EFFECTS OF TRANSPORT PROCESSES TO THE DEPOSITION AND QUALITY OF ATMOSPHERIC PRESSURE CHEMICAL VAPOUR DEPOSITED GRAPHENE

BY

FATIN BAZILAH BINTI FAUZI

A thesis submitted in fulfilment of the requirement for the degree of Doctor of Philosophy (Engineering)

Kulliyyah of Engineering
International Islamic University Malaysia

FEBRUARY 2021

ABSTRACT

Until now, producing homogeneous chemical vapour deposited graphene with zero defects remains a challenge. The research on chemical aspects has been extensively explored either through experiments or computational studies. Given that it is a mass-transport limited process for atmospheric-pressure CVD (APCVD), the gas-phase dynamics and interfacial phenomena at the gas-solid interface (i.e., the boundary layer) is a crucial controlling factors. In this research, the importance of CVD fluid dynamics aspect was emphasised through fundamental studies at both gas-phase and gas-solid phase. As a preliminary study, an extensive review of available APCVD literature provided information on the relationship of graphene quality and its corresponding growth parameter. From these parameters, Reynolds number was calculated with the consideration that it is a ternary gas mixture. This was then compiled into a CH_4-H_2-Ar ternary plot which predicts the quality of graphene and Reynolds number at all gas compositions. Higher Reynolds number was found to be promising for high-quality graphene deposit which could be obtained at the gas composition range of $\leq$1% of CH_4, $\leq$10% of H_2, and $\geq$90% of Ar. Following this, a customised homogenous gas with properties similar to mixture of CH_4, H_2 and Ar was used in our computational fluid dynamics (CFD) of APCVD graphene. The in-depth details on gas-phase dynamics, interfacial phenomena, particularly the boundary layer and mass transport during the deposition process, were studied. Conditions, where gravity parameter is vital or could be safely neglected in CFD, was also determined. CFD model also allowed a close-up view of the boundary layer at the gas-solid interface. This was found to provide the most reasonable estimation of boundary-layer thickness formed on top of substrate for a bounded flow system like in a CVD. Higher Reynolds number formed thinner boundary layer. Consecutively, the relationship between the deposited graphene quality with Reynolds number, boundary-layer thickness and mass transport were explored. Calculated mass transport coefficient shows a good correlation to graphene thickness but not it's defect density which suggests that graphene defects are more dependent on factors other than fluid dynamics. At the highest Reynolds number of 84, few-layer graphene with monolayer ratio, I_{2D}/I_G of $\sim$0.67 and defect ratio, I_D/I_G of $\sim$0.45 was obtained. Wherein the quality of graphene improves when the I_D/I_G decreased by 90% and I_{2D}/I_G increased by 60%. Based on the experimental and computational studies, transport process was shown to have a vital role in the APCVD graphene growth.

خلاصة البحث

لا يزال إنتاج بخار كيميائي متجانس غير معيوب من الجرافين المترسب تحديًا حتى يومنا هذا. تم القيام بالعديد من الأبحاث في الجوانب الكيميائية على نطاق واسع إما من خلال التجارب أو الدراسات الحسابية. بالنظر إلى أنها عملية نقل جماعي محدودة للضغط الجوي APCVD(CVD)، فإن ديناميكيات الطور الغازي والظواهر البينية في السطح البيني الغازي الصلب (أي الطبقة الفاصلة) هي عوامل التحكم الحاسمة. تم التأكيد على أهمية ديناميكيات APCVD من خلال الدراسات الأساسية في كل من المرحلة الغازية والمرحلة الغازية الصلبة في هذا البحث .كدراسة أولية، قدمت مراجعة شاملة لأدبيات APCVD المتاحة معلومات حول العلاقة بين جودة الجرافين وعامل النمو المقابل لها. من بين هذه العوامل، تم حساب رقم رينولدز مع الأخذ في الاعتبار أنه خليط غازي ثلاثي. تم جمعه بعد ذلك في مخطط CH_4–H_2–Ar الثلاثي والذي يتوقع جودة الجرافين ورقم رينولدز في جميع التركيبات الغازية. تم التوصل إلى أن أرقام رينولدز العالية تُعد واعدة بنسبة للجودة العالية لرواسب الجرافين والتي يمكن الحصول عليها في نطاق تكوين الغاز الذي يبلغ أقل من 1٪ من CH_4، 10٪ من H_2، و90٪ من Ar. بعد ذلك، تم تطوير نموذج غاز متجانس مخصص بشكل أكبر لديناميات السوائل الحسابية (CFD) من جرافين APCVD. تمت دراسة التفاصيل المتعمقة حول ديناميكيات الطور الغازي والظواهر البينية، خاصة الطبقة الفاصلة والنقل الجماعي أثناء عملية الترسيب. تم أيضًا تحديد الظروف التي تكون فيها عوامل الجاذبية أمرًا حيويًا أو يمكن إهمالها بدون عواقب في CFD. يسمح نموذج CFD أيضًا برؤية قريبة للطبقة الفاصلة في السطح البيني الغاز الصلب. تم العثور على هذا لتوفير أكثر تقدير منطقي لسُمك الطبقة الفاصلة لنظام تدفق محدود كما هو الحال في CVD. تم إثبات عدم صحة التقدير التقريبي الآخر المعتمد على نموذج Blasius. شكل رقم رينولدز الأعلى طبقة حد أقل سمكًا. وتم استكشاف العلاقة بين الجرافين المترسب ورقم رينولدز وسمك الطبقة الفاصلة والنقل الجماعي. يُظهر عامل النقل الجماعي المحسوب ارتباطًا جيدًا بسُمك الجرافين ولكن لا يُشير إلى كثابة معيوبة، والذي يشير إلى أن عيوب الجرافين تعتمد بشكل أكبر على عوامل أخرى غير ديناميكيات السوائل. أثناء تطبيق أعلى رقم لرينولدز (البالغ 84) ، تم الحصول على عدد قليل من الجرافين مع نسبة أحادية الطبقة I_{2D}/I_G بقيمة 0.67∽ ونسبة العيوب I_D/I_G ∽0.45. تحسنت جودة الجرافين عند انخفاض I_D/I_G بنسبة 90٪ وزادت I_{2D}/I_G بنسبة 60٪. بناءً على الدراسات التجريبية والحسابية، تبين أن لعملية النقل دور حيوي في نمو جرافين APCVD.

APPROVAL PAGE

The thesis of Fatin Bazilah Binti Fauzi has been approved by the following:

Mohd Hanafi Bin Ani
Supervisor

Syed Noh Bin Syed Abu Bakar
Co-Supervisor

Waqar Asrar
Internal Examiner

Azrul Azlan Bin Hamzah
External Examiner

Akram Zeki Khedher
Chairman

DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

Fatin Bazilah Binti Fauzi

Signature ..... Date 20 February 2021

INTERNATIONAL ISLAMIC UNIVERSITY MALAYSIA

DECLARATION OF COPYRIGHT AND AFFIRMATION OF FAIR USE OF UNPUBLISHED RESEARCH

EFFECTS OF TRANSPORT PROCESSES TO THE DEPOSITION AND QUALITY OF ATMOSPHERIC PRESSURE CHEMICAL VAPOUR DEPOSITED GRAPHENE

I declare that the copyright holders of this thesis are jointly owned by the student and IIUM.

By signing this form, I acknowledged that I have read and understand the IIUM Intellectual Property Right and Commercialisation policy.

Affirmed by Fatin Bazilah Binti Fauzi

…….……..

Signature

20 February 2021

……..

Date

ACKNOWLEDGEMENTS

In the name of Allah, Most Gracious, Most Merciful.
May the blessing and peace of Allah be upon our Prophet Sayyidina Muhammad ibn Abdullah (peace be upon him), and upon his families, his companions and all his godly followers.

Alhamdulillah and praise to Allah SWT for being able to finish my studies. First of all, I would like to give my special thanks to my honourable supervisor, Dr Mohd Hanafi Bin Ani for his countless guidance and advice throughout my study. This also goes to my co-supervisor with my field-supervisor, Dr Syed Noh Syed Abu Bakar and Dr Mohd Ambri Mohamed.

I would like to express my gratitude to my colleagues (Edhuan Bin Ismail, Mukhtaruddin Bin Musa, Mohd Shukri Bin Sirat) and the members of Corrosion Lab 2 for their help and friendly support. Many thanks to IIUM laboratory staffs in Kulliyyah of Engineering especially Br. Ibrahim (SEM laboratory), UPNM and UKM laboratory staffs for their help and expertise.

I would also like to thank the Ministry of Higher Education (MOHE) for Long-term Research Grant Scheme (LRGS15-003-0004) and IIUM for their funding and facilities.

The constant encouragement from my parents and my family as a continued source of inspiration is like a breath of fresh air every time I needed it. Their faith in me pushed me to be the best, to explore this learning path and to pursue my dream. For that, I am eternally grateful.

Thank you very much.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
AFM	Atomic Force Microscope
AP	Atmospheric Pressure
APCVD	Atmospheric-Pressure CVD
ASTM	American Society for Testing and Materials
CFD	Computational Fluid Dynamics
CNT	Carbon Nanotube
CVD	Chemical Vapour Deposition
Eq.	Equation
LP	Low Pressure
LPCVD	Low-Pressure CVD
MFC	Mass Flow Controller
OM	Optical Microscope
PMMA	Polymethyl Methacrylate
ppm	parts per million
RF	Radio Frequency
rpm	revolutions per minute
SAED	Selected Area Electron Diffraction
sccm	standard cubic centimetre per minute
SEM	Scanning Electron Microscope
STP	Standard Pressure and Temperature
TC	Thermocouple
TEM	Transmission Electron Microscope
UHVCVD	Ultrahigh-Vacuum CVD

LIST OF SYMBOLS

Å	Angstrom
Ar	Argon
atm	Atmosphere
BCl_3	Boron trichloride
C	Carbon
CH_4	Methane
cm	Centimetre
cm^{-1}	Wavenumber
Cu	Copper
D	Tube diameter
$FeCl_3$	Iron chloride (III)
GPa	Gigapascal
Gr	Grashof number
H_2	Hydrogen gas
He	Helium gas
K	Kelvin
k	Kilo
kg	Kilogram
Kn	Knudsen number
L	Tube length
M	Molar
m	Meter
min	Minute
mm	Millimetre
mm^2	Millimetre squared
N_2	Nitrogen gas
P	Pressure

Pa	Pascal
Q	Volumetric flow rate
r	Radius
Re	Reynolds number
S	Siemens
s	Second
SiB_4	Silicon boride
SiH_4	Silane
sq	Square
T	Temperature
TPa	Terapascal
V	Volt
W	Watt
ZnO	Zinc oxide
δ	Boundary-layer thickness
μ	Viscosity
μm	Micrometre
π	Pi (3.14159265359)
ρ	Density
Ω	Ohm

CHAPTER ONE

INTRODUCTION

This chapter provides the research background starting from the significance of graphene, its production method and the challenges in the production of high-quality large-area graphene that is currently the obstacle to its widespread use. With the current status of graphene research introduced, a vital point in the production process which is fluid dynamics is discussed. From there, issues in this field of study will be highlighted and the objectives of this research are stated.

1.1 STUDY BACKGROUND

1.1.1 Properties and Production of Graphene

Carbon-based material was recently discovered to have extraordinary properties for various applications. Fabrication of carbon materials especially graphene, also known as 'wonder material', have gained massive research interest in a short duration due to its spectacular structural and electronic properties. Graphene is a 2D material made of a single atomic layer of graphite consisting of sp^2 carbon atoms in hexagonal lattices. It is the basic building block for other graphitic materials in other dimensions. Graphite is composed of a stack of many graphene layers forming a 3D structure; CNT is graphene in a tubular shape forming a 1D structure; fullerene is graphene in a spherical shape with some hexagonal lattices replaced by pentagon lattices forming a 0D structure. In contrast, sp^3 carbons form 3D carbon allotropes as diamonds and supercubane tetrahedral, BC8. Figure 1.1 shows the structures of all graphitic materials in all

dimensions and graphene is the basic structure with a single atom thick carbon layer (Oganov, Hemley, Hazen, and Jones, 2013).

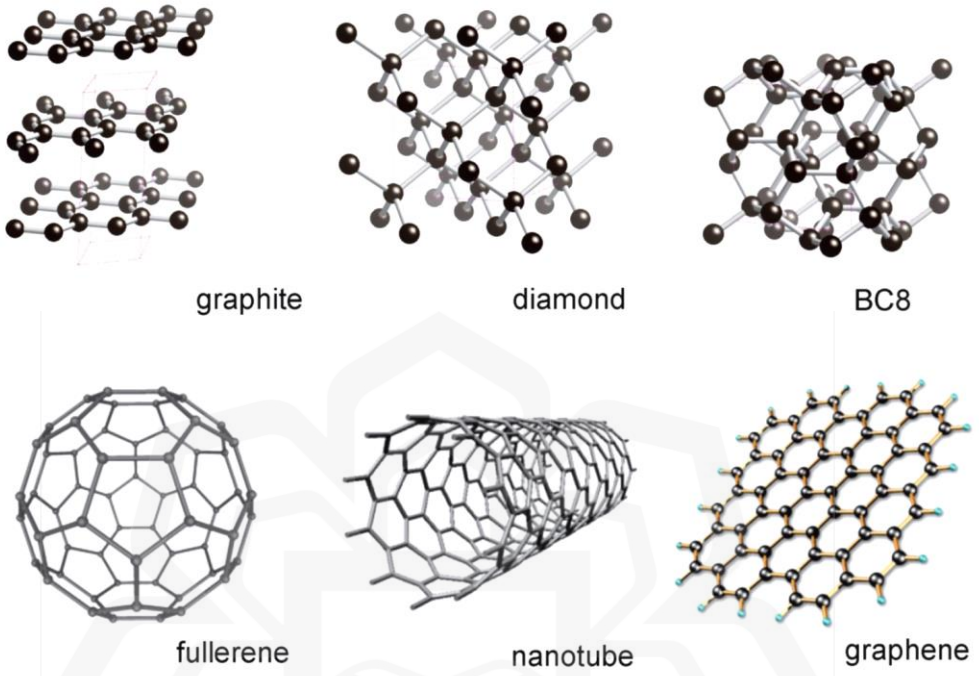

Figure 1.1 Structures of carbon allotropes in all dimensions (Oganov et al., 2013).

Theoretically, graphene has been studied for about sixty years and its superior characteristics beyond other materials' characteristics were discovered forty years later. Since 2004, graphene has gained massive interest with many applications relying on its superior properties and strength. Geim and Nosolev from Manchester University first discovered it that awarded them the Nobel Prize. It has become a reference for describing properties of other carbon allotropes (Geim and Novoselov, 2007).

Composed of carbons in sp^2-hybridised bonds, it forms benzene rings with delocalised electron clouds. The sp^2 bonds provide excellent structural strength and fracture strength of ~1 TPa Young's modulus and 130 GPa, respectively (Lee, Wei, Kysar, and Hone, 2008). As a comparison, iron only has Young's modulus of 211 GPa.

Its delocalised π-electron clouds give rise to its conductivity. Its bulk conductivity is $0.96 \times 10^6\ \Omega^{-1}\ cm^{-1}$, higher than Cu which is $0.60 \times 10^6\ \Omega^{-1}\ cm^{-1}$. Graphene is the thinnest material (~3.35 Å) with remarkable properties such as high electron mobility at room temperature ($\sim 2–2.5 \times 10^5\ cm^2\ V^{-1}\ s^{-1}$), high optical transmissivity (2.3%), exceptional thermal conductivity (4800–5300 $W\ m^{-1}\ K^{-1}$) and high electrical conductivity (2000 $S\ cm^{-1}$) (Mayorov et al., 2011). Compared to conventional conductive materials such as metals and semiconductors, single-layer graphene possesses a sheet resistivity of 31 $\Omega\ sq^{-1}$ while maintaining its transparency and flexibility. Single-layer graphene was found to allow 98 % of visible light to pass through it (Zhao et al., 2014). Due to its benzene-like structure, pristine graphene is chemically inert giving chemical stability in a wide range of conditions.

No other materials can beat the superior characteristics of graphene. These particular properties of graphene have generated lots of interest and have been explored for more than fifty years. All the above properties are the reason why graphene is known as a ‘wonder material’. These characteristics give graphene the potential ability to be used in many fields of applications including optoelectronics, flexible solar cell, bio-sensing, nanocomposites, and energy storage devices (Ani et al., 2018; Azam et al., 2017; Mishra, Boeckl, Motta, and Iacopi, 2016). However, such characteristics only apply to high-quality graphene. Until now, it is still a challenge to produce high-quality large-area graphene consistently.

Currently, many methods have been developed to synthesise graphene in various dimensions, shapes, and quality (Novoselov et al., 2012). These methods can be categorised into bottom-up or top-down approaches. The top-down approach is the process where the hexagonal lattice graphene sheets are split from its large carbon building structures such as graphite and CNT. Meanwhile, a bottom-up approach is a

process building up new carbon hexagonal lattice of graphene from carbon precursors such as hydrocarbon molecules (Tour, 2014; Yi and Shen, 2015).

The interest in graphene spiked since the first successful mechanical exfoliation of monolayer graphene was reported by Nosolev and Geim in 2004 (Novoselov et al., 2004). This method is essentially a top-down approach. Since then, researches on graphene productions have been widely explored resulting in many new methods as shown in Figure 1.2 which sorts each method in terms of quality and cost for mass production (Novoselov et al., 2012). The highest quality of graphene can be produced using mechanical exfoliation, but this method is costly for mass production and produces only flakes. This method is only used for research purposes.

Meanwhile, liquid exfoliation is a method to produce graphene on a large scale with the cheapest production cost. But through this method, the poorest quality of graphene was produced. Graphene that was produced thus were unable to be used in nanoelectronics applications. Alternatively, growth on silicon carbide, CVD and molecular assembly has produced good quality graphene for nanoelectronics applications.

CVD has become the most favourable method for graphene production in terms of cost and quality compared to other methods. It can produce high-quality graphene with small defects (Zhang et al., 2013). Furthermore, CVD is well-known for its simplicity, scalability, large size of continuous graphene sheets, and reasonable material quality (Vlassiouk, Fulvio, et al., 2013). In addition, modifications of the CVD reactor, such as plasma-enhanced CVD (Braeuninger-Weimer, Brennan, Pollard, and Hofmann, 2016; Jacob et al., 2015) or flame deposition CVD (Ismail et al., 2017; Memon et al., 2011), have also been reported for graphene production. Due to the above reasons, rapid CVD graphene research is predicted to continue for the next few decades.

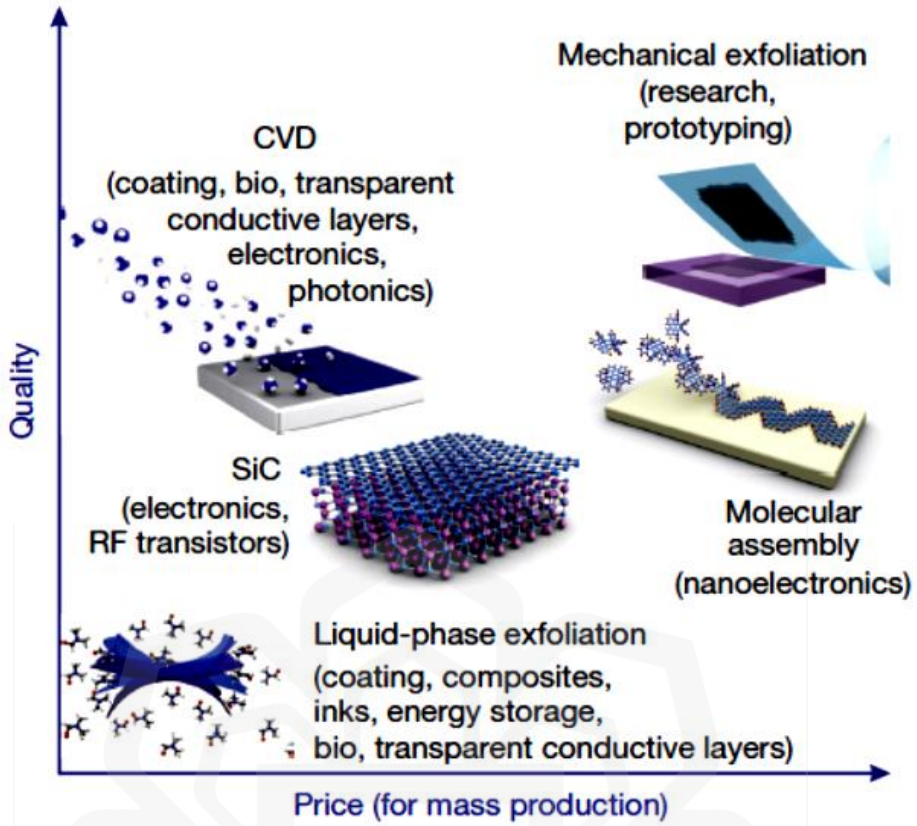

Figure 1.2 Graphene production in terms of methods, cost and quality (Novoselov et al., 2012).

1.1.2 CVD

The use of CVD for graphene production is not a new finding. It is a bottom-up approach where graphene will be deposited on the substrate through chemical reactions of the hydrocarbon species at a temperature range of 573 K to approximately 1273 K. Figure 1.3 shows the schematic diagram of a typical tube-furnace CVD system (Miao, Zheng, Liang, and Xie, 2011).

Carbon sources usually used for graphene deposition comes from hydrocarbons such as ethylene, methane, benzene, ethanol as well as polymers in any particular form but mostly in the gas form (Li et al., 2011; Yao et al., 2011). The gases that enter the reactor will be controlled by MFC, then the reaction will take place at the reactor where the substrate will be placed within it. The reaction can be any pressure condition. The