

Report

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**Graphene: a review of the
state of the art and future
metrology applications**

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ABSTRACT

Metrology has a long history, over the past fifty years at least, of providing the first application of new science. The unexpected discovery of the existence of a true 2D isolated material, graphene, is a new and important material which was only discovered in 2004. Apart from fundamental physics interests it is becoming clear that it also has considerable metrological potential. This report includes a detailed literature search summarising the present state of the art of this new material, outlining prospects for longer term research work, ending with conclusions about future possible directions for NPL research. We also include suggestions for leading edge metrology (such as Quantum Hall Effect (QHE), SET, quantum resistor and capacitor, spintronics, quantum spin Hall effect), and the possibility of a number of enabling new sensor types in this area. A second component of this report describes our preliminary experimental work on preparation, identification, processing and characterisation of graphene samples, including AFM, SEM, confocal microscopy analysis, transport properties and optical response.

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Approved on behalf of the Managing Director, NPL
by (*Susan Evans*), Director, *Industry & Innovation Division*

Table of Contents:

1. Executive Summary	1
2. Introduction.....	2
2.1 <i>Background</i>	2
2.2 <i>The Electronic Structure of Graphene</i>	3
3. Graphene: a Brief History of Preparation and Experiments	4
3.1 <i>Single layer graphene fabrication.....</i>	4
3.1.1 <i>Layer by layer preparation– from graphene to graphite in 10 steps</i>	4
3.2 <i>Epitaxial growth of graphene.....</i>	5
3.3 <i>Preparing devices on graphene.....</i>	5
3.4 <i>SPM study of single layer graphene.....</i>	6
3.4.1. <i>Optical method for rapid graphene identification</i>	6
3.4.2 <i>AFM/STM imaging of graphene</i>	7
3.4.3 <i>TEM imaging of graphene</i>	7
3.4.4 <i>Raman Spectroscopy of Graphene</i>	7
3.5 <i>Electrons in graphene: ballistic massless Dirac fermions.....</i>	9
3.6 <i>The Quantum Hall Effect (QHE) and Chirality</i>	9
3.7 <i>Metallic FET and QDs in few-layer graphene.....</i>	11
3.8 <i>Induced Superconductivity in Graphene</i>	12
3.9 <i>Spintronics and Spin Quantum Hall Effect in Graphene</i>	13
4. Preliminary NPL experimental results	14
4.1 <i>Sample preparation.....</i>	14
4.2 <i>Few Layer Graphene Identification</i>	16
4.3 <i>AFM characterisation</i>	17
4.4 <i>Experimental Raman Measurements on Graphene.....</i>	19
4.5 <i>Deposit electrodes and transport measurements</i>	21
4.6 <i>Future plans</i>	23
5. Graphene future and potential benefits to NPL	23
5.1 <i>QHE (Quantum Hall Effect) at room temperature.....</i>	24
5.2 <i>Possible tests of the quantum electrical triangle</i>	24
5.3 <i>Quantum capacitance of CNTs/graphene</i>	25
5.4 <i>Single Electron Transistors using Graphene</i>	25
5.5 <i>Spintronics and the Spin QHE in Graphene</i>	25
5.6 <i>Nano-ribbons and applications (QDs, spintronics and ‘Valley-tronics’)....</i>	26
5.7 <i>Nanoelectronics: ballistic transport.....</i>	28
5.8 <i>QED.....</i>	28
6. Conclusions.....	28
7. Acknowledgement:.....	29
8. References.....	30

1. Executive Summary

Metrology has a long history of providing the first application of new science over the past fifty years. The unexpected discovery of the existence of a true 2D isolated material, graphene, in 2004 has yielded a dramatic new scientific laboratory in which, again, metrological applications are very likely within the next few years. The first three years of existence of this research topic have led to the publication of more than one hundred research and review papers and the rate of publication is still increasing.

Graphene completes the range of remarkable *reduced dimension* structures containing only the element carbon with sp^2 bonding. This began with the zero dimensional (0D) fullerenes ('buckyballs'), continued through the 1D carbon nanotubes and ends with 2D graphene. Each reduced dimension has introduced radical new behaviour and graphene proves to be no exception. To summarise some of the most surprising observations:

Graphene exhibits

- ❑ Dispersion-free density of states, mimicking the Dirac equation for massive relativistic particles
- ❑ The quantum Hall effect *at room temperature*
- ❑ Proximity induced superconductivity at temperatures above 1K, with long decay lengths, making fabricated Josephson junctions feasible.
- ❑ Extremely long spin polarisation decay lengths, making graphene highly promising for spintronics applications.
- ❑ Possible new topological quantum standard of spin conductance
- ❑ Gate control of carrier density and sign, allowing samples with metallic levels of conductivity to be switched by an electric field from p-type to n-type.
- ❑ Minimum quantum conductivity and quantum capacitance in graphene devices

This list reflects the situation at the time of writing this report (November 2007). We may anticipate that the fundamental physics surprises from graphene have not yet been exhausted.

In asking how metrology may benefit from the above possibilities the most direct impact may come through the quantum Hall effect where graphene based devices may allow the precise realisation of quantised resistance standards to be made at temperatures far above the millikelvin region currently required. There will almost certainly be a trade-off between low temperatures and high magnetic fields in the preferred operating point for such a standard. Looking further ahead one may anticipate that graphene may enable a single-chip test of the quantum electrical triangle with high precision since Josephson junctions with graphene barriers have already been demonstrated to exhibit microwave induced constant voltage steps and we have proposed (see below) that graphene ballistic resistors may be the ideal missing component in a yet-to-be-realise coherent quantum current standard.

As well as direct opportunities for existing metrology developments the use of graphene-based charge and spin devices will present future challenges for metrology, in the demands for novel forms of measurement and even of physical parameters (e.g. spin current) which will be required. For these reasons it is important that NPL becomes actively involved in graphene research in order to play a leading role in the expected rapid and important developments already beginning to take place.

2. Introduction

2.1 Background

Single layer graphite (graphene), first prepared by Geim et al.¹, is a new and important material which was only discovered in 2004. It continues in the line of development of low dimensional crystalline materials containing only carbon. Starting with the zero dimension fullerenes, progressing through one dimensional carbon nanotubes, two-dimensional graphene completes the sequence. These materials all exhibit interesting and unique properties and graphene, the latest addition, is no exception. Apart from fundamental physics interests it is becoming clear that it also has considerable metrological potential. The quantum Hall effect (QHE) in graphene was predicted theoretically in 2005² and preliminary observations made recently^{3,4,5}. *With direct relevance to future development of the SI Quantum Hall Effect measurement*, there is a possibility to compare the value of R_K deduced from the existing standard based on semiconducting materials (operating at low temperature) with that from a graphene QHE device. The latter might even be usable at room temperature. Furthermore, during the course of this research project we have proposed that it may prove possible to realise nanoscale versions of each of the three quantum electrical standards using graphene based systems. Not only would this allow a test of the quantum electrical triangle of standards in a completely new material but it may also allow the realisation of localised standards in quantum circuits. The project has also included some preliminary experiments involving preparation, bonding and characterisation of graphene samples.

In the following paragraph we summarise in bullet point form the remarkable properties of graphene which have already been identified.

- Its electronic properties can be controlled with an externally applied voltage – this is key in the field of electronics.
- It exhibits a pronounced ambipolar electric field effect – that is to say charge carriers can be tuned continuously between electrons and holes.
- Very high mobilities ($\mu > 1.5 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), even at room temperature
- The mobility is weakly dependent on temperature T so μ depends on impurity scattering and could potentially be increased by another order of magnitude.
- In graphene μ stays high even at high carriers concentrations ($n > 10^{12} \text{ cm}^{-2}$)
- Ballistic transport is possible at RT (over a length scale currently up to $0.4 \text{ } \mu\text{m}$ at 300 K)
- Very high sustainable current densities ($> 10^8 \text{ A/cm}^2$ – see supporting material to reference 1).
- QHE is visible in graphene even at RT, although large fields ($\sim 30 \text{ T}$) are required.
- Graphene could be used as the basis for sensitive gas sensing
- Charge carriers in graphene mimic relativistic particles and are best described starting with the Dirac equation. Electrons in graphene behave as massless Dirac fermions. This is due to the conical shape of the dispersion relation for graphene which is found in the neighbourhood of the points in the Brillouin zone where the band gap approaches zero⁶.

We will discuss each of the above issues in more detail later in the report.

2.2 The Electronic Structure of Graphene

In graphene, the carbon atoms are arranged in a honeycomb pattern, with each atom bound to three neighbours through strong, covalent bonds. This gives graphene exceptional structural rigidity within its layers. Because a carbon atom has four electrons available for bonding, each atom also contributes one unbound electron that is itinerant through the crystal, giving graphene its second distinctive characteristic — excellent electrical conductivity. However the mobile electrons in graphene are not the same as those in two-dimensional semiconductor structures. In a simple conventional metal or semiconductor a conduction electron can be modelled as a particle that obeys Newton's laws of motion, provided it is ascribed an effective mass, m^* , which takes into account the interaction between the electron and the semiconductor's crystal lattice. The dispersion relationship, linking the kinetic energy E with the momentum of the electron $\mathbf{p} = \hbar\mathbf{k}$ (where $\hbar$ is Planck's constant and $\mathbf{k}$ is a vector representing the wave number of the electron) is quadratic in $\mathbf{k}$, and their quantum mechanical behaviour can be described by the non-relativistic Schrödinger equation with appropriate modifications arising from the band structure of the material which depends critically on the crystal structure.

In contrast, the earliest experimental observations^{3,7,4} show that, in the honeycomb structure of graphene, the relation between energy and momentum of the conduction electrons is linear (Fig. 1 – taken from ref. 4). This is reminiscent of Einstein's theory of relativity for massless particles — which travel at the speed of light — and suggests that electrons in graphene obey a two-dimensional version of the relativistic quantum theory introduced by Paul Dirac in 1928. Electrons in graphene are, of course, not actually massless, and their typical velocity at the Fermi level ($8 \times 10^5 \text{ m s}^{-1}$) is almost 400 times lower than the speed of light in a vacuum — although still much higher than the speed typical of electrons in semiconductors.

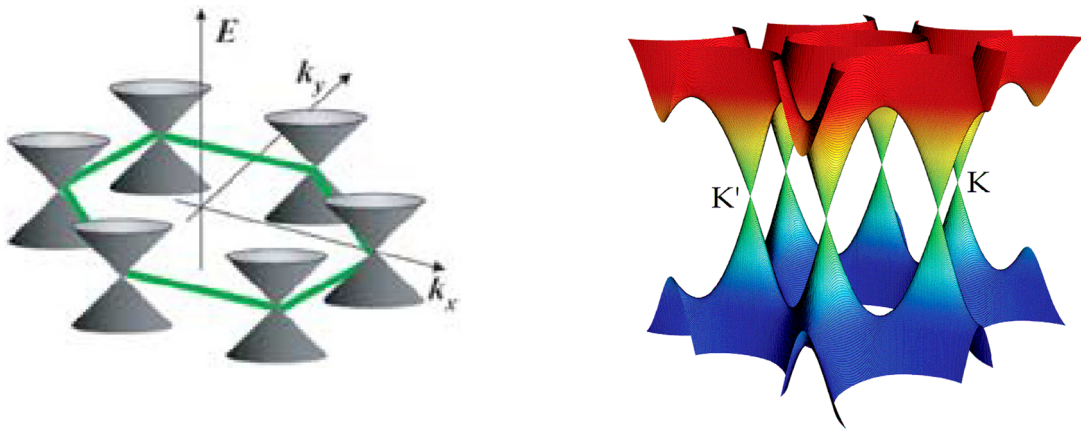


Fig. 1 Schematic of band structure of graphene showing the conical energy bands, touching at the Dirac points.

In the two-dimensional reciprocal k -space that corresponds to the 2- D physical structure of graphene conduction and valence bands in graphene form conically shaped bands, touching only at a point (known as the Dirac point). It is around this region that the dispersion relationship $E(k)$ is linear. There are two inequivalent Dirac points in the Brillouin zone, related by time-reversal symmetry. This gives rise to two distinct

valleys in the band structure and symmetry considerations show that intervalley scattering between them should be suppressed in pure samples⁸. This will have significant influence on the potential for graphene device applications which we will discuss further below.

The term graphene is now applied to any sample of graphite having less than about ten layers of carbon atoms. The electronic structure *rapidly evolves* with the number of graphene layers. Single layer and double layer graphene are the most interesting as their electronic structures are quite distinct from each other and from bulk graphene. (These properties will be explored in detail below). With layers ranging from three to around nine (sometimes this refers as Few Layer Graphene (FLG)) the electronic structure becomes increasingly complex, conduction and valence bands begin to overlap and by the time ten layers are reached the properties are virtually indistinguishable from bulk graphite.

3. Graphene: a Brief History of Preparation and Experiments

3.1 Single layer graphene fabrication

The unusual properties of graphene were predicted many years before anyone was successful in preparing samples⁹. In fact for many years it was assumed that graphene would not exist as a stable material, the belief being that a single layer of carbon atoms would ‘buckle’ into an irregular structure, since thermal fluctuation energies would exceed crystal binding energies¹⁰. Geim’s group at Manchester University was the first to show that this is not the case using a mechanical abrasion method to produce tiny flakes of graphite which turned out to consist of layer numbers ranging from tens down to single layers¹.

3.1.1 Layer by layer preparation– from graphene to graphite in 10 steps

The first successful preparation method¹ begins with 1mm thick sample of high quality highly oriented pyrolytic graphite (HOPG), the surface of which is patterned into an array of micron-sized mesas, by dry etching. This patterned surface is pressed against a glass surface which has been spin-coated with a thin layer of photoresist. On baking to harden the photoresist the mesa regions can be detached from the bulk graphene to be retained on the glass. Using adhesive tape successive layers of graphite can be removed from any mesa until, with care, only a few layers remain in place. Thin graphite flakes left attached to the photoresist are released in acetone and a Si wafer (with a 300 nm thick SiO₂ layer on top) is dipped into the solution and washed in water and propanol. Some flakes attach to the wafer’s surface and then ultrasound cleaning in propanol is used to remove mostly thick flakes.

Another method was developed by Kim’s group.¹¹ They used micromechanical manipulation techniques to extract mesoscopic graphite crystallites with thickness from 10 to 100 nm from bulk HOPG. First the arrays of graphite micropillars (~2x2x4 μm) have been fabricated using micropatterning and masked anisotropic oxygen plasma etching, then attached to a graphite block on the AFM cantilever to use as AFM tip. By operating the AFM in contact mode with load on the graphite mounted cantilever, thin graphite samples have been transferred onto a SiO₂/Si substrates.

An even simpler method¹² was described by the Geim's group. This involves rubbing a fresh surface of HOPG against another surface (virtually any solid surface is suitable), which leaves a variety of flakes attached to it. It is found that a very small fraction of these flakes consists of graphene of only a few layers. The problem with both the methods outlined is to identify the flakes which have only a few layers. Note that the thickness of even ten layers is only around 4 nm, more than two orders of magnitude less than the wavelength of visible light. For both mechanical abrasion methods the optimal intrinsic properties of the graphene flakes are best realized if an annealing phase at around 400°C is carried out.

3.2 Epitaxial growth of graphene

Although the mechanical abrasion methods have been very useful in producing the first samples of high quality graphene, which have yielded remarkable results, the promise of graphene as a unique and applicable material for real electronic applications will only be fulfilled if deposition techniques appropriate to high volume production can be developed. The best approach to date seems to involve vacuum graphitisation of single crystal silicon carbide¹³. The steps involved in production of the layers begin with hydrogen etching of a commercial silicon carbide wafer to produce atomically flat surfaces. The next step is vacuum graphitisation which produces an ultrathin epitaxial graphite layer on the surface. Metal contacts (Pd or Au) may be evaporated on to this surface and patterned by e-beam lithography. A final oxygen plasma-etch defines the graphene structure. The group from Georgia Tech.¹³ has shown that these samples exhibit many of the unique electronic properties demonstrated earlier by the mechanically abraded samples, including the Dirac point conduction anomalies, magnetotransport oscillations and electron phase coherence extending over 1 μm . Devices extending over many square microns have been fabricated and bonded successfully. It remains the case at the time of writing that these epitaxial grown samples do not have as high a quality as the mechanically abraded versions.

A chemical method to produce graphene sheets has been recently investigated by group at the University of California.¹⁴ The technique begins with oxidation of graphite to produce graphite oxide, a compound which is dispersible in water, into individual small plates. These are then deposited onto Si/SiO₂ substrates, and chemical reduction proceeds, producing graphene sheets. This process is indicated by a 10000-fold increase in electrical conductivity. Tapping mode atomic force microscopy measurements show the resulting platelets exhibit only one to two layer graphene steps. The group have patterned electrodes onto a reduced graphite oxide film and demonstrated a field effect response to gate voltage variations between +15 and -15 V. Temperature dependent conductivity measurements indicate that the graphene-like sheets exhibit semiconducting behaviour.

3.3 Preparing devices on graphene

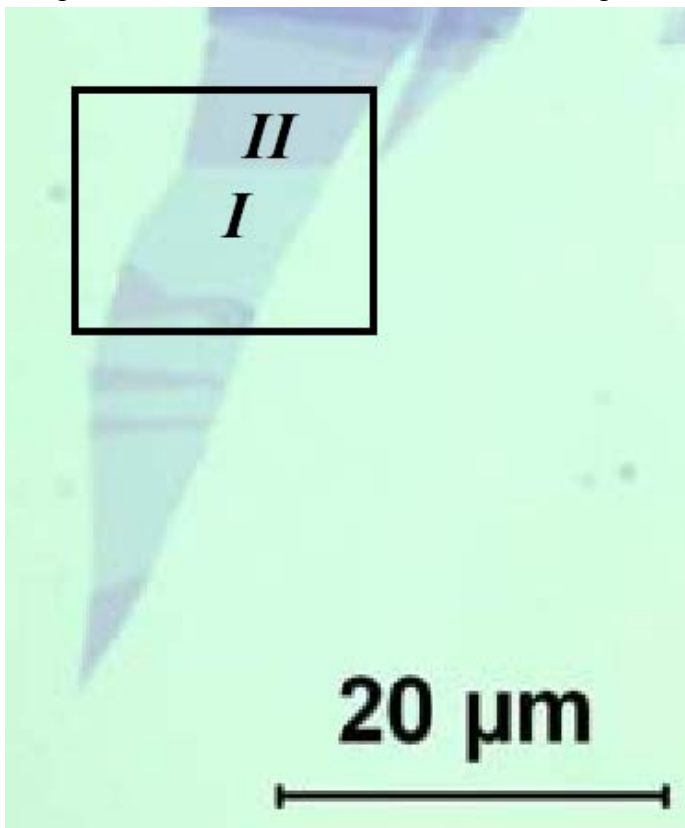
Novoselov et al¹ used electron-beam lithography to prepare resist masks of a desired geometry on top of the graphene films. Then they used dry etching in an oxygen plasma to remove the graphitic material from everywhere but underneath the mask. The next lithography step defined contact regions on top of the prepared mesas. This was followed by deposition of a 100 nm layer of Au (with a 5nm Cr underlayer to improve adhesion) and the standard lift-off procedures.

The Columbia University group¹¹ used essentially the same procedure but only a 30nm thick layer of Au – with a 5nm Cr adhesion layer – is thermally evaporated to make the electrodes. For multilayer graphene, the resulting gold-to-graphene contacts had a typical resistivity of $<50 \Omega$ per μm of their length, roughly independent of thickness. For Few Layer Graphene (FLG), contact resistances were typically about 1 k Ω and varied strongly with gate voltage, in line with changes in resistivity ρ of FLG itself. In both cases, the contacts exhibited linear I-V characteristics without any evidence for the Schottky barrier, even down to nV biases.

3.4 SPM study of single layer graphene

3.4.1. Optical method for rapid graphene identification

Graphitic films thinner than 50 nm are transparent to visible light but, by a fortunate



outcome, nevertheless can easily be seen on the SiO₂ surface because the extra optical path changes the interference colours. Thus the colour for a 300 nm wafer is violet-blue and the extra thickness due to graphitic films shifts it to blue, then lighter blue, then white. Novoselov et al reported (in ref. ¹) that at thicknesses d less than ~ 2 nm graphene films are no longer visible, even via the interference shift, as it becomes too small. However, Zhang et al. are able to detect the optical contrast of single layer graphene. (thickness 0.8 nm) – see region I in Figure 2 (taken from ref. ¹⁵).

Fig. 2 Optical micrograph of thin graphene flake, illustrating the visibility of a single graphene layer under suitable conditions (see Zhang et al.¹⁵)

For large-area optical searching for graphene to succeed it is vital that the oxide layer on the Si is of the right thickness. For example, only a 5% difference in SiO₂ thickness (315 nm instead of the current standard of 300 nm) can make single-layer graphene completely invisible¹⁶. Another ‘good’ oxide thickness is found to be ~ 100 nm. The advantage of the optical method outlined above is that it allows a large number of flakes within a field of view to be instantly screened for suitable thickness. Other methods,

such as SEM and AFM, can give more accurate results for this parameter, at the cost of much reduced scanning speed.

3.4.2 AFM/STM imaging of graphene

The separation of successive layers in bulk graphene is around 0.4 nm. For a graphene flake deposited on a SiO₂ surface Novoselov et al. found¹² that there existed a ‘dead’ layer d between graphene and SiO₂ which varied from sample to sample and ranged from $d \sim 0.5 - 1.0$ nm. The lower value is consistent with expectations for an atomically smooth contact between graphene and SiO₂ surfaces, however this thickness was only found for graphene patches of rather small sizes $\sim 1 \mu\text{m}^2$. More commonly, they observed $d \sim 1.0$ nm. They attributed this to a layer of absorbed water captured between graphene and SiO₂. Therefore, a graphene layer with an apparent thickness $d \sim 1.0$ to 1.6 nm as measured by AFM can contain only 1, 2 or maximum 3 layers of graphene. Note that the interlayer distance in bulk graphite is $\sim 3.35 \text{ \AA}$ (i.e. ~ 0.4 nm). Zhang et al.¹⁵ also found that the apparent thickness of a single layer of graphene was 0.8 nm, thus suggesting a ‘dead layer’ of 0.4 nm.

Novoselov et al. and Zhang et al.^{15,17} suggested that AFM contact mode is more reliable than tapping mode as a method for determining the thickness of graphene, due to the different interaction of an AFM tip with SiO₂ and graphene (tips were found to be more strongly attracted to SiO₂). However they found that contact mode AFM imaging could destroy samples consisting of only a few graphene layers, by peeling the films off the SiO₂ surface and then ripping them apart, or by scratching their surface. As scratches are detrimental to electrical continuity, they avoided the use of AFM for imaging of the films chosen for fabrication of electronic devices. Since scanning tunnelling microscopy (STM) measurements require a conducting sample Novoselov et al.¹ deposit a Au film around 2D crystallites to provide electrical contact.

3.4.3 TEM imaging of graphene

When the 2D cleaved material is deposited directly on holey carbon films the route of preliminary identification of 2D crystallites in an optical microscope becomes impossible. To find them on top of holey carbon among thicker flakes, a different procedure has been developed¹². First, scanning electron microscopy imaging at low acceleration voltages (at ~ 500 V) is used. Then the flakes that were found most transparent in the SEM were studied by AFM (i.e., directly on top of the holey carbon substrate) to define their thickness and select single-layer crystals. Then TEM images were taken.

3.4.4 Raman Spectroscopy of Graphene

Raman spectroscopy provides a sensitive method for determining small changes in electronic or phononic properties of condensed matter samples, without the need for attaching measurement probes. Raman studies of carbon nanotubes were used extensively in the early papers to further the understanding of phonon and electron density of states. It was not surprising that researchers were quick to use the same technique to look at graphene samples.

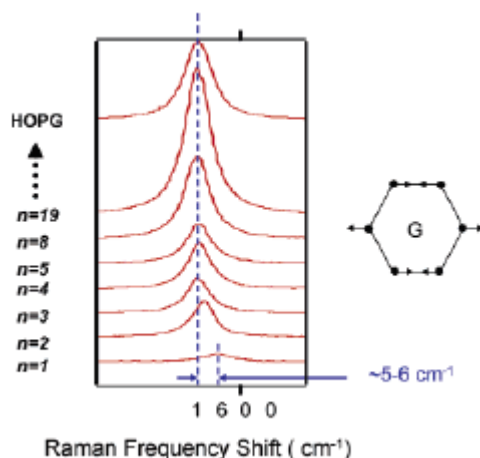


Fig. 3 The first order Raman G-band lines for a series of supported graphene flakes. The stacked plot labels each flake with the number n of layers. Note the shift in the Raman line. Relative to bulk graphite its position shifts linearly upwards in frequency proportional to $1/n$. (Gupta et al.¹⁸)

Most of the work to date on Raman properties of graphene has concentrated on four lines related to those within the spectrum of graphite, the G line (around 1580 cm^{-1}) and its overtone G' line around 3250 cm^{-1} , together with the D line at around 1330 cm^{-1} and its overtone D' line at 2700 cm^{-1} . The D line is of particular interest to our study in that, even in bulk graphite, its presence is indicative of a finite crystallite size and its strength is directly proportional to defect or grain boundary density. In graphene too its intensity increases strongly in the region of crystallite edges and the steps between layer numbers within graphene flakes. In addition its frequency shifts significantly with the frequency of laser excitation.

Gupta et al.¹⁸ reported early results which showed there exist a number of Raman lines in the spectrum of FLG which are shifted from those observed in bulk graphite and that they show a characteristic shift with n the number of layers in the sample. In principle a simple measurement of the peak frequency of one such line should allow the immediate identification of the number n of layers in a graphene flake. A second important paper by Ferrari et al.¹⁹ confirmed the downward shift in the G line with increasing n number but went further to show that the D line shape and width depends on proximity of the excitation region to the edge of a flake or a grain boundary. They confirmed the predicted strong shift in D band frequency with excitation frequency, due to a double resonance effect, as seen first in bulk graphite²⁰. A combined study using AFM and Raman²¹ showed that both Raman intensity and linewidth may also be correlated with n value for a number of different lines. An important qualification to the simple model of line centre shifts with n has been pointed out in a recent paper. These authors²² measured the frequency shift of the graphene Raman lines with temperature and showed that the temperature coefficients were such that a change of temperature by one to two hundred degrees could mask or exaggerate the n based lineshift. Such levels of heating have been predicted and observed in Raman measurements on small samples, where, although the total incident laser power may be only $\sim\text{mW}$, the power density is very large due to the small laser spot size associated with a high magnification microscope

objective. Thus care must be taken to avoid heating if Raman spectroscopy is to be used for accurate metrology on graphene samples.

3.5 Electrons in graphene: ballistic massless Dirac fermions

In the first experimental paper the nature of the carriers in few-layer graphene (FLG) was found to be hole-like with very high mobility. Novoselov et al.^{3,1} found that it was possible to change the position of the resistivity peak by annealing their devices in vacuum, which usually resulted in shifting of the peak close to zero gate voltages. They also noticed that exposure of the annealed films to either water vapour or NH₃ led to p- and n-doping, respectively. They thus concluded that intrinsic FLG is a mixed-carrier material. The same authors showed graphene to exhibit the properties of a highly gate-tunable conductor, having extremely high mobility even at room temperature, as great as $1.5 \times 10^4 \text{ T}^{-1}$. The specific properties vary radically as the number n of layers changes from one upwards.

They found (and other authors have supported these results) that:

- graphene's conductivity never falls below a minimum value corresponding to the quantum unit of conductance even when concentrations of charge carriers tend to zero (i.e. the maximum resistivity $\rho_{max} \sim 6.5 \text{ k}\Omega = h/4e^2$ – the 4 in the denominator arising from the 4 fold degeneracy in graphene – $2 \times$ spin and $2 \times$ valley/sublattice degeneracy). Note that it is the resistivity (conductivity) and not the resistance (conductance) that is quantised in graphene, reflecting the 2D nature of the material.
- the integer quantum Hall effect in graphene is anomalous in that it occurs at half-integer filling factors, but at integer factors for bilayer graphene (see following section);
- the cyclotron mass m_c of massless carriers in graphene is described by $E = m_c c^{*2}$ (where c^* is the carrier velocity in graphene $\sim 10^6 \text{ m s}^{-1}$) and $m_c \sim 0.02\text{--}0.07 m_0$ where m_0 is the free electron mass – therefore even though the linear spectrum of fermions in graphene implies zero rest mass, their cyclotron mass is not zero.
- Graphene mobility (μ) = $15,000 \text{ cm}^2/\text{Vs}$ (from 10 to 100 K, independent of T)

3.6 The Quantum Hall Effect (QHE) and Chirality

More surprises were in store when the transverse conductance of graphene samples was measured. The Hall effect has been an important tool in analysing the properties of conductors, especially the carrier density and the sign of the charge carriers. More recently the observation of quantised Hall effect in 2D semiconductor samples at very low temperatures has led to a topological standard of quantum resistance which has been implemented in NMIs throughout the world to maintain electrical standards at the highest level. Unsurprisingly groups involved in electrical measurements on graphene were quick to look at the Hall effect in this material. At around the same time both Novoselov et al.³ and Zhang et al.⁴ observed the quantum Hall effect in graphene with pronounced plateaus in high fields at around 4K. The spacing of the plateaus was unexpected, not following the conventional sequence $(4e^2/h)N$, where N is integer. Instead the plateaus correspond to half-integer N so that the first plateau occurs at $2e^2/h$ and the sequence is $(4e^2/h)(N+1/2)$. The transition from the lowest hole to the lowest

electron Landau level in graphene requires the same number of carriers as the transition between other nearest levels. This results in a ladder of equidistant steps in σ_{xy} that are not interrupted when passing through zero. This unusual fractional QHE in single layer graphene reverts to a more ‘normal’ QHE in bilayer graphene (see fig. 4 –these are figures 1a and 4 from Novoselov et al.³). The following figure 5 shows related results from Zhang et al..⁴

Following these experimental observations two theory papers appeared quite rapidly, explaining all the main features of the observed results^{2,23,24,25,26}.

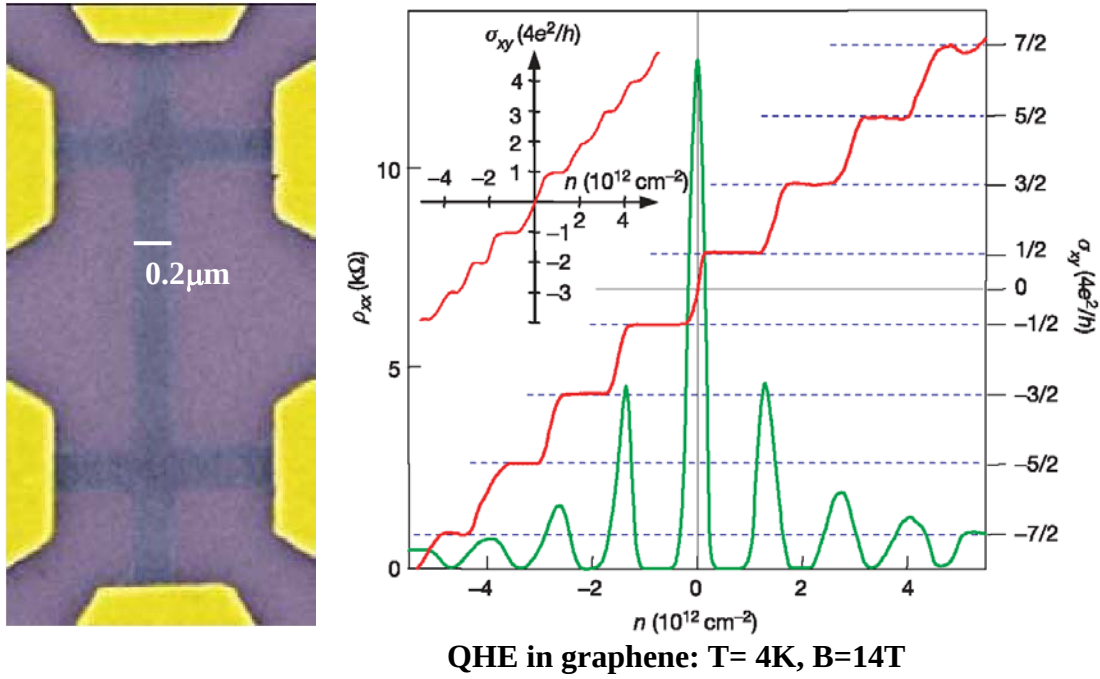


Fig. 4 Half-integer quantum Hall effect in single layer graphene. Inset shows results for bi-layer graphene. (Taken from Novoselov et al..³)

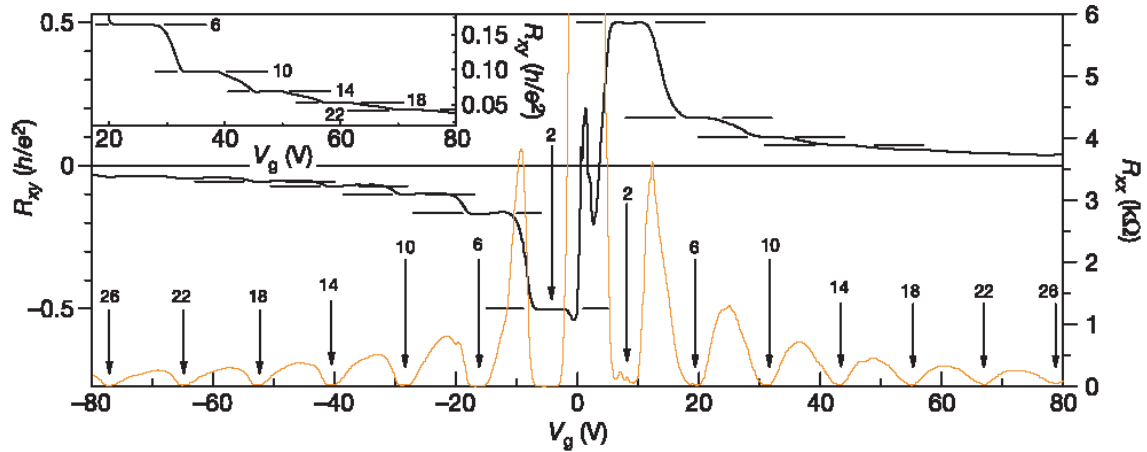


Fig. 5 Single layer graphene quantum Hall effect, showing anomalous plateau spacings, from Zhang et al.⁴.

3.7 Metallic FET and QDs in few-layer graphene

The Manchester group of Geim et al. demonstrated a metallic field effect transistor (FET) on few-layer graphene¹ in which the conducting channel can be switched between 2D electron and hole gases by changing the gate voltage (see Fig 6 below these are taken from ref. 1). They found a mobility (μ) for FLG in the range from 3,000-10,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, in the same range as that found by other groups^{27, 28} which was independent of absolute temperature. The mean free path was remarkably long, $\sim 0.4 \mu\text{m}$ with maximum carrier concentrations $n = 3 \times 10^{13} \text{ cm}^{-2}$, so that ballistic conduction may be observed in samples of mesoscopic size. The mean free path remains at least this great, even at room temperature and in samples which have been doped significantly²⁹. This paper suggests that that micron-size graphene sensors are capable of detecting individual events when a gas molecule attaches to or detaches from the sensor's surface. Such a gas sensor has important implications for single entity detection and metrology.

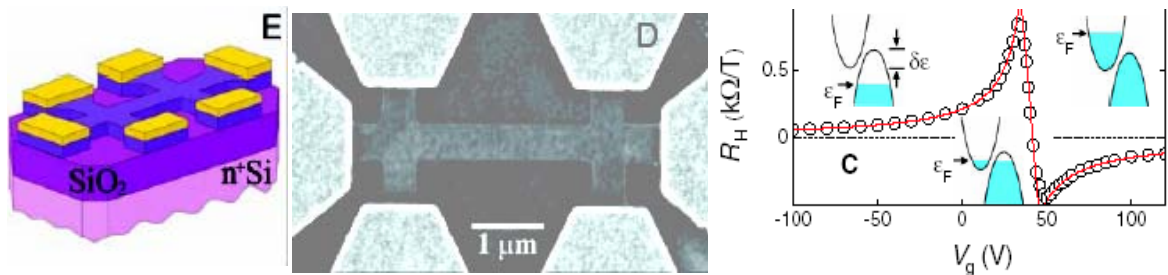


Fig. 6. Schematic view of the graphene FET device (E), STM image of one of devices made from FLG (D) and Hall coefficient R_H vs. gate voltage V_g at $T=5 \text{ K}$. (Take from Novoselov et al.¹)

Even more interesting for applications is the fact that small graphene flakes can be considered as single isolated quantum dots (QDs). This was first demonstrated by

Bunch et al.³⁰ who measured the magnetic field and electric gate voltage dependence of the two point resistance over a range of temperatures from 1.5 K down to 100 mK. The electrodes were attached by first locating a thin flake by AFM and then using e-beam lithography to pattern tracks onto it. Contact resistances produced by this method varied over a wide range. Interestingly for high contact resistance values the voltage biased flakes showed a transport current periodic in the gate voltage, as it was varied between -10 mV and $+10$ mV. This indicated the flakes were small enough and sufficiently isolated electrically to exhibit coulomb blockade effects. The results were analysed to indicate that the capacitive coupling to the flake was much greater from the source and drain electrodes than it was from the gate electrode. The authors concluded that thin tunnel barriers existed between S and D electrodes and the flake although they were unable to determine the exact nature of these. Related results on open quantum dot behaviour were reported by the Georgia Tech group³¹.

3.8 Induced Superconductivity in Graphene

Proximity effect induced superconductivity in graphene has been observed at temperatures below 1 K³². As for the metallic field effect, a gate voltage was able to change carrier nature from electrons to holes and proximity-effect induced superconductivity was observed in both regimes. Closely spaced aluminium superconducting electrodes (with Ti intermediate layer for improved contact to graphene) were deposited on FLG samples. In the normal state of the electrodes the QHE could be observed and the plateau spacings could be used to identify the number of layers present in the graphene samples. Cooling the two-terminal structure to 30 mK, well below the superconducting transition temperature of the electrodes, resulted in observation of a true supercurrent between them. The graphene weak link demonstrated the Josephson effects, both in terms of the modulation of the supercurrent flowing by a magnetic field and the induction of constant voltage Shapiro steps under the influence of microwave irradiation (see fig. 7).

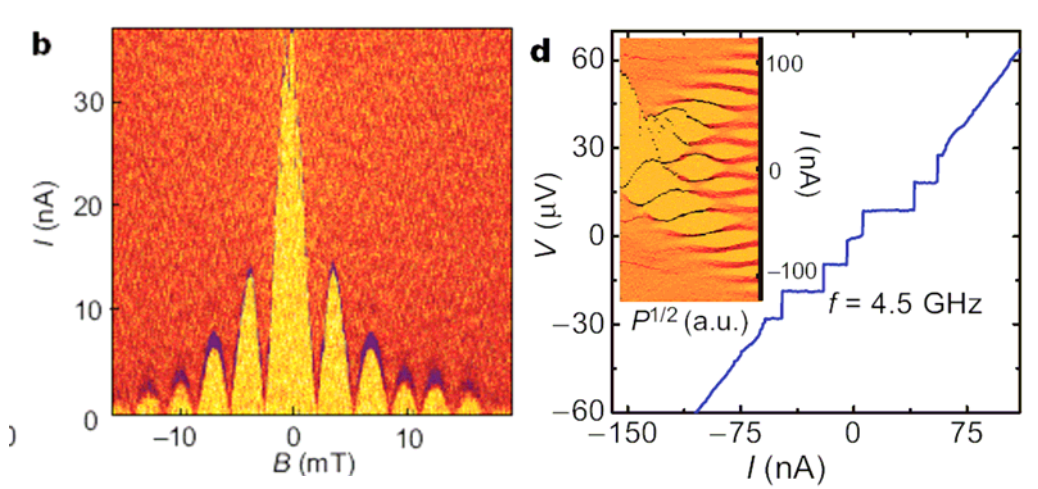


Fig. 7 a) Magnetic field modulation of proximity induced Josephson critical current of graphene weak-link. b) Microwave induced Shapiro steps in the same device, under irradiation at 4.5 GHz. The inset shows the variation of constant voltage step amplitude with microwave power (Heersche et al.³¹)

A second group has recently shown that the proximity effect induced superconductivity in graphene can be observed at temperatures above 1 K³³. In this work a Ga focussed ion beam is used to decompose a metallo-organic tungsten compound to produce deposited electrodes of contaminated tungsten which superconducts with a $T_c > 4$ K. These electrodes are deposited with small separation on a FLG graphene layer. For electrodes separated by as much as 2.5 μm the transition temperature of the graphene is as high as 1.7 K, although on this length scale no Josephson current is observed. In addition the authors claim to have evidence of multiple Andreev reflections from the influence of the superconducting normal interfaces existing towards the centre of the graphene sample.

3.9 Spintronics and Spin Quantum Hall Effect in Graphene

Spintronics is a key topic for research in condensed matter physics at present, driven partly by the promise of commercial applications in the near term and partly by the challenge of understanding a new degree of freedom available to those who study transport properties in low-dimensional systems or novel materials³⁴. Very recently another novel aspect of spintronics has attracted much attention. This is the existence of a spin Hall effect, corresponding to the separation of spin states of charge carriers in the presence of an applied magnetic or electric field, without the need for any charge current^{35,36,37,38,39}. Theoretical studies of the spin transport properties of graphene have been published since the earliest days of the graphene explosion^{40,41,42,43}. The weak spin-orbit coupling present in graphene makes spintronics particularly promising as the spin relaxation time can be expected to be long. In addition most of the carbon nuclei do not possess a nuclear spin so this is another reason for expected low conduction electron spin scattering rates.

A recent experimental paper has confirmed a number of these expectations. Tombros et al.⁴⁴ showed that a spin valve could be formed from a single graphene layer with suitable bottom gate electrode provided by n-doped Si below an insulating SiO_2 layer. A thin overlay of Al_2O_3 provides tunnel barriers between the graphene and each of four electrodes of metallic Cobalt which form parallel ferromagnetic stripes across the graphene strip. The experiments involve measuring the non-local transport properties by injecting spin polarised current between two electrodes while measuring the voltage drop between two electrodes separated from the injecting pair. The magnetic field applied in the direction perpendicular to the substrate was varied between + and – 100 mT, remaining within the coercive field range of the electrodes. Spin selective transport was observed at room temperature in some devices and spin valve operation was also observed at lower temperatures. The spin coherence length was shown to be greater than 300 nm. It was necessary to employ tunnel junction barriers between electrodes and graphene to avoid problems with resistivity mismatch which was observed in high transparency, low resistance ferromagnetic-graphene interfaces.

The promising spin-related properties of graphene suggest that the spin Hall effect may be observable and demonstrated to be a useful platform for future spintronics developments in which NPL could actively participate. The quantum spin Hall effect has also been theoretically discussed in some detail⁴⁵.

4. Preliminary NPL experimental results

4.1 Sample preparation

Highly-oriented pyrolytic graphite (HOPG) was chosen as a starting material. In our experiment two types of HOPG have been used: HOPG-Grad SPI-1 and HOPG-Grad SPI-2 (<http://www.2spi.com>). The more expensive HOPG Grade SPI-1 is highly ordered (the lateral grain size is typically up to about 3 mm but can be as large as 10 mm) and has excellent crystalline perfection (with a mosaic angle $\sim 0.4^\circ \pm 0.1^\circ$). HOPG-Grade SPI-2 is slightly less highly ordered than grade SPI-1 (the lateral grain size is more typically up to 0.5 mm) with a mosaic angle of about $0.8^\circ \pm 0.2^\circ$. But it is cheaper than grade SPI-1 and also is expected to have better adhesion to SiO_2 since the cleavage steps are slightly irregular.

We have used a silicon substrate with a 300 nm thick layer of SiO_2 grown on the surface. The thickness of SiO_2 is crucial for finding the graphene flakes using an optical confocal microscope. To allow us to repeatedly identify the same graphene flakes using the confocal microscope, the AFM or Raman microscope the Si/ SiO_2 substrate has been patterned with an array of identification marks using photolithography and electron beam lithography. An SEM image of these marks is shown in Fig. 8.

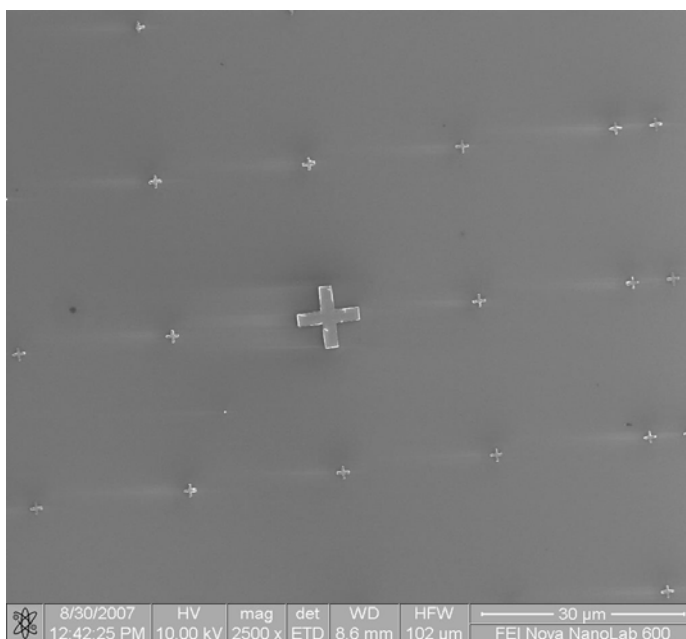


Fig. 8. SEM image of the marked SiO_2/Si substrate. The distances between small marks are either $20\mu\text{m}$ or $5\mu\text{m}$

The initial experiment to prepare the graphene sample began by scraping some HOPG grade SPI-1 with a Stanley knife onto the patterned SiO_2 substrate, then rinsing off excess HOPG material with isopropanol. The sample was later imaged with the confocal microscope (see section below). This method results in a wide variation of graphene flake sizes and shapes.

In order to prepare graphene samples with more reproducible shapes and sizes (so that, for example, four leads may be attached to a Hall bar), we patterned HOPG samples using focussed ion beam lithography (FIB) by milling the surface into an array of different shapes and sizes of mesa. For a possible Hall bar the mesa size chosen was a $6\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ rectangle, the diameter of circular shapes was $4\text{ }\mu\text{m}$ with a distance between circles of $2\text{ }\mu\text{m}$. In each case the height of the mesa above the surrounding substrate was from 300 nm to 500 nm (see SEM images in Figs. 9 and 10). The flexibility of the pattern generation capability of the FIB milling technique is that a wide variety of shapes and sizes may be milled on a single substrate in a short time.

For the FIB milling, 30 kV Ga ions with a beam current of 1 nA, have been used. Higher currents would result in a shorter milling time, but the chosen parameters minimised the total ion dose to the HOPG. The time is about 30 minutes per set of structures.

Subsequently we used same method as above to scrape flakes from the patterned graphite samples onto SiO_2 , followed by later analysis by confocal microscope and other SPM techniques. In future we will explore different methods for preparing graphene samples.

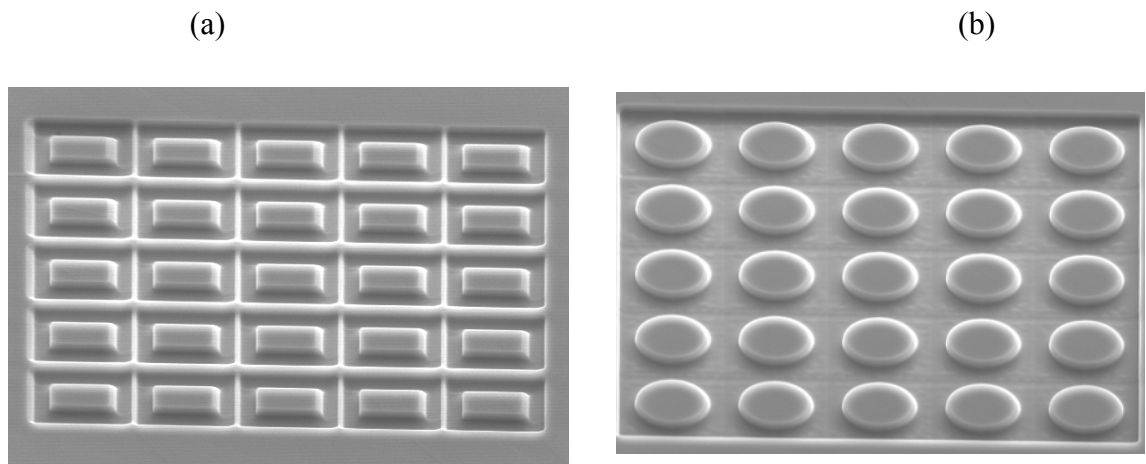


Fig 9. SEM image of (a) the quantum hall bar sample post, the size of the Hall bar is $6\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$. (b) the circles sample post with diameter $4\text{ }\mu\text{m}$.

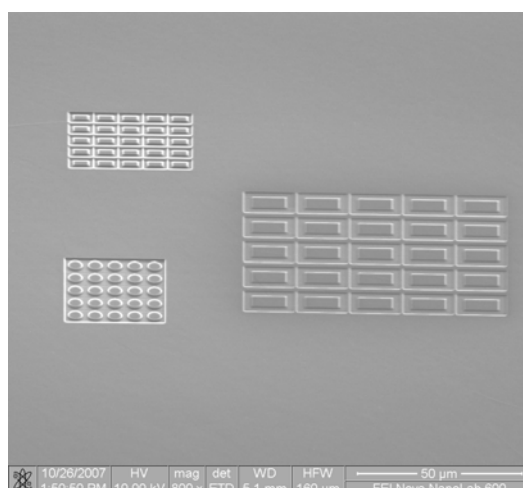


Fig 10. SEM image of the different sample posts on same HOPG substrate.

4.2 Few Layer Graphene Identification

Using the scraping method described above the variation of flake thickness is very large, ranging from 1 or 2 nm up to hundreds of nm. Since only flakes consisting of just a few ($n \leq 10$) layers of graphite show interesting properties it is necessary to find a rapid screening method for flakes. The Si substrate is imaged in a confocal optical microscope. The presence of the SiO_2 layer causes the perceived colour of the flakes to vary dramatically depending on the number n of layers in the flake. The observation of this effect was what allowed Geim's group at Manchester to make rapid progress with the earliest experiments on graphene. Under normal circumstances graphitic films thinner than 50 nm are transparent to visible light but nevertheless can easily be seen on the SiO_2 surface because of the added optical path that shifts the interference colours. For a 300 nm SiO_2 wafer the thinner flakes appear purple, the thicker ones white and the colour progression of white– light blue – deep blue – purple corresponds to the thickness of graphite flakes from thickest to thinnest. Fig. 11 shows an example image from the confocal microscope. The SiO_2 substrate has a purple colour overall. The large bright cross and regular dots are the substrate markers, and the graphite flakes appear on the substrate as different colours from white through light blue to deep blue. Four deep blue flakes (sample a to d) were rapidly identified and imaged for further investigation. The position of a flake is captured by acquiring images at successive zoom levels from 100 $\times$, 50 $\times$ 20 $\times$ and 10 $\times$. The thickness of the graphite flakes can be estimated by step measurements using the confocal microscope (Fig. 12), but for flakes thinner than about 10 nm this is not possible due to limited resolution of the microscope.

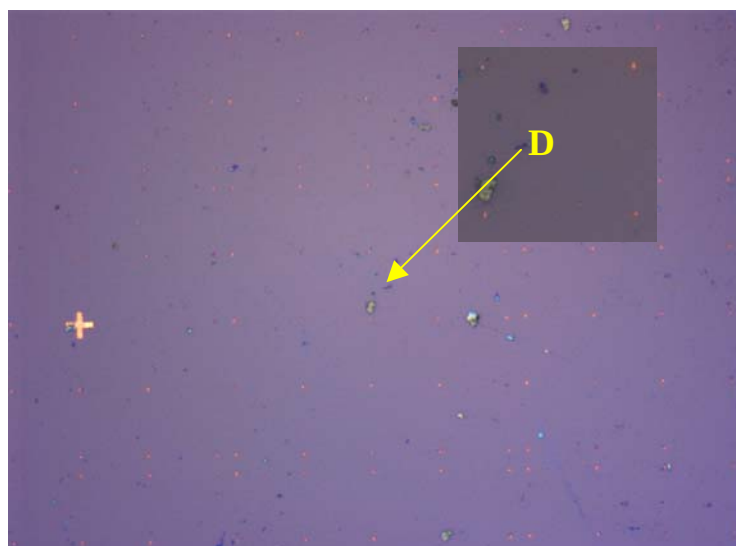


Fig. 11. Confocal microscope image of the graphite flakes at 50x zoom. Inset shows image of flake sample d at 100x zoom.

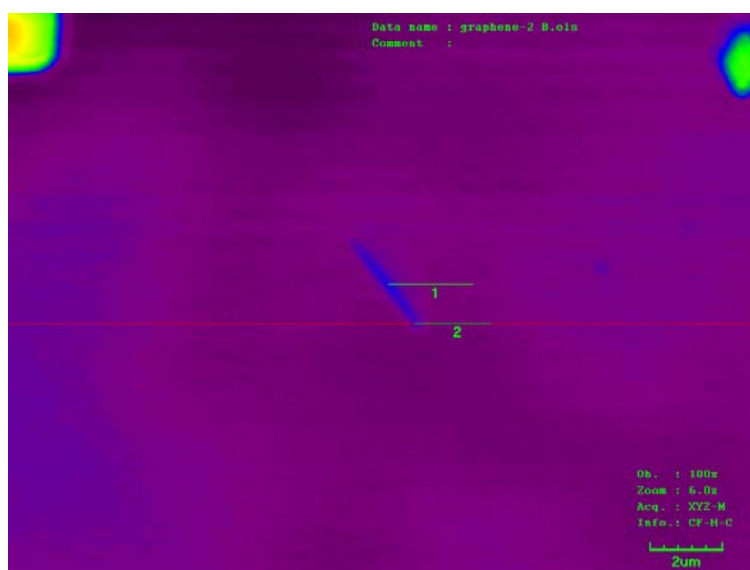


Fig 12. Image of the graphite flakes by confocal microscope. The thickness of the graphite flakes can be estimated by step measurement using confocal microscope (see table 1 for results corresponding to position on the sample 1 and 2 respectively).

Table 1: Step measurement of the sample (graphene-2 B) for position 1 and 2 (image see Fig 12)

Position	Width[μm]	Height[μm]	Length[μm]	Angle[Degree]	Upper[μm^2]	Lower[μm^2]
1	2.3958	0.029	2.396	0.6935	0	0.0244
2	2.1458	0.016	2.1459	0.4272	0	0.0158

4.3 AFM characterisation

For a FLG flake the thickness of the sample is much less than 10 nm since one layer graphene is only about 0.35 nm thick and for $n > 10$ graphene layers approach very

closely the properties of bulk graphite. The confocal microscope does not have sufficient depth resolution to accurately estimate the sample thickness when it is below around 10-20 nm. In order to characterise the flakes we have used atomic force microscopy (AFM). Sample profiles were imaged using various AFM instruments (MultiMode, Digital instrument and Nanoscope) after the confocal optical images were taken. In our AFM measurements the graphite flakes (sample b, c and d) were imaged with the AFM having located the positions of these promising flakes identified using the confocal microscope. Fig. 13 shows a typical AFM image of a graphene flake. Various image analyses of different regions of several graphene flakes have been taken (one example is shown in Fig. 14). We have assessed both the thickness, lateral extent and surface roughness of the flakes. For flake sample C the thickness in region I is 2.5 nm and region II is 3.3 nm. The cross-section trace shows a sharp vertical step edge between neighbouring regions. Since one layer graphene is only 0.35 nm and also considering an additional 'dead layer' between graphene and the SiO₂ surface which is typically ~0.3 nm, this implies that in region I we have only 5~6 layers of graphene and in region II layers less than 10 layers. Note that the size of these FLG flakes is greater than 1 μm x 2 μm , sufficient to allow us to deposit the electrodes for future transport properties measurement.

We also investigated the effect of subsequent sonication treatment of the graphene samples. The sample is placed in a beaker with isopropanol in a bath sonicator at 120% power for 15 minutes, then dried with an air duster. Thanks to the substrate marking array the same region of the sample could then be imaged again with AFM. The flakes inspected had not been moved detectably and neither had their thickness changed, following this vigorous sonication treatment.

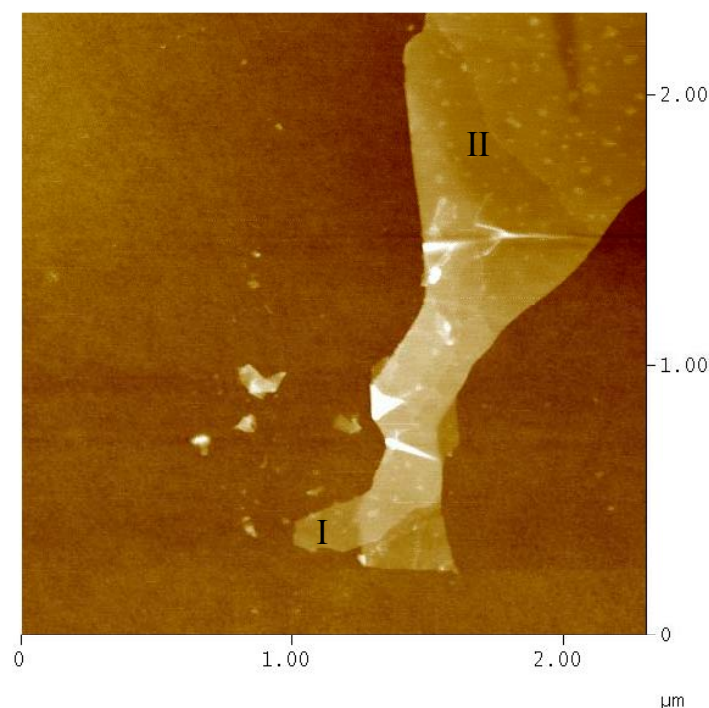


Fig. 13. AFM image of a graphene flake (sample c). Thickness in region I is 2.5nm and region II is 3.3nm, which corresponds to 5 and 9 layers graphene, respectively.

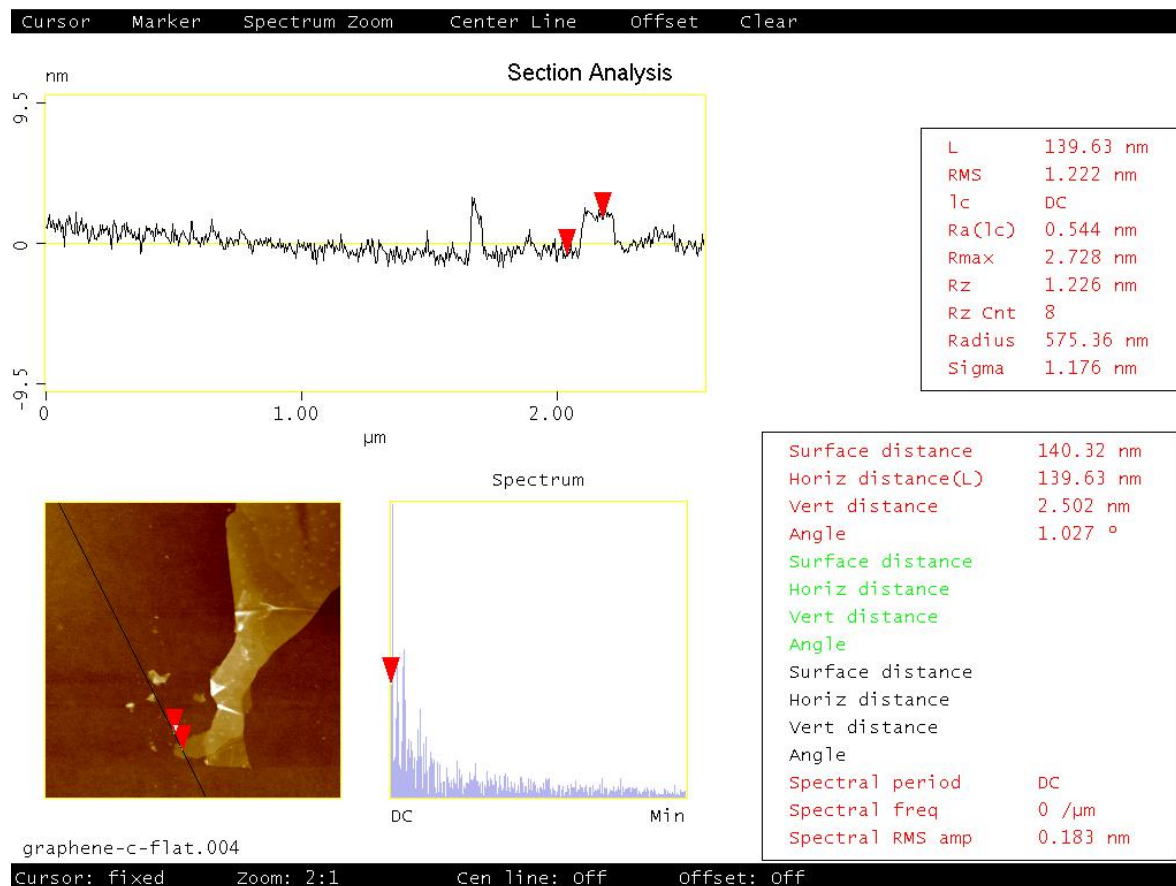


Fig. 14 AFM image analysis of a graphene flake (sample C) in region I (see fig 13).

4.4 Experimental Raman Measurements on Graphene

As part of this NPL Exploratory Strategic Research Project it has been possible to study one or two of the graphene samples produced at NPL using the Raman microscope in Prof. Cohen's group at Imperial College. This multi-laser system has been described elsewhere⁴⁶. Raman measurements were made on graphene flakes, produced by scraping, and supported on a Si wafer with 300nm thick cap-layer of SiO₂. Preliminary optical inspection in a x100 microscope and a LEXT Confocal microscope allowed rapid identification of suitably thin graphene flakes. Then, having located the same flakes using a grid of markers previously evaporated onto the substrate, Raman spectra were taken using a Renishaw RM-2000 CCD spectrometer coupled to an Olympus BH-2 microscope. Spectra were obtained with x50 short working distance and long working distance objectives resulting in a laser spot of approximately 1.5 micron diameter. Measurements were made using a 633nm HeNe laser with power ranging from 0.05 to 5 mW and a 514 nm Ar⁺ ion laser with power ranging from 0.05 to 20 mW. Spectra were collected with a range of integration times dependent on the specific measurement. Note that this system is also equipped with a scanning mapping stage which allows the sample to be translated by steps of order 1 μm or less. Also a Linkam

temperature stage allows measurements to be made over a wide temperature range between 293 and 73 K.

Figure 15 shows a spectrum of the D and G lines taken with 633 nm irradiation on a portion of a graphene flake (region I in the insert) which is believed, from AFM direct measurement, to be 5 layers thick. Region II is at least one layer thicker. The results of fitted profiles for D and G lines for both regions are shown in Table 2. Two or three entries are shown for each line, for independent curve fits to the spectra. These indicate that, with integration times of 300 s, it is possible to achieve centre frequency and linewidth values which are repeatable to within around 0.2 cm^{-1} in good circumstances. This implies that for any flake comparable in size to the laser spot size the n value should be unambiguously identified. Mapping scans of larger flakes should allow detailed information of edge and grain properties and temperature dependence of both Stokes and anti-Stokes spectra could enable interesting information on the nature of single and double resonance in this fascinating new material.

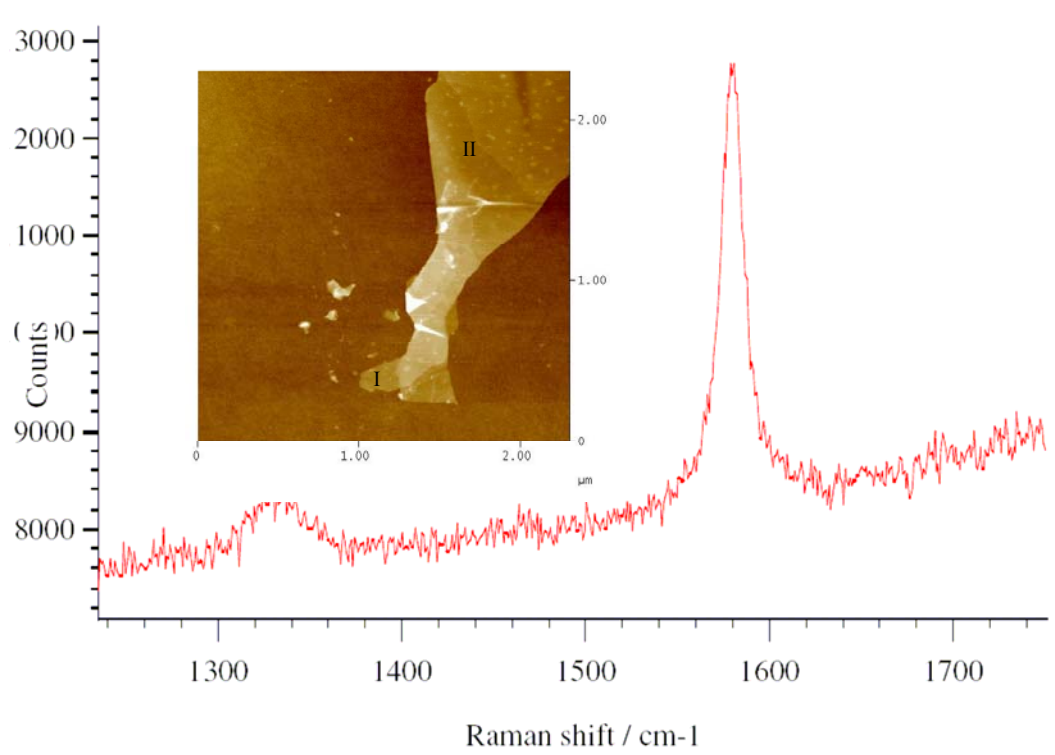


Fig. 15. Raman spectrum of D and G lines from Region I of the graphene flake shown in the insert which is an AFM tapping mode scan of the flake.

Table 2 Raman measurement results of the graphene sample 1C.

Region	Centre frequency (cm^{-1})	Width (cm^{-1})	Height (a.u)
I D line	1330.88	38.284	598.32
	1330.88	38.263	598.39
G line	1580.54	14.97	4437.1
	1580.36	14.79	4454.6
	1580.31	14.77	
II D line	1330.02	39.31	928.9
	1330.37	41.56	976.9

G line	1580.69		
	1580.71	14.40	8432.9

4.5 Deposition of electrodes and transport measurements

For an initial trial for making electrical contact to graphene samples, tungsten (W) electrode strips have been directly deposited onto our sample 1C by FIB, followed by three bonding pads (150 μ m square) using the same material. The W conductor was produced from tungsten octocarbonyl, using the same process that produces rather low resistivity tracks which superconduct above 4K.

In order to make transport measurements the device was then wire bonded to a chip holder with Al bond wires direct to W contact pads (see Fig. 16). The direct wire bonding to these pads proved successful. This opens the road for future fabrication devices by FIB, since it is not necessary to use photolithography and complex masking procedures to produce contact electrode pads for many cases.

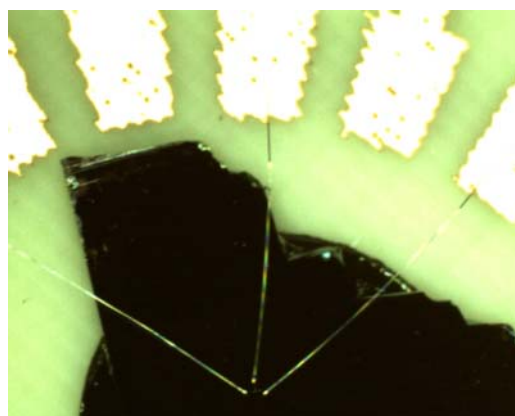


Fig. 16. Photo micrograph of the wire bonding direct from W pads to chip holder. Note that the external electrode connection numbers used in the later experiments were nos. 1, 4 and 6 from left to right.

Due to the small size of the flake 1C only three electrodes could be fitted onto it so it was necessary to carry out three terminal measurement on the sample. We measured the total 2-terminal resistances between the external electrical connections, allowing us to estimate that the contact resistance is not greater than about 7 to 8 k Ω (see table). For the 3-terminal measurements the current applied to the device was varied from 10 μ A to 10 μ A and a Keithley 2400 source meter was used for this measurement. Power dissipated in the device was not more than about 1 μ W. We have tested all combinations of three terminals to allow estimates of contact resistance for different contacts. The results are shown in table 3.

Table 3: 2 and 3 terminal resistance measurements for graphene sample 1C at room temperature with gate voltage $V_g = 0$.

Electrical connection leads No.	2-Terminal resistance (k Ω)	Electrical common connection lead No. (I-, V-)	V+ and I+ connection lead No.	3-Terminal Graphene resistance (k Ω)
1 to 4	7.6	6	V+ (4); I+ (1)	9.45

4 to 6	7.4	4	V+ (1); I+ (6)	64.4
1 to 6	8.6	1	V+ (6); I+ (4)	63.0

Next the response of the graphene to an applied back-gate voltage was measured. The SiO₂ substrate provides the gate insulator, being around 300 nm thick. A gate voltage applied to the graphene sample was varied from 0 to +15 V. Fig. 17 and 18 show the I-V and dV/dI-V with gate voltage 5 V. We found that the resistance changes from 63.5 k Ω to 70.5 k Ω for an applied gate voltage from 0 V to +15 V at room temperature (see Fig.19). Due to the thick gate oxide it will be necessary to apply higher voltages to observe more significant changes in resistance.

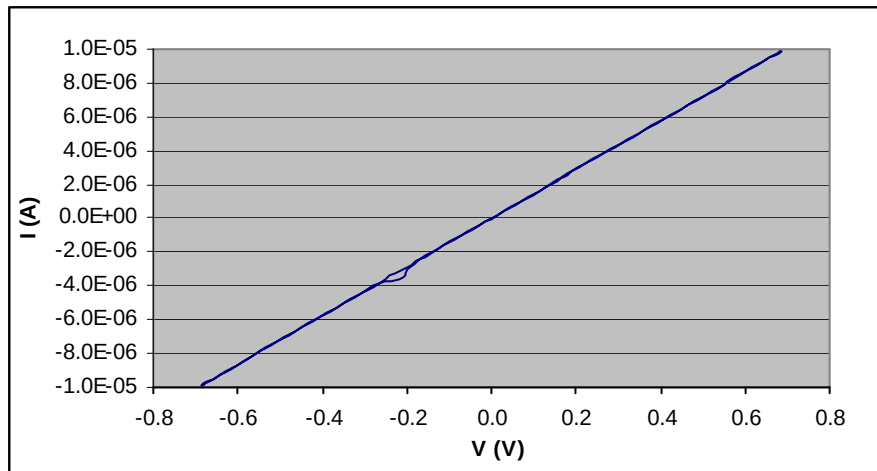


Fig. 17. I-V curves for graphene sample 1C using leads 1 as common electrical connection with applied gate voltage 5V.

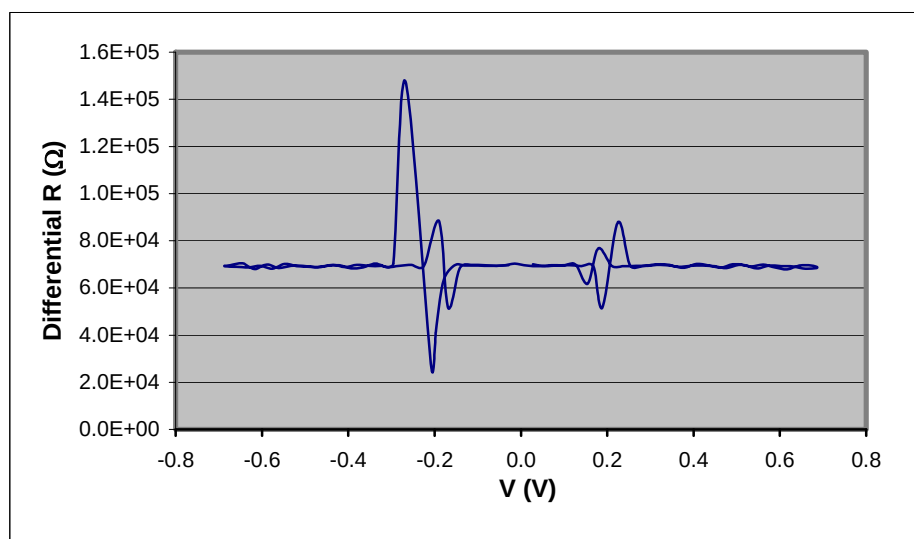


Fig. 18 Differential resistance (dV/dI)-V curves for graphene sample 1C using leads 1 as common electrical connection with applied gate voltage 5V.

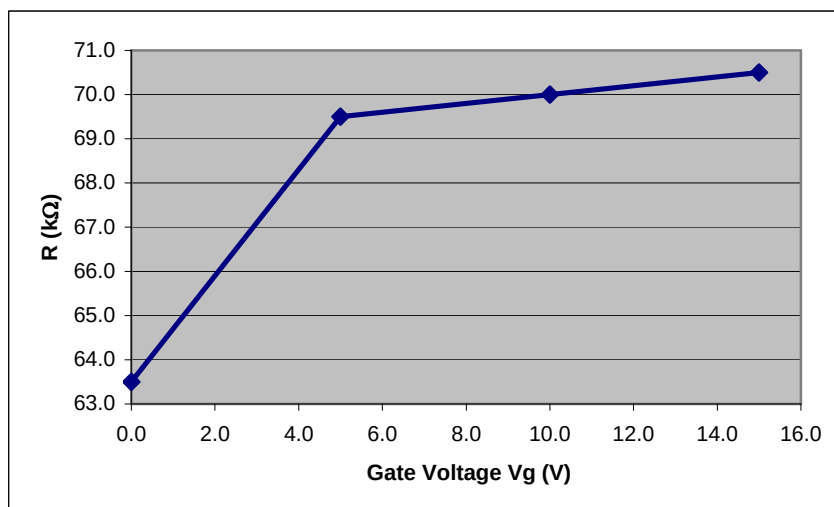


Fig. 19. Preliminary results of resistance of the graphene vs. applied gate voltage.

For a few preliminary transport measurements we have shown that attaching low contact resistance electrodes to graphene by FIB direct writing is encouraging and we have implemented a transport measurement system which may be used for future experiments. The system as built will also allow operation at low temperatures but there was insufficient time during this project to test any samples.

4.6 Future plans

In any future extension of this work we will explore different methods for preparing graphene samples in order to enable the controlled size, shape and thickness of the graphene samples. Further investigations of the interfaces between metallic electrodes and graphene will be important for understanding the range of potential graphene applications, especially in metrology. Particularly interesting will be the use of FIB deposited *W*-based electrodes since other work within the Quantum Detection Group has already demonstrated the extremely useful superconducting properties of this direct-write thin film material. This should provide an important route towards mixed device direct quantum electrical triangle realisation, each component being based on graphene.

5. Graphene future and potential benefits to NPL

A major challenge facing NPL and other NMIs in the coming decade is the requirement that traceable metrology will be needed at the nanoscale both for conventional ‘classical’ physical quantities such as voltage and current (a significant challenge in itself) but also, and much more challenging, the influence of novel physics at the nanoscale is producing the requirement to measure quite different physical parameters such as the degree of spin polarisation in nanoscale structures, or the measurement of spin current density, a physical parameter for which at the present time there is no agreed unit of measure. A third ‘prong’ of the nanoscale metrology trio of challenges relates to the fact that at the nanoscale quantum effects begin to emerge, even at room

temperature. Condensed matter metrology has long been insulated from the issues of true quantum measurement by the nature of the ensemble averages and the close energy level spacings that most macroscopic measurements involve. This is becoming no longer true. Graphene, along with other high quality crystalline structures such as carbon nanotubes and fullerenes, demonstrates all of the above issues in a single simple material made from pure carbon. In the following paragraphs we summarise those aspects of graphene's properties which provide both promise and challenge for future generations of metrologists.

5.1 QHE (Quantum Hall Effect) at room temperature

As described above in section 3.6 the Quantum Hall Effect in graphene takes on a number of surprising features. From the point of view of metrology perhaps the most significant issue is that the QHE has been observed at room temperature in graphene. This is more than two orders of magnitude higher than for other 2DEG semiconducting systems and three orders of magnitude above the temperature at which precise measurements involving the QHE are made. Thus there is the possibility of a simplified QHE resistance calibration system which will not require deep cryogenic refrigeration. At the time of writing the magnetic field required to produce reasonable plateaus in R_{xy} for the graphene samples at room temperature is as high as 30 T, a field not easily achieved in continuous operation. But essentially there is a trade-off between operating field and temperature so that, for example, operating at $T \sim 77$ K (the boiling point of liquid nitrogen) the required field is expected to be reduced by a factor of 4 compared with room temperature, corresponding to a more modest field of ~ 8 T, easily attainable with a superconducting magnet.

In addition the interesting chiral aspects of the QHE in graphene allow the possibility of comparing the plateaus in graphene with those in a conventional 2DEG semiconducting sample since the physics in the two situations is markedly different.

5.2 Possible tests of the quantum electrical triangle

The previous section has dealt with an important metrological application of graphene. The Quantum Hall Effect does not exhaust its potential. We have also proposed single electron transport (SET) and Josephson Junction (JJ) devices operating at relatively easily achieved cryogenic temperature (~ 2 K). Successful realisation of these devices would make quantum electrical standards easier to use, and enable a portable quantum electrical triangle realisation based on a single material. Graphene bias resistors provide the possibility to realise the predicted but as yet unachieved quantum phase slip standard. Unlike the other stochastic quantum current standards so far being evaluated a quantum phase slip current standard would possess coherent synchronised single electron or pair transport and has the potential to reach accuracy levels comparable with that of the Josephson voltage standard.

NPL is in a good position to become the first laboratory to exploit the possibilities of graphene. Some possible high-profile 'firsts' could be:

- First demonstration of metrologically-accurate QHE resistance standard at room temperature (1-2 years).
- First demonstration of metrologically-accurate JJ voltage standard at temperature higher than 4 K (2-3 years).

- First quantum phase-slip current standard (using graphene bias resistors, 3-5 years).
- First practical bench-top, quantum electrical standard (5 years).
- First metrological triangle realisation in a single material (5-10 years).

5.3 Quantum capacitance of CNTs/graphene

A major new phenomenon in electrical measurement which has emerged over the past few years is the concept of quantum capacitance. In classical metrology we are used to the idea of electrostatic capacitance, that is the energy of a body as a result of its geometry in relation to its surroundings. (The calculable capacitor typifies this entirely classical approach). When the discrete energy level structure of a body becomes significant, usually due to its size reducing to the scale where the energy level spacing becomes comparable with thermal energies $k_B T$, at an operating temperature T) then additional energy contributions must be included in the calculation of capacitance. Thus for a conductor in which the carriers are fermions the addition of extra charges will require the addition of kinetic energy to allow for the extra filling of energy levels around the Fermi energy. In addition the correlated motion of electrons can reduce this energy. Note that the total capacitance C is inversely proportional to energy so the first effect reduces the total C whereas the second one increases it. The gate isolation capacitance in graphene can be made very small (see ref. ²⁹) and this enables easy investigation of the quantised capacitance effect.

5.4 Single Electron Transistors using Graphene

When considering the potential of graphene SET devices, perhaps here the most promising aspect of graphene for metrologists is that FET transistors based on graphene are expected to operate up to THz frequencies. This has been identified as a key strategic area for NPL science. Similarly quantum dots and single electron transistors made from FLG are expected to extend the performance of these devices as realised in conventional materials.

5.5 Spintronics and the Spin QHE in Graphene

The curious spin effects predicted and already observed in graphene (see section 3.9 above) has led to suggestions that spin qubits could be realised in graphene⁴⁷. These could be based on quantum dots on graphene nano-ribbons (with ribbon widths $\sim 30\text{nm}$) and with semiconducting armchair boundaries. Why an armchair nanoribbon? Because an armchair nanoribbon creates a gap in the graphene spectrum: and the presence of a gap is a prerequisite for the formation of a tuneable QD. Note that this is a semiconducting armchair ribbon, as opposed to a metallic one (a third of armchair nano-ribbons are metallic) (see also the nano-ribbons section). The advantage is that these qubits will have longer spin coherence time. This is because for quantum dots formed in semiconductor heterostructures the major sources of spin decoherence have been identified as 1) the spin-orbit interaction, i.e. coupling the spin to lattice vibrations and 2) the hyperfine interaction of the electron spin with the surrounding nuclear spin. But in carbon-based materials the spin-orbit coupling is weak owing to the relatively low atomic weight of carbon, and natural carbon consists predominantly of the zero-spin isotope ^{12}C , for which the hyperfine interaction is absent. This is why graphene (and CNTs) are such good candidates.

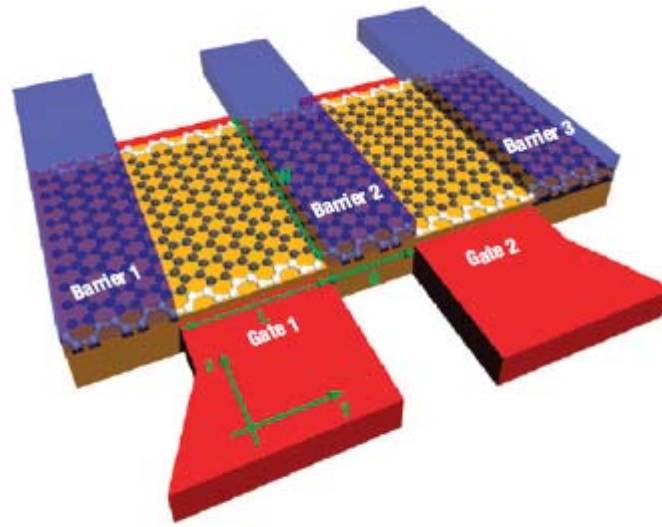


Fig. 20. Schematic diagram of a graphene double quantum dot. (Figure taken from ref. ⁴⁴).

The figure 20 (from ref. ⁴⁴) shows a schematic diagram of a graphene double quantum dot. Each dot is assumed to have length L and width W (about ~ 30 nm). The structure is based on a ribbon of graphene (grey) with semiconducting armchair edges (white). Confinement is achieved by tuning the voltages applied to the ‘barrier’ gates (blue) to appropriate values such that bound states exist. Additional gates (red) allow one to shift the energy levels of the dots. Virtual hopping of electrons through barrier 2 (thickness d) gives rise to a tuneable exchange coupling J between two electron spins localized in the left and the right dots. The exchange coupling is then used to generate universal two-qubit gates.

5.6 Nano-ribbons and applications (QDs, spintronics and ‘Valley-tronics’)

There are two types of nano-ribbons, which, as for carbon nanotubes, are defined depending on the boundary conditions of the edges. The open 2D nature of graphene makes these boundary conditions less-restrictive than for CNTs. For edge state of the graphene: **armchair** ribbons (a) and **zig-zag** ribbons (b) (See Fig. 21, this is taken from ref. ⁴⁸, in which Nakada, in collaboration with the Dresselhaus group at MIT, considered the edge states in graphene ribbons some eight years before realisation of the material).

In an *armchair* nanoribbon the ribbon width critically controls whether the system is metallic or insulating. The system is metallic when $N=3M-1$, where M is an integer and N denotes the number of dimer lines for armchair ribbons and the number of zigzag lines for zigzag ribbons. For the insulating ribbons, the direct gap decreases with increasing ribbon width and tends to zero in the limit of very large N – in a similar manner to the gap in CNTs as the diameter increases. The chance of opening a gap in the graphene spectrum makes armchair nanoribbons good candidates for making QDs as explained by Trauzettel (see ref. ⁴⁴ – and see the section above).

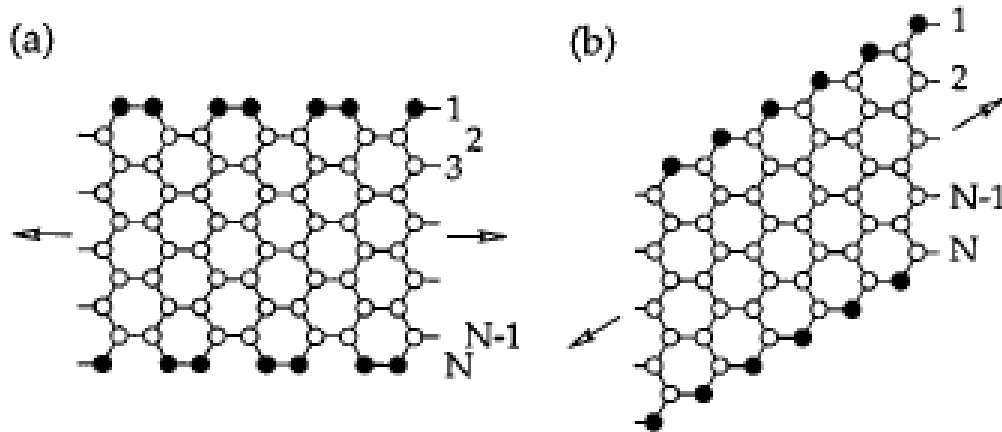


Fig. 21. Schematic of a) arm-chair and b) zig-zag nanobibbons. (From ref. ⁴⁶)

However, no gap is created in a *zig-zag* nanoribbon. In a zigzag graphene nanoribbon there are peculiar *localized electronic states at each edge*. These edge states (which are extended along the edge direction) decay exponentially into the centre of the ribbon, with decay rates depending on their momentum. These localised edge states in *zig-zag* nano-ribbons make them ideal candidates for information carrying devices.

One possible application of *zig-zag* nano-ribbons is in the field of **spintronics** as suggested in a paper by the Louie group at Berkeley⁴⁹. This arises because the edge states of the zig-zag ribbons are expected to have opposite spin orientations which, more importantly, can be controlled by external homogeneous **electric** fields applied across the zigzag graphene nanoribbons. With control from an external electric field the nano-ribbons will behave as half-metals. Half metallic materials have a great potential in the field of spintronics because they have asymmetric electronic states for the different spins. In half-metals electrical current can be completely spin polarized, as a result of the coexistence of metallic nature for electrons with one spin orientation and insulating nature for electrons with the other. One example of a half-metallic material is manganese perovskite, however, the results implied by Son's⁴⁸ theoretical work open a new path to explore spintronics at the nanometre scale, based on graphene.

The *zig-zag* nanoribbons and their unusual band structure could also be used to create devices that have no analogue in silicon-based electronics. One such example is put forward in a theory paper by Rycerz et al.⁵⁰. In zig-zag nano-ribbons carriers travelling in different directions along the edge states of the ribbon do so in different valley states (see also Falko⁵¹), and Rycerz et al. suggest that the ability to differentially populate — or polarize — the valley states of graphene could be used to represent information, in the same way that charge is used in digital electronics, or spin in the emerging field of spintronics. This would yield a new field unique to graphene: '**valley-tronics**'.

A key question is: How wide does a nano-ribbon need to be before its properties become the same as those of 2D graphene? (or, how thin does a graphene ribbon need to be before we should start worrying about edges?) However, in ref. 44 they used a 30

nm wide armchair ribbons, in ref. 47 the zig-zag nanoribbon was 8.6 nm wide and in ref. 46 it was 6.7 nm wide.

5.7 Nanoelectronics: ballistic transport

One of the attractions of graphene, compared with the well known ballistic transport properties of carbon nanotubes, is that graphene ribbons can in principle be patterned to any length and width and the transport properties can be appropriately tailored. Ballistic electron transport in graphene was observed very early in the history of the subject. Recently Gunlycke et al.⁵² have carried out more detailed calculations of the expected electrical ballistic properties of graphene nanoribbons and predict that for a ribbon as narrow as 11 nm will have a mean free path as great as 70 μm .

Titov and Beenakker⁵³ have considered the influence of using a ballistic graphene weak link in a Josephson junction. The vanishing density of states at the Dirac points and the ballistic transfer through the weak-link implies that the normal state resistance of a weak link of width W and length L tends to a maximum value of R_N where

$$R_N \sim \frac{h}{e^2} \frac{L}{W}$$

Thus the resistance can be tuned to an almost arbitrary value by geometric tuning of the barrier. Yet at the same time the $I_c R_N$ product for the device remains essentially constant, at a value Δ/e where Δ is the energy gap of the superconductor. This observation may prove useful for future implementation of a graphene based electrical quantum triangle implementation.

5.8 QED

The prediction and subsequent observation that graphene carriers obey an analogue of the Dirac relativistic quantum mechanics equation have led to the suggestion that graphene may provide a suitable condensed matter test-bed for the Klein paradox of relativistic quantum mechanics. This refers to a proposal^{54,55,56} that the transmission probability by tunnelling through a barrier which is high compared with the particles kinetic energy is not strongly energy dependent. In fact as the barrier height becomes very large the transparency of the barrier (that is the tunnelling probability) tends to unity.

6. Conclusions

This report has attempted to review the varied but important properties of this new material, with emphasis on future relevance to metrology. In addition this exploratory strategic research project has carried out preliminary experimental work on preparation, identification, processing and characterisation of graphene samples, including AFM, SEM, confocal microscopy, transport properties and optical response. This experimental phase was highly successful, given the very limited amount of time available, only around 12 days in total. Collaboration with external groups including Surrey University, Imperial College and Cambridge University meant that much extra leverage on this labour resource was achieved.

The importance of this new material, both for metrology and for basic science and the demonstration of the availability of all the skills at NPL to exploit these properties suggests to the authors that this would present a promising area of development for future NPL research whether in a Strategic Research funded route or through NMS programmes. The topic falls firmly within two strategic priority areas for NPL science, namely nanoscience and quantum metrology. Many important outcomes may be expected, including leading edge metrology, the positioning of NPL as a leader in a major new field and high profile publications in top journals.

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8. References

- ¹ K. S. Novoselov, A.K. Geim, S. V. Morozov, D. Jian, 'Electric Field Effect in Atomically Thin Carbon Films', *Science* v.306, pp.666-9 (2004).
- ² V. P. Gusynin and S. G. Sharapov, 'Unconventional Integer Quantum Hall Effect in Graphene', *Phys. Rev. Lett.* Vol. 95, 146801 (2005).
- ³ K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jia, 'Two-dimensional gas of massless Dirac fermions in graphene', *Nature* v.438, pp.197-200 (2005).
- ⁴ Zhang, Y., Tan, J. W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* 438, 201–204 (2005).
- ⁵ K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim and A.K. Geim, 'Room temperature Quantum Hall Effect in Graphene', *Science* v.315, pp.1379 (2007).
- ⁶ C L Kane, 'Erasing electron mass', *Nature* vol. 438, pp 168-9 (2005).
- ⁷ Yuanbo Zhang, Joshua P. Small, Michael E. S. Amori, 'Electric Field Modulation of Galvanomagnetic Properties of Mesoscopic Graphite', *Phys. Rev. Lett.* v.94 176803(2005).
- ⁸ Morpurgo, A. F. & Guinea, F., 'Intervalley scattering, long-range disorder, and effective time reversal symmetry breaking in graphene', *Phys. Rev. Lett.* Vol. 97, 196804 (2006).
- ⁹ Semenoff, G. W., 'Condensed-matter simulation of a three-dimensional anomaly', *Phys. Rev. Lett.* 53, 2449–2452 (1984).
- ¹⁰ Landau, L. D. & Lifshitz, E. M. *Statistical Physics, Part I* (Pergamon, Oxford, 1980).
- ¹¹ Yuanbo Zhang, Joshua P. Small, William V. Pontius, and Philip Kim, 'Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices', *Appl. Phys. Lett.* Vol. 86, 073104 (2005).
- ¹² Novoselov, K. S. et al. 'Two-dimensional atomic crystals', *Proc. Natl Acad. Sci. USA* 102, 10451–10453 (2005).
- ¹³ Berger, C. et al. 'Electronic confinement and coherence in patterned epitaxial graphene', *Science* 312, pp.1191–1196 (2006).
- ¹⁴ Scott Gilje, Song Han, Minsheng Wang, Kang L. Wang and Richard B. Kaner,† 'A Chemical Route to Graphene for Device Applications', *Nano Lett.* 7, 3394-3398 (2007).
- ¹⁵ Zhang, Y., Tan, J. W., Stormer, H. L. & Kim, P. 'Experimental observation of the quantum Hall effect and Berry's phase in graphene', *Nature* 438, 201–204 (2005) see supplementary information, available on line.
- ¹⁶ A K Geim and KL Novoselov, 'The rise of graphene', *Nature Mats.*, 6 pp.183-91(2007).
- ¹⁷ K. S. Novoselov, A.K. Geim, S. V. Morozov, D. Jian, 'Electric Field Effect in Atomically Thin Carbon Films', *Science* v.306 (2004) pp.666-9 see supplementary information, available on line.
- ¹⁸ Gupta, A., Chen, G., Joshi, P., Tadigadapa, S. & Eklund, P. C. 'Raman scattering from high-frequency phonons in supported n-graphene layer films', *Nano Lett.* 6, 2667–2673 (2006)
- ¹⁹ A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth and A. K. Geim, 'Raman Spectrum of Graphene and Graphene Layers', *Phys. Rev. Lett.* Vol. 97 p187401(2006).
- ²⁰ C Thomsen and S Reich, 'Double Resonant Raman Scattering in Graphite', *Phys. Rev Lett* vol.85 pp.5214-7 (2000).
- ²¹ D Graf, F Molitor, K Ensslin, C Stampfer, A Jungen, C Hierold, and L. Wirtz, 'Spatially Resolved Raman Spectroscopy of Single-and Few-Layer Graphene', *Nano Letters* vol. 7, pp.238-42 (2007).
- ²² I. Calizo, F. Miao, W. Bao, C. N. Lau & A. A. Balandin, 'Variable temperature Raman microscopy as a nanometrology tool for graphene layers and graphene-based devices', *Appl. Phys. Lett.* Vol. 91, p71913 (2007).
- ²³ K. S. Novoselov, E. McCann, S. V. Morozov, V. I. Fal'ko, M. I. Katsnelson, U. Zeitler, D. Jiang, F. Schedin and A. K. Geim, 'Unconventional Quantum Hall Effect and Berry's Phase of 2π in Bilayer Graphene', *Nature Physics*, Vol. 2 p177-180 (2006).
- ²⁴ N. M. R., Peres, F. Guinea, & A. H Castro Neto, 'Electronic properties of disordered two-dimensional carbon', *Phys. Rev. B* vol. 73, 125411 (2006).
- ²⁵ E. McCann and V. I. Fal'ko, 'Landau-Level Degeneracy and Quantum Hall Effect in a Graphite Bilayer', *Phys. Rev. Lett.* vol. 96, 086805 (2006).
- ²⁶ L. Sheng, D. N. Sheng, F. D. M. Haldane, and Leon Balents, 'Odd-Integer Quantum Hall Effect in Graphene: Interaction and Disorder Effects', *Phys. Rev. Lett.* vol. 99, 196802 (2007).

-
- ²⁷ Zhihong Chen, Yu-Ming Lin, Michael J. Rooks, Phaeton Avouris, 'Graphene Nano-Ribbon Electronics', Preprint at <http://arxiv.org/abs/cond-mat/0701599v1> (2007).
- ²⁸ Nikolaos Tombros, Csaba Jozsa, Mihaita Popinciuc, Harry T. Jonkman & Bart J. van Wees, 'Electronic spin transport and spin precession in single graphene layers at room temperature', *Nature* 06037 (2007).
- ²⁹ Schedin, F. et al., 'Detection of individual gas molecules by graphene sensors'. *Nature Materials* vol. 6, pp. 652-655 (2007).
- ³⁰ J. Scott Bunch, Yuval Yaish, Markus Brink, Kirill Bolotin, and Paul L. McEuen, 'Coulomb Oscillations and Hall Effect in Quasi-2D Graphite Quantum Dots', *Nano Lett.* Vol. 5 pp. 287-90 (2005)
- ³¹ Claire Berger, Zhimin Song, Tianbo Li, Xuebin Li, Asmerom Y. Ogbazghi, Rui Feng, 'Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics', *J.Phys.Chem. B* Vol. 108, pp. 19912-6 (2004).
- ³² Heersche, H. B., Jarillo-Herrero, P., Oostinga, J. B., Vandersypen, L. M. K. & Morpurgo, 'A. F. Bipolar supercurrent in graphene', *Nature* 446, pp56-9 (2007).
- ³³ A.Shailos, W. Nativel, A. Kasumov, C. Collet, M. Ferrier, S. Guéron, R Deblock & H Bouchait, 'Proximity Effect and Multiple Andreev Reflections in Few-Layer-Graphene', *Europhysics Letters* v.79 pp.57008-12 (2007).
- ³⁴ Stuart A. Wolf, 'Spintronics, Electronics for the Next Millenium', *J. Supercond.* Vol. 13 pp.195-9(2000).
- ³⁵ J. Wunderlich, B. Kaestner, J. Sinova and T. Jungwirth, 'Experimental Observation of the Spin-Hall Effect in a Two-Dimensional Spin-Orbit Coupled Semiconductor System', *Phys Rev Lett.* Vol. 94, 47204(2005).
- ³⁶ Biqin Huang, Douwe J. Monsma & Ian Appelbaum, 'Experimental realization of a silicon spin field-effect transistor', *Appl. Phys. Lett.* Vol. 91, 72501 (2007).
- ³⁷ J. Sinova, D. Culcer, Q. Niu, N. A. Sinitsyn, T. Jungwirth, and A. H. MacDonald, 'Universal Intrinsic Spin Hall Effect', *Phys. Rev. Lett.* Vol. 92, 126603(2004).
- ³⁸ Markus König, Steffen Wiedmann, Christoph Brüne, Andreas Roth, Hartmut Buhmann, Laurens W. Molenkamp, Xiao-Liang Qi, Shou-Cheng Zhang, 'Quantum Spin Hall Insulator State in HgTe Quantum Wells', *Science* vol.318, pp.766-70 (2007).
- ³⁹ J. Wunderlich, B. Kaestner, J. Sinova and T. Jungwirth, 'Experimental Observation of the Spin-Hall Effect in a Two-Dimensional Spin-Orbit Coupled Semiconductor System', *Phys Rev Lett.* Vol. 94, 47204(2005).
- ⁴⁰ Zutic, I. & Fuhrer, M., 'A path to spin logic', *Nature Phys.* Vol.1, p85–86 (2005).
- ⁴¹ Hill, E. W., Geim, A. K., Novoselov, K., Schedin, F. & Blake, P, 'Graphene spin valve devices', *IEEE Trans. Magn.* 42 (10), p2694 (2006).
- ⁴² Huertas Hernando, D., Guinea, F. & Brataas, 'A. Spin orbit coupling in curved graphene, fullerenes, nanotubes and nanotube caps', *Phys. Rev. B* 74, 155426 (2006)
- ⁴³ Trauzettel, B., Bulaev, D. V., Loss, D. & Burkard, G., 'Spin qubits in graphene quantum dots', *Nature Phys.* Vol.3, p192–196 (2007)
- ⁴⁴ Nikolaos Tombros, Csaba Jozsa, Mihaita Popinciuc, Harry T. Jonkman & Bart J. van Wees, 'Electronic spin transport and spin precession in single graphene layers at room temperature', *Nature* v. 448, pp571-4 (2007)
- ⁴⁵ C. L. Kane and E. J. Mele, 'Quantum Spin Hall Effect in Graphene', *Phys. Rev. Lett.* Vol. 95, 226801 (2005)
- ⁴⁶ R. C. Maher, L. F. Cohen, J. C. Gallop, E. C. Le Ru and P. G. Etchegoin, 'Temperature-Dependent Anti-Stokes/Stokes Ratios under Surface-Enhanced Raman Scattering Conditions', *J.Phys. Chem. B* vol. 110, pp.6797-6803 (2006)
- ⁴⁷ Bjorn Trauzettel, Denis V. Bulaev, Daniel Loss And Guido Burkard, 'Spin qubits in graphene quantum dots', *Nature Physics* vol. 3 pp.192-196 (2007).
- ⁴⁸ Kyoko Nakada, Mitsutaka Fujita, Gene Dresselhaus and Mildred S. Dresselhaus 'Edge state in graphene ribbons: Nanometer size effect and edge shape dependence', *Phys. Rev. B* vol. 54 pp17954-7 (1996).
- ⁴⁹ Young-Woo Son, Marvin L. Cohen & Steven G. Louie, 'Half-metallic graphene nanoribbons', *Nature* vol. 444 pp 347-50 (2006).
- ⁵⁰ A. Rycerz, J. Tworzydło and C. W. J. Beenakker, 'Valley filter and valley valve in graphene', *Nature Phys.* (2007).
- ⁵¹ V I Falko, 'Quantum information on chicken wire', *Nature Phys.* Vol. 3 pp. 151-2 (2007).
- ⁵² D. Gunlycke, H. M. Lawler, and C. T. White, 'Room-temperature ballistic transport in narrow graphene strips', *Phys. Rev. B* vol. 75, 085418(2006).

⁵³ M. Titov and C. W. J. Beenakker, ‘Josephson effect in ballistic graphene’, Phys. Rev. B vol.74, 041401 (2006).

⁵⁴ O. Klein, ‘Die reflexion von elektronen an einem potentialsprung nach der relativistischen dynamik von Dirac’, Z. Phys. 53, 157-165 (1929).

⁵⁵ M. I. Katsnelson, Zitterbewegung, ‘Chirality and minimal conductivity in graphene’, Eur. Phys J. B v.51, pp.157-160 (2006).

⁵⁶ M. I. Katsnelson, K. S. Novoselov and A.K. Geim, ‘Chiral tunnelling and the Klein paradox in graphene’, Nature Phys v.2, pp.620-625 (2006).