Growth Conditions of Graphene Grown in Chemical Vapour Deposition (CVD)
(Keadaan Tumbesaran Grafin yang Dihasilkan dengan Pemendapan Wap Kimia)

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ABSTRACT

The fabrication of high quality graphene has become the main interest in current chemical vapour deposition (CVD) method due to the scalability for mass production of graphene-based electronic devices. The quality of graphene is determined by defect density, number of layers and properties changed such as electron mobility, transparency and conductivity as compared to the pristine graphene. Here, we did a study on the effects of reaction conditions such as methane, CH_4 concentration and deposition time towards the quality of graphene produced. We found that by lowering both CH_4 concentration down to 20% and deposition time to 5 min, a better quality graphene was produced with higher I_{2D}/I_G ratio of 0.82 compared to other reaction condition. Through the analysis, we concluded that there are two important parameters to be controlled to obtain high quality graphene.

Keywords: Chemical vapour deposition (CVD); graphene; optimization

ABSTRAK

Penghasilan grafin yang berkualiti tinggi menjadi tumpuan utama dalam kaedah pemendapan wap kimia (CVD) pada masa kini kerana ia boleh diskalakan untuk pengeluaran peranti elektronik berasaskan grafin secara besar-besaran. Kualiti grafin diukur daripada jumlah kecacatan, jumlah lapisan dan perubahan sifat lain seperti pergerakan elektron, ketelusan dan daya konduksi jika dibandingkan dengan grafin asli. Di sini, kami telah menjalankan kajian perubahan keadaan tindak balas seperti kepekatan metana, CH_4 dan masa pemendapan terhadap kualiti grafin yang dihasilkan. Kami telah mengenal pasti dengan menurunkan kedua-dua kepekatan CH_4 sehingga 20% dan masa pemendapan sehingga 5 min akan menghasilkan kualiti grafin yang lebih baik dengan nisbah I_{2D}/I_G sebanyak 0.82 lebih tinggi berbanding keadaan tindak balas lain. Menerusi analisis ini, kami menyimpulkan bahawa terdapat dua parameter penting yang perlu dikawal untuk menghasilkan grafin yang berkualiti tinggi.

Kata kunci: Grafin; pemendapan wap kimia (CVD); pengoptimuman

INTRODUCTION

Since its debut in 2004, graphene has become the main interest amongst research societies due to its superlative characteristics such as high electron mobility (Bolotin et al. 2008), transparency (Nair et al. 2008) and high strength (Lee et al. 2008) that will allow it to be used in many applications especially in the electronic industries. Therefore, mass production of high quality graphene is a must. In recent years, CVD have shown the capability to produce graphene in large scale with promising quality by using Cu as the catalyst or substrate to decompose hydrocarbon gas such as methane, CH_4 (Chan et al. 2013; Faggio et al. 2013; Li et al. 2009)graphene is limited to small sizes because it is produced mostly by exfoliating graphite. We grew large-area graphene films of the order of centimeters on copper substrates by chemical vapour deposition using methane. The films are predominantly single-layer graphene, with a small percentage (less than 5%. However, most of the graphene produced was multilayered with a polycrystalline structure that consists of many graphene domains which have been separated by grain boundaries thus degrading several of its properties (Huang et al. 2011; Song et al. 2012; Yazyev &Louie 2010). The graphene domains are believed to form due to the morphology of polycrystalline Cu such as defects, surface roughness and grain boundaries that acted as nucleation sites (Han et al. 2011) and cause uneven growth of graphene during the deposition process. Thus, multiple graphene domains are formed at various orientations and in certain conditions could even overlap with other domains. As a result, multilayer graphene with a polycrystalline structure is produced.

There are several approaches taken to tackle this problem. One of them is by removing surface imperfections through various pretreatments such as Cu electropolishing (Luo et al. 2011) and hydrogen, H_2 annealing (Ibrahim et al. 2015; Jung et al. 2014) that causes graphene domain density and its overall thickness could be controlled. Apart from that, one group oversaw the approach of growing graphene epitaxially on Cu(111) and Cu(100) film to fabricate a single layer graphene (Hu et al. 2012) and it seems that there is a preferred surface orientation for single

layer graphene to grow (Ishihara et al. 2011; Wood et al. 2011) thus showing that Cu crystal structure do have effect on the quality of graphene growth. Additionally, surface orientation of Cu might also affect the domain structures of the graphene produced (Ogawa et al. 2012). However, the influence of substrate's surface orientation towards the formation of high quality graphene is still not fully understood. Another approach taken was by controlling the reaction parameters such as temperature, pressure and the gas composition (Yang et al. 2014) in order to produce a better graphene quality. Despite of all these efforts to improve the quality of graphene, the real understanding towards graphene growth mechanism is not yet fully understood.

Nucleation of new phases exists when supersaturation of solute in solution occurs thus inducing an increase in Gibbs free energy. In order to reduce the energy of the system, the solute will segregate from the solution forming other phases that are stable. Classical theory of deposition cited that Gibbs volume free energy for nucleation are as follows (Sree Harsha 2006):

$$\Delta G_v = \frac{-kT}{\Omega} \ln \frac{C}{C_0} = \frac{-kT}{\Omega} \ln (1+\sigma),$$ (1)

where is Gibbs volume free energy; is the atomic volume; C is the concentration of solute; C_0 is the equilibrium concentration; and is the supersaturation defined as $(C-C_0)/C_0$. As the increases, the supersaturation of solute happens thus initiating segregation, which will reduce the Gibbs free energy.

Nucleation density is basically caused by the rate of deposition of the solute species, which is carbon in this case. The higher the rate of carbon deposition, the higher the nucleation density, thereby, would produce a fine grain polycrystalline graphene. The rate of deposition is controlled by the amount of carbon species supplied during the deposition process. Therefore, by understanding the nucleation and growth theory, this research intends to develop the optimized condition for graphene growth by manipulating the reaction condition especially methane (CH$_4$) gas concentration and deposition time to produce better graphene.

METHODS

SAMPLE PREPARATION

Commercially available polycrystalline Cu was used with foil thickness of 0.15 mm. They were cut into 10 by 10 mm, polished by using 1 micron alumina polish and ultrasonically cleaned with distilled water for 5 min.

GRAPHENE GROWTH

The furnace setup is shown in Figure 1 where three types of gases involved in the graphene growth process are Ar, H$_2$ and CH$_4$.
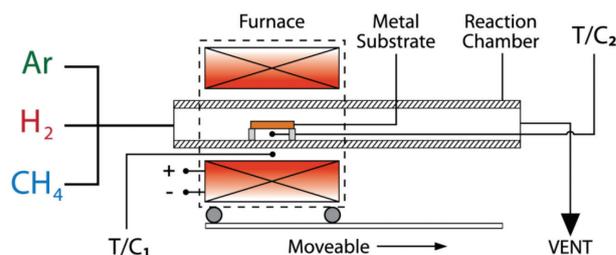

FIGURE 1. Furnace setup for graphene growth process

First, the sample was loaded into a 15 mm diameter quartz reactor as shown in Figure 1. The reactor was purged by using Ar gas to make sure that air inside the reactor was removed. The total flow rate used during the process is 50 sccm at ambient pressure and was kept constant throughout the experiment.

Annealing process started when the temperature reached 1000ºC for 30 min with the introduction of 20% H$_2$ in Ar gas.

Subsequently, the graphene growth was initiated by the introduction of CH$_4$ gas in the presence of Ar 20% H$_2$ gas according to the reaction time and CH$_4$ concentration shown in Table 1. The reaction temperature remained at a constant 1000ºC throughout the whole experiment.

After that, the furnace was moved from the reaction place for accelerated cooling under a flow of Ar 20% H$_2$ with the cooling rate of ~113ºC min⁻¹. Then, H$_2$ gas supply was shut off and 100% Ar was kept flowing for 15 min to make sure that all H$_2$ gas was completely removed from the furnace.

TABLE 1. Reaction time and CH$_4$ concentration used during graphene growth process at 1000˚C

Reaction time (min)	Concentration (%)
5	20
	60
15	20
	60
30	20
	60

CHARACTERIZATION

The morphology of graphene was studied using optical microscope (OLYMPUS BX-41-M) and the quality of graphene produced was indicated by using Raman spectroscopy machine (UniRAM 3500) with a wavelength of 532 nm and wave number ranging from 0 to 4000 cm⁻¹. The Raman spectroscopy was conducted directly onto Cu substrates without performing any graphene transfer process. Despite the fluorescence effects of Cu, it has been reported that the graphene spectra on Cu is still reliable enough (Costa et al. 2012).

RESULTS AND DISCUSSION

OPTICAL MICROSCOPY (OM)

Figure 2 shows the OM images taken after graphene deposition process was done at respective reaction time and CH_4 concentration. By observing these images, it could be seen that there were very large Cu grain boundaries (highlighted with dotted lines) with differing color contrasts. Additionally, near perfect parallel striations could be noticed within each grain boundaries but at various orientations as shown by the arrows in Figure 2. Later, Raman analysis proved that this deposited striations to be graphene. First of all, the different orientations of these striations indicated different surface orientation for the deposited graphene. It could be safely concluded that this is due to the polycrystalline nature of the Cu substrates where the differing orientation of Cu grain was influencing the deposited graphene. Next, the color contrast of the striation within each grain is also worth noting. The bands of light and dark contrast in each grain were believed to originate from the differing thickness of the deposited graphene (Borah et al. 2015). However, this disparity in contrast gradually disappeared with increasing CH_4 concentration which suggests an improvement in homogeneity of the graphene deposit. Besides, it seems that there is a preferred direction for graphene to grow in each Cu grains, which was limited by the grain boundaries at any reaction condition and shows that the growth of the graphene started at the grain boundaries of Cu.

Figure 3 shows the graph of Cu grain density over reaction time at respective CH_4 concentration. From this figure, it can be seen that the grain density decreases for both CH_4 concentration as the deposition time increases, showing that longer reaction time could produce lower Cu grain density. This could be understood as longer reaction time yields larger Cu grain size since the reaction temperature at 1000ºC is sufficiently high enough to promote the growth of Cu crystals thus producing lower grain density (Ago et al. 2015; Borah et al. 2015). Since
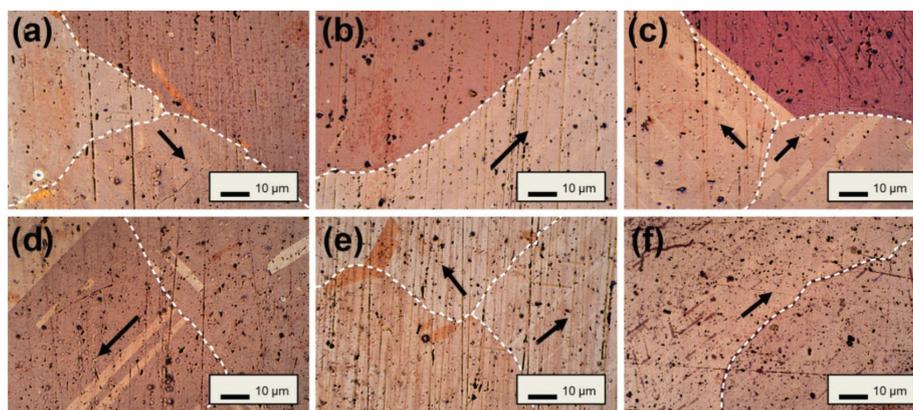

FIGURE 2. OM images of as-grown graphene on top of Cu substrates, (a) 5 min, 20% CH_4 (b) 15 min, 20% CH_4 (c) 30 min, 20% CH_4 (d) 5 min, 60% CH_4 (e) 15 min, 60% CH_4 and (f) 30 min, 60% CH_4
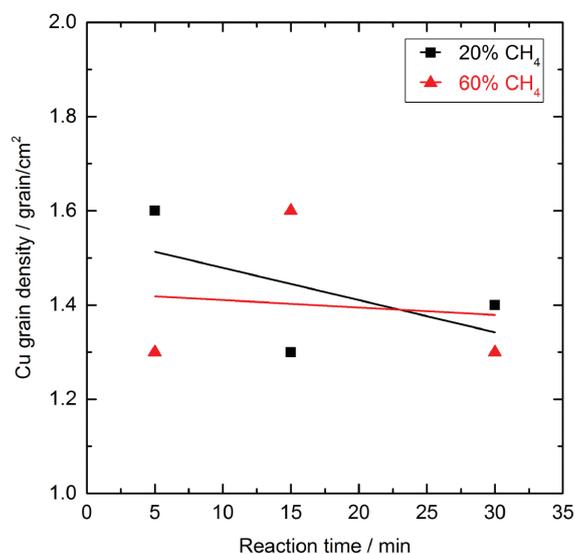

FIGURE 3. Change of Cu grain size against reaction time

lower grain density is desirable for high quality graphene growth, future works will attempt to optimize the pretreatment annealing procedure based on this data.

RAMAN SPECTROSCOPY

All Raman test was done directly on the deposited graphene without doing any transfer process. Based on the result shown in Figure 4, it can be seen that all deposited carbon showed the graphitic peak such as D-band, G-band and 2D-band (Malard et al. 2009) which shows that all of them are graphene.

The existence of D-band determines the amount of defect presence in the deposited graphene. All of them appear at ~1390 cm^{-1} shifted about 40 cm^{-1} from the theoretical graphene peak of 1350 cm^{-1} (Childres et al. 2013). This can be explained due to existence of large amount of defects on the graphene produced such as grain boundaries (Yu et al. 2011). Besides that, there is another defect peak known as D+G-band appearing at ~2920 cm^{-1}. This peak emerged due to large defects contained in the deposited graphene (Dresselhaus et al. 2010). In Figure 4(a), we can see that at 20% CH$_4$ concentration, there is no significant change in D-band intensity indicating that all of the deposited graphene contained approximately the same amount of defects as the deposition time increased. Only when the concentration was changed to 60% CH$_4$, fluctuation of D-band intensity appeared, showing that they have inconsistent amount of defects as shown in Figure 4(b).

2D-band represents the graphene layer thickness by analyzing the peak's shape and calculating its full-width half maximum (FWHM) and it only appears at certain graphene thickness. Typical graphene has FWHM of about 24 cm^{-1} (Malard et al. 2009) and any FWHM broader than that represents multilayer graphene. 2D peak with the highest intensity was obtained at 20% CH$_4$ and 5 min reaction time with a FWHM of ~86 cm^{-1}. Other conditions yield a very broad 2D peak which suggests a short reaction time and low CH$_4$ concentration is desirable for the formation of monolayer graphene.

The other way to identify the amount of layers in graphene can be done through the calculation of I$_{2D}$/I$_G$ ratio as decrease in layers would give higher ratio (Childres et al. 2013). Analyzing the peak ratios in Figure 4, it can be seen from Figure 5 that I$_{2D}$/I$_G$ ratio is getting smaller as the deposition time increases for both 20% and 60% indicating increment in graphene layers. Lower CH$_4$ concentration seems to have higher I$_{2D}$/I$_G$ ratio and the highest ratio calculated is 0.82 for the 5 min reaction. This shows a short reaction time and low CH$_4$ concentration is the optimal condition for monolayer graphene growth and this complies with the report that lower CH$_4$ concentration reduces the nucleation density of graphene and forming a uniform layer of graphene (Liu et al. 2011)but also substantially influenced by the quality of Cu substrate and how the Cu substrate is pretreated. It is found that the micro-topography of the Cu surface strongly affects the uniformity of grown graphene while the purity of the Cu film determines the number of synthesized graphene layers at low pressure conditions. On the other hand, a minimum partial pressure of hydrocarbon is required for graphene to cover the Cu surface during graphene growth. The optimized bilayer graphene exhibits a maximum hole (electron. In our study, the reduction in CH$_4$ concentration is expected to have the same effect.

Based on the Raman results discussed, it can be identified that the graphene produced is still multilayered and in defective form. However, it is understood that the quality of graphene can be controlled by manipulating the CH$_4$ concentration and reaction time. This information is very useful and should become a benchmark for the next optimization process to fabricate a high quality graphene.
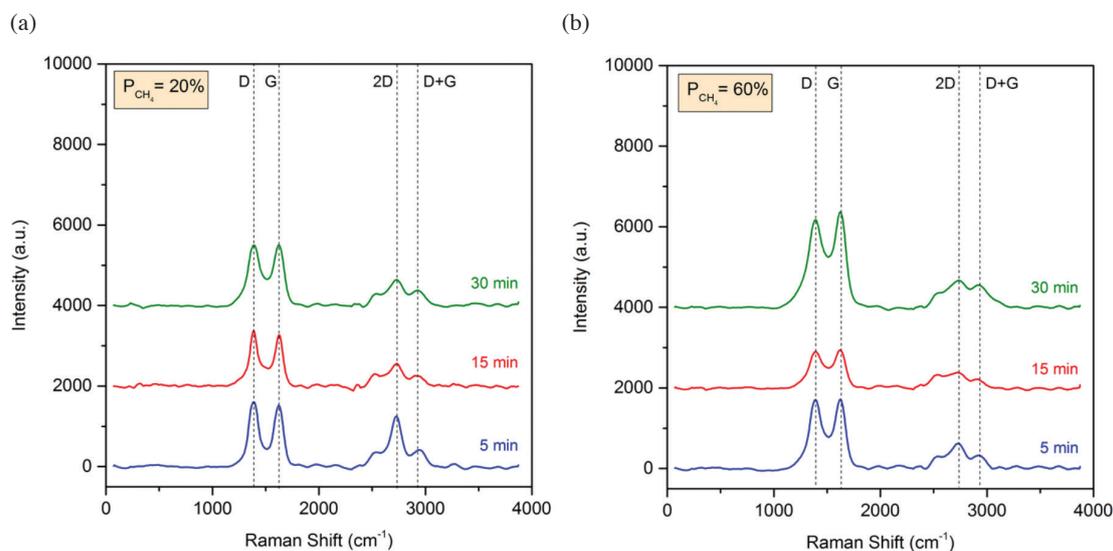

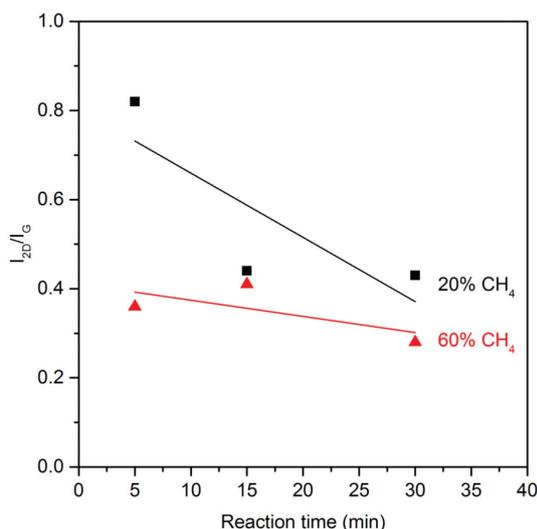FIGURE 4. Raman spectroscopy of graphene on Cu (a) with 20% CH$_4$ (b) with 60% CH$_4$ during deposition process

FIGURE 5. Change of I_{2D}/I_G ratio against reaction time

CONCLUSION

In order to summarize, graphene has been successfully fabricated by using ambient pressure CVD. The graphene produced has inconsistent number of graphene layers within each Cu grains as the color contrast of the striations observed from the OM images seems to suggest. When higher CH_4 concentration was used, there was a marked reduction in the color contrast assuming a more homogeneous deposition. This is affirmed by Raman spectra as well which shows an overall improvement in the quality of the deposited graphene. Besides that, from the striations there are preferred directions for graphene to grow in each Cu grains which then limited by the Cu grain boundaries. The Cu grain density per cm^2 was also calculated and it shows that higher reaction time will produce lower grain density. From the Raman, it can be identified that the graphene produced is highly defective as there is an existence of D-band which shifted about 40 cm^{-1} higher from the theoretical peak and the appearance of D+G band at ~2920 cm^{-1}. FWHM of 2D band for all samples exceeds 24 cm^{-1} which shows that graphene produced is multilayered. From the I_{2D}/I_G plot, lower CH_4 concentration of 20% and deposition time of 5 min yields the thinnest layer of graphene from all the samples obtained. Although the quality of the graphene produced is low but the pattern for optimization process has now been understood. Better quality graphene could be produced by decreasing the CH_4 concentration and deposition time. This finding is expected will be useful to improve the quality of graphene production in the future.

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