INFLUENCE OF GAS FLOW INSIDE CIRCULAR TUBE USING COMPUTATIONAL FLUID DYNAMICS FOR GRAPHENE SYNTHESIS VIA CHEMICAL VAPOUR DEPOSITION

BY

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ABSTRACT

Since its discovery in 2004, graphene has been tipped as the material that can boost various applications' development. Among the methods developed to produce graphene in large-scale is chemical vapour deposition (CVD). CVD is viewed as the most cost-efficient method besides having the potential to synthesize high-quality graphene. Despite this potential, it requires excellent control in various aspects, including fluid dynamics inside the CVD tube. Further studies need to be done especially near the substrate to understand further the effect of fluid dynamics on the graphene synthesis process via CVD. One of the subsidiaries of fluid dynamics near the substrate was the boundary layer thickness. This is the first layer where carbon needs to pass through to be at the substrate's surface. Changing the tilting angle is one of the ways to change the boundary layer thickness. In this study, the simulation was done for horizontal CVD with different tilting angle, and then graphene was synthesized in the lab based on the simulation results. This is to understand the effect of substrate tilting to the fluid behaviour inside the CVD tube and the graphene produce. The simulation was done using ANSYS® FLUENT where a 1m tube was divided into three sections which are the calm, heating and outlet section. A constant temperature of 1273K was supplied at the heating section wall, and the other two sections were exposed to room temperature. A substrate was placed in the heating section with a tilting angle of 8°,15°,30°,45°,60° and 75°. Based on the simulation at a 0° angle, the boundary layer thickness becomes thicker as the flow moves from the front to the rear of the substrate. For other tilting angles, the boundary layer thickness became thinner as the flow moved from the front to the end of the substrate. Higher tilting angle produced a thinner boundary layer, but the non-uniformity of the boundary layer thickness over the substrate surface also became more prominent. Tilted substrate also caused vortices at the side of the substrate where the larger the tilting angle, the larger vortices produced. Therefore, lower substrate angle was preferred for graphene synthesis as it has a more uniform boundary layer and smaller vortices. For the synthesis process, the 1cm x 1cm copper substrate was placed inside the CVD tube with a tilting angle of 8° and 15° with a flow rate of 100 sccm, 200sccm, and 300sccm for each synthesis process. A larger substrate angle was also chosen, which is 60° but only for 300 sccm of flow rate. Based on the Raman spectroscopy result, higher velocity will give thinner graphene for 8° and 15° substrate angle. For 8° substrate angle, the defect ratio increases as the flow rate increase while for 15°, it is vice versa. The graphene produce on top of the 8° and 15° substrate is constantly thin throughout the substrate, but for 60° substrate angle, the graphene becomes thinner from the front to the rear of the substrate. The defect on graphene produce on 60° substrate is also very high. This shows that the tilting angle plays a vital role in changing the graphene quality produced via CVD.

ملخّص البحث

منذ اكتشاف الجرافين في عام 2004 وقد تم التكهن على أنها المادة التي يمكن أن تعزز التطور في مختلف التطبيقات. ومن بين الأساليب المتقدمة لإنتاج الجرافين عبر نطاق واسع هو عن طريق الترسيب الكيميائي للبخار (CVD). CVD تعتبر الطريقة الأكثر فعالية من حيث التكلفة وإلى جانب امتلاك الإمكانات لتوليف جرافينات عالية الجودة. وعلى الرغم من هذه الإمكانات, إلا أنها تتطلب سيطرة كبيرة في مختلف الجوانب بما في ذلك السلوك الديناميكي السائل داخل أنبوب الـCVD. هناك حاجة إلى مزيد من الدراسات وخاصة بالقرب من المادة المتفاعلة من أجل فهم تأثير ديناميكيات السوائل على عملية تصنيع الجرافين عبر الـCVD. سماكة الطبقة الحدودية تعتبر ة واحدة من فروع ديناميكية السوائل بالقرب من المادة المتفاعلة. وهذه هي الطبقة الأولى حيث يحتاج الكربون إلى المرور من أجل أن يكون على سطح المادة المتفاعلة. يعد تغيير زاوية الإمالة إحدى طرق تغيير سماكة الطبقة الحدودية. في هذه الدراسة, تم إجراء المحاكاة للترسيب الأفقي للبخار الكيميائي بإستخدام مادة متفاعلة مختلفة وقد تم تصنيع الجرافين في المختبر بناءً على نتيجة المحاكاة. وهذا لفهم تأثير إمالة المادة المتفاعلة إلى سلوك السوائل داخل أنبوب الـCVD وإنتاج الجرافين. وقد تم إجراء المحاكاة بإستخدام ANSYS® FLUENT حيث تم تقسيم أنبوب طوله متر واحد إلى 3 أقسام وهي: القسم الهادئ, قسم التدفئة وقسم للمخرج. ودرجة حرارة ثابتة تبلغ 1273K قد زود في جدار قسم التدفئة وأما القسمان الآخران فقد بقيا على درجة حرارة الغرفة. المادة المتفاعلة بزاوية الركيزة بمعدل 8°, 15°, 30°, 45°, 60° و 75° تم وضعه في قسم التدفئة. إستنادا على المحاكاة بزاوية 0 أصبح سمك الطبقة الحدودية أكثر سمكاً حيث يتحرك التدفق من الأمام إلى الجزء الخلفي من المادة المتفاعلة. بالنسبة للزوايا الأخرى,سمك الطبقة الحدودية يصبح أرق حيث يتحرك التدفق من الأمام إلى الجزء الخلفي من المادة المتفاعلة. كلما كانت الزاوية أعلى كلما تنتج طبقة حدودية رقيقة ولكن الفرق هنا يكمن في سمك الطبقة الحدودية ستصبح أكبرعلى مدار المادة المتفاعلة وبالتالي تجعلها غير موحدة. وأيضا أي مادة متفاعلة بزاوية تسبب دوامات على جانبها, وكلما كانت الزوايا أكبر كلما نتجت دوامات أكبر. وبناء على ذلك, تم إختيار زاوية أصغر للمادة المتفاعلة من أجل تأليف الجرافين لأنها تحتوي على طبقة حدودية أكثر إتساقا وتسبب دوامات أصغر. بالنسبة لعملية التوليف, 1 متر x 1 متر من الركيزة النحاسية تم وضعها داخل أنبوب الـCVD بزاوية معدلها 8° و 15° مع تدفق بمعدل 100sccm, 200sccm, و 300sccm لكل محاكاة. بالإضافة إلى أن زاوية ركيزة أكبر قد تم إختيارها بمعدل 60° ولكن من أجل 300sccm من معدل التدفق. وحسبا لنتيجة Raman للتحليل الطيفي, لكل 8° و 15° زاوية الركيزة, بسرعة أعلى قد تنتج جرافين أكثر رقاقة. ولـ 8° زاوية ركيزة, تزداد نسبة الخلل مع زيادة معدل التدفق بينما بنسبة 15° تكون النتيجة على النحو الآخر. الجرافين المنتج للركيزة فوق 8° و 15° تكون رقيقة بإستمرار في جميع أنحاء الركيزة ولكن إذا كانت زاوية الركيزة بنسبة 60° سيصبح الجرافين أكثر رقاقة من الأمام إلى الجزء الخلفي من الركيزة. الخلل الناتج من الجرافين الموضوع على ركيزة 60° سيكون مرتفعا جدا. وهذا يوضح أن زاوية الركيزة تلعب دورا حيويا يمكن أن يغير جودة الجرافين التي تم إنتاجها عبر الـCVD.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Mechanical Engineering).

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LIST OF ABBREVIATIONS

CFD	Computational fluid dynamics
CVD	Chemical vapor deposition
GaAs	Gallium arsenide
HOPG	High ordered pyrolytic graphite
Si	Silicon
SiO_2	Silicon oxide
MIT	Massachusetts Institute of Technology
Re	Reynold number
Gr	Grashof number
Nu	Nusselt number
Pr	Prandtl number
Ri	Richardson number
Ra	Rayleigh number
2D	Two dimensional
LP	Low pressure
AP	Atmospheric pressure
LPCVD	Low-pressure chemical vapour deposition
APCVD	Atmospheric pressure chemical vapour deposition
CNT	Carbon nanotube
I_D/I_G	Defect ratio
I_{2D}/I_G	Monolayer ratio

LIST OF SYMBOLS

σ	Sigma
π	pi
μ	Viscosity
v_y	Velocity along y
v_x	Velocity along x
g	Gravity
ρ	Density
p	Pressure
d	Diameter
l_c	Calm section
l_h	Heated section
l_o	Outlet section

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Graphene is a layer of interconnected carbon ring that is an atom thick connected in honeycomb hexagonal lattice pattern. Meanwhile, if a few layers of graphene were stacked together it becomes graphite which is a substance used as pencil lead, if it is rolled in a cylindrical shape, it becomes carbon nanotube, and if it is wrapped into a rounded form it becomes fullerenes (Neto, Guinea, & Peres, 2006; Yu et al., 2016)

Graphene is the strongest material discovered by human, which is 100 times stronger than steel (Hibino, 2013) and graphene has superior carrier mobility and lower resistivity. This makes graphene the most outstanding material for conductor and semiconductor in nano electric such as photovoltaic cell, energy storage, ultrafiltration, optical electronics and many more (Bhaviripudi, Jia, Dresselhaus, & Kong, 2010; Muñoz & Gómez-aleixandre, 2013). But all of these outstanding characteristics are only found in pristine graphene. Graphene that had been produced up to this day still not able to be used for all of the application stated above because there is a structural imperfection in the graphene produce("15 Years of Graphene Electronics," 2019; Bhaviripudi et al., 2010; Huang et al., 2011; Kleijn et al., 2007; Pollard et al., 2014). A lot of researches have been done to overcome this problem and try to produce high-quality graphene on a large scale (Chen, Dai, et al., 2015; Li, Huang, & Li, 2015; Li et al., 2012; Novoselov, Geim, Morozov, & Jiang, 2004).

There are a few ways to produce graphene. The best method of producing graphene will be exfoliated graphene, which is presently the closest to flawless (Aydin et al., 2015; Li et al., 2012). Other than that, there is epitaxial growth (Tetlow et al., 2014), reduction of graphene oxide(Li, Wang, et al., 2009), and chemical vapour deposition (CVD). Among these methods, CVD has been the most promising approach because it is relatively inexpensive, transferable, and can produce high quality and large-area graphene films (Chen, Zhang, & Chen, 2015; Deokar et al., 2015; Muñoz & Gómez-aleixandre, 2013).

In CVD of graphene, most researches were focused on material properties such as, gas composition (Bhaviripudi et al., 2010; Deng, Liu, & Peng, 2019; Shin, Dresselhaus, & Kong, 2014), substrate use (Muñoz & Gómez-aleixandre, 2013; Novoselov & Castro Neto, 2012; Pham, Huynh, Do, & Ngo, 2019) and temperature that affects the graphene synthesis (Chen, Zhang, et al., 2015; Frank & Kalbac, 2014; Seah, Chai, & Mohamed, 2014). Most of these works were experimental works where the parameters selection for the experimental setups are based on the researcher's experiences. Furthermore, the experimental works required a lot of funds to sustain a research project. However, with the advancement of computer technology nowadays and the ability of the computational fluid dynamics (CFD) software today, it could cut the cost for an experimental project by predicting the outcome for every experiment and by describing what is the physical phenomena within an experimental setup. Experimental work can be carried out after a simulation work to confirm and validate the simulation results.

In addition, the CFD method also enables researchers to study parameters such as the boundary layer effect which is invisible to the naked eyes. The boundary layer, which is the first layer that carbon needs to pass through before reaching the substrate (Bhaviripudi et al., 2010), is mostly neglected by most researchers. By controlling the boundary layer thickness, it could enhance the production of graphene by producing uniform graphene on top of the substrate (Chen, Zhang, et al., 2015; Kleijn et al., 2007). Thus, more research should be done to further understand the effect of boundary layer on the graphene produce.

1.2 STATEMENT OF PROBLEM

To date, there is no single method to mass-produce high-quality graphene. Many aspects need to be discovered, and a lot of research needed to get the best condition to synthesize graphene. CVD processes involve heat transfer, mass transfer, surface reaction, and gas-phase reaction. All these processes are interdependent and to produce an optimized condition to synthesize graphene based on experiment alone is almost impossible. In an experiment, the physical phenomena and the gas state inside the CVD tube is not known thus making it difficult for researchers to explain the influence of parameters in CVD setup for graphene synthesis. Besides that, a lot of variables is restricted to machine availability, and the cost is high. Introducing CFD into this research area will significantly improve and optimize the development process. CFD not only can provide a graphical representation of data that show condition inside the CVD tube but also the simulation is only restricted to the computer power available, and the cost could be reduced.

On the other hand, boundary layer acts as the first layer that carbon needs to pass through before it could be diffused on the substrate and produce graphene on it. Therefore, it is essential that more studies need to be made to understand further about the boundary layer thickness effect to the graphene produce. These can be achieved by changing the tilting angle of the substrate that will cause the boundary layer thickness to change.

1.3 RESEARCH OBJECTIVE

This research project aims to achieve the following objectives:

1. To determine the effect of substrate tilting angle to the flow pattern near the substrate and the boundary layer on top of the substrate.
2. To synthesize graphene based on the studied tilting angle and analyze its effect on graphene quality by using Raman Spectroscopy through analyzing the monolayer ratio (I_{2D}/I_G) and defect ratio (I_D/I_G)

1.4 RESEARCH SCOPE

This study mainly focuses on the effect of fluid mechanics inside the CVD tube with the gas used for the simulation is single gas which is argon as it is the primary gas use for graphene synthesis via CVD. The chemical reaction that will also influence graphene quality is not considered for the simulation. The graphene quality will be determined by using graphene synthesis in the lab using the CVD method, and then it will be characterized by using Raman Spectroscopy.

CHAPTER TWO

LITERATURE REVIEW

2.1 GRAPHENE

Graphene is a layer of graphite. In theoretical words, graphene is an allotrope of carbon that is made of very tightly bonded carbon atoms organized into honeycomb hexagonal lattice, as shown in Figure 2.1. Graphene was found by Geim and Novoselov at the University of Manchester in the year 2004 (K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, 2016) but the idea of graphene was introduced by Boehm, Setton and Stumpp (1994). In the year 2010, Geim and Novosolov had been awarded a noble prize in physic for their work.

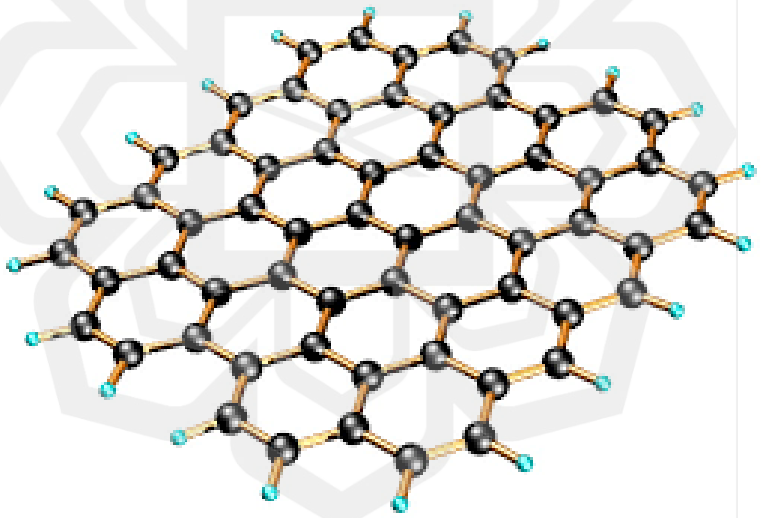

Figure 2.1 The structure of graphene (Lasky, 2015)

Graphene is very strong material due to its crystal structure which is a single layer of the carbon atom that is in the form of the hexagonal lattice with each of the carbon atoms shares one sigma (σ) bond. The fourth bond is a pi (π) bond, oriented in the z-direction (out of the plane). One can visualize the π orbital as a pair of symmetric lobes oriented along the z-axis and centre on the nucleus (Cooper et al., 2012). A three-dimensional stack of graphene sheets is graphite, which is a familiar material in daily life. Graphene is also the basic element of fullerenes and carbon nanotubes, which are well-known carbon nanostructures (Neto et al., 2006).

Graphene possessed several physical strengths that are more advantageous compared to other materials. It has a breaking strength of 42 Nm^{-1}, which is 100 times stronger than steel. From an electrical perspective, graphene is a very potent charge carrier, with mobility of 200000 $cm^2V^{-1}s^{-1}$ at room temperature. This is 100 times higher than silicon. Graphene has high thermal conductivity, making it attractive for photovoltaic cells, which is ten times higher than Cu. Graphene's optical absorption coefficient of 2.3%, which is about 50 times higher than the optical absorption coefficient of gallium arsenide (GaAs) make it more attractive to many electronics applications. All these properties had attracted many researchers to study more about graphene as it can be used in a lot of fields.

2.2 METHOD OF PRODUCING GRAPHENE

There are a few methods to produce graphene such as sputtering, mechanical exfoliation, epitaxial growth, and CVD. Among this method, CVD is considered the most promising way in terms of cost and quality for mass production of graphene (Novoselov et al., 2012). Figure 2.2 shows the comparison of graphene quality from different methods.

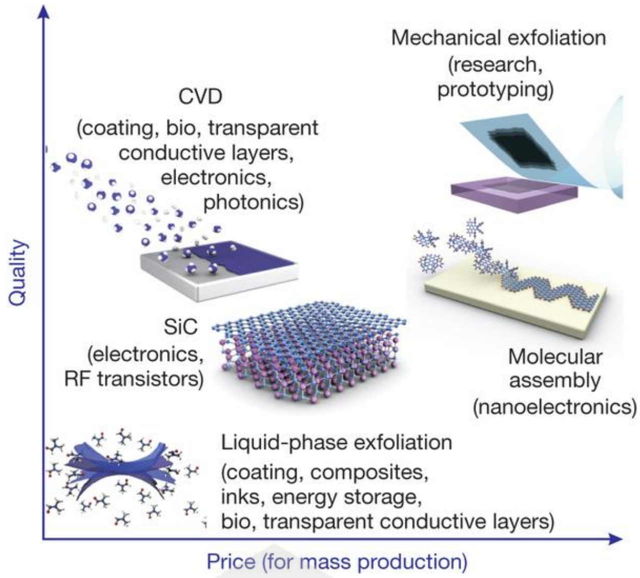

Figure 2.2 Comparison of graphene growth methods with the quality and the cost of each technic. (Novoselov et al., 2012)

2.2.1 Mechanical Exfoliation.

Mechanical exfoliation can produce high-quality graphene, but the cost is very high. This technique is not suitable for mass production of graphene, but it is good at producing a small amount of graphene for research purposes. The first graphene was found using this technique.

This technique is relatively very easy. First, as in Figure 2.3(a) fresh piece of Scotch tape is taken. The adhesive side is pressed onto the Highly Ordered Pyrolytic Graphite (HOPG) for about ten seconds. The tape is then gently peeled away with thick shiny layers of graphite attached to it as in Figure 2.3 (b). The tape with layers from the HOPG was refolded upon a clean adhesive section of the same piece of the tape, and then the tape is unfolded. This process is repeated several times until the end of the tape is no longer shiny but becomes dark/dull and grey. These graphite layers on the tape are transferred onto the surface of the Si/SiO_2 wafers by gently pressing them onto the tape for some time (figure 2.3(c)) and then peeling off (figure 2.3(d)). The wafers are then examined using various characterization techniques.

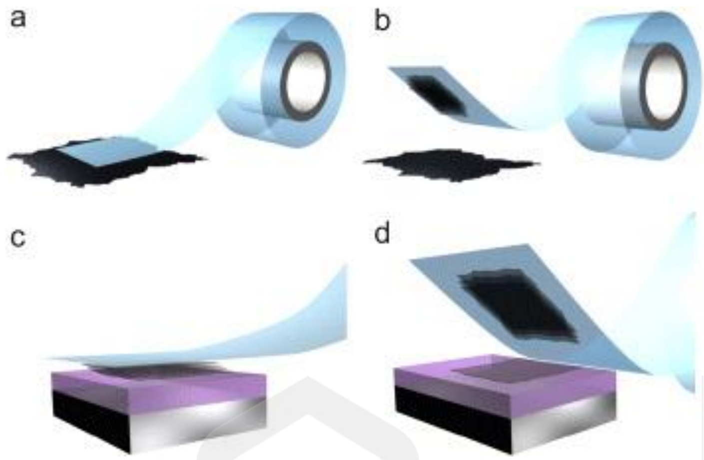

Figure 2.3 Illustration of mechanical exfoliation technics in producing graphene. (Novoselov et al., 2012)

2.2.2 Liquid Phase Exfoliation

This method is about the similar as mechanical exfoliation where graphite was exfoliated to get graphene. Instead of using scotch tape to mechanically exfoliate the graphite, graphite exposed to a solvent that will split the graphite into individual platelets and continue to expose the graphite platelets will turn out to be a few monolayer flakes (Hernandez et al., 2008). These flakes can be deposited as a thin film on any surface.

Beside using graphite or graphite oxide, unzipping of single-wall carbon nanotubes can also be used to get graphene using liquid phase exfoliation. This is more expensive, but better quality and uniform graphene can be harvest(Jiao et al., 2009; Kosynkin et al., 2009).

Although this method is cheap, the quality of graphene produce is far from perfect. This method had been used to produce graphene based paint that eventually can be printed on electronics and act as electromagnetic shielding, heat dissipation, smart windows and many more (Novoselov et al., 2012).

2.2.3 Chemical Vapor Deposition (CVD)

Chemical vapour deposition (CVD) can be traced back to prehistory. MIT chemical engineer, Professor Karen Gleason said in MIT news website “When the cavemen lit a lamp and soot was deposited on the wall of a cave,”(Chandler, 2015) that was the basis of CVD. Basically, CVD is a process for the synthesis of thin films via chemical reactions between molecules in the gas phase and on a surface of a metal substrate.

Nowadays, CVD is basic in manufacturing thin films such as in solar cell, and many electronic devices. CVD opened the way in producing a variety of material that cannot be produced using other technique. CVD has the capability of producing highly dense and pure materials. Besides that, it can produce uniform films with good reproducibility and adhesion reasonably high deposition rates. Using CVD, the surface morphology and orientation of the end products may be controlled by controlling the parameters in the CVD process. Other than that, the cost by using this technique is relatively cheap compared to other techniques(Novoselov et al., 2012). The comparison to other synthesis methods can be seen in Figure 2.2. compared to other popular techniques, CVD could produce good quality graphene at a lower price.

In 2009 Xuesong et al (2009) had established a large area high quality and uniform graphene synthesis via CVD which is in order of centimetre. Before this could be established, most graphene synthesis could only be synthesis in less than 1000μm^2 in size. The finding by Xuesong et al (2009)is a huge breakthrough that confirms it is possible to produce high quality and uniform graphene using the CVD method. The