



**THE INFLUENCE OF DEPOSITION PARAMETERS
AND CRYSTALLINITY OF COPPER SUBSTRATE ON
THE FORMATION OF APCVD DERIVED GRAPHENE**

BY

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ABSTRACT

Since its debut in 2004, graphene has created a ‘gold rush’ in the researches world due to its superlative characteristics that could benefit a lot in many application such as electronics and aerospace. In order to utilize its characteristics into commercial applications, a large scale production of graphene with high quality is necessary. Chemical vapor deposition (CVD) has been reported to be one of the suitable methods to produce graphene in a large scale through decomposition of methane gas, CH₄ at high temperature with the presence of transition metals such as Cu as the catalyst. Typically, the graphene produced is polycrystalline which consists of many small graphene domains that could deteriorate its performance. It is believed that the polycrystallinity of the graphene was produced due to the usage of polycrystalline substrates that might influence the growth of the graphene during CVD. Hence, this study intends to investigate the effects of Cu substrate crystallinity towards formation of graphene in CVD. The graphene was deposited in a closed reactor at 1000 °C with the presence of argon (Ar), hydrogen (H₂) and methane (CH₄) gases of 0.6:0.2:0.2 gas ratios for 30 minutes. The Cu substrates were varied into polycrystalline and single crystal Cu of (100),(110) and (111) orientations. The as-grown graphene was then analyzed using Raman spectroscopy and the optical microscope (OM). The Raman spectra show the existence of graphene peak for all the Cu substrates. The calculation of I_D/I_G ratio revealed that the polycrystalline Cu possessed the lowest amount of defects followed by Cu(100), Cu(110) and Cu(111). Besides that, I_{2D}/I_G ratio fluctuated between 0.22 to 0.34 suggested that the surface orientation is not a major factor that could control the graphene layer thickness at these reaction conditions. It is understood that at high CH₄ concentration, lattice mismatch plays an important role in controlling the growth of the graphene. Large lattice mismatch of Cu(111) causes a highly defective graphene to be produced. These findings thus would give a new insight in the understanding of the graphene growth at high CH₄ concentration in CVD.

خلاصة البحث

ظهر الجرافين لأول مرة في 2004 جعل الباحثين في رحلة دائمة للبحث عن الذهب وهذا يعود إلى خصائصه المميزة والتي قد تفيد في الكثير من المجالات كالإلكترونيات والطيران. ولكي نستغل خصائصه في تطبيقات تجارية، يتوجب علينا إنتاج كمية من الجرافين ذو الجودة العالية. الترسيب الكيميائي للبخار (Chemical vapor deposition) يعتبر أحد أنسب أساليب إنتاج الجرافين عن طريق تحليل غاز الميثان (CH_4) في درجة حرارة عالية مع وجود أحد المعادن الانتقالية كالحاس كحفز للعملية. عادةً، الجرافين المنتج هو متعدد الكريستالات و يحتوي على العديد من عناصر الجرافين الصغيرة التي قد تؤثر سلبًا على الأداء. من المعتقد أن تعددية الكريستالات الخاصة بالجرافين ترجع لاستخدام ركائز متعدد الكريستالات والتي قد تؤثر على نمو الجرافين أثناء عملية الـCVD. لذلك، فهذا البحث يقوم بدراسة تأثير كرسالتية ركيزة الحاس على تكوين الجرافين في الـCVD. تم تخزين الجرافين في مُفاعل في درجة حرارة 1000 مئوية مع وجود غاز الأرجون (Ar) بنسبة 0.6، وغاز الهيدروجين (H_2) بنسبة 0.2، وغاز الميثان (CH_4) بنسبة 0.2 لمدة 30 دقيقة. تم تنويع ركائز الحاس بين الحاس متعدد الكريستالات والحاس ذو الكريستال الواحد بتوجهات مختلفة (100) و(111) و(110). تم تحليل الجرافين الأصلي باستخدام مطيافية رامان و المجهر الضوئي (OM). أشارت نتائج مطيافية رامان وجود ذروة للجرافين لكل ركائز الحاس (Cu). كما أن نتائج نسبة I_D/I_G تشير إلى أن الحاس (Cu) متعدد الكريستالات يحمل أقل نسبة عيوب يتبعه Cu(100) و Cu(110) و Cu(111). إضافة إلى ذلك، تغيرت نسبة I_{2D}/I_G بين 0.22 و 0.34 وهذا الاختلاف يشير إلى أن اتجاه السطح الخارجي لا يمكن اعتباره عامل رئيسي مُساهم في سماكة طبقة الجرافين في ظروف هذا التفاعل. من المعروف أنه في وجود نسب عالية من الميثان، يلعب عدم تطابق الشبكية (lattice mismatch) دورًا مهمًا في التحكم بنمو الجرافين، وذلك يعود إلى أن نسبته العالية في حاس (111) Cu تسببت في إنتاج جرافين به الكثير من العيوب. لذلك، فهذه النتائج قد تلفت نظرنا إلى فهم أكبر لنمو الجرافين في نسب عالية لغاز الميثان أثناء عملية الترسيب الكيميائي للبخار CVD.

APPROVAL PAGE

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DECLARATION

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*In the name of Allah, the Most Gracious and the 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 and upon his companions and
upon all his godly followers.*

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LIST OF ABBREVIATIONS

2D	Two-dimensional
APCVD	Ambient-pressure chemical vapor deposition
CNT	Carbon nanotube
CVD	Chemical vapor deposition
EBS	Electron backscatter diffraction
FCC	Face-centered cubic
FWHM	Full-width half maximum
<i>g</i>	Gas
ITO	Indium Tin Oxide
<i>l</i>	Liquid
LEED	Low-energy electron diffraction
LPCVD	Low pressure chemical vapor deposition
LPE	Liquid-phase exfoliation
M	Metal
MFC	Mass flow controller
MO _x	Metal Oxide
OLED	Organic light-emitting diode
OM	Optical microscope
PET	Polyethylene terephthalate
<i>s</i>	Solid
SSA	Specific surface area
STM	Scanning tunneling microscope
TC	Thermocouple
UHV	Ultra-high vacuum
UHVCVD	Ultra-high vacuum chemical vapor deposition
XRD	X-ray diffraction

LIST OF SYMBOLS

$^{\circ}\text{C}$	degree Celcius
$^{\circ}\text{C}/\text{min}$	degree Celcius per minute
4N	99.99%
5N	99.999%
a	lattice parameter
\AA	angstrom
$a_o(f)$	lattice parameter of the film
$a_o(s)$	lattice parameter of the substrates
atm	standard atmosphere
C_2H_2	acetylene
C_2H_4	ethylene
C_3H_6	propylene
c_{cu}	carbon supersaturation
c_{eq}	equilibrium supersaturation
cm^2	square centimeter
cm^{-2}	reciprocal square centimeter
$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	square centimeter per volt-second
c_{nuc}	critical point of supersaturation
Cu	copper
eV	electron volt
f	lattice mismatch
GPa	gigapascal
I_{2D}/I_G	ratio of 2D-band over G-band intensity
I_D/I_G	ratio of D-band over G-band intensity
J/m^2	Joule per square meter
m^2	square meter
m^2/g	square meter per gram
meV	milli electron volt
mL/min	milliliter per minute
N_b	number of broken chemical bonds
nm	nanometer
Pa	pascal
P_{gas}	gas partial pressure
ppm	part per million
TPa	terapascal
W/mK	Watt per meter-kelvin
θ	theta
λ	wavelength
μm	micrometer
γ	surface energy
ε	bond strength
π	pi
ρ_a	surface atomic density
σ	sigma

CHAPTER ONE

INTRODUCTION

1.1 RESEARCH BACKGROUND

Better performance technology can improve human lifestyles and it has always been the motivation for the development of semiconductor industries for years. In the pursuit to fulfil the demand for a better performance, semiconductor industries have brought silicon (Si) to its limitation of scaling closer to 7 nm (IBM, 2014). Smaller scaling than this value will disrupt its property as a semiconductor material due to the occurrence of quantum tunnelling effects (Moammer, 2015). Accordingly, the search for alternative materials to replace Si is crucial in order to continue the miniaturization trend of the Moore's Law.

This motivation then led to the discovery of two-dimensional carbon-based material, known as graphene in 2004 (Novoselov et al., 2004). In brief, graphene could be described as a single layer carbon packed in a hexagonal lattice structure, as shown in Figure 1.1. Although graphene is very thin at only one atom thick, it possesses several outstanding characteristics, such as high mechanical strength and high electron mobility that could benefit not only the semiconductor industries, but other industries in the field of biomedical, aerospace, and corrosion.

In order to utilize graphene characteristics in commercial applications, a large-scale production of high-quality graphene is necessary. Until recently, the highest quality of graphene produced is by using a mechanical exfoliation technique, which is restricted only to the fundamental study and it is quite impossible to scale-up the production. Therefore, there is an urgent need to find feasible fabrication techniques to produce a large-scale high-quality graphene.

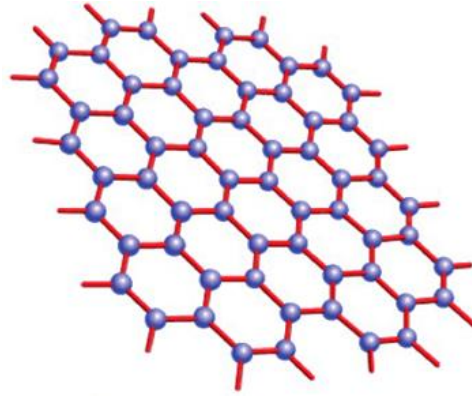


Figure 1.1 The basic structure of graphene (<http://graphene.nus.edu.sg/content/graphene>).

1.2 PROBLEM STATEMENT

Chemical vapour deposition (CVD) is known to be one of the promising techniques to grow graphene in a large area (Bonaccorso et al., 2012; Li, Pan, Awan, & Avent, 2014; Obraztsov, 2009). Basically, during CVD, graphene is grown by dissociating short chains of hydrocarbon gases, such as methane (CH_4) into carbon and hydrogen gases (H_2) at high temperature in the presence of transition metal substrates as the catalyst.

Despite the versatility of the CVD technique to produce large-scale graphene, most of the graphene produced using CVD are polycrystallines, which consist of small crystallite graphene domains that are oriented at different directions and separated by grain boundaries, as shown in Figure 1.2. The presence of grain boundaries has resulted in the degradation of several graphene properties, for example, electronic and mechanical properties (Song et al., 2012; Yazyev & Chen, 2014; Yazyev & Louie, 2010). This issue will subsequently prevent graphene from being utilized, particularly in the electronic industries, as they need a steady and high-quality graphene.

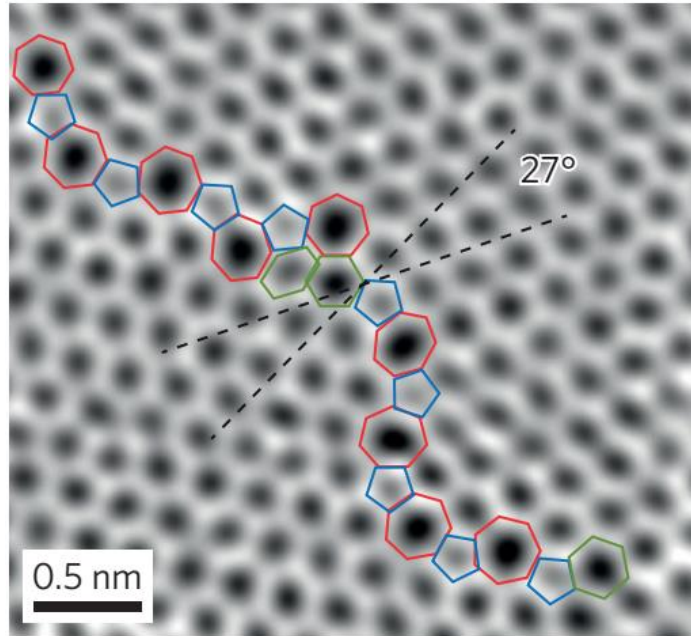


Figure 1.2 TEM images of two graphene domains with 27° rotation connected by the grain boundaries (Huang et al., 2011).

The formation of the polycrystalline graphene is believed to be due to the high density and random nucleation of graphene domains on the Cu surface during CVD. These misaligned graphene domains will then grow and coalesce to form one large continuous layer of graphene, with a high degree of polycrystallinity. Since graphene is grown on top of metal substrates, the existence of multiple surface orientations of the substrates plays an important role in causing the random nucleation of the graphene domains (Wood et al., 2011).

The usage of single crystal substrates might be one of the alternatives to grow single crystal graphene (Ago et al., 2012) since they consist of only one terminated surface orientation throughout the surface. As a result, this will prevent the random nucleation of graphene. There are three common types of surface orientations for face-centered cubic structured (FCC) metal substrates like Cu, which are known as (100), (110) and (111). Ishihara et al. (2011) claimed that higher quality graphene could be

produced on the Cu(111) facet compared to on other Cu facets, such as Cu(100). Ogawa et al. (2012) also made the same claim, whereby Cu(111) could produce a single domain graphene, while Cu(100) consisted of multi-domain graphene with two orientations.

However, none of the previous studies had comprehensively compared the quality of graphene produced on all types of surface orientations. In addition, the influence of graphene formation on each surface orientation is still not fully understood. This study, thus aimed to determine the influence of each surface orientation on the formation of graphene using the CVD technique. A better understanding of the influences of substrate crystallinity towards the formation of graphene might lead to the fabrication of high-quality single crystal graphene.

1.3 RESEARCH OBJECTIVES

The study aims to achieve the following objectives:

- a) To fabricate graphene by using CVD technique at ambient pressure and to identify deposition parameters that influencing its properties.
- b) To study the effect of substrate crystallinity on the formation of graphene.

1.4 SCOPE AND LIMITATION

This study is focused mainly on the influences of substrate crystallinity on the formation of graphene. The qualities of graphene in terms of defects and layer intensities can be quantified by measuring the I_D/I_G and I_{2D}/I_G ratios. The substrates used in this study are restricted only to Cu because it has lower carbon solubility, which could produce a single-layer graphene. In addition, Cu was also chosen because it is highly available and low cost for graphene fabrication. In this study, the Cu

consisted of polycrystalline and single crystal Cu. The chosen fabrication technique was the CVD, conducted at ambient pressure. The reaction parameters were fixed for all types of Cu crystals, namely, the reaction temperature, the partial pressure of the gases involved, and the reaction time according to the optimised conditions conducted using polycrystalline Cu.

1.5 CONTRIBUTION OF THE REASEARCH

The main purpose of this study was to clarify the fundamentals of the effect of substrate crystallinity, especially the surface orientations, towards the quality of graphene produced through the CVD technique. Fundamental aspects such as lattice mismatch, grain boundaries, surface energy, and growth mechanism are also included in the following discussions to provide a better overview of graphene growth.

This study also determined which surface orientation could provide the highest quality graphene. With that, future researches could focus on other factors that could affect the formation of high-quality graphene. The most important point of this study was to identify the importance of using single crystal substrates to produce high-quality graphene.

In addition, this study was also focused on CVD technique conducted at ambient condition. The purpose was to maintain low-cost and retain the simplicity of the process for commercialisation as demanded by the industry.

1.6 THESIS ORGANIZATION

This thesis has been divided into five chapters. **Chapter One** discusses the background of the study, which includes the limitations of the silicon-based technology that led to the discovery of graphene as an alternative material for

semiconductor devices. This chapter also introduces graphene according to its chemical and physical properties, along with the constraints that are preventing it from being commercialized. This chapter also includes problem statements, objectives, scopes, and limitations, as well as the contributions of this study.

Chapter Two covers the literature review related to this research. This chapter discusses substrate crystallinity, mechanisms of the CVD, and reviews previous researches related to graphene. **Chapter Three** discusses the research methodology, which is divided into several subtopics, namely, furnace design and setup, substrates preparation, the growth of graphene, and characterization techniques. In addition, all materials and equipment used in this study are also recorded in this chapter.

Chapter Four presents the results and discussion of this study, which include the analysis results of X-ray diffraction (XRD), the optical microscopy (OM), and the Raman spectroscopy. These analyses were selected to study the effect of substrate crystallinity on graphene formation and its quality.

Chapter Five presents the conclusion and future development subsequent to this study. All conclusions were derived from the result analyses in the previous chapter. Thus, further exploration is needed to better understand graphene growth mechanism using CVD technique for future development of high-quality graphene.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter discusses current graphene fabrication techniques, including the quality and the size of the resulting graphene. This chapter is also focused on the fabrication of graphene using the CVD technique; its basic setup and details of graphene growth mechanism that could lead to the formation of polycrystalline graphene. A review of previous studies has shown that the best way to control the polycrystallinity of graphene was by controlling the reaction parameters and the metal surface conditions. The discussion on the crystallinity of Cu substrates is also included, especially on its effect on the formation of graphene.

2.2 OVERVIEW OF GRAPHENE

As described previously, graphene is a monolayer of carbon, packed in a hexagonal structure and exists in two-dimensional (2D). Graphene is also the basic structure for other graphitic-based carbon allotropes, such as graphite, carbon nanotubes (CNT), and fullerenes, which exist in other dimensionalities, as shown in Figure 2.1 (Geim & Novoselov, 2007). The research on graphene has been started as early as 1947 in order to investigate the electronic properties of graphite (Wallace, 1947). By declining the instability theory of the existence of 2D materials (Fradkin, 1986), graphene was first successfully isolated from graphite in 2004. Novoselov and his team had experimentally isolated graphite layers using a scotch tape (Novoselov et al., 2004). Since then, a tremendous amount of researches has been conducted on graphene. This could be proven by Figure 2.2 that shows the drastic increment of research

publications regarding graphene from 2004 until 2013 (Plume, 2014). Randviir, Brownson, and Banks (2014) also estimated that about 40 publications regarding graphene were published per day in 2013. The reason for this fame is its superlatives properties that could be beneficial in future applications, especially in electronics, aerospace, and medical industries.

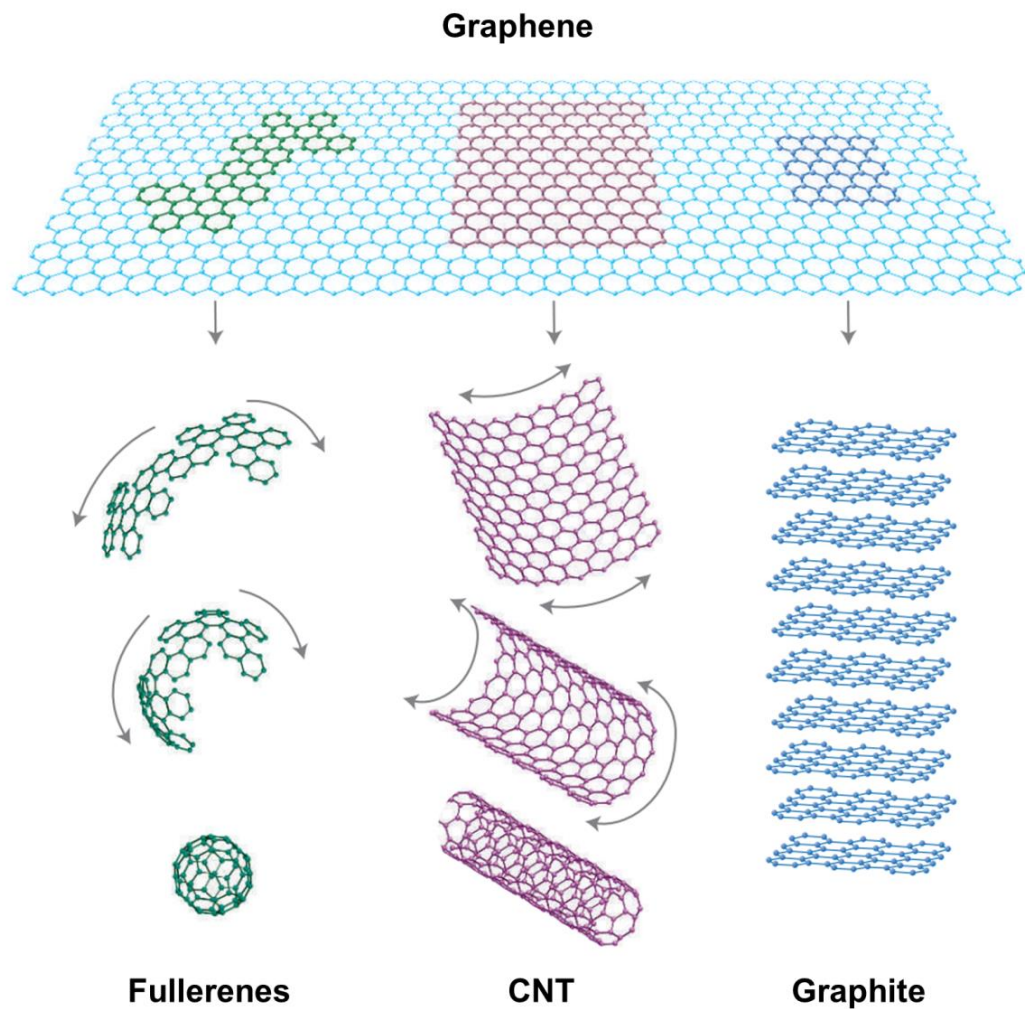


Figure 2.1 Graphene as the basic structure for other graphitic-based allotropes of carbon; fullerenes, CNT and graphite (Geim & Novoselov, 2007).