

Growth of Multi-Layered Graphene Using Organic Solvent-PMMA Film as the Carbon Source under Low Temperature Conditions

Alaa Y. Ali, Natalie P. Holmes, John Holdsworth, Warwick Belcher, Paul Dastoor, Xiaojing Zhou

Abstract—Multi-layered graphene has been produced under low temperature chemical vapour deposition (CVD) growth conditions by utilizing an organic solvent and polymer film source. Poly(methylmethacrylate) (PMMA) was dissolved in chlorobenzene solvent and used as a drop-cast film carbon source on a quartz slide. A source temperature (T_{source}) of 180 °C provided sufficient carbon to grow graphene, as identified by Raman spectroscopy, on clean copper foil catalytic surfaces. Systematic variation of hydrogen gas (H_2) flow rate from 25 standard cubic centimeters per minute (sccm) to 100 sccm and CVD temperature (T_{growth}) from 400 to 800 °C, yielded graphene films of varying quality as characterized by Raman spectroscopy. The optimal graphene growth parameters were found to occur with a hydrogen flow rate of 75 sccm sweeping the 180 °C source carbon past the Cu foil at 600 °C for 1 min. The deposition at 600 °C with a H_2 flow rate of 75 sccm yielded a 2D band peak with $\sim 53.4 \text{ cm}^{-1}$ FWHM and a relative intensity ratio of the G to 2D bands ($I_{\text{G}}/I_{\text{2D}}$) of 0.21. This recipe fabricated a few layers of good quality graphene.

Keywords—Graphene, chemical vapour deposition, carbon source, low temperature growth.

I. INTRODUCTION

IN recent years, liquid carbon sources for CVD of graphene have attracted interest among researchers because of the materials available and the reduction in cost compared to a gaseous carbon source [1], [2]. The choice of molecule to act as the carbon source when growing graphene via thermal decomposition is based on the C-H binding energy in the source compound as to grow graphene using methane (CH_4) molecules as the carbon source requires a high temperature of $\sim 1000 \text{ °C}$ due to the high C-H binding energy (4.56 eV) [3], while the use of solvent residing in a polymer matrix as the hydrocarbon source has the potential to lower the synthesis temperature due to the utilization of preformed ring structures. PMMA solvated in chlorobenzene, PMMA solid and benzene have been reported as successful carbon sources for the growth of graphene at low temperature using the CVD method [4]-[6].

In our study, multilayered graphene was grown on pre-annealed copper foil ($\sim 900 \text{ °C}$) at low growth temperatures

(400-800 °C). Graphene layers were identified via Raman spectroscopy with measurements made directly on the copper catalyst. After the transfer of graphene, transmission electron microscopy (TEM) revealed the hexagonal structure of uniform layers of graphene. Generally, graphene layers prepared from organic solvent and polymer as carbon source is an interesting way to investigate the growth mechanism of graphene at low temperature.

II. EXPERIMENTAL SECTION

PMMA (Sigma Aldrich) was dissolved in chlorobenzene solvent at a concentration of 100 mg/ml. PMMA-chlorobenzene was drop cast onto quartz glass slides and inserted into the CVD tube furnace to form the carbon source. The catalyst was electro-polished copper foil (Cu) (25 μm thickness), thermally annealed at 900 °C for 1 hour under hydrogen (H_2)/argon (Ar) atmosphere 50:100 sccm respectively. The electrochemical polishing (custom-built electrochemistry cell) was applied to copper foil substrates before the thermal annealing in order to make the surface of the catalyst more uniform, as the uniformity of the copper catalyst surface and the crystal size has a significant effect on the growth layers of graphene [7], [8]. H_2 gas was utilized in the pre-annealing condition of copper to clean and reduce the oxidation of the Cu surface [3]. Furthermore, the Ar gas atmosphere was used to minimize and limit the level of oxygen (O_2) in the CVD chamber during thermal annealing [9].

Graphene layers were deposited on cleaned Cu foil at a range of low temperatures for growth, ~ 400 to 800 °C , with a range of H_2 flow rates, 25 to 100 sccm, and a T_{source} of 180 °C. The quality of graphene films was verified through Raman spectroscopy before a wet transfer method was utilised. This analysis method was based on an intensity ratio of $I_{\text{G}}/I_{\text{2D}}$ peaks, and these peaks are the most significant features in the Raman spectrum of graphene, with peak locations G $\sim 1580 \text{ cm}^{-1}$ and 2D $\sim 2700 \text{ cm}^{-1}$. Raman spectroscopy can also be a powerful technique to determine the number of layers of graphene grown on the catalyst [10]. A Renishaw inVia Raman spectrometer was used to characterize the quality of graphene films at each growth condition. For Raman mapping, an XploRA PLUS Raman microscope from HORIBA Scientific was used for identifying the quality of graphene layers up to $100 \times 100 \mu\text{m}$. The Raman microscope is equipped with atomic force microscopy (AFM) functionality with a 532 nm (green) laser, , 400 nm spot size

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and 1 nm step size.

The purification of the Cu catalyst surface was tested via X-ray photoelectron spectroscopy (XPS). A non-monochromatic X-ray source (Omnivac) using Al K α (1486.6 eV) radiation and Scienta detector was used to analyse the surface of cleaned Cu foil to provide information about the chemical state and elemental composition of the sample. The pressure in the analysis chamber with sample under X-ray illumination was typically 3.0×10^{-9} mbar, with a base pressure of 4×10^{-10} mbar.

In this work, thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Diamond TG/DTA to characterise the decomposition temperature of PMMA-chlorobenzene drop cast matrices. Fourier transform infrared spectroscopy (FTIR) was utilized to investigate the presence of solvent residing in the PMMA polymer matrix forming the carbon source for graphene growth. A Perkin Elmer Spectrum Two FTIR with a total range of 8300 to 350 cm^{-1} at a best resolution of 0.5 cm^{-1} was used for measuring the intensity of infrared attenuation as a function of wavenumber. The morphology and thickness of graphene films were analysed through atomic force microscopy (AFM) on an Asylum Research Cypher AFM. The crystal lattice structure of graphene was imaged using TEM on a JEOL 2100 with operating voltage of 80-200 kV and varying magnification ranges (10,000 to 100,000 x).

III. RESULTS AND DISCUSSION

Generally, a native oxide layer covers the copper foil because of oxygen gas reacting with the metallic copper surface. Fig. 1 reveals the level of elemental oxygen on the copper surface before and after thermal annealing as determined by X-ray photoelectron spectroscopy (XPS). The oxygen level peak decreased indicating the thermal annealing process for copper foil in a hydrogen and argon atmosphere, was an effective way to remove the oxide layers from the surface; enhancing graphene catalysis.

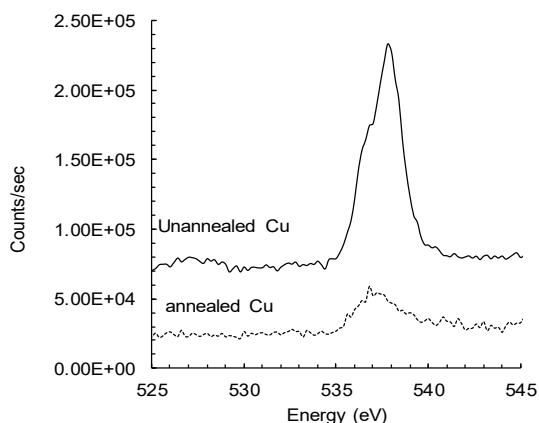


Fig. 1 XPS spectrum of thermally annealed Cu foil

Thermal degradation of chlorobenzene-PMMA was carried out using TGA analysis. Fig. 2 shows the thermal

decomposition of pure PMMA (as powder) and PMMA composite with chlorobenzene under nitrogen (N_2) atmosphere. Thermal pyrolysis of PMMA-chlorobenzene dried at 180 $^{\circ}\text{C}$, and air dried, were conducted with a starting temperature of 30 $^{\circ}\text{C}$ and maximum temperature of 500 $^{\circ}\text{C}$. The initial degradation phase of PMMA powder occurs via decomposition of PMMA molecules at temperatures of around 200 $^{\circ}\text{C}$ in N_2 atmosphere, followed by accelerated weight loss above 300 $^{\circ}\text{C}$. These observations are in agreement with the known thermal decomposition of PMMA into monomers at 220 $^{\circ}\text{C}$ and subsequent C-C scission at temperatures of more than 300 $^{\circ}\text{C}$ [11]. In the drop-cast PMMA film, the weight loss started from room temperature and plateaued at around 150 $^{\circ}\text{C}$ followed again by sharp weight loss above 350 $^{\circ}\text{C}$. The random scission degradation of PMMA occurs by homolytic scission of a methoxycarbonyl side group, then β scission at about 350-400 $^{\circ}\text{C}$ [12]. By contrast, chlorobenzene can exist as clusters or pools of molecules of different sizes in the PMMA matrix [13]. Consequently, the chlorobenzene molecules are released from the polymer matrix across a range of low temperatures since the chlorobenzene molecules in PMMA matrix do not exist as bulk chlorobenzene with a standard boiling point.

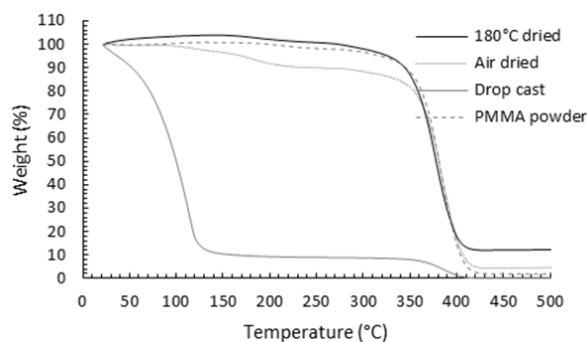


Fig. 2 TGA curves of chlorobenzene-PMMA films prepared as follows: 180 $^{\circ}\text{C}$ dried (grey line), air-dried (dotted line), drop cast wet film (solid line), compared to pure PMMA powder (dashed line)

The Raman spectrum of graphene was used to map out the area of material deposited by the CVD and identify the graphene layers, typically deposited as multilayers of graphene, on the Cu foil before transferring the layers onto a target substrate. From Fig. 3, the characteristic Raman spectral peaks of the G band at $\sim 1582 \text{ cm}^{-1}$ and 2D band at 2690 cm^{-1} are clearly apparent. The full width at half maximum (FWHM) of the 2D band peak and the ratio of the peak heights (presented in Table I) are good measures of the quality and presence of the graphene layers. Furthermore, the D band located at $\sim 1350 \text{ cm}^{-1}$ in the Raman spectrum relates to the defect level in graphene giving further information on the quality of graphene films. The D peak intensity is weak compared to other features. The intensity ratio of the G to 2D band is ~ 0.21 for a H_2 gas flow rate of 75 sccm. This ratio is typical for CVD-derived multi-layered graphene with defects such as domain boundaries [14]. Domain boundaries in

graphene layer can be represented via the D band. The dehydrogenation of benzene molecules from PMMA-chlorobenzene requires a low activation energy on Cu (111) of ~ 1.47 eV for growth of graphene [15]. However, using benzene as carbon source for synthesis of graphene because of its low activation energy could not lead to large graphene domains and continuous graphene films [5], [16]. Based on the quality of graphene layers at temperature growth (600°C), it can be considered as suitable thermal energy for growth a good quality of graphene layers.

The Raman analysis indicated that a few layers of graphene grew under these conditions [10]. The ratio of the G to 2D Raman bands is a convenient measure by which to map the surface for the presence of graphene [16]. A mapped area of $100\ \mu\text{m} \times 100\ \mu\text{m}$ is shown in Fig. 4 (a) where the red areas correspond to graphene formation from the source and CVD process with evidence of micrometer sized multi-layer graphene flakes matched with the optical image of graphene on Cu in Fig. 4 (b).

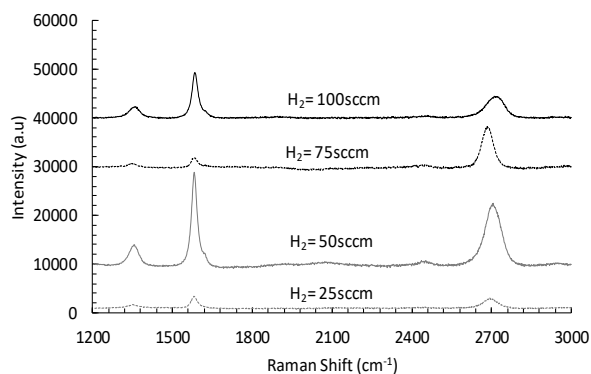


Fig. 3 Raman spectra of graphene films grown at different H_2 gas flow rates at $T_{\text{growth}} 600^\circ\text{C}$.

TABLE I
VARIATION OF GRAPHENE FILM QUALITY AT $T_{\text{GROWTH}} 600^\circ\text{C}$ WITH VARIED H_2 GAS FLOW RATE

H_2 flow rate (sccm)	G position (cm^{-1})	2D position (cm^{-1})	I_G/I_{2D}	$2D_{\text{FWHM}}$ (cm^{-1})
25	1579	2694	1.16	64.56
50	1581	2707	1.5	71.7
75	1581	2685	0.21	53.37
100	1584	2711	2.11	80.71

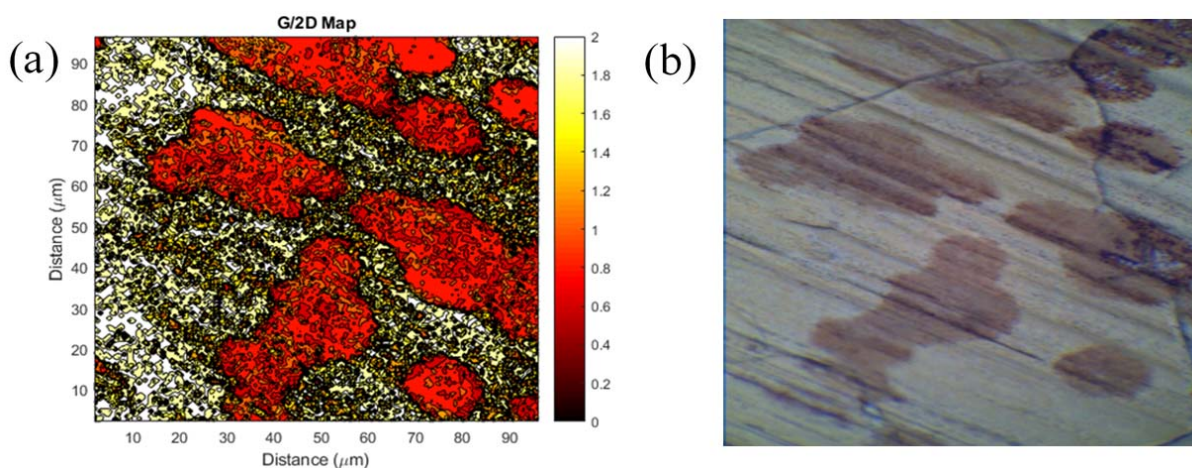


Fig. 4 (a) Raman G/2D peak ratio map ($100\ \mu\text{m} \times 100\ \mu\text{m}$) showing graphene at $T_{\text{growth}} 600^\circ\text{C}$ with H_2 gas flow rate 75 sccm, (b) position-matched optical image of Raman mapped area

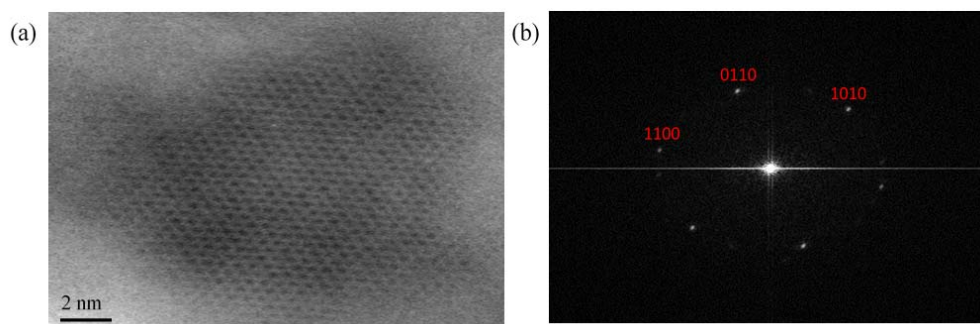


Fig. 5 (a) TEM image of graphene layers suspended on Cu grid and (b) The electron diffraction pattern of carbon atoms in graphene

The graphene layers were transferred onto a Cu TEM grid after the Cu foil was etched away using the wet transfer method [17]. These suspended graphene layers were imaged under a TEM at 200 kV (Jeol 2100 TEM) as shown in Fig. 6 (a) and the hexagonal structure of the graphene is clearly evident. The layers of graphene closer to the source are white in the image with a bright contrast while the layers further away from the source, and focal plane, of the TEM appear darker.

The electron beam of the TEM may be utilized to create nano-area electron diffraction patterns (SAED) that may identify the number of layers in the suspended graphene flakes. This measurement may be realized by varying the incidence angle between the graphene sheet and the electron beam. The electron diffraction pattern in Fig. 5 (b) from the graphene sample is indicative of electron diffraction from a single layer of graphene. The dark field in the TEM image is due to the objective aperture and the incident beam alignment selecting scattered electrons over a very small angle.

The quality of graphene is based on the atomic arrangement of carbon in a planar hexagonal lattice to create, ideally, a single layer graphene sheet. Once formed graphene is a candidate for inclusion in electronic and optoelectronic applications. This work has shown that a drop-cast PMMA-dichlorobenzene matrix is a good source for low temperature film growth.

The surface morphology and thickness of graphene film (~1 nm) can be measured by AFM as shown in Fig. 6. The presence of some defects is clear, which are significantly higher than the substrate which has been attributed to residential contamination of PMMA [18], used to mechanically support the graphene film during the transfer process.

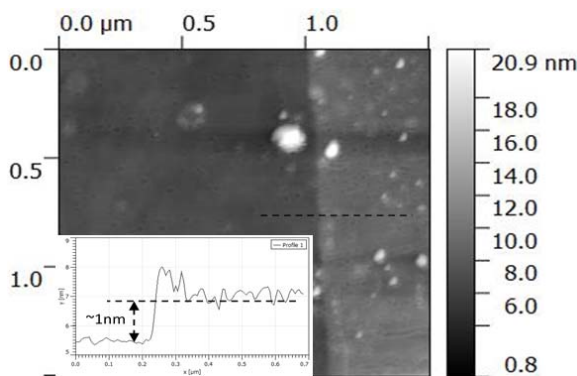


Fig. 6 AFM image of a graphene film prepared at $T_{\text{growth}} 600\text{ }^{\circ}\text{C}$ with H_2 gas flow rate of 75 sccm transferred onto Si substrate

IV. CONCLUSION

The significance of this work lies in the identification of the carbon source characteristics and CVD parameters to allow low temperature growth of graphene on a clean electropolished copper substrate. The flow rate of H_2 gas was optimized to improve the quality of the graphene film and a rate of 75 sccm was identified for the $T_{\text{growth}} 600\text{ }^{\circ}\text{C}$ deposition

to give the highest quality film. Multi-layers of graphene were deposited on Cu foil from the PMMA-chlorobenzene source. This carbon source was a good material for decreasing the decomposition temperature for the formation of graphene layers.

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REFERENCES

- [1] Yao, Y., et al., *Controlled Growth of Multilayer, Few-Layer, and Single-Layer Graphene on Metal Substrates*. The Journal of Physical Chemistry C, 2011. 115(13): p. 5232-5238.
- [2] Campos-Delgado, J., et al., CVD synthesis of mono- and few-layer graphene using alcohols at low hydrogen concentration and atmospheric pressure. Chemical Physics Letters, 2013. 584(Supplement C): p. 142-146.
- [3] Muñoz, R. and C. Gómez-Aleixandre, *Review of CVD Synthesis of Graphene*. Chemical Vapor Deposition, 2013. 19(10-11-12): p. 297-322.
- [4] Li, Z., et al., Low-Temperature Growth of Graphene by Chemical Vapor Deposition Using Solid and Liquid Carbon Sources. ACS Nano, 2011. 5(4): p. 3385-3390.
- [5] Sun, Z., et al., *Growth of graphene from solid carbon sources*. Nature, 2010. 468(7323): p. 549-552.
- [6] Sulaiman, K., et al., *Matrix assisted low temperature growth of graphene*. Carbon, 2016. 107(Supplement C): p. 325-331.
- [7] Zhang, B., et al., Low-Temperature Chemical Vapor Deposition Growth of Graphene from Toluene on Electropolished Copper Foils. ACS Nano, 2012. 6(3): p. 2471-2476.
- [8] Pavel, P., et al., Ultrasoft metallic foils for growth of high quality graphene by chemical vapor deposition. Nanotechnology, 2014. 25(18): p. 185601.
- [9] Hu, J., et al., Roles of Oxygen and Hydrogen in Crystal Orientation Transition of Copper Foils for High-Quality Graphene Growth. Scientific Reports, 2017. 7: p. 45358.
- [10] Wei, W., et al., Control of thickness uniformity and grain size in graphene films for transparent conductive electrodes. Nanotechnology, 2012. 23(3): p. 035603.
- [11] Zeng, W.R., S.F. Li, and W.K. Chow, *Review on Chemical Reactions of Burning Poly(methyl methacrylate) PMMA*. Journal of Fire Sciences, 2002. 20(5): p. 401-433.
- [12] Grassie, N. and H.W. Melville, *C-Degradation. The mechanism of the thermal degradation of polymethyl methacrylate*. Discussions of the Faraday Society, 1947. 2(0): p. 378-383.
- [13] Ouano, A.C. and R. Pecora, Rotational Relaxation of Chlorobenzene in Poly(methyl methacrylate). 1. Temperature and Concentration Effects. Macromolecules, 1980. 13(5): p. 1167-1173.
- [14] Reina, A., et al., Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. Nano Lett, 2009. 9(1): p. 30-5.
- [15] An, W., X.C. Zeng, and C.H. Turner, *First-principles study of methane dehydrogenation on a bimetallic Cu/Ni(111) surface*. The Journal of Chemical Physics, 2009. 131(17): p. 174702.
- [16] Levendorf, M.P., et al., *Transfer-Free Batch Fabrication of Single Layer Graphene Transistors*. Nano Letters, 2009. 9(12): p. 4479-4483.
- [17] Nguyen, V.T., et al., Synthesis of multi-layer graphene films on copper tape by atmospheric pressure chemical vapor deposition method. Advances in Natural Sciences: Nanoscience and Nanotechnology, 2013. 4(3): p. 035012.
- [18] Park, H., et al., Graphene As Transparent Conducting Electrodes in Organic Photovoltaics: Studies in Graphene Morphology, Hole

Transporting Layers, and Counter Electrodes. Nano Letters, 2012. 12(1): p. 133-140.

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