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Graphene Research Support

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14. ABSTRACT There was a steady increase in average flake size in the years following the initial isolation of monolayer grapheme in 2004, but even by 2008, flakes rarely exceeded 1000 μm^2. As part of the research for this grant, carefully analyzed the factors that affect flake size, including: graphite source (natural, HOPG, Kish), type of adhesive tape, number of cleaves, substrate material and roughness, substrate cleaning (sonication, piranha etch, oxygen plasma, etc.) and temperature. They found that the number of graphite cleaves and the substrate cleaning procedures were the most common factors that limited flake size. By cleaving only 5-10 times (typical number of cleaves in previous procedures was >20) and cleaning with oxygen plasma, we were able to routinely prepare flakes >100, 000 μm^2 and occasionally >1 mm². With flakes more than 100 μm in diameter, a wider range of experiments became possible. Optical scanning measurements over large regions, ellipsometry, infra-red-spectroscopy and capacitance devices have yielded interesting results. Occasionally when preparing large flakes, air can get trapped between the substrate and the grapheme, forming bubbles. The shape of these bubbles can be controlled with a gate voltage, potentially allowing for grapheme-based adaptive focus lenses.					
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Organisation	Graphene Industries Ltd. Manchester Centre for Mesoscience & Nanotechnology Oxford Road Manchester, UK

Flake size improvement

There was a steady increase in average flake size in the years following the initial isolation of monolayer graphene in 2004, but even by 2008, flakes rarely exceeded $1000 \mu\text{m}^2$. As part of the research for this grant, we carefully analysed the factors that affect flake size, including: graphite source (natural, HOPG, Kish), type of adhesive tape, number of cleaves, substrate material & roughness, substrate cleaning (sonication, piranha etch, oxygen plasma etc.) and temperature.

We found that the number of graphite cleaves and the substrate cleaning procedure were the most common factors that limited flake size. By cleaving only 5-10 times (typical number of cleaves in previous procedures was >20) and cleaning with oxygen plasma, we were able to routinely prepare flakes $>100,000 \mu\text{m}^2$ and occasionally $>1 \text{ mm}^2$ (example flake shown in fig 1).

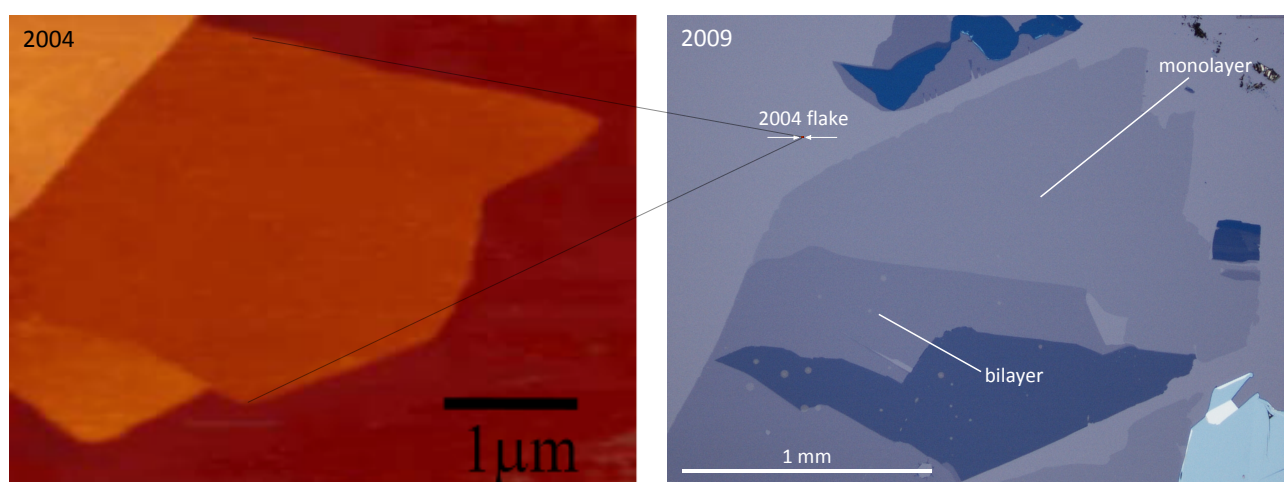


Figure 1: Left: AFM image of one of the first monolayer flakes [Novoselov et al. Science, 2004]. Right: graphene flake containing mono- and bilayer regions on 90 nm SiO_2 , largest known single crystal flake produced to date and visible to the naked eye.

With flakes more than $100 \mu\text{m}$ in diameter, a wider range of experiments became possible. Optical scanning measurements¹ over large regions, ellipsometry², infra-red spectroscopy³ and capacitance devices⁴ have

yielded interesting results.

Occasionally when preparing large flakes, air can get trapped between the substrate and the graphene, forming bubbles. The shape of these bubbles can be controlled with a gate voltage, potentially allowing for graphene-based adaptive focus lenses⁵.

[1] ZH Ni, LA Ponomarenko, RR Nair, R Yang, S Anissimova, IV Grigorieva, F Schedin, **P Blake**, ZX Shen, EH Hill, KS Novoselov, and AK Geim, *On resonant scatterers as a factor limiting carrier mobility in graphene*, Nano Lett **10** (2010), no. 10, 3868–3872

[2] VG Kravets, AN Grigorenko, RR Nair, **P Blake**, S Anissimova, KS Novoselov, and AK Geim, *Spectroscopic ellipsometry of graphene and an exciton-shifted van Hove peak in absorption*, Phys. Rev. B **81** (2010), 155413*

[3] AB Kuzmenko, L Benfatto, E Cappelluti, I Crassee, D van der Marel, **P Blake**, KS Novoselov, and AK Geim, *Gate tunable infrared phonon anomalies in bilayer graphene*, Physical Review Letters **103** (2009), no. 11, 116804*

[4] LA Ponomarenko, R Yang, RV Gorbachev, **P Blake**, AS Mayorov, KS Novoselov, MI Katsnelson, and AK Geim, *Density of states and zero Landau level probed through capacitance of graphene*, Phys. Rev. Lett. **105** (2010), 136801

[5] T Georgiou, L Britnell, **P Blake**, RV Gorbachev, A Gholinia, AK Geim, C Casiraghi, and KS Novoselov, *Graphene bubbles with controllable curvature*, Appl. Phys. Lett. **99** (2011), no. 9, 093103–3*

Graphene flakes on other substrates

As part of our research into the effects of substrate material on flake preparation/yields, we were able to isolate graphene on materials other than oxidised silicon, including gold for scanning tunneling measurements⁶, quartz for optical measurements² and thin layers of pmma - enabling flake transfer to boron nitride substrates⁷.

[6] Z Klusek, P Dabrowski, P Kowalczyk, W Kozłowski, W Olejniczak, **P Blake**, M Szybowicz, and T Runka, *Graphene on gold: Electron density of states studies by scanning tunneling spectroscopy*, Applied Physics Letters **95** (2009), no. 11, 113114*

[2] Kravets et al., *Spectroscopic ellipsometry of graphene and an exciton-shifted van Hove peak in absorption*, full details are in the *Flake size improvement* section.

[7] AS. Mayorov, RV Gorbachev, SV Morozov, L. Britnell, R Jalil, LA Ponomarenko, **P Blake**, KS Novoselov, K Watanabe, T Taniguchi, and AK Geim, *Micrometer-scale ballistic transport in encapsulated graphene at room temperature*, Nano Lett **11** (2011), no. 6, 2396–2399

Graphene Membranes

We refined our technology⁸ for making graphene membranes and explored the application of TEM imaging of viruses and biological molecules⁹.

[8] **P Blake** and T Booth, *Method of forming an ultra-thin sheet suspended on a support member*, US patent application 12/934,325 (2010)

[9] RR Nair, **P Blake**, JR Blake, R Zan, S Anissimova, U Bangert, AP Golovanov, SV Morozov, AK Geim, KS Novoselov, and T Latychevskaya, *Graphene as a transparent conductive support for studying biological molecules by transmission electron microscopy*, Applied Physics Letters **97** (2010), no. 15, 153102

Hexagonal Boron Nitride

In 2010, Dean et al. [Nat Nano 5, 722-726] showed that hexagonal boron nitride (hBN) was an excellent substrate for graphene. We found that hBN was also an excellent capping material for graphene⁷.

We were able to isolate and characterise¹⁰ mono-, bi- and trilayer hBN using similar techniques that we developed for graphene. 2D insulators such as hBN are an essential building block for graphene heterostructure devices.

[7] Mayorov et al., *Micrometer-scale ballistic transport in encapsulated graphene at room temperature*, full details are in the *Graphene flakes on other substrates* section.

[10] RV Gorbachev, I Riaz, RR Nair, R Jalil, L Britnell, BD Belle, EW Hill, KS Novoselov, K Watanabe, T Taniguchi, AK Geim, and **P Blake**, *Hunting for monolayer boron nitride: Optical and raman signatures*, Small **7** (2011), no. 4, 465–468*

Notes

*AFOSR was not included in the acknowledgement section for these papers; apologies for the oversight.