Raman Studies on Pre- and Post-Processed CVD Graphene Films Grown under Various Nitrogen Carrier Gas Flows

K P Beh, F K Yam, Raed Abdalrheem, Y Z Ng, F H A Suhaimei, H S Lim, M Z Mat Jafri

School of Physics, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia.

Abstract. In this work, graphene films were grown on copper substrates using chemical vapour deposition method under various N₂ carrier flow rate. The samples were characterized using Raman spectroscopy. Three sets of Raman measurements have been performed: graphene/Cu (as-grown samples), pre-annealed graphene/glass, and post-annealed graphene/glass. It was found that the Raman spectra of graphene/Cu samples possessed a hump-shaped baseline, additionally higher signal-to-noise ratio (SNR) that leads to attenuation graphene-related bands. Significant improvement of SNR and flat baseline were observed for graphene films transferred on glass substrate. Further analysis on the remaining sets of Raman spectra highlighted minute traces of polymethyl methacrylate (PMMA) could yield misleading results. Hence, the set of Raman spectra on annealed graphene/glass samples would be suitable in further elucidating the effects of N₂ carrier flow towards graphene growth. From there, higher N₂ flow implied dilution of methanol/H₂ mixture, limiting interactions between reactants and substrate. This leads to smaller crystallite size and lesser graphene layers.

1. Introduction
Graphene can be described as a single layer of sp²-hybridized carbon atoms arranged in a honeycomb network. Dubbed as the “wonder material of the 21st century”, graphene possesses many unique and superior properties and can be found in a wide range of applications. Some notable features of graphene includes active electro-optic effects, high optical transparency, electrical and thermal conductivity. Having such unique characteristics allowed graphene to be included in devices such as optical modulator, smart windows, transistors, and thermal interface material [1-6].

A wide varieties of method have been developed for graphene growth, such as chemical vapour deposition (CVD), reduced graphene oxide (rGO) route, and electrochemical exfoliation [7-10]. Among the aforementioned techniques, CVD is well received since it is capable of large area growth, additionally allowing flexible controls over the number of graphene layers through fine tuning process parameters. With proper fine-tuning of process parameters, monolayer graphene with dimensions up to tenths of centimetre can be fabricated [7].

The CVD method for graphene growth consisted of many parameters such as precursor types, flow rate, substrate, growth duration, temperature, and so on. In general, monoatomic carbon source such as methane is preferred and copper is a well-received substrate due to poor solubility of carbon source that leads to two-dimensional (2D) growth [8, 11]. Since monolayer graphene ascribed to the thickness of single carbon atom, the precursors concentration should be properly regulated. This could be achieved through dilution of the carbonaceous source with an inert gas, such as argon or nitrogen. Hence, the gas ratio between, e.g. methane and argon served as an essential parameter in controlling the graphene layers growth [11].
Graphene possessed a strong affinity towards incident light source; hence, many of their characteristics could be determined. Raman spectroscopy, which well known for its non-destructive testing, is widely used in characterizing graphene films. Properties of graphene such as defect levels, crystallite size, and layer numbers could be determined from its respective Raman spectrum [12-15]. However, in case for CVD grown graphene, particularly utilizing copper substrate, Raman measurement would be more challenging. The consequence of performing Raman measurements on graphene/Cu samples have led to an overall attenuation of the Raman bands, additionally producing artifact signals such as hump-shaped baseline [16]. Hence, additional process such as transferring of graphene film to other substrates are necessary in order to yield reliable results [17-19]. Still, direct Raman probing on as-grown CVD graphene would be useful from qualitative perspective.

In this work, graphene films were grown on copper substrate using CVD method. Methanol/H\textsubscript{2} mixture served as the reactants while that of N\textsubscript{2} being the carrier gas and diluent. The flow rate of N\textsubscript{2} was varied from 600 to 2000 sccm. Raman measurements were performed on all samples under three conditions: graphene/Cu (as-grown); graphene/glass (transferred); and annealed graphene/glass (post-annealing process).

2. Methodology

Copper plates are cut into 2×2 cm\textsuperscript{2} using a guillotine. A “T” was stamped on the edge for easy identification of the top surface. Next, the copper plates are sonicated in 5% Decon 90 solution for 15 minutes to remove surface impurities such as oils.

Prior electropolishing, the copper plates are subjected for thermal annealing to improve its crystallinity. The copper plates are loaded into a ceramic crucible that subsequently inserted into a tube furnace. After connecting the end seals, the furnace was ramped up to 1000°C under N\textsubscript{2} flow of 1000 sccm in order to remove any residue air. Upon achieving that, 200 sccm of H\textsubscript{2} was introduced. H\textsubscript{2} would reduce any surface oxides present, resulting in a clean and pure copper surface. The annealing process lasted for 3 hours. After that, H\textsubscript{2} was shut off and the furnace was purged with 1000 sccm of N\textsubscript{2}. The copper plates were allowed to cool under N\textsubscript{2} stream prior removal.

A two electrodes electrochemical cell was setup for electropolishing. Here, the copper plates would serve as the anode, while that of brass plate being the cathode. The electrolyte used here consisted of 65% phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) solution. The electropolishing was done potentiostatically around 2 V, lasted for 20 minutes each. A mirror-like surface was obtained in the end.

The CVD growth of graphene on Cu plate is described as follows. The copper plates were inserted into a 1-inch quartz tube, subsequently loaded into the cold zone of a 2-inch diameter tube furnace. After sealing both ends and established proper piping connections, 3000 sccm of N\textsubscript{2} was flown for 5 minutes in order to remove residue air. Next, 200 sccm of H\textsubscript{2} was introduced for 10 minutes. This step is necessary to remove any possible surface contaminants such as native oxides. Additionally, this provide an ultrafine polishing towards the already electropolished copper surface. After that, 1000 sccm of N\textsubscript{2} was used to remove residue H\textsubscript{2}. Then, for the graphene growth, 30 sccm of H\textsubscript{2} is bubbled into a gas bubbler containing pure methanol, while N\textsubscript{2} was used to dilute the reactants. The flow of N\textsubscript{2} during this stage varies from 600 to 2000 sccm. After graphene growth, the samples were allowed to cool down for 15 minutes under N\textsubscript{2} flow prior removal.

The graphene film grown on copper substrate required to be transferred onto glass substrate for further characterizations. To do that, polymethyl methacrylate (PMMA) layer was spin-coated on the graphene/Cu substrate around 2000 rpm for 10s. The PMMA film was dried cured at 180°C. The graphene films were delaminated using electrochemical process, where PMMA/graphene/Cu served as the cathode, while Pt wire being the anode. The electrolyte used was 0.5 M aqueous sodium chloride (NaCl), and a constant potential of 5 V was used to trigger the delamination process.

The delaminated PMMA/graphene films were washed several time in DI water prior overlaid on glass substrate. The PMMA layer were removed through dissolving in acetone. For complete removal of residue PMMA, the samples were heat-treated at 400°C for 15 minutes in a tube furnace.
Raman spectroscopy (Jobin Yvon HR 800) with incident laser source of 514.5 nm that operates at 20 mW was used to perform measurements on all graphene samples.

3. Results and Discussions
Raman spectroscopy has been widely used in characterizing graphitic samples such as graphene and carbon nanotubes. For graphene sample, additional information such as defects, crystallite size, and number of layers could be obtained from Raman spectrum. Despite the superiority of Raman measurement, the properties of the spectrum can be affected by external factors such as incident wavelength and substrate. The former was omitted in this study since a monochromatic incident source of 514.5 nm was used. On the other hand, the latter holds certain degree of importance for CVD graphene growth, given that copper substrate is typical in such process.

Figure 1 shows a compilation of Raman spectra obtained under various conditions: graphene/Cu, graphene/glass, and annealed graphene/glass. All Raman spectra displayed two notable peaks for graphene, that is, G and 2D band. This shows the presence of graphene can be easily determined while remained on copper substrate. The absence or relatively weak D band indicative of high quality graphene [13].

Figure 1. Raman Spectra of (a) graphene/Cu, (b) graphene/glass, and (c) annealed graphene/glass samples.
Despite all Raman spectra represented graphene grown under different \( \text{N}_2 \) carrier, some differences could be noted. In the Raman spectra of graphene/Cu samples, a humped-shaped baseline and higher signal-to-noise (SNR) ratio (relative to other spectra) could be noted. Both attributed to the presence of copper substrate, where the free carriers within induced scattering sites, attenuating the overall signal strength. While advanced mathematical methods could be adopted in removing the baseline and lowering overall noise level, the latter effectiveness dwindled since it depended on the characteristics of the raw data. For example, the presence of D band, which essential in determining defects level, could be ambiguous in graphene/Cu samples due to poor SNR and hump-shaped baseline. After transferring to glass substrate and post-annealed, the state of D band become discern and was confirmed to be present but weak.

Performing Raman spectroscopy on graphene/Cu samples would provide qualitative aspects of the graphene samples. Prior in-depth analysis, the graphene film often required to be transferred to other substrate, such as SiO\textsubscript{2}/Si or glass. From Figure 1, the Raman spectra of graphene/glass and annealed graphene/glass exhibited flat baseline and better SNR. From there, D band was confirmed present but with weak intensity, which signified graphene samples of high quality i.e. low defect levels. With better SNR, the G band 2D band become more prominent. Interestingly, the relative intensity ratio between 2D and G bands, denoted as \( I_{2D}/I_G \) showed a dependency towards \( \text{N}_2 \) carrier flow. Although significant changes were brought upon transferring graphene from copper to glass substrate, however, it should be noted that the Raman spectra between pre- and post-annealed conditions differed from each other. Their differences would be revealed upon further analysis.

CVD grown graphene often possessed large crystallite size. This can be calculated using Tuinstra-Koenig relation [10, 20]:

\[
L_a (\text{nm}) = (2.4 \times 10^{-10}) \times \lambda^4 \times \left(\frac{I_D}{I_G}\right)^{-1}
\]

Where \( L_a \) is the crystallite size, \( \lambda \) is the incident wavelength (514.4 nm in this study); \( I_D/I_G \) is the relative intensity ratio between D and G band.

![Figure 2. Plot of average crystallite size, \( L_a \) against \( \text{N}_2 \) carrier flow rate.](image-url)
The plot of \( L_a \) against \( N_2 \) carrier flow rate is shown in Figure 2. From Figure 2, graphene/Cu and graphene/glass exhibited an increasing trend with \( N_2 \) carrier flow, while that of annealed graphene/glass showed otherwise, i.e. decreasing trend. The difference in trend requires further analysis on the nature of Raman data sets in order to choose a suitable candidate that best described the effects of \( N_2 \) carrier flow towards graphene growth. Based on Tuinstra-Koenig relation, \( L_a \) depended on \( I_{D}/I_{G} \), which implied the intensity of D band to be taken into account. As graphene/Cu samples have lower SNR and D band intensity, the latter was further attenuated, thus producing less reliable results compared to the rest, which unfavourable for in-depth analysis. Meanwhile, the behavioural differences between graphene/glass and annealed graphene/glass samples were likely caused by the presence of impurities, that is, PMMA. In order to transfer graphene from copper to glass substrate, a layer of PMMA was spin coated on graphene/Cu. This layer would act as film support, additionally allowing better visualization of the sample for subsequent handling. Upon successful transferring of PMMA/graphene to glass substrate, the former would be removed by dissolving in acetone. The main challenge here was thorough removal of PMMA, which proved to be challenging. Various works have indicated the presence of PMMA residue as thin as 1 nm remained despite thorough washing [21]. This could affect the overall graphene quality. Hence, post-annealing sessions have become a necessity in effectively removing PMMA residues, given that PMMA decomposed into gaseous compounds around 400°C. In short, annealed graphene/glass samples would have the least impurities, thus the corresponding dataset would provide a more accurate representation of the effects of \( N_2 \) carrier towards graphene growth. From there, the decrease in \( L_a \) with respect to \( N_2 \) carrier flow was attributed to the reactants-substrate interactions. \( N_2 \), aside being a carrier gas, it could dilute methanol/H\(_2\) mixture in this work. As the \( N_2 \) carrier flow increases, the amount of reactants that undergone decomposition and subsequent nucleation of copper surface become limited. Hence, the growth of larger crystallite domains become hindered.

![Graph showing the relationship between \( I_{2D}/I_{G} \) ratio and \( N_2 \) carrier flow rate.](image)

**Figure 3.** Plot of \( I_{2D}/I_{G} \) ratio against \( N_2 \) carrier flow rate.
The consequence of diluting the reactants would also limit the number of graphene layers to be grown. In general, the determination of graphene layers could be done using by taking the intensity ratio of 2D to G band (denoted as $I_{2D}/I_G$). Figure 3 shows a plot of $I_{2D}/I_G$ against $N_2$ flow rate. At glance, all data set presented an increasing trend. Interestingly, the behaviour of $I_{2D}/I_G$ for graphene/Cu samples differed from that of graphene/glass and annealed graphene/glass. For graphene/Cu samples, $I_{2D}/I_G$ trend only exhibited significant changes above 1400 sccm of $N_2$ carrier flow (omitting the anomalous case at 1200 sccm). With $N_2$ flow at 2000 sccm, an $I_{2D}/I_G$ as high as 2.5 was obtained, suggesting possible monolayer growth. Meanwhile, the indistinguishable changes below 1400 sccm could be attributed to poor SNR, which limits detection. Upon transferring to glass substrate, a linear behaviour of $I_{2D}/I_G$ was noted. Between pre- and post-annealed graphene/glass samples, $I_{2D}/I_G$ become distinguishable above 1200 sccm of $N_2$ carrier flow. At 2000 sccm, $I_{2D}/I_G$ for annealed graphene/glass ~1.5, suggesting mono- to bilayer graphene, while that of graphene/glass ~ 0.9, indicating the presence of bilayer graphene. The behavioural differences of $I_{2D}/I_G$ in both data sets could well described the interaction of PMMA towards the π-bonds of graphene [21]. In general, monolayer graphene possessed localized π-bonds, which enhanced the double resonance process hence higher 2D band. The intense 2D bands would retained its feature even with two layers of monolayer graphene stacked over each other, since the π-bonds remained localized. As the graphene layers increases during growth, the π-bonds delocalized, forming van der Waals forces between graphene sheets. Hence, lower intensity of 2D band is to be expected. It was likely that PMMA disrupted the localized π-bonds on graphene sheet, forming functional groups, which inadvertently lowering the overall intensity of 2D bands. For lower $N_2$ flow, as the π-bonds were already delocalized due to multilayer graphene growth; hence, it is difficult to gauge the contributions from PMMA. Overall, the $I_{2D}/I_G$ analysis have highlighted the importance of impurities removal for accurate Raman measurements.

4. Conclusions
Raman spectroscopy is essential in determining the characteristics of graphene. However, analytical Raman studies on CVD grown graphene can be challenging since copper substrate contributed in attenuation of the signal strength that limits useful data extraction. Despite transferring graphene film to glass substrate improved SNR, the presence of PMMA residue could produce misleading results, e.g. $L_a$ and higher counts on graphene layers. Post-annealing of graphene/glass proved effective in removing PMMA residues, also yield better and reliable results. From there, it was found that higher $N_2$ carrier flow dilute methanol/H$_2$ mixture, which limits reaction/substrate interaction. Consequently, this lead to smaller $L_a$ (from 500 to 200 nm on average) and lesser graphene layers, with $I_{2D}/I_G$ as high as 2.5 was obtained.

Acknowledgments
This work is financially supported by the grant “Clad (Topological Insulators and Transition Metal Dichalcogenides) Planar Photonic Devices” (203/PFIZIK/6770002), which is under the LRGs grant “Graphene and Other 2 Dimensional Nanomaterial” (grant no.: LRGs(2015)/NGOD/UM/KPT) from Ministry of Higher Education (MOHE) of Malaysia. In addition, the author, K.P. Beh, would like to thank Universiti Sains Malaysia (USM) for awarding Post-Doctoral Fellowship Scheme to pursue his post-doctoral studies. All supports from USM and various parties are gratefully acknowledged.
References

[1] Park W, Guo Y, Li X, Hu J, Liu L, Ruan X, Chen Y P 2015 The Journal of Physical Chemistry C 119 26753
[2] Reserbat-Plantey A, Schadler K G, Gaudreau L, Navickaite G, Guttinger J, Chang D, Toninelli C, Bachtold A, Koppens F H 2016 Nature communications 7 10218
[3] Hu Y, Pantouvaki M, Van Campenhout J, Brems S, Asselberghs I, Huyghebaert C, Absil P, Van Thourhout D 2016 Laser & Photonics Reviews 10 307
[4] Echtermeyer T J, Milana S, Sassi U, Eiden A, Wu M, Lidorikis E, Ferrari A C 2016 Nano Lett 16 8
[5] Fernández-Rossier J, Palacios J J, Brey L 2007 Physical Review B 75 205441
[6] He Q, Wu S, Gao S, Cao X, Yin Z, Li H, Chen P, Zhang H 2011 ACS Nano 5 5038
[7] Zhou H, Yu W J, Liu L, Cheng R, Chen Y, Huang X, Liu Y, Wang Y, Huang Y, Duan X 2013 Nature communications 4 2096
[8] Yu P, Lowe S E, Simon G P, Zhong Y L 2015 Curr Opin Colloid Interface Sci 20 329
[9] Yang H, Li H, Zhai J, Sun L, Yu H 2014 Ind Eng Chem Res 53 17878
[10] Shanmugam R, Rangarajan M, Devanathan S, Sathe V G, Senthilkumar R, Kothurkar N K 2016 Materials Research Express 3 125601
[11] Ferrari A C, Meyer J C, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov K S, Roth S, et al. 2006 Phys Rev Lett 97 187401
[12] Beams R, Gustavo Cancado L, Novotny L 2015 J Phys Condens Matter 27 083002
[13] Ferrar A C, Basko D M 2013 Nat Nanotechnol 8 235
[14] Lenski D R, Fuhrer M S 2011 J Appl Phys 110 013720
[15] Costa S D, Righi A, Fantini C, Hao Y, Magnuson C, Colombo L, Ruoff R S, Pimenta M A 2012 Solid State Commun 152 1317
[16] Lee H C, Liu W-W, Chai S-P, Mohamed A R, Aziz A, Khe C-S, Hidayah N M S, Hashim U 2017 RSC Adv 7 15644
[17] Marta B, Leordean C, Istvan T, Botiz I, Astilean S 2016 Appl Surf Sci 363 613
[18] Chen Y, Gong X L, Gai J G 2016 Advanced science 3 1500343
[19] Naghd S, Rhee K Y, Kim M T, Jaleh B, Park S J 2016 Carbon letters 18 37
[20] Suk J W, Lee W H, Lee J, Chou H, Piner R D, Hao Y, Akinwande D, Ruoff R S 2013 Nano Lett 13 1462