

Fabrication and transport properties of graphene-based nanostructures

Submitted by Roman V. Gorbachev to the University of Exeter as a
thesis for the degree of Doctor of Philosophy in Physics
June, 2009

This thesis is available for Library use on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.

I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Roman V. Gorbachev
June, 2009

Abstract

In this work fabrication and studies of transistor structures based on an atomic sheet of graphite, graphene, are described. Since graphene technology is in its early stages, the development and optimisation of the fabrication process are very important. In this work the impact of various fabrication conditions on the quality of graphene devices is investigated, in particular the effects on the carrier mobility of the details of the mechanical exfoliation procedure, such as environmental conditions and humidity, source of graphite and wafer cleaning procedure. In addition, a comparison is made between the conventional e-beam lithography and lithography-free fabrication of samples. It was also demonstrated that water and other environmental species play an important role in graphene-to-substrate adhesion and can also contribute to the carrier scattering in graphene.

A technique for creating suspended metal gates was developed for the fabrication of graphene p-n-p structures, and charge transport has been studied in such top-gated graphene devices. Depending on the relation between the carrier mean free path and the length of the top-gate we have realized three distinct transport regimes through the p-n-p structure: a) diffusive across the structure; b) ballistic in the regions of p-n junctions but diffusive in the n-region; c) ballistic across the whole p-n-p structure. The second regime has revealed the chiral nature of carriers in graphene. This was demonstrated by comparing the experimental resistance of a single p-n junction with results of electrostatic modeling in the diffusive model. In the third regime we have observed oscillations of the device resistance as a function of carrier concentration in the n-region, which are also dependent on magnetic field. These oscillations have been demonstrated to be a direct consequence of a Fabry-Perot-like interference effect in the graphene p-n-p structures.

Acknowledgements

I would like to express my gratitude to many people who helped me during the period of my PhD studies.

First of all, I am very grateful to my supervisor Prof. Alex Savchenko for his encouragement and support throughout these years. Special thanks goes to Andrew Kretinin and Dave Horsell for sharing their knowledge and experimental experience. It was priceless and much appreciated.

I would like to thank other PhD students: Fedor Tikhonenko and Sasha Mayorov for the assistance they provided at all levels of the research, Adam Price for helping me to improve my English skills, Alexey Kaverzin and Alexey Kozikov to whom I was lucky to work with.

I must also acknowledge all the technical support in the Physics Department. Some things would never have been possible without the help of Paul Wilkins, Stephen Tuckett, Kevin White, Peter Cann, Matthew Wears and Phil Slade. Dave Manning and Adam Woodgate did a great job making sure the supply of liquid helium never stopped. The Stores never ceased to be a treasury full of useful things thanks to John Meakin. I would also like to thank the office staff for all the times their assistance helped me along the way.

Separate thanks to Massimo Gludini for sharing his knowledge of SPM, Kostya Novoselov (Manchester University) for very useful discussions about graphene, Geb Jones and David Anderson (Cavendish Laboratory) for the communication concerning e-beam lithography.

My PhD studies would not have been possible without the financial assistance of the Overseas Research Student Award Scheme and the University of Exeter, and I express my gratitude to them.

I would like to thank my friends George Zorinyants and Tatyana Voronina, Fedor and Natasha Ogrin, Alexander Beloglazov, Andrey Kondratyuk, Olga Mihal'chenko, Sergey Levin and, especially, Julia Lalina for supporting me and having fun together.

And last but not least, I would also like to thank my family for the opportunity to have a good education and support they provided me through all the years of my study.

Contents

Abstract	2
Acknowledgements	3
Contents	4
List of Figures	8
List of Tables	15
Introduction	16
1 Basic theoretical concepts of graphene	18
1.1 Graphene dispersion relation. Tight binding approximation	18
1.2 Low energy approximation. Dirac Hamiltonian. Berry phase	22
1.3 Chirality, DOS	26
1.4 Transistor structure: graphene on n-Si/SiO ₂	28
1.5 Carrier scattering in graphene on SiO ₂	29
1.6 Conclusion	31
2 Experimental methods of graphene fabrication	32
2.1 Introduction	32
2.2 Wafers for graphene deposition	34
2.2.1 General information	34
2.2.2 Cleaning methods	35
2.2.3 Surface topography	36
2.2.4 Water on SiO ₂	37
2.3 Graphite	39

2.3.1	General information	39
2.3.2	Adhesion to graphite surface	41
2.4	Conventional graphene deposition	43
2.5	Environmental graphene deposition	44
2.6	Thin flakes search and identification	46
2.7	AFM study of graphene and its environment	47
2.7.1	Introduction	47
2.7.2	Step height measurements	48
2.7.3	Morphology of graphene on silica	50
2.7.4	Effect of high electric field on SiO ₂ wafers	51
2.7.5	Contamination induced by electric field	53
2.7.6	Contamination after fabrication and annealing	54
2.8	Conclusion	57
3	Device Fabrication	58
3.1	Introduction	58
3.2	Electron Beam Lithography	59
3.3	Elphy quantum. Exposure logistics	61
3.4	Spatial energy distribution. Proximity effect.	63
3.5	E-beam resists	65
3.6	Multilayer resist. Development	68
3.7	Metalization. Undercut profile. Lift-off	69
3.8	Packaging and bonding	72
3.9	“Old” fabrication route	73
3.10	“New” fabrication route	74
3.11	Example of graphene Hall-bar fabrication	75
3.12	Shaping graphene flakes	80
3.13	Samples storage and handling	81
3.14	Flake suspension and further technology development	83
3.15	Summary	84
4	Transport in graphene flakes	86
4.1	Introduction	86
4.2	Experimental setup	86

4.3	Basic characterisation	87
4.4	Annealing and Doping	
	Samples Statistics	89
4.5	Review of scattering mechanisms	92
4.6	Temperature dependencies of the conductivity: experimental results	95
4.7	Transport in high magnetic field	96
	4.7.1 Specifics of high B behaviour in graphene	96
	4.7.2 Experimental observation of resistance in high B	97
4.8	Weak Localisation	100
4.9	Conclusion	101
5	Suspended bridge fabrication	102
5.1	Introduction	102
5.2	General technique	103
5.3	EBL and resist	104
	5.3.1 Focusing and exposure	104
	5.3.2 Resist intermixing	105
5.4	Undercut profile and dose selection	106
5.5	Way forward	109
5.6	Conclusion	111
6	Transport in top-gated structures	112
6.1	Transmission through a single p-n junction	112
6.2	Characteristic lengths of a p-n-p structure, effects of disorder	115
6.3	Experimental results: overview	117
6.4	Electrostatic modeling	119
6.5	Diffusive and ballistic regimes of a single p-n interface	121
6.6	Fully ballistic regime of the p-n-p structure	124
6.7	Transport through p-n-p structure in magnetic field	128
6.8	Conclusion	131
7	Further developments and suggestions	132
	Bibliography	134

A Inserts

141

List of Figures

1.1	Graphene honeycomb crystal lattice. (a) Two independent sublattices are shown with different colour, yellow rhombus is the primitive cell. (b) Graphene lattice in the reciprocal space, yellow fill shows two possible selections of the Brillouin zone.	19
1.2	Band diagram of graphene in the nearest neighbours approximation according to relation 1.12.	22
1.3	Lines of the constant energy for the graphene dispersion relation 1.12.	23
1.4	Change from the hexagonal Brillouin zone to the diamond-shaped. . .	23
1.5	Illustration for the chirality in graphene – yellow and blue colours denote chirality of 1 and -1.	27
2.1	Different termination of the oxide surface.	34
2.2	TAFM surface image of silicon dioxide, 1 - roughness distribution and 2 - autocorrelation function for the given image.	37
2.3	Water H-bonded to silanol terminated SiO ₂	38
2.4	Dependence on the relative humidity of: water film thickness on SiO ₂ by XPS study (left axis) and the surface potential measured by Kelvin-probe AFM (right axis) [32].	38
2.5	Hexagonal graphite lattice arranged in Bernal $A\bar{B}$ stacking.	40
2.6	SEM image of natural graphite, scale bar 100 μm	40
2.7	Micrometer size water droplets on graphite surface [36].	41
2.8	Comparison of binding energies of molecules on graphite surface obtained from the friction experiments to other values in literature. From [41].	42
2.9	Nitto adhesive tape (blue) with graphite flakes (black).	43
2.10	Chamber for environmental graphene deposition.	44

2.11	Density of deposited graphite as a function of relative humidity. . . .	45
2.12	Optical image of a multi-step flake under optical microscope, (a) with white light source, (b) green filtered. Scale bar is 20 μm . 1 and 2 denote single layer and bilayer parts.	47
2.13	Schematics of scanning probe microscope.	48
2.14	TAFM image of a folded graphene flake. Insets give the height profiles averaged over rectangular boxes 1 and 2, respectively.	49
2.15	TAFM image of a graphene flake. Number 1 denotes SiO_2 , 2 – graphene single and 3 – triple-layer regions.	50
2.16	Flake manipulation using the AFM tip. (a) TAFM scan of the initial flake, b – folded flake, c – zoomed area indicated on image b.	52
2.17	Effect of local charging of silicon dioxide. Scale bar is 2 μm	52
2.18	Topography of pristine flake (a), phase contrast image of contaminated (b) and heavily contaminated (c) flake. All images have the same scale and were acquired in the same region.	54
2.19	Topography of a pristine graphene flake on silica (left) and a sample which passed the conventional contact fabrication procedure (right).	55
2.20	Effect of annealing on topography of graphene devices: (a) a sample annealed in helium at 150° C; (b) single line scan showed as the white dashed line in (a); (c) annealed in Ar/H ₂ mixture at 400° C; (d) summary table for topography measurements. Scale bar is 1 μm	56
3.1	Schematic of an electron beam microscope.	60
3.2	Pattern fragmentation before the exposure. Numbers shown default left-to-right exposure order.	61
3.3	Gaussian contribution from forward scattering (solid line) and back-scattering (dashed dot line) for low (a) and high (b) beam energy. Proximity effect: initial pattern (c), actual dose distribution (d) and profile of developed resist (e).	64
3.4	Metal contacts to a graphene flake. Left - correct dose distribution and shape, right - distortion due to the proximity effect. Scale bar 1 μm	64

3.5	Developed resist thickness plotted against exposure dose. Solid line is normal resist; dashed line is the same resist with higher molecular weight, short dashed – with broad distribution of molecular weights.	66
3.6	Structure of PMMA polymer.	67
3.7	PMMA reaction under electron or UV irradiation.	68
3.8	Structure of the P(MMA-MAA) copolymer.	69
3.9	Illustration of the ‘shadow’ effect during metal evaporation using two sources.	71
3.10	Lift-off in the acetone distiller.	71
3.11	A piece of silicon wafer with a graphene sample glued and bonded to a package.	72
3.12	Back side of the package for the further electrical connections.	72
3.13	Standard technological route. Dotted block can be placed in any of two positions.	74
3.14	Second technological route.	75
3.15	Optical image of uncovered flake on 275 nm silicon dioxide surface (in white light).	77
3.16	Optical image of the flake covered with ~ 100 nm PMMA layer and the 4 nearest crosses (green light).	77
3.17	Structure design superimposed on the optical image of a graphene flake.	78
3.18	Optical image of the developed contact pattern.	79
3.19	Optical image of the finished sample.	79
3.20	Plasma etching of graphene flakes: (a) initial optical image of a flake, (b) Hall-bar design (black lines), (c) final device after the etching and contacts fabrication. Scale bar is $2 \mu\text{m}$	81
3.21	SEM image of the sample damaged by ESD.	82
3.22	SEM image of the sample damaged by thermal shock. A split in the flake can be seen around the contact.	82
3.23	SEM image of (left side) suspended and (right side) collapsed parts of a graphene flake, tilt 45°	84

4.1	Characterization of a graphene sample: a - resistivity (left scale, black) and conductivity (right scale, red) as a function of the carrier concentration, b - carrier mobility (left scale, black) and mean free path (right scale, red) as a function of the carrier concentration.	88
4.2	(a) Effect of annealing on the $R(V_{bg})$ dependence of single and bilayer graphene samples. Inset shows optical image of the sample. (b) Statistical results on the graphene mobilities plotted against peak values of the sheet resistance. Black circles denote standard fabrication technique, blue dots – flakes deposited in dry argon, red dots – lithography-free technique.	90
4.3	Lithography-free graphene device. Flake length is $\sim 20 \mu\text{m}$	91
4.4	(a) Conductance as a function of back-gate voltage for different temperatures, top black curve shows result of the linearization procedure. (b) Extracted values of R_{\min} as a function of temperature. (c) Slope α as a function of temperature. Colours denote different samples.	95
4.5	Shubnikov-de Haas oscillations (a) and Hall effect (b) as a function of magnetic field for three different concentrations indicated as coloured dots on $R(V_{bg})$ in the inset of (b). Temperature is 4 K, carrier mobility for the studied range on V_{bg} is $\mu = 12000 \text{ cm}^2/\text{Vs}$	98
4.6	Left axis: quantum lifetime as a function of the carrier concentration for different temperatures (corresponded data shown as symbols, see colour-code). Right axis: momentum relaxation time (refers to solid line) calculated from $R(V_{bg})$	99
4.7	R_{xx} as a function of B for $n = 1.5 \cdot 10^{12} \text{ cm}^{-2}$, $T = 50 \text{ mK}$. The filling factor values are found from the position in B of centers of minima in R_{xx}	99
4.8	The longitudinal (black and red, left axis) and transverse (green and blue, right axis) conductivity as a function of gate voltage, with $T = 5.6 \text{ K}$ $B = 12.5 \text{ T}$	99
5.1	Stages of suspended gate fabrication: a – electron beam exposure, b,c – resist development, d – metalization and e – lift-off.	104
5.2	Contamination spot grown using 20 second point-like exposure.	105

5.3	PMMA dissolution rates, taken from [99].	106
5.4	Undercut profile for different resist configurations. Bilayer (a) (span) and triple layer (b) (pillar), (c) (span) resist techniques.	106
5.5	Developed resist thickness against the exposure dose for the two different resist layers. Red lines d_{span} and d_{pillars} illustrate a correct exposure doses for the different regions of suspended bridge.	107
5.6	SEM image of three different bridges made with 45° tilt to the surface. Image (b) shows the optimal span dose, whilst (c) and (a) are overexposed and underexposed cases, respectively.	108
5.7	Bridge clearance as a function of the span dose. Three curves show 60, 75 and 150 nm wide patterns resulting in 90, 105 and 150 nm real span width, respectively.	108
5.8	Nanotube suspension: a nanotube embedded into resist (a), illustration for metal clamping (b).	110
5.9	MWCN manipulation on a graphene sample. Initial (a) and final (b) positions of the nanotube (highlighted with the green arrow) imaged with TAFM.	111
6.1	Illustration of chiral tunneling through a sharp p-n junction (see text).	112
6.2	Tunneling through a smooth p-n junction.	113
6.3	Illustration for different transport regimes inside p-n-p structure: from (a) fully diffusive to (c) fully ballistic.	115
6.4	Oscillations in (a) transmission coefficient and (b) resistance as a function of the potential depth under the top gate from [104]. Inset shows scaling of the peak positions as a function of $n^{2/3}$, where n is the peak number.	117
6.5	Sample S2: (a) SEM image and (b) resistance in high magnetic field (see text)	118
6.6	Top-gate dependence of the resistance for different values of $V_{\text{bg}} = V_{\text{bg}}^{\text{off}} + i[\text{V}]$, where $i = 1\dots 9$, from top to bottom.	119
6.7	Colour-scale plot of the resistance as a function of V_{tg} and V_{bg} (sample S1). Coloured arrows refer to the line sweeps in Fig.6.6.	119

6.8	Electrostatic modeling reported in [94]: (a) Geometry of top gated structure used in the calculations, (b,c,d) potential profile along the flakes S1,S2,S3 at fixed V_{bg} and different V_{tg} . Bold bars indicate the mean free path length.	120
6.9	(a) Resistivity of samples S1, S2 and S3 as a function of V_{bg} , at $T = 50$ K and $V_{tg} = 0$. (b,c,d) The resistance of samples S1, S2 and S3, respectively, as a function of V_{tg} (values of V_{bg} shown as symbols in (a)). The empty circles show the result of the modeling assuming diffusive transport of carriers.	122
6.10	Resistance as a function of V_{tg} showing an oscillatory behaviour for a small values of l_{pnp} in the range of V_{tg} between 19 and 32 V.	124
6.11	The oscillations at 4.2 K: reproducibility test for a different mesoscopic realization, curves shifted by 0.5 k Ω	124
6.12	Reproducibility test for the dependence shown in Fig.6.10. Black and red curves denote different sweep directions.	125
6.13	Temperature dependence of the oscillations. The curves are shifted by 0.5 k Ω	125
6.14	Results of electrostatic modeling for sample S4: (a) potential profile along the flake calculated for different top-gate voltages; (b) dependence of l_{pnp} and the potential depth ε on the top-gate voltage; (c) the parabolic fit for the potential shape (see text).	127
6.15	Comparison of the observed peak positions (black dots) with the theoretically predicted values (red dots and line) [104].	128
6.16	Shift of the oscillations in magnetic field: red curve $B = 0$, blue $B = 300$ mT.	129
6.17	Grey-scale plot of resistance as a function of V_{tg} and B showing a shift of the oscillations.	129
6.18	Magnetoresistance up to 1.5 T for three different regions on the $R(V_{tg})$. Solid lines are the weak localisation fits.	130
A.1	Modification done to Heliox VL cryostat cold-finger. Allows quick and reliable connection of the sample packages to the cryostat wires. . .	141

- A.2 Low temperature part of the experimental insert used for characterisation study of graphene samples and annealing in a transport dewar. 142
- A.3 Environmental chamber for doping experiments. Insert with the sample nest, heater and environmental gauges (top) and a chamber body with transparent optical window, gas inlet and pumping port. . . . 143

List of Tables

6.1	Summary of measured samples.	118
-----	--------------------------------------	-----