AFRL-AFOSR-UK-TR-2012-0042

Graphene Research Support

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EOARD Grant 09-3021

Report Date: September 2012

Final Report for 15 August 2009 to 14 August 2010

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Air Force Research Laboratory
Air Force Office of Scientific Research
European Office of Aerospace Research and Development
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REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From – To)*
10 September 2012	Final Report	15 August 2009 – 14 August 2010

4. TITLE AND SUBTITLE

Graphene Research Support

5a. CONTRACT NUMBER

FA8655-09-1-3021

5b. GRANT NUMBER

Grant 09-3021

5c. PROGRAM ELEMENT NUMBER

61102F

6. AUTHOR(S)

Peter Blake

5d. PROJECT NUMBER

5d. TASK NUMBER

5e. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

EOARD
Unit 4515 BOX 14
APO AE 09421

10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/AFOSR/RSW (EOARD)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

AFRL-AFOSR-UK-TR-2012-0042

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

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 µm2. 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 µm2 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.

15. SUBJECT TERMS

EOARD, Electronic Devices, Electronic Materials, graphene

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18, NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			SCOTT DUDLEY, Lt Col, USAF
UNCLAS	UNCLAS	UNCLAS	SAR	5	19b. TELEPHONE NUMBER *(Include area code)* +44 (0)1895 616162

Final Report for AFOSR Award FA8655-09-1-3021

Proposal Title	Graphene Research Support
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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 µm^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 µm^2 and occasionally >1 mm^2 (example flake shown in fig 1).

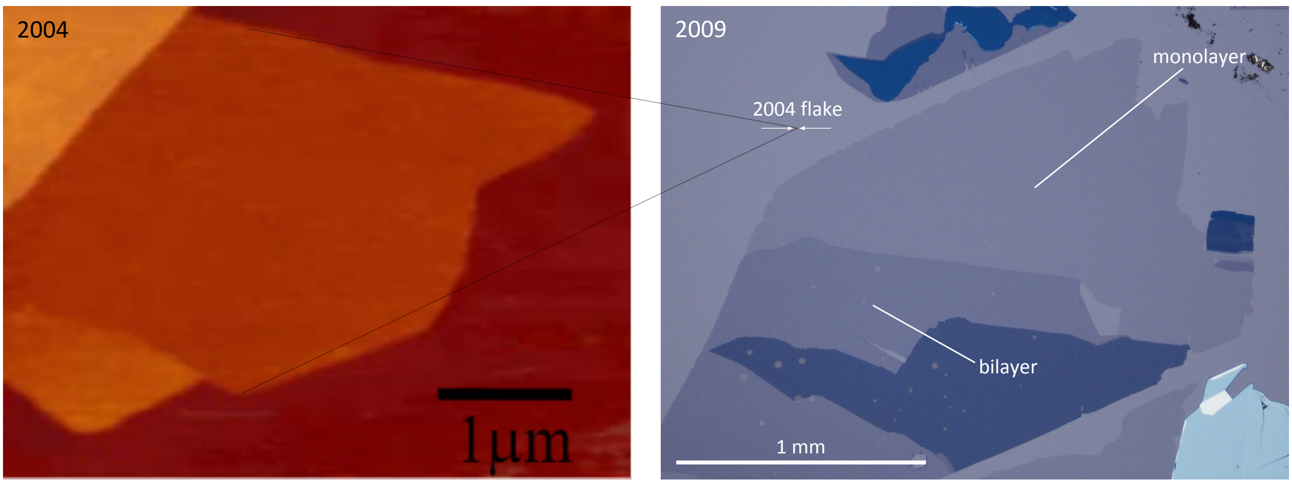

Figure 1: Left: AFM image of one of the first monolayer flakes [Novoselov et al. Science, 2004]. Right: graphene flake containing mono- and bilayer regions on 90 nm SiO_2, largest known single crystal flake produced to date and visible to the naked eye.

With flakes more than 100 µm in diameter, a wider range of experiments became possible. Optical scanning measurements[1] over large regions, ellipsometry[2], infra-red spectroscopy[3] and capacitance devices[4] have

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yeilded 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 lenses[5].

[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 measurements[6], quartz for optical measurements[2] and thin layers of pmma - enabling flake transfer to boron nitride substrates[7].

[6] Z Klusek, P Dabrowski, P Kowalczyk, W Kozlowski, 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

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Graphene Membranes

We refined our technology[8] for making graphene membranes and explored the application of TEM imaging of viruses and biological molecules[9].

[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 Latychevskaia, *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 graphene[7].

We were able to isolate and characterise[10] 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 heterostucure 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.

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