Atmospheric Pressure Chemical Vapour Deposition Growth of Graphene for the Synthesis of SiO$_2$ Based Graphene Ball

(Pertumbuhan Grafin melalui Endapan Wap Kimia Tekanan Atmosfera untuk Sintesis Bebola Grafin Berasaskan SiO$_2$)

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ABSTRACT

Graphene is a prominent carbon nanomaterial with fascinating characteristics such as high conductivity and very high charge carrier mobility at low temperatures. Numerous synthesis methods for graphene have been established. Chemical vapour deposition (CVD) is among the most successful methods to fabricate high-quality graphene. However, metal-catalyzed growth is used in virtually all of the CVD techniques mentioned. To remove these metal catalysts and relocate the graphene to the necessary dielectric substrate (SiO2/Si or quartz), complex and sophisticated post-growth methods must be used, which limits the usage of graphene in practical electronic components. In the present work, we conducted a preliminary study to determine the suitable methane(CH$_4$) flowrate, which could be used to synthesise SiO$_2$ based graphene ball. Few-layer graphene was grown on a large area of copper(Cu) surface using 20 sccm CH$_4$ in atmospheric pressure CVD (APCVD). The influence of CH$_4$ flowrate on graphene growth has been investigated. Graphene was deposited on a metal catalyst substrate at optimum temperatures of 1000 °C.

Keywords: Atmospheric pressure chemical vapour deposition; graphene; graphene ball; methane flowrate

ABSTRAK

Grafin merupakan bahan nano karbon ulung dengan ciri-ciri menarik seperti mempunyai sifat kekonduksian ion yang tinggi dan mobiliti pembawa cas yang amat tinggi pada suhu rendah. Banyak kaedah sintesis grafin yang mantap dibuat dan telah diiktiraf. Endapan wap kimia (CVD) merupakan antara kaedah yang paling berjaya dalam menghasilkan grafin berkualiti tinggi. Walau bagaimanapun, pertumbuhan logam pemangkin telah digunakan dalam hampir semua teknik CVD. Untuk menyingkirkan pemangkin logam ini dan memindahkan grafin ke substrat dielektrik yang diperlukan (SiO$_2$/Si atau kuarza), kaedah pascapertumbuhan yang kompleks dan canggih perlu digunakan dan hal ini telah mengehadkan penggunaan grafin dalam komponen elektronik praktikal. Dalam penyelidikan ini, kami telah menjalankan kajian awal untuk menentukan kadar aliran metana (CH$_4$) yang sesuai, yang boleh digunakan untuk mensintesis bebola grafin berasaskan SiO$_2$. Grafin beberapa lapisan telah ditanam di kawasan besar permukaan tembaga (Cu) menggunakan 20 sccm CH$_4$ dalam CVD tekanan atmosfera (APCVD). Pengaruh kadar aliran CH$_4$ pada pertumbuhan grafin telah dikaji. Grafin telah didepositkan pada substrat pemangkin logam pada suhu optimum 1000 °C.

Kata kunci: Bebola grafin; endapan wap kimia tekanan atmosfera; grafin; kadar aliran metana

INTRODUCTION

Graphene is a stunning two-dimensional carbon allotrope composed of a monolayer of sp^2 bonded carbon atoms with a carbon atom at each vertex in a hexagonal configuration. The key study of Novoselov et al. (2004) ignited interest in graphene. Three-dimensional graphite is formed by piling graphene layers; carbon nanotubes are formed by rolling graphene sheets, and fullerene is a zero-

dimensional graphene. Graphene has many remarkable properties, including electron mobility greater than 2.105 cm^2/Vs at room temperature, 1 TPa of Young's Modulus, approximately 5000 Wm/K thermal conductivity at room temperature, 2.3% optical absorption, and the ability to be functionalized by a wide range of organic species (Cao 2014; Zhen & Zhu 2018; Zhu et al. 2010). The list of applications that could benefit from graphene is possibly limitless, for instance in biomedical applications (Hamzah et al. 2017), biosensors (Jamil et al. 2018), field-effect transistors (Khalid et al. 2015), energy generation and storage (Son et al. 2017), and could contribute as a leading material in the fight against pneumonia outbreak of coronavirus disease 2019 (COVID-19) (Palmieri & Papi 2020) to mention a few.

As a result, there are numerous investigations on graphene in the literature. There are various ways of producing graphene, each with its own set of advantages: Mechanical exfoliation (Yi & Shen 2015), synthesis of silicon carbide (Mishra et al. 2016), liquid-phase exfoliation (Xu et al. 2018) and CVD. Among all, the CVD method has been successfully utilized to grow high-quality graphene and has proven to be reliable. Much effort has been expended to improve the overall performance of the CVD method, such as studying the elastic strain energy and the influence of surface energy (Sirat et al. 2019), understanding the relationship between parameters affecting the quality of CVD-grown graphene and metal substrate selection (Ani et al. 2018) and investigating gas-phase dynamics during graphene deposition (Fauzi et al. 2020).

CVD refers to the process of depositing material as a thin film onto substrates from vapour species through chemical reactions. The most common carbon precursor is CH_4 gas, which is delivered to the reaction chamber through a gas distribution system. The CVD process is classified into two categories based on total reaction pressure: low-pressure CVD (LPCVD) and atmospheric pressure CVD (Jafari et al. 2014) and atmospheric pressure CVD (APCVD). In terms of low-cost and simple graphene generation, APCVD is likely the most appealing technology since it eliminates the need for pumping devices (Reckinger et al. 2013). Because of its low carbon solid solubility (<0.001 %) and comparably limited catalytic effect on CH_4, as well as its inexpensive cost, Cu is the most commonly used substrate for graphene deposition (Antonova 2013). Temperature (Nalini et al. 2018), pressure (Fauzi et al. 2020), growth and annealing time (Nguyen et al. 2013; Wang et al. 2016) are only a few of the parameters that might impact graphene growth. The gas flow rate is another important factor to consider.

However, in order to make practical electrical components, the as-grown graphene must be transferred from the metal catalyst surface to another suitable substrate via a series of complex operations. Various impurities, folds, defects, and cracks in graphene are unavoidable throughout this transfer technique. This might lead to a decrease in the quality and properties of graphene films. As a result, graphene sheets must be grown directly on dielectric substrates without any transfer step.

In this research, we show how to develop a few layers of graphene utilising the CVD technique over a broad area of Cu surface using CH_4 at atmospheric pressure. In particular, we conducted a preliminary investigation to establish the optimal methane (CH_4) flowrate for the production of SiO_2 nanoparticles-based graphene balls.

EXPERIMENTAL DETAILS

Before graphene growth, the Cu foil (99.9% purity; 50 μm thick) 10 by 10 mm is sonicated in ethanol for 5 min, then in distilled water for 5 min, subsequently in IPA for 5 min, and finally gently blown dry with nitrogen. The substrate was cleansed to eliminate any leftover organic elements and contaminants. As illustrated in Figure 1, the sample is immediately deposited on a porcelain boat placed into a horizontal quartz tube (inner diameter = 25.4 mm, length = 1200 mm) at room temperature. Before graphene growth, the quartz tube was sealed and then purged with Ar/H_2 for 30 min under atmospheric pressure. This procedure is carried out to flush the air contained in the quartz tube. While Ar/H_2 gas flowed, the system was heated to 1000 °C at a ramping rate of 33 °C/min. The Cu foil was annealed at 1000 °C for 30 min in an Ar/H_2 environment to enhance the Cu grain size and assure the elimination of native oxide and a smooth Cu surface. Graphene is then grown by admitting mixed gases of Ar/H_2 and CH_4 at various flowrates (Table 1) for 30 min. In this investigation, the overall flow rate was set at 100 sccm. After growth, CH_4 was shut off for the cooling step. The graphene/Cu samples were cooled from 1000 °C to room temperature using an Ar/H_2 environment, as illustrated in Figure 2.

Using the bubbling process, the graphene/Cu samples were subsequently transferred to glass substrates. To guarantee good adherence of the PMMA on the graphene/Cu samples, a thin layer of PMMA was spun-coated on them at 4000 rpm for 10 s before baking them at 140 °C for 4 min. Using an aqueous $FeCl_3$ solution, the PMMA/graphene was removed from the copper foil.

The floating PMMA/graphene film is washed in distilled water, transferred to a SiO$_2$ piece, and air dried. Finally, PMMA is removed from the sample by immersing it in acetone for 10 min.

To determine the existence of graphene on Cu substrates, Raman spectroscopy was performed using confocal micro-Raman imaging spectroscopy (DXR2Xi, Thermo Scientific). The wavelength of excitation was 532 nm, and the exposure duration was 0.1 s. A 900 line mm-1 diffraction grating and a 50 μm spectrograph aperture were employed. These studies were carried out directly on Cu substrates, with no graphene transfer procedure. Field emission scanning electron microscopy (FESEM, Zeiss Merlin) was used to examine the sample's morphology after they had been transferred to SiO$_2$ substrates.
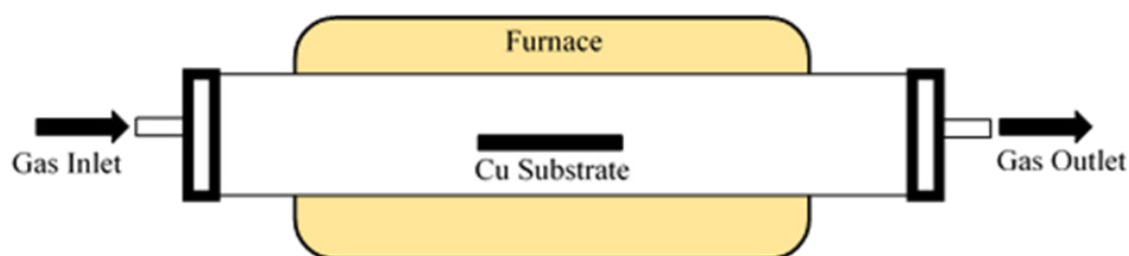

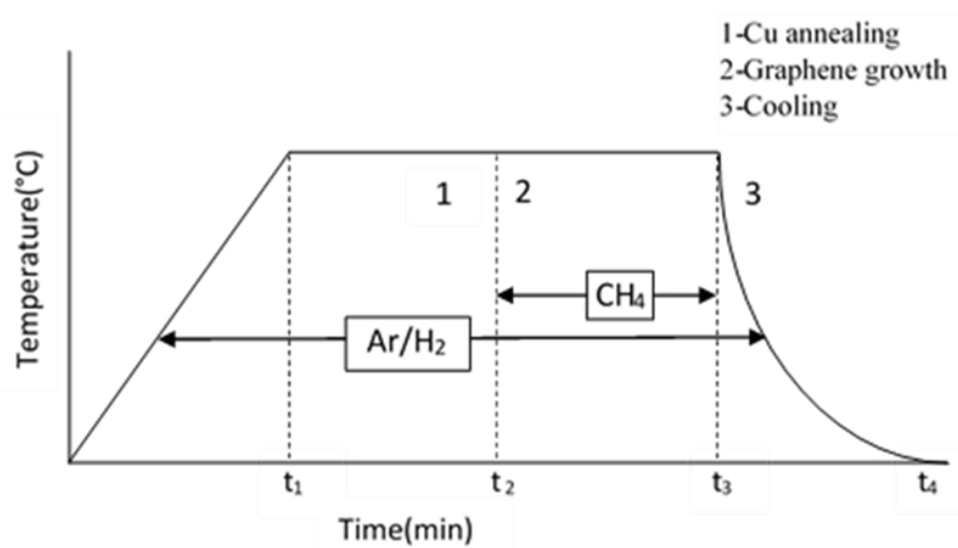FIGURE 1. Experimental setup of APCVD graphene growth on Cu foil

FIGURE 2. Graphene growth protocol

TABLE 1. Evaluated flow rate for the growth process

Heating	Purging	Growth flow rate [sccm]		Cooling
T (°C)	Time [min]	CH$_4$	Ar/H$_2$	Gas
1000	30	60	40	Ar/H$_2$
1000	30	20	80	Ar/H$_2$

RESULTS AND DISCUSSION

Raman spectroscopy has advanced into a powerful, non-invasive tool for analyzing graphene and related materials (Childres et al. 2013). This spectroscopic approach has been used to assess the structural and physical characteristics of graphitic components, showing valuable information on the atomic structure of edges, the presence of disorder, defects, charges, and strain (Moreno-Bárcenas et al. 2018). Graphene Raman spectra are based on the D, G, and 2D bands, which are expected to be about 1350 cm^{-1}, 1580 cm^{-1}, and 2680 cm^{-1}, respectively (Gajewski et al. 2016). D band provides a good indicator for determining the amount of disorder in the sample. The G band corresponds to the in-plane vibration of sp^2 carbon atoms, whereas the 2D band represents graphene thickness (Dresselhaus et al. 2010). I_D/I_G ratio measurement is a well-known tool for determining defect density, whilst I_{2D}/I_G ratio measurement offers details on the number of layers in a graphene sample.

In this study, the CH_4 gas flowrate was investigated by keeping all other parameters constant. Figure 3 depicts the Raman spectra of graphene produced at various CH_4 flowrates. Only the sample grown with a flowrate of 20 sccm of CH_4 shows the presence of standard graphene D, G, and 2D-bands, whereas the sample grown with a flowrate of 60 sccm of CH_4 shows the formation of amorphous carbon. The 2D band was clearly visible in the 20 sccm sample but not in the 60 sccm sample when the flowrates were compared.
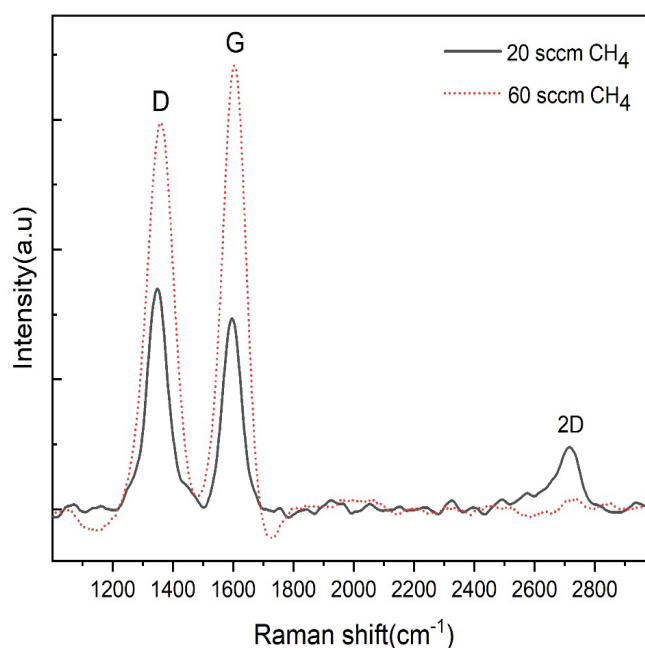

FIGURE 3. Raman spectra of graphene grown with different CH_4 flowrate

The peak ratios of I_D/I_G and I_{2D}/I_G were calculated to assess the quality of graphene on Cu foil. Table 2 displays the computed ratios. Based on the high I_D/I_G ratios, defects were discovered in the 20 sccm sample (Childres et al. 2013). Its existence, however, is predicted due to surface imperfections in the Cu substrate (Zhang et al. 2016). Furthermore, in this work, our CVD reactors operate at atmospheric pressure where some oxygen will be present. The presence of oxygen in the CVD reactors most likely contributes to defects during the formation of graphene grains on the Cu foil (Robinson et al. 2013).

In the 20 sccm sample, the I_{2D}/I_G ratio was 0.324. The existence of graphene from a few layers to multilayers is indicated by an I_{2D}/I_G less than 1 (Nguyen et al. 2013). The I_{2D}/I_G ratio of the 20 sccm sample was 0.324, indicating the development of a few layers of graphene. This information is critical in understanding why low flow rates are required for higher graphene quality. This indicates that reducing the flow of CH_4 gas results in fewer flaws and an increase in the thickness and uniformity of graphene quality.

TABLE 2. Evaluated flow rate for the growth process

Flowrate [sccm]	I_D/I_G ratios	I_{2D}/I_G ratios
60	NA	NA
20	1.146	0.324

The morphology of graphene was examined using a field emission scanning electron microscope (FE-SEM). Figure 4 shows a 20 sccm sample with a continuous graphene sheet on SiO_2 substrates. Graphene domains tend to merge with one other, leaving only tiny gaps in between. Each graphene domain is usually flat and smooth, which is ideal for the production of graphene electrical devices.
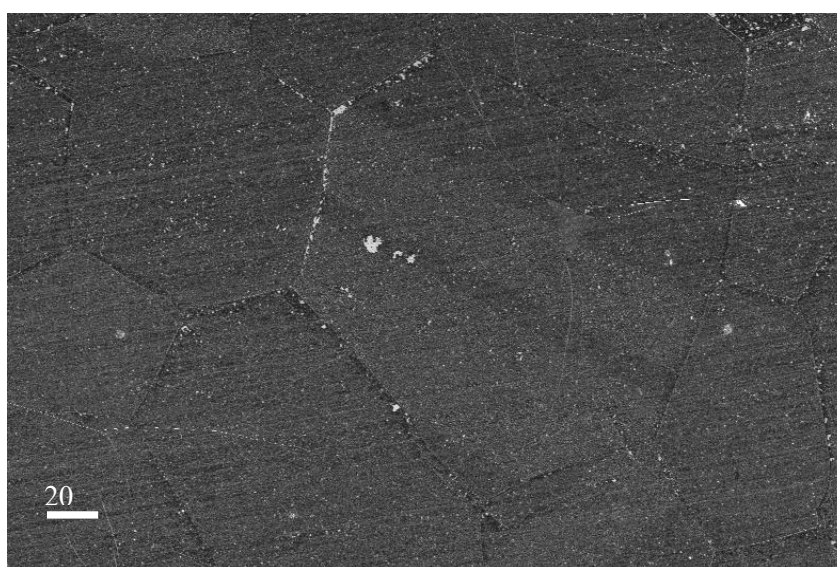
FIGURE 4. FE-SEM images of grown with 20 sccm CH_4

Conclusions

We have explored the effect of CH_4 gas flow on the synthesis of graphene on the Cu surface. Before this investigation, all the other growth parameters were optimized. Two extreme conditions of CH_4 flow rate have been chosen, including 20 sccm and 60 sccm, which are predicted to give significant results to grow graphene at atmospheric pressure. Few layers of graphene were successfully synthesized on the Cu surface by the APCVD method in a vacuum-free system with 20 sccm of CH_4 flowrate. The outcome of this research provides a starting point to establish the optimal methane (CH_4) flowrate for the production of SiO2 nanoparticles-based graphene balls.

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