent of methane precursors. In this work, graphene defects are shown to be caused by the presence of O_2 during CVD synthesis. This affects the physical and chemical properties of the synthesized graphene. Furthermore, the graphene device fabricated to explore the TE properties with PG exhibited the highest Seebeck coefficient. In addition, stable performance of graphene TE device under vacuum and in air conditions allows it to be used for a multitude of sensing applications.

5 Metal decorated graphene

5.1 Prelude

Though CVD graphene has been reported for various applications. In nanoelectronics and nanophotonics, the performance has greatly suffered from the presence of defects which might have evolved from the precursors during CVD growth as mentioned in chapter 4. In this chapter, graphene is hybridized with metal nanoparticles to overcome the limitations by promoting charge transfer and to bridge the grain boundaries in order to improve the electrical performance.

5.2 Introduction

So far, graphene has been widely reported for biosensing [6] and carbon electronics [5]. They have been successfully demonstrated as a carbon catalyst for photocatalysis [112] and electrocatalysis [113] as well. An assortment of applications ranging from drug delivery, food contamination discovery, health monitoring, bioimaging, etc. have been explored. However, the presence of grain boundaries and intragranular defects have resulted in detrimental effects on the electrical conductivity. The defect sites are packed with mainly sp^3 carbon and other oxygen species. These defect sites are usually high energy centers with the capability of carrying out catalysis and redox reaction as well as the capturing of atoms. To overcome this issue, graphene is often functionalized with other materials to improve its performance.

A number of publications [114, 115] have reported on the metal and metal oxides nanoparticles/graphene hybridized system to form graphene nanocomposites. Examples include Au, Ag, Pt, Pd Fe_3O_4 , TiO_2 , ZnO, NiO [116, 117]. [116,

117].[116, 117].[116, 117].[116, 117].[116, 117].[116, 117]. Generally, the hybridizations are carried out by the following methods: hydro/solvo-thermal treatment, electrochemical, electron beam/sputter deposition, UV photoreduction and reduction with hydrides/ hydrazine in the absence or presence of capping agents [118]. In addition, graphene synthesis from graphene oxide has shown the capability of reducing graphene oxide to form graphene/metal-NPs composites [119]. In particular, Au nanoparticles are well known for the enhancement in the optical field due to the localized surface plasmon resonance effect. The fabrication techniques and precursors used will greatly affect the size of the synthesized NP. The functionalization of graphene with NP could alter the mechano-optoelectronics properties of the pristine graphene to suit different applications.

In the first part of this work, Au metal nanoparticles (NPs) were hybridized by four different methods. The outcomes of the hybridization were studied and evaluated. In this case, the evaluation was carried out to ascertain the efficiency and the level of “environmental-friendliness” of the methods to form graphene hybrids. The discussed reduction methods are spontaneous reduction via charge transfer, chemical reduction using NaBH_4 , ultraviolet (UV) photoreduction with spin coating of Au solution and without spin coating.

The second part of this work emphasized on a shortlisted method of reducing Au as well as other metal NPs, such as Ag and Pt onto graphene. Characterization techniques were used to investigate the thermoelectric effect of nanoparticles on graphene. The functionalization was performed using UV photoreduction after metal-containing inorganic compounds were drop cast onto the graphene surface.

This method was regarded as the most effective and green among the four reduction methods. The effects of UV photoreduction of different metal nanoparticles were compared and the thermoelectric power factor of graphene-NP hybrids were evaluated.

5.3 Hybridization of metal NPs-decorated graphene

The fabrication process of graphene and graphene device have been illustrated in chapter 3. The methodology remained unchanged. Here, four different reduction methods for Au-decorated graphene would be elaborated. HAuCl_4 purchased from Sigma Aldrich (Merck) was dissolved in DI water to make up for a 2 mg/ml Au containing solution. Then, the solution was subjected to the following treatments to obtain Au-decorated nanostructure:

- i. Spontaneous reduction via charge transfer. In a beaker containing 1 ml of Au solution, the graphene sample was placed in a Teflon holder and suspended in it. The setup was then stirred in dark for one hour.
- ii. Chemical reduction using NaBH_4 . A second graphene sample was placed and suspended in the beaker containing 1 ml of Au solution. The setup was stirred in the dark for one hour followed by the addition of 1 gram of NaBH_4 . The setup was stirred for an additional 30 minutes.
- iii. UV photoreduction. A drop of the prepared solution was pipetted onto the graphene sample. Then the sample was subjected to an 400 W Xenon lamp for approximately two minutes.

- iv. UV photoreduction for spin-coated metal-containing solution. A modification to the UV photoreduction method whereby a drop of Au solution was pipetted onto the sample, followed by spinning at 2000 rpm for 30 seconds. Then the sample was subjected to an 400 W Xenon lamp for approximately two minutes.

Finally, the sample was washed using DI water and was blown dry with N₂ for all reduction methods.

The hybridization of Ag-decorated graphene and Pt-decorated graphene was performed in a similar manner as described above for the formation of graphene-Au. In this case, AgNO₃ and H₂PtCl₆ were purchased from Sigma-Aldrich (Merck) and were prepared in separate beakers to make up for a 2 mg/ml metal containing solution. The reduction was then carried out with UV photoreduction as described above.

5.4 Results and discussion

5.4.1 Comparative study of Au reduction methods for graphene – Au NPs hybridization

The reduced Au-decorated graphene samples were visualized using field emission scanning electron microscopy (FESEM) as shown below. It has a spatial resolution of less than 2nm. Figure 39 and 40 show the surface of the graphene before and after hybridization, respectively. It is observed that the surface of the freshly prepared graphene is free of particles at the same magnification whereas Au NPs were seen in all the above mentioned reduction methods.

The differences between the reduction methods are investigated. It is proven that the surface of graphene is capable of undergoing spontaneous charge transfer where Au_{3+} is reduced to Au_0 [120]. Ionic Au_{3+} in the solution was attracted to the negatively charged graphene surface which was subsequently captured and reduced. The reduced Au NPs were approximately 10 nm in diameter with the exclusion of a few larger NPs as shown in figure 40A.

Figure 39 Surface of CVD graphene.

Figure 40 Size distribution of Au NPs when reduced by various reduction methods on CVD graphene. A) Spontaneous reduction via charge transfer, B) Photoreduction using UV, C) in NaBH_4 and D) Spin dropped Au solution prior to UV reduction. The red arrows indicate the presence of 10 nm size Au NPs.

Chemically reduction of Au^{3+} to Au^0 using NaBH_4 was found to be effective and produced a high concentration of NPs [121]. From figure 40C, a high concentration of Au NPs could be seen distributed homogeneously on the graphene surface. NaBH_4 reduction allows good AuNP size control with an average particle diameter measured to be about 10 nm. However, similar-sized NPs could be seen on Si/SiO_2 substrate surface too. This showed that the chemical reduction method using NaBH_4 was unable to differentiate the reduced surface, regardless if it is a substrate or graphene surface. This might be detrimental in certain applications due to the altered characteristics of the substrate.

Au NPs produced by the photoreduction method using UV showed particle size of 10 and 100 nm in general (figure 40B). Although fewer Au NPs were seen reduced in the spin dropped process due to the reduced amount of Au solution on the graphene surface prior to reduction, larger Au NPs were dominated the surface (figure 40D). This could be due to a two-step process involved in the UV photoreduction process, namely (1) surface charge transfer process that forms small NPs and (2) UV initiated agglomeration that form larger NPs.

Table 7 Comparison of different reduction methods

Reduction Methods	Size of Au NPs	Distribution of Au NPs	Controllable NPs size?
Spontaneous	10nm	Widespread on Graphene	No
NaBH ₄	10nm	Widespread on Graphene and Si substrate	No
Spin drop UV	10nm – 100nm	scarce	Yes
UV	10nm – 100nm	scarce	Yes

Here, various methods reduced Au-decorated graphene samples were subjected to XPS elemental analysis. It confirmed that the Au element was present in all reduction methods. Peaks corresponding to Au 4f_{7/2} and 4f_{5/2} can be seen in figure 41. Both peaks were found in the vicinity of 84.0 and 88.0 eV and no Au₃₊ was seen. This shows that the Au₃₊ ions have been effectively reduced on the graphene surface to Au₀. [122].

Figure 41 XPS spectra of Au 4f from the Au NPs fabricated using various reduction methods

Generally, compared with the XPS spectra of pristine graphene, the peak associated with C1s became predominant as the graphene was reduced as shown in figure 42, while the peak associated with O1s was weakened (figure 43) after reduction. This indicates that the graphene was deoxygenated and reduced to form Au-decorated graphene [123]. Here, XPS spectra of C1s and O1s from the UV photoreduction method were used to compare with the pristine graphene to illustrate the change and the discussion will be extended in the following section.

Figure 42 C1s XPS spectra of UV reduced Au-decorated graphene compare to Pristine graphene.

Figure 43 O1s XPS spectra of UV reduced Au-decorated graphene compare to Pristine graphene.

In this work, fabricated CVD graphene was successfully functionalized with nanometer-sized Au NPS using various reduction methods. Both UV and surface reduction methods have shown promising results in producing desirable sized particles for various applications and depending on the applications, various metal NPs can be reduced on the graphene surface.

5.4.2 Metal NPs-decorated Graphene for thermoelectric power factor enhancement

Recently, graphene has been explored as the next-generation thermoelectric nanogenerator (g-TENG). However, this development is impeded by the low electrical conductivity and high charge carrier scattering due to the presence of defects [124]. In view of this, researchers have turned to doping, nano-patterning and forming graphene – polymer nanocomposites to address the issues. These methods proposed are, however, limited in terms of 1) the need of using harsh doping conditions, 2) suffering from fabrication errors, and 3) out-gassing when used in the vacuum environment, respectively.

After the work on comparative study of Au reduction methods for Au-decorated graphene hybridization, UV photoreduction has been shortlisted as a green, effective and efficient reduction method. Besides Au NPs, Ag and Pt NPs were used to compare the effect of UV photoreduction and the hybridized system was explored as a possible thermoelectric generator by examined and evaluated the thermoelectric power factor.

5.4.2.1 TEM visualization of metal NPs on graphene

Figure 44 shows the transmission electron microscopy (TEM) images of the deposited nanoparticles on samples. Au NPs tend to aggregate into nanoclusters

and are measured to be approximately 10nm in diameter. Au NP are generally irregularly shaped. Ag NPs, on the other hand, are circular in shape and are highly dispersive. Ag NPs are much smaller and measured to be around 3.5 nm in diameter. Pt NPs, on the other hand, are observed to be 3.8 nm on average in diameter and have large variation in sizes, just like Au NPs. However, Pt NPs are circular in shape, similar to that of Ag NPs. All three types of NPs were prepared in a similar reduction environment.

Figure 44 TEM images of graphene-metal NPs (A,B: Au; C,D: Ag; E,F: Pt).

5.4.2.2 Characterization of fabricated samples using XPS and Raman

The nature of the UV photo-reduced nanoparticles on the graphene surface were elucidated using XPS (figure 45). Figure 45A shows UV reduced Au 4f core at 87.8 and 83.9 eV which correspond to the binding energy of Au4f_{5/2} and Au4f_{7/2}, respectively [125]. Figure 45B reveals Ag 3d spectrum at 374.9 (Ag3d_{3/2}) and 368.4 (Ag3d_{5/2}) eV [126] with a peak splitting of 6.5 eV which corresponds to metallic silver (Ag⁰) [127]. Figure 45C shows the four deconvoluted peaks that are assigned to Pt₂₊ and Pt₀. Pt₂₊ peaks are found to be at 72.1 and 75.4 eV which correspond to Pt4f_{7/2} and Pt4f_{5/2}, respectively. Pt₀ peaks are located at 70.5 and 73.5 eV [128]. There is no Pt₄₊ peak found in this study. XPS analysis shows the complete reduction of Au and Ag.

Figure 45 XPS spectra of functionalized graphene with A) Au, B) Ag and C) Pt.

The nature of doping and the influence of metal nanoparticles on graphene electronic characteristic was done using Raman spectroscopy. Figure 46 is arranged in graphical order as follows: A, D, G is the Raman spectra for Au-decorated Graphene, B, E, H for Ag-decorated Graphene and C, respectively, I

for Pt-decorated Graphene. As shown in figure 46A, and B, the defect (D) peak which presents at 1340cm^{-1} is observed to enhance when Au and Ag were reduced by UV. This effect was attributed to the surface-enhanced Raman scattering (SERS) [129, 130]. D peak of Pt-decorated Graphene which is shown in figure 46C, however, decreased as a result of rechannelling of electrons at Pt-decorated Graphene chemical interface as well as Pt_2^+ interaction with the oxygen group at the defect sites.

Figure 46D – F and 46G – I refer to the shift of G and 2D peaks, respectively. It is observed that the G band of Pt-decorated graphene is red-shifted by $\Delta G = 1.16$, 0.76 and 0.76 cm^{-1} while the 2D band is red-shifted by $\Delta 2D = 2.45$, 6.36 and 4.40 cm^{-1} [131]. Also from Zabel *et al.*, it is known that the ratio of $\Delta 2D / \Delta G$ was reported to be $1.9 - 2.5$ in the case of pure uni/ bi-axial strain. Here, the calculated ratios of $\Delta 2D / \Delta G$ are 2.11 , 8.37 and 5.79 for Au-decorated Graphene, Ag-decorated Graphene, and Pt-decorated Graphene, respectively. The higher than expected values of $\Delta 2D / \Delta G$ could be the results of multiple perturbations due to the tensile strain introduced by surface physisorption of metal nanoparticles and doping. As discussed in [132], the interaction of the NPs on graphene has resulted in the generation of electrostatic forces among them which led to the strain distortion to the graphene lattice. In general, tensile strain would induce a red shift on G and 2D bands whereas compressive strain would result in a blue shift for the bands. On the other hand, n doping will cause blue shifting of G band and red shifting of the 2D band. For p-doping, both G and 2D peaks are observed to be blue shifted [133].

The higher $\Delta 2D / \Delta G$ ratio of Graphene - Ag found in this work can be explained by 1) a sharp increase in local strain within the graphene sp^2 network following the addition of Ag NPs in Graphene - Ag. 2) n-doping of graphene by Ag NPs with electron transfer from Ag to graphene [134] which resulted in blue and red shifting of G and 2D band, respectively. For the case of Graphene - Au, the ratio of $\Delta 2D / \Delta G$ is within the limit as reported by Zabel *et al* [131]. Similarly, the presence of large Au NPs has attributed to significant local tensile strain on the underlying graphene network where adsorption energy increases with the size of NPs [135].

As the perturbation factors will cause varying degrees of influence on the graphene sp^2 network, it warrants an independent study to properly ascertain the effect of these factors.

Figure 46 Raman spectra for Graphene-Au (A-C), Graphene-Ag (D-F) and Graphene-Pt (G-I). (A,D,G), (B, E, H) and (C, F, I) are the corresponding sequential D, G and 2D peaks for Graphene-Au, Graphene-Ag, and Graphene-Pt, respectively. Guidelines and arrows have been inserted into selected figures to indicate red shifting of G and 2D peaks.

5.4.2.3 The effect of metal NPs on the Seebeck coefficient and power factor

Fabricated metal NPs-decorated graphene (Au, Ag, Pt) samples were probed for Seebeck coefficient (S) and sheet resistance (R_{sh}) measurement with regard to pristine graphene samples. In this case, for consistency, Seebeck coefficient measurement was done in a vacuum chamber to minimize the effect of air convection that could cause the temperature difference to lower between hot and cold junctions.

The formula for the Seebeck coefficient from equation (2) is as follow [136]:

$$S = -\frac{\Delta V}{\Delta T} \quad (2)$$

where ΔV is the potential drop and ΔT is the temperature difference between the hot and cold junctions.

Sheet resistance, on the other hand, was measured using a four point probe setup [137]. To invoke a clearer understanding of the effect of metal NPs-decorated graphene, the ratio of PF_{after}/PF_{before} was adopted. The thermoelectric power factor (PF) is given as [138]:

$$PF = S^2 \sigma \quad (31)$$

PF is a function of the Seebeck coefficient and electrical conductivity. The equation for the ratio of PF_{after}/PF_{before} is as follow:

$$PF \text{ ratio} = \frac{PF_{after}}{PF_{before}} = \frac{S_{after}^2}{S_{before}^2} \cdot \frac{R_{before}}{R_{after}} \quad (32)$$

Table 8 Compiled Seebeck coefficient, resistance and PF ratio. SD = standard deviation

	Mean Seebeck ratio (SD)	Mean Resistance ratio (SD)	
Sample	S_{after} / S_{before}	R_{before} / R_{after}	PF Ratio
Au-decorated Graphene/ Pristine	0.76 (0.03)	5.26 (0.46)	3.04
Ag-decorated Graphene/ Pristine	1.04 (0.06)	1.43 (0.02)	1.55
Pt-decorated Graphene/ Pristine	0.94 (0.08)	1.33 (0.07)	1.18

Table 8 shows the measured Seebeck coefficient, mean resistance and PF ratio of Au-decorated Graphene, Ag-decorated Graphene, and Pt-decorated Graphene to pristine graphene. Minimum change in Seebeck coefficients were observed in Ag-decorated Graphene, and Pt-decorated Graphene system, indicating the intrinsic characteristic of the systems were not significantly affected by the surface hybridization by Ag and Pt NPs. As a result, the Seebeck coefficient ratio of Ag-decorated Graphene, and Pt-decorated Graphene to pristine graphene remained the same. A 25% drop in Seebeck coefficient with reference to pristine graphene was observed in Au-decorated Graphene hybridized system. This drop could be attributed to a thermal coupling effect that lowers the local temperature between the Au and graphene [139]. The change in the temperature difference resulted in the drop in Seebeck coefficient due to a larger ΔT denominator in Equation (2).

In addition to the change in the Seebeck coefficient of the hybridized systems, the overall conductivity of the systems changed as well. Sheet resistance (R_s) was measured using a four point method. Then, the sheet resistance was numerically calculated using the Van der Pauw's equation [140]. The measurement is done when a current is flowing along one edge of the sample (eg. I_{12}) and the voltage (eg. V_{34}) across the opposite edge is measured. Thus resistance ($R_{12,34}$) can be calculated using equation (33):

$$R_{12,34} = \frac{V_{34}}{I_{12}} \quad (33)$$

The sheet resistance of an arbitrary shape sample can be obtained by measuring the resistance along a vertical edge ($R_{12,34}$) and the corresponding one along the

horizontal edge ($R_{23,41}$). Finally, the actual sheet resistance can be obtained by solving the following formula:

$$e^{-\pi R_{12,34}/R_s} + e^{-\pi R_{23,41}/R_s} = 1 \quad (34)$$

Table 9 Compiled sheet resistance and the SD of pristine, Au-decorated Graphene, Ag-decorated Graphene, and Pt-decorated Graphene, respectively.

	Pristine	Au-decorated Graphene	Ag-decorated Graphene	Pt-decorated Graphene
R_s (Ω/sq)	528.38	100.4	369.35	398.95
Standard Deviation (Ω/sq)	38.73	4.83	24.41	15.46

The sheet resistances of the different graphene samples are shown in Table 9. The hybridized graphene sheet resistances arranged in ascending order as follows: (lowest) Au-decorated Graphene < Ag-decorated Graphene < Pt-decorated Graphene < Pristine (highest). The results corresponded to the intensity of the defect peaks as revealed in the Raman spectra. Electrons transferred from metal NPs to graphene has caused the red shifting of G and 2D peaks. It resulted in the decrease of overall sheet resistance in all three hybridized systems [141]. High electrical conductivity of metal NPs could be the main contributing reason to the decrease in sheet resistance. The lower resistance value of Au-decorated Graphene could be attributed to the Au NPs nanoclusters being agglutinated at the graphene defect sites and grain boundaries [142]. Thus, it is postulated that the large Au NPs are able to minimize the grain boundary resistance. It could be done by forming conducting bridges

across the boundary and lower the resistance, allowing charge carriers to pass through with ease.

Finally, the power factor of the hybridized system which is a function of Seebeck coefficient and electrical conductivity changes as different metal NPs attaches to the surface of graphene. The enhancement of PF with respect to the pristine graphene is as follow: Au-decorated Graphene ($3.04 \text{ } \Omega/\square$) > Ag-decorated Graphene ($1.55 \text{ } \Omega/\square$) > Pt-decorated Graphene ($1.18 \text{ } \Omega/\square$) > Pristine ($1.00 \text{ } \Omega/\square$). In this case, it can be seen that the power factor of Au-decorated Graphene has been enhanced more than three times than the pristine graphene.

5.5 Summary

In summary, graphene was successfully functionalized with Au NPs with different reduction methods and with Ag and Pt NPs with UV photoreduction method. Metal NPs-decorated Graphene hybridized systems were probed for the subsequent measurement in electrical conductivity and Seebeck coefficient. Although it was shown that the Seebeck coefficient of Au-decorated Graphene decreased by 25%, it yielded a three times improvement in thermoelectric power factor due to a five times reduction in sheet resistance. This increase in thermoelectric PF would, in turn, enhance the overall thermoelectric performance.

6 Thermoelectric Beyond Graphene

6.1 Prelude

Both pristine graphene and metal-(Au, Ag, Pt) functionalized graphene display p-type doping characteristics in the Seebeck coefficient. To facilitate the fabrication of an IR thermopile, the exploration of a n-type material to compliment the p-type graphene is vital. In this chapter, 2D materials $\text{Bi}_2\text{O}_2\text{Se}$ and MoS_2 are explored as the potential n-type materials.

6.2 Introduction

Exploration of 2D materials beyond graphene leads to another class of material. They are commonly termed as transition metal dichalcogenides (TMDs). TMDs are monolayer 2D materials where a layer of metal atoms is sandwiched between two layers of chalcogenide atoms. The similarity between the 2D TMDs and graphene is the unique planar structure which is held together by the van der Waals (vdWs) force [143]. As TMD 2D materials are quantum confined in thickness, their unique structural property improves the TE properties owing to an enhanced density of states energy dependence when compared to their bulk counterparts. Similar to the previous chapters on graphene performance, TMDs promises excellent electrical, as well as excellent physical properties. This is, in part due to the presence of direct band gaps and high carrier mobility. As such, these materials are highly applicable in the fields of nano-transistors, optoelectronics and even as thermoelectric devices. Several reports have shown that a number of these materials to possess a high Seebeck coefficient and at the same time with ultralow thermal conductivity [12, 57, 144-147]. Given its

promising characteristics, 2D TMDs have received wide interest among the research community.

The perspectives of this PhD work are two folds: in the first part of this chapter, I will showcase a simulation work using COMSOL Multiphysics on the thermoelectric properties of molybdenum disulfide (MoS_2). This material exhibits a high power factor on a single crystal. In the second part of this chapter, some experimental results on bismuth oxidelenide ($\text{Bi}_2\text{O}_2\text{Se}$) will be presented. Previously, Yu *et al* [148] simulated the outcomes on a 2D sheet of $\text{Bi}_2\text{O}_2\text{Se}$ using DFT-based calculations and Boltzmann transport equation (BTE). In that work, Yu *et al* evaluated the electronic and thermal transport properties of $\text{Bi}_2\text{O}_2\text{Se}$. The authors determined that the ZT is larger than SnSe_2 , shedding a new light on this material. Oxides TMDs are stable in air at elevated temperatures, while it is both lightweight and environmentally friendly. Interestingly, it possesses many qualities desirable for potential commercial applications in the area of energy harvesting.

Thus, it is highly possible to construct effective thermoelectric material from $\text{Bi}_2\text{O}_2\text{Se}$. The fabrication, characterization and thermoelectric properties of $\text{Bi}_2\text{O}_2\text{Se}$ will be discussed in this chapter.

6.3 Molybdenum Disulfide (MoS_2)

MoS_2 is one of the earlier synthesized TMDCs with a direct bandgap of 1.8 eV when grown or exfoliated. As a monolayer, it exhibits very different physical and electronic characteristics from its bulk form. In such a case, a direct bandgap is obtained in mono and a few layers MoS_2 . It addresses the zero bandgap obstacle

encountered in graphene and offers excellent performance for a wide spectrum of applications e.g. optical, flexible electronics, energy harvesting among others. To enable high volume manufacturing and industry compatible process of 2D TMDCs into devices, layer-controllable and reproducible wafer-scale growth of the materials are necessary. To date, their growth has been largely dependent on the sublimation process and the transport of solid precursors in the reactor to the substrate. The critical control of growth parameters such as vapour and gas-phase chemistry hampered the large scale growth required by the manufacturers. To address the issues of uneven and small area growth for these materials, a customized cold wall chemical vapour deposition (CVD) system (figure 47) has been acquired.

Figure 47 Customized cold wall CVD system.

6.3.1 Growth and Characterization

The customized cold wall CVD grown MoS₂ shows promising results. Therefore, a few different runs were performed to determine the batch-to-batch consistency of MoS₂ grown on silicon wafers. Figure 48 shows the schematic diagram of the cold wall CVD system. The cold wall CVD system utilizes an easy to vaporize solid precursor such as Mo(CO)₆ to achieve stable process control in the vapour phase. On the other hand, users have full control over most of the growth parameters. These parametric controls include substrate temperature, precursors (Mo(CO)₆, C₂H₆S₆) temperature and flow rate of the carrier and reaction gases.

Figure 48 Schematic plot of cold wall CVD for large scale MoS₂ growth.

The substrate holder is capable of accommodating one 6-inch wafer. The wafer is resistively heated by direct current which can be closely monitored and regulated. Large scale, uniform growth was shown in figure 49 where two 6-inch sapphire wafers were compared before and after MoS₂ growth.

Figure 49 Visual inspection of large scale, uniform MoS₂ growth on 6-inch sapphire substrate.

Here, Raman and Photoluminescence (PL) spectroscopy was used to characterize the thickness and quality of the MoS₂ film. A total of 5 positions were taken to verify the characterization of the film. The optical measurement was first initiated at the center of the wafer. Progressively, different points were measured from the wafer center and then outward. As shown in figure 50, Raman shift spectra were collected and compared. Monolayer MoS₂ exhibits a unique spectrum in the PL due to its transition from indirect to direct bandgap semiconductor. A broad photoluminescence spectrum centered at 662nm was observed. It corresponds to the PL peak of the monolayer MoS₂ as described in the literature. Raman signature of monolayer MoS₂ was shown in E_{12g} and A_{1g} modes and is around 385cm⁻¹ and 405cm⁻¹ respectively. Both Raman and PL peak positions were observed at all locations. This shows that the cold wall CVD growth process is able to produce film thickness and quality that are uniform and consistent.

However, further tuning is required to optimize the growth recipe of MoS₂ and the growth of other 2D TMDCs will also be conducted using this new system.

Figure 50 (A) Raman and (B) PL spectrum of as-grown MoS₂ taken at different positions. Position 1 denotes the center of the 6-inch substrate and position 5 denotes the edge of the substrate.

Figure 51 shows the atomic force microscopy (AFM) image of as-grown MoS₂ flakes grown using the cold wall CVD system. The deposited film consists of small triangle flakes, of which, the total thickness, including flakes stacking on top of each other, is less than 10 nm. The sizes of the triangles flakes are generally uniform. Upon measurement, the size of one triangle is around 450 nm, and the thickness corresponds to monolayer MoS₂, which is 0.65 nm.

Figure 51 (A) AFM image of as-grown MoS₂ film and (B) measured height profile using a customized cold wall CVD system.

Despite the success in growing large scale and uniform MoS₂ using the cold wall CVD system, further fine tuning of the growth recipe is required. At this stage, it is necessary to optimize the growth conditions. Once the optimal growth condition has been achieved, it would achieve excellent electrical properties of the MoS₂ film.

6.3.2 Theoretical Discussion

The temperature gradient of MoS₂ as a thermoelectric material on the Si/SiO₂ substrate is simulated using COMSOL Multiphysics. Upon determining the steady-state temperature gradient across the hot and cold junctions, Seebeck coefficient, can be derived and calculated from the Mott relation [149]:

$$S = \frac{\pi^2 k_B^2 T}{3e} \left. \frac{d \ln(\sigma(E))}{dE} \right|_{E=E_F} \quad (35)$$

In the study shown by Buscema et al [149], temperature gradient along MoS₂ generates three components of Seebeck coefficient, namely (1) Seebeck coefficient that is proportional to specific heat of electrons, S_e , where $S_e \propto \frac{dE_e}{dT} \propto c_{el}$, E_e is the electron energy and c_{el} is the specific heat of electrons. (2) Seebeck coefficient that follows the diffusive flow of electrons, S_μ , where $S_\mu = \frac{1}{e} \frac{d\mu}{dT}$, e is the electron charge. Also, (3) Seebeck coefficient that is induced by diffusion of lattice phonons, $S_{lattice}$, where $S_{lattice} \propto \alpha \frac{c_{lattice}}{eN}$, α is the electron-phonon coupling, $c_{lattice}$ is the specific heat of lattice phonons and N is electron density. Figure 52(A) shows the schematic drawing of simulating temperature gradient using COMSOL Multiphysics and figure 52(B) shows the time taken to reach steady-state, and (C) shows the temperature distribution in the device.

Figure 52 (A) Schematic of simulating temperature gradient using COMSOL Multiphysics, (B) Time to reach steady-state, (C) Temperature distribution graph.

Table 10 shows the values of material properties utilized for thermal gradient simulation using COMSOL Multiphysics. Aluminium is used as a second thermoelectric material in the simulation. TiN acts as an broadband absorber.

	MoS ₂	Aluminum	SiO ₂	TiN
Thickness (nm)	1	1	280	100
Density (kgm ⁻³)	5060	2700	2200	5430
Specific heat capacity (JKg ⁻¹ K ⁻¹)	176	900	680	337
Thermal conductivity (Wm ⁻¹ K ⁻¹)	103	205	1.3	11.29

Table 10 Materials' properties used in simulation.

The largest temperature simulated gradient between the hot and cold junctions for MoS₂ is determined to be 0.219 K. In a separate study, the calculated Seebeck coefficient based on the Boltzmann transport equation is approximately

300 $\mu\text{V/K}$ [12]. Thus, this indicates that MoS_2 could be a potential n-type thermoelectric material.

6.4 Bismuth Oxyselenide ($\text{Bi}_2\text{O}_2\text{Se}$)

Interest in the family of oxychalcogenides is on the rise ever since the reports on promising optoelectronic applications [150-152]. Due to the indifferent electrical conductivity and often high thermal conductivity in n-type TE materials, the interest in this area is high among the research community for better n-type TE materials. Sparked by the success of its p-type counterparts (BiCuSeO) in TE performance ($ZT \sim 1.5$) and high chemical and thermal stability for oxygen-containing compounds, bismuth oxyselenide ($\text{Bi}_2\text{O}_2\text{Se}$) has received much attention in the recent years as a promising n-type TE material [6, 148, 153].

Here, CVD growth of large crystalline $\text{Bi}_2\text{O}_2\text{Se}$ is described and the measured TE properties are discussed. In addition, potential improvement in TE properties using intercalation is also suggested.

6.4.1 Growth and Characterization

Figure 53A shows the schematic diagram of the CVD chamber layout when growing $\text{Bi}_2\text{O}_2\text{Se}$. The growth took place in a temperature-controlled tube furnace where the temperature can reach 1200 °C. The fused quartz tube is 1200 mm in length and 50 mm in outer diameter. The tube can be divided into three segments where one of the precursors, Bi_2O_3 is placed at the center and the other precursor, Bi_2Se_3 , is placed at the inlet of the gas, 8 cm away from Bi_2O_3 . The substrate used for Bi_2O_3 deposition is f-mica and is placed 12 cm downstream from Bi_2O_3 . Initially, the chamber was pumped down to 6.0×10^{-2} Torr. Then 170 sccm of Ar

gas was introduced into the chamber to maintain a base pressure of 350 – 400 Torr. The chamber was subsequently heated to 620 °C in 25 minutes and the reaction was allowed to take place for the next 40 minutes. Next, the heater was switched off and the chamber was allowed to air cool to room temperature. Finally, the chamber was vented with Ar gas to reach atmospheric pressure and the grown $\text{Bi}_2\text{O}_2\text{Se}$ on mica removed from the chamber [58].

Figure 53 (A) Schematic diagram of Bi₂O₂Se using the CVD method. (B) As a grown optical image of Bi₂O₂Se, crystal size ~ 50 μm. (C) Raman spectrum of Bi₂O₂Se showing the characteristic A_{1g} peak at 159.1 cm⁻¹. (D) AFM measurement of the thickness of the as-grown Bi₂O₂Se crystal, measured thickness around 12 nm.

Figure 53B shows a single as grown $\text{Bi}_2\text{O}_2\text{Se}$ crystal on the f-mica substrate. The size of the crystal is measured to be around $50\text{ }\mu\text{m}$. Further characterization on the crystal is done using Raman spectroscopy and AFM, showing the characteristic A_{1g} peak at 159.1 cm^{-1} (Figure 53C) and the crystal thickness to be around 12 nm (Figure 53D).

6.4.2 Results and Discussion

6.4.2.1 Thermal conductivity

The thermoelectric effect of a material is determined by its figure of merit, ZT . For many 2D materials, thermal conductivity is known to be a major consideration. To date, thermal conductivities of 2D materials have been mainly characterized by Raman spectroscopy. The method is regarded as the most conventional and non-destructive [56, 154, 155]. The increase in temperature on the 2D materials is due to the localized heating effect brought about by the focused laser. It causes anharmonic lattice vibrations and thermal expansion. Thus, by measuring the laser power-induced phonon softening at various temperatures one is able to obtain the thermal conductivity of the material [156].

To facilitate the measurement, $\text{Bi}_2\text{O}_2\text{Se}$ is suspended on a holey Si/SiO_2 substrate. The diameter of the holes beneath $\text{Bi}_2\text{O}_2\text{Se}$ is around $5\text{ }\mu\text{m}$ to ensure highly accurate thermal conductivity measurement. Also, it is noteworthy to mention that the laser spot size is around $0.5\text{ }\mu\text{m}$ in diameter. The main purpose of the holes is to reduce heat dissipation induced by the laser during measurement via conduction. The Raman spectra of a 12 nm thick $\text{Bi}_2\text{O}_2\text{Se}$ is shown in figure 54 with varying incident laser power (A) and temperature (C). In situ temperature-dependent Raman spectra were acquired from 80 K to 300 K

and a drastic redshift was observed. This shift was attributed to the anharmonic lattice vibrations and thermal expansion [157]. The evolution of the A_{1g} peak frequency with respect to the temperature was linearly fitted by the equation $\omega = \omega_0 + \chi T$, where ω_0 is the Raman peak at 0 K and χ is the slope of the first order temperature coefficient, $\partial\omega/\partial T$. Here, the slope ($\partial\omega/\partial T$) is calculated to be $0.00921 \text{ cm}^{-1}\text{K}^{-1}$. An increase in the laser power gives rise to higher local temperature of the suspended film which results in phonon softening. Figure 54D shows the frequency fitting of A_{1g} at varying laser power and the slope ($\partial\omega/\partial P$) is $-2.19259 \text{ cm}^{-1}(\text{mW})^{-1}$.

Figure 54 Temperature- and laser power-dependent Raman spectra of 12nm thick suspended $\text{Bi}_2\text{O}_2\text{Se}$. (A) Temperature-dependent (C) Laser power-dependent. Linear fitting of the A_{1g} peak frequency as a function on (B) laser power and (D) temperature, respectively.

Thermal conductivity of suspended Bi₂O₂Se can be obtained by comparing the experimental value ($\partial T/\partial P$) with the calculated value of $\partial T_m/\partial P$ from solving heat dissipation equations through boundary conditions.

The heat dissipation equations for films within the suspended region and outside are as shown in equations (36) and (37):

$$\kappa \frac{1}{r} \frac{d}{dr} \left[r \frac{dT(r)}{dr} \right] + q(r) = 0 \quad (r < R) \quad (36)$$

$$\kappa' \frac{1}{r} \frac{d}{dr} \left[r \frac{dT'(r)}{dr} \right] - \frac{G}{h} [T'(r) - T_0] = 0 \quad (r > R) \quad (37)$$

where κ and κ' are the thermal conductivities of the suspended and supported films, respectively. r is the distance between the laser position and hole center. $T(r)$ and $T'(r)$ are the temperature distribution in and out of the hole, respectively. The radius for the hole is $R = 2.5 \text{ } \mu\text{m}$. G is the interfacial thermal conductance between Bi₂O₂Se and the substrate, which is $50 \text{ MWm}^{-2}\text{K}^{-1}$ for 2D materials [56]. $q(r)$ is the volumetric optical heating and T_0 is the room temperature presented in Kelvin. The laser-induced weighted average temperature inside the laser spot from this Raman experiment is described in equation (38):

$$T_m = \frac{\int_0^R T(r) q(r) r dr}{\int_0^R q(r) r dr} \quad (38)$$

By solving the above heat dissipation equations, temperature profiles for $T(r)$ and $T'(r)$ are expressed as follow:

$$T(r) = c_1 - 2c_2 \ln r + c_2 Ei \left[1, \left(\frac{r}{r_0} \right)^2 \right] \quad (39)$$

$$T'(r) = c_3 K_0 \left[0, r \sqrt{\frac{G}{\kappa' h}} \right] + T_0 \quad (40)$$

Where K_0 is the Bessel function of the second kind [56], Ei is the exponential integral, r_0 is the half of the width of the Gaussian beam which is 0.425 μm . Together with the boundary conditions as listed in equations (41) and (42) :

$$T(R) = T'(R) \quad (41)$$

$$T'(r) = T_0(r \rightarrow \infty) \quad (42)$$

the temperature profile $T(r)$ within the suspended hole can be expressed as a function of thermal conductivity under different laser powers. With all the parameters in check, the average temperature T_m inside the laser spot can be calculated and thus the measured thermal conductivity of $\text{Bi}_2\text{O}_2\text{Se}$ is around 10 $\text{Wm}^{-1}\text{K}^{-1}$.

6.4.2.2 Seebeck Coefficient

Using a similar test structure for Seebeck coefficient measurement for graphene, the Seebeck coefficient of the n-type $\text{Bi}_2\text{O}_2\text{Se}$ is measured to be 555 $\mu\text{V/K}$ (Figure 55A) at room temperature. In the same setup, a lower Seebeck coefficient of 420 $\mu\text{V/K}$ is obtained at 275 K.

Figure 55 (A) Seebeck coefficient of n-type Bi_2O_2Se measured at 300 K. (B) Seebeck coefficient of Bi_2O_2Se at 275 K and 300 K.

These results show the potential of Bi_2O_2Se to be used as a high temperature thermoelectric material. The confirmation of its Seebeck coefficient at higher temperatures will be investigated in the future.

To complete the picture, future work is required to develop specific instruments. Particularly it is useful to have equipment that affords quick and accurate ways to quantify the material properties across a broad temperature range. Currently, we are constructing a cryostatic stage to carry out resistivity and Seebeck coefficient measurements from 77 K to 700 K. Although the results presented here are encouraging, there is still room for the improvement of ZT .

In view that the superlattice nature of 2D materials is ideal for the construction of thermoelectric devices, we will modulate the electronic and thermoelectric properties of 2D materials. We will first focus on Bi_2O_2Se since its growth has been established in our lab. So far, we have the capability to grow single crystal and polycrystalline Bi_2O_2Se . Our proposal is to carry out energy filtering using ions intercalation to improve the TE figure of merit (ZT). The benefit of energy

filtering is three folds: (i) distort the band structure of the material and the effective mass of the carriers, (ii) act as scattering centers for phonons reducing the thermal conductivity only hot carriers overcome the energy barrier while cold ones are scattered. If the potential barrier is appropriate, the loss in σ can be overcome by a substantial increase in S , i.e. the resultant power factor $S^2\sigma$ is larger. (iii) modulate S coefficient and change its sign (n to p-type i.e negative S to positive S). The objective is to modulate the sign of the Seebeck coefficient from positive to negative by selecting ions to be intercalated in electrolyte. Our goal is to achieve a negative correlation material where σ and κ exhibit opposite trends in order to achieve high ZT .

6.4.3 Summary

The studies carried out in this chapter have shown that CVD grown 2D materials are potential candidates for a number of thermoelectric applications. The Seebeck coefficients measured for CVD graphene and $\text{Bi}_2\text{O}_2\text{Se}$ range from 160 to 555 $\mu\text{V/K}$. Materials must exhibit a very low thermal conductivity (κ) while both electrical conductivity (σ) and Seebeck coefficient (S) must be large. In bulk materials, these transport coefficients are interrelated. The term $S^2\sigma$ i.e. the power factor is optimized for degenerated narrow gap semiconductors with $n \simeq 10^{19} \text{ cm}^{-3}$. This factor relates to the electronic band structure of the compound: a large dispersive band (small effective mass) around the Fermi level E_F results in a large σ , while a sharp increase in the density of states (large effective mass) leads to larger S . Yet, increasing the carrier density n increases the electrical conductivity, which is detrimental to S . It causes S to decrease. As for the thermal conductivity (κ), it is dominated by the phonons contribution κ_l due to heat conduction. Strategies to reduce this include alloying. This might affects the

electrons and holes mobility and could reduce σ . Various physical concepts such as e.g. anharmonicity, Rashba effect, spin Seebeck, topological states, resonant levels, and energy filtering among others have been introduced to tailor the TE properties.

7 Future works – Graphene-based thermopile with heat absorber and F-doped graphene as low thermal buffer

Many graphene research has shown that the 2D material possesses excellent optical, electrical and thermal properties unseen in bulk graphite material. For example, phonons promoted thermal conductivity in graphene have been experimentally shown to be as high as 1500 – 5000 W/mK [158]. Despite a high Seebeck coefficient and electrical conductivity, high thermal conductivity affects the overall ZT negatively. FOM (ZT) is governed by the square of the Seebeck coefficient multiplied by the electrical conductivity over that of thermal conductivity. To overcome the intrinsic nature of graphene, hybrid layered fabrication has been proposed and showcased.

Although the transfer of graphene over a void is proven to be effective for thermal isolation, the construction is not sufficiently mechanically robust for use as a detection device [159]. Alternatively, graphene has been reported to be transferred onto insulating materials. The thin films would hold the graphene sheet firmly in place. These materials include that of, amorphous oxides such as SiO_2 [160, 161], insulating 2D material like hexagonal boron nitride (hBN) [162] and polymers such as polydimethylsiloxane and parylene [163, 164]. [163, 164]. [163, 164]. [163, 164]. [163, 164]. [163, 164]. [163, 164]. However, those insulating materials pose some disadvantages. Despite being a CMOS compatible thin film, SiO_2 is prone to thermal bleed due to relatively high cross-plane and in-plane thermal conductivity. The presence of dangling bonds on the SiO_2 substrates can interact with the graphene layer, inducing oxygen doping. Such interaction can create a downshift in Fermi energy for the graphene film

[165]. Furthermore, its thermal conductivity depends on the deposition method [166].

White graphene, or hBN, is an attractive and excellent electrical insulator. It has a similar lattice constant to graphene which allows the layers to be bound tightly by Van der Waal's forces [167]. Although hBN has been reported to be an excellent thermal shock resistance layer, it possesses high thermal conductivity with an experimental reported value between 220-420 W/mK [168]. For this, it might not be a viable thermal insulating choice to support graphene for this application.

Polymers possess low electrical and thermal conductivities. Past research studies revealed that many polymers have low thermal conductivity at all temperatures [169]. Low thermal conductivity has been well characterized previously and it is largely influenced by the degree of crystallinity, temperature and crystallite orientation [170]. The shortfalls of polymers are as such: low glass transition temperature (up to 260 °C for fluorocompounds), and its ability to outgas which is detrimental for encapsulated and/or vacuum packaged detectors.

So far, various elements have been substitutionally doped into graphene successfully [8]. These include elemental N, B, F and O [9-12]. Interestingly, fluorine-doped graphene has attracted much attention. F-doped graphene, or commonly known, fluorinated graphene (FG), is a semi-metal/insulator in nature with bandgap up to 3.58 eV [13]. Bandgap can be varied by modulating the stoichiometry of C_xF_y . So far, precursors for introducing F atoms into CVD grown graphene are XeF_2 and CF_4 [171, 172]. In the earlier

reports, F atoms are dominantly found at defects sites [14]. However, at higher substitution concentration, C: F = 1:1 has been synthesized [173]. To date, FG has found applications in hydrophobic coating, lubricant and electrode material [15, 16].

7.1 Methods

FG was prepared according to the previously reported methods [17]. Briefly, CVD synthesized monolayer graphene was wet transferred onto SiO₂/Si wafers. Thereafter, samples were fluorinated by timed exposure to CF₄ plasma treatment at reduced pressure. Exposure time ranges from 10 to 30 min. In subsequent sections, prepared samples are denoted as follows: FG (pristine), FG10, FG20, and FG30. FG was lithographically patterned to rectangular strip with dimension 64 μ m x 16 μ m. Then, the samples were electrically connected by electron beam evaporation metallization with 80 nm / 20 nm (Au / Ti) by electron beam deposition.

7.2 Characterization

Prepared samples were subjected to various tools to elucidate its characteristics. Seebeck coefficient measurement was performed under vacuum conditions. The probes were fitted with sharpened tungsten needles. A patterned microheater was powered by a standalone power supply. X-ray photoemission spectroscopy was performed on all the samples to further verify that all fluorine atoms were lost during the thermal treatment step.

7.3 Results and Discussion

CVD graphene was synthesized using CH_4 as a carbon source. Subsequently, the graphene samples were fluorinated by subjecting to different holding times with CF_4 as an F source. The results of the fluorination process were characterized using XPS as shown in figure 56. XPS spectra for FG10 can be observed from figure 56A and B. Brief fluorination results in the introduction of a small quantity of F in the graphene structure with the presence of C-F and C-CF at 288.3 and 285.9 eV, respectively. Increasing fluorination time to 20 min results in the formation of CF_2 , CF- CF_n at 292.6 and 290.6 eV as seen in figure 56C and D. The increase in C-F peak area suggests an increase conversion of carbon SP_3 to SP_2 . Correspondingly, the C-CF peak area decreases in response to more fluorination of carbon centers. Furthermore, the presence of the CF_2 peak reveals the fact that some of the carbon centers are double fluorinated with increasing fluorination time. When fluorination time was set to 30 min, an additional CF_3 peak at 293.6 eV was recorded. Unlike fluorinated samples, pristine graphene does not exhibit any C-F containing peak.

Figure 56 Results of fluorination process using XPS.

Raman spectroscopy was performed using a 532 nm laser as an excitation source. As shown in figure 57A, D peaks of pristine graphene and fluorinated graphene samples are present at 1350 cm^{-1} . For clarity, the plasma-assisted fluorinated samples are not considered fluorographene as D and G peaks can be seen in all samples. Due to the wider bandgap in fluorographene, the emitted laser is insufficient to excite the molecules resulting in zero

response. The local distortion by the presence of multiple C-F affects the overall graphene crystal structure. In all, it can be thought of as a compressive stress on the global structure.

Figure 57 Raman spectroscopy of FG.

This work should be continued with the transfer of graphene using either wet or dry transfer technique onto FG. Subsequently, the cross-plane and in-plane thermal conductivity of the graphene-FG unit should be quantified experimentally. Cross-plane doping and interaction of dangling F atoms with the graphene's graphitic network and C-O defects must be carefully examined experimentally and computationally.

7.4 Device fabrication of thermocouple with absorber

This Thesis in its entirety dedicates to the study of thermoelectric characteristics of 2D materials. Thus far, all devices are constructed with an in-plane linear microheater positioned approximately 4 μm away from the hot junction. Realistically, in an operating thermopile, the hot junction of both p- and n-type

thermocouple arms is connected to a heat absorber. Heat collected at the absorber would effect a change to the hot junction temperature. The heating effect is governed by the Planck's law.

At present, most thermopiles have heat absorbers are made of carbon black or gold black [174, 175]. Some of these have been organized into vertical stacks to improve absorption [176]. On the other hand, nanomaterials such as carbon nanotube forests have been explored as mid-infrared absorber [177]. Increasingly, titanium nitride has been explored as broadband mid-infrared absorbers. One advantage of the use of titanium nitride (TiN) is a thin film (< 10 nm) is required in many applications [178].

7.5 Titanium nitride (TiN) thin-film absorber

As such, Ti_xN_y thin films were reactively sputtered onto SiO_2/Si substrate. Sputtering conditions were varied to explored the possibility of obtaining a TiN film of different stoichiometries. In particular, Ar and N_2 gas flow rates were varied with the Ti target RF sputtered at 300 W.

Sputtered samples were subjected to FTIR measurement calibrated in the presence of SiO_2/Si wafers. The obtainable result is shown in figure 58. The best optimal TiN was fabricated with no Ar flow and N_2 flow at 50 sccm. The absorber has an absorbing range between 3.3 and 5.7 μm . However, lower N_2 flow results in poor light absorption. On the other hand, the increase in Ar results in similarly poor MIR absorption. Due to the limitation of the attached N_2 flow meter, which has a ceiling flow rate of 50 sccm, it can only be guessed that a higher N_2 flow rate could ensure better TiN quality.

Figure 58 FTIR spectrum of fabrication TiN absorber.

The fabricated TiN thin film can then be incorporated onto the graphene-, 2D material- FG TE device. The proposed process flow is as shown in figure 59. Firstly, synthesized FG are transferred onto a SiO₂/Si substrate. Graphene and other 2D materials are transferred onto the FG. EBL was then carried out to pattern the p- and n- types materials. This is followed by the deposition of TiN and a second EBL for the metallization of metal leads. Optional wire bonding could be carried to larger bond pads for testing.

Figure 59 Process flow of integrating TiN absorber onto graphene TE device.

7.6 Meta-absorber - Simulation

On the other hand, meta absorber could be a possible alternative to regular thin-film absorber. Due to its ability to provide high quality (Q) factor selection of wavelength, it is a hot research topic lately [179]. Normally, repeating unit cells of meta atoms are fabricated on an intended substrate. These meta atoms are typically constructed of metal [180] or dielectrics [181]. Strong light-matter interaction exists due to the presence of those subwavelength structures. Depending on the geometrical profile, a certain wavelength of light can be strongly absorbed. As such, meta absorber is simulated using Lumerical FDTD. The setup of the simulation is as follows: A thin Au (50 nm) is coupled at the top of a Si substrate. A 100 nm thick SiO₂ layer is simulated above that of the Au film.

Finally, circular Au disks of diameter $0.8 < r < 1.4 \text{ } \mu\text{m}$ are placed above the dielectric layer with a fixed period of $3.2 \text{ } \mu\text{m}$. One such unit is simulated. The results are as shown below. It is within expectation that smaller disks would results in absorption at shorter wavelength. When $r = 0.8 \text{ } \mu\text{m}$, the absorption appears at about $4.9 \text{ } \mu\text{m}$. When $r = 1.4 \text{ } \mu\text{m}$, the absorption peak red shifted to $7.1 \text{ } \mu\text{m}$. The full width half maximum is roughly 250 nm . Q factor is then calculated to be approximately 30. Although meta absorber promises to offer high absorbance, specific in wavelength, it is not an optimal choice for the fabrication of a broad band absorber. The reasonings proposed are as such: High cost associated with microfabrication and narrow absorption band. For effective scanning of a range of data, many such nanodisks (radius and periods) have to be simulated, designed and fabricated. This potentially increases the cost of ownership given that requirement varies from different projects. This results in the need to acquire masks to support specific jobs.

Figure 60 Simulation results of the proposed meta-absorber.

Therefore, it might make more economical sense to build broadband absorber as demonstrated previously with TiN thin film.

8 Conclusion

In this thesis, the concept of utilizing 2D materials for use as a thermoelectric device is examined. The main intent of this work is to realize an infrared responsive thermal detector. In chapter 2, the principles of thermoelectricity are discussed. It is further shown that by reducing the dimensionality of a material, its intrinsic properties would change accordingly. Often, the alterations in physiochemical properties can be leveraged upon for the construction of a thermoelectric device.

In chapter 3, the growth and fabrication of a p-type graphene-based TE device is demonstrated. Lab-grown graphene was subjected to a series of characterization tools to elucidate its properties. It was shown that CVD produced monolayer graphene is typically defective which limits its use as a TE structure. The origin of defects was investigated in detail in chapter 4. To understand the origin of the defects, graphene was grown in methane precursors containing different amounts of O_2 and non-reactive N_2 . It was revealed by Raman spectroscopy that with the introduction of O_2 , the amount of surface defects on graphene increases. This is likely due to the oxidation of methane to form methanol and formaldehyde. The molecules are then incorporated into the graphene superlattice. Furthermore, it has been shown that the presence of non-reactive N_2 could introduce a physical barrier by blocking CH_4 atoms from effective dehydrogenation. In all, the technique discussed could be used to tune the amount of defects present on graphene at will.

Later on in chapter 5, four different techniques are explored for hybridizing defective graphene with metal nanoparticles. In this case, noble metals such as

Au, Ag, and Pt were reduced on the graphene surface. Among the proposed methods, photoreduction is confirmed to be the most preferred technique. During photoreduction, metal nanoparticles, with small distribution in particle diameter, were deposited on graphene. Graphene-Au samples demonstrated the highest improvement. In this case, the thermoelectric power factor was calculated to be three times that of pristine graphene. The power factor improvement can be arranged in the following order: (low) graphene-Pt < graphene-Ag < graphene-Au (high).

With the characterization of p-type graphene in previous chapters, the synthesis of n-type TE materials has been reported in chapter 6. CVD MoS₂ and Bi₂O₂Se were grown in cold wall and hot wall CVD systems respectively. In this instance, the calculated Seebeck coefficient of both MoS₂ and Bi₂O₂Se have been determined to be 300 and 555 $\mu\text{V/K}$. The Seebeck coefficient and the overall ZT can be tuned by energy filtering by altering the intercalated ion type and concentration.

Numerous future works have been proposed in chapter 7. In this chapter, unfinished works on thermal absorber and solid support are discussed. For the former, meta surface-based absorber has been compared to broadband absorber. Although meta absorber enables a specific wavelengths to be absorbed, microfabrication of the structure remains to be challenging. On the other hand, TiN broadband absorber deposited by reactive sputtering is capable of absorbing light between 3-5 μm . While air-supported graphene has shown good thermal insulation, it is not feasible to suspend 2D material thermocouples. A solid support has to be explored. It has been identified that fluorinated

graphene with poor thermal insulation is a promising platform. Initial work shows that fluorinated graphene with a high C: F ratio is a poor conductor of heat.

9 List of Publications

Journal

- 1) Li Lynn Shiau, Simon Chun Kiat Goh, Xingli Wang, MinMin Zhu, Mamina Sahoo, Chuan Seng Tan, Chao-Sung Lai, Zheng Liu and Beng Kang Tay, Effects of precursors' purity on graphene quality: synthesis and thermoelectric effect, AIP Advances (2020) (Schedule for publication in the April issue)
- 2) Li Lynn Shiau, Simon Chun Kiat Goh, Xingli Wang, MinMin Zhu, Chuan Seng Tan, Zheng Liu and Beng Kang Tay, Graphene – metal nanoparticles for enhancing thermoelectric power factor, IEEE Transactions on Nanotechnology, 2019, DOI: 10.1109/TNANO.2019.2948077
- 3) Qinyu Kong, Laurence Bodelot, Berengere Lebental, Yu Dian Lim, Li Lynn Shiau, Boris Gusarov, Chong Wei Tan, Kun Liang, Congxiang Lu, Chuan Seng Tan, Philippe Coquet, Beng Kang Tay, Novel three-dimensional carbon nanotube networks as high performance thermal interface materials, Carbon, Vol 132, 2018, pp. 359-369
- 4) Julia Gusakova, Xingli Wang, Li Lynn Shiau, Anna Krivosheeva, Victor Shaposhnikov, Victor Borisenko, Vasilii Gusakov, Beng Kang Tay, Electronic properties of bulk and monolayer TMDs: Theoretical study within DFT framework, Physica Status Solidi (a), 1700218, DOI: 10.1002/pssa.201700218

Conference Paper

- 1) Li Lynn Shiau, Xingli Wang, Simon Chun Kiat Goh, Kailiang Chuan, Henrik Ernst, Beng Kang Tay, First demonstration of gate voltage-less chemical

vapour deposition graphene for non-vacuum thermoelectric study, SPIE Defense + Commercial Sensing 2018, DOI: 10.1117/12.2304794

- 2) Li Lynn Shiau, Beng Kang Tay, Comparative Study of Gold Reduction Methods for Functionalizing Chemical Vapor Deposited Graphene, IEEE NEMS 2019.

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