Properties of Graphene

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Abstract

The resistivity and Hall effect of monolayer graphene were measured and compared with the results obtained in A. Geim and K. Novosolov's 2004 paper 'Electric Field Effect in Atomically Thin Carbon Films'[1]. The resistivity was found to peak at (10.7 ± 0.2) kΩ and the Hall coefficient was found to have a local maximum at (-65 ± 15) kΩT^{-1}, varying significantly from the results in the aforementioned paper.

1. Novosolov, K.S., Geim, A. K, Morozov, S. V, Jiang, D., Zhang, Y, Dubonos, S. V, Grigorieva, I. V, Firsov, A. A. 2004. Electric Field Effect in Atomically Thin Carbon Films. *Science*. **306**(5696), pp. 666-669.

1 Introduction

Since being first isolated in 2004 [1] , there has been a great deal of research into graphene. The material's electrical properties are of particular interest due to its unique band structure with an infinitesimally small band gap. As traditional silicon semiconductor devices approach theoretical limits of performance[2], it is hoped that graphene will herald a new era of modern electronics characterised by carbon-based semiconductor devices.

To do this, it is crucial to understand how applying a variable electric field across graphene can be used to alter its electric properties. In this experiment the resistivity and Hall effect in graphene are explored under varying electric fields by applying a 'gate' voltage across graphene. We then compare these results to those reported in the famous 2004 Nobel prize-winning paper 'Electric Field Effect in Atomically Thin Carbon Films'.

2 Theory

2.1 Fundamentals of graphene structure

Graphene is a carbon-based material consisting of a basis of two carbon atoms on a two-dimensional triangular lattice[3]. This gives graphene its famed 'honeycomb' structure, which can be seen in Figure 1.

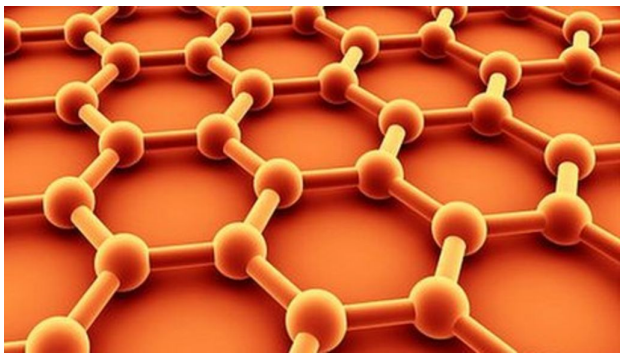

Figure 1: The 'honeycomb' structure of graphene. Each carbon atom has four valence electrons. Three form σ-bonds with adjacent atoms and the fourth is in a weak π-bond, similar to the valence electron configuration of a benzene ring[4].

The energy of the fourth carbon atom is often estimated using the 'tight-binding model'. The wavefunction of the electron is assumed to be periodic with the structure of the graphene lattice and by making this assumption, we calculate the energy of the π-bonded electron in reciprocal space, $E(\underline{k})$ to be

$$E(\underline{k}) = \pm\gamma\sqrt{1+4\cos\left(\frac{3k_x a}{2}\right)\cos\left(\frac{\sqrt{3}k_y a}{2}\right)+4\cos^2\left(\frac{\sqrt{3}k_y a}{2}\right)} \tag{1}$$

where a is the distance from each atom to its nearest neighbour, $\underline{k}$ is the position vector in k-space with components k_x and k_y and γ is a factor approximately equal to 2.8 eV. This

expression is derived in detail in 'Introduction to the Physical Properties of Graphene' by Jean-Noël Fuchs[5]. The expression is shown graphically in Figure 2.

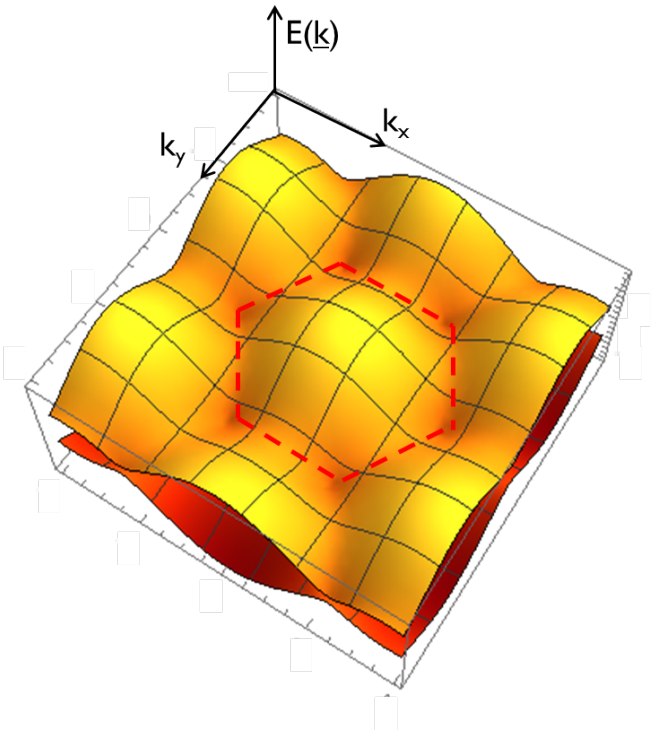

Figure 2: The energy of the π-bonded electron in reciprocol space. The first Brillouin zone is outlined by the red dotted line. The corners of the Brillouin zone have zero energy and are thus 'Dirac points' or 'Dirac cones'.

The first Brillouin zone forms a hexagon in k-space [6], the corners of which are points of zero energy, known as 'Dirac points' or 'Dirac cones'. These are shown in more detail in Figure 3.

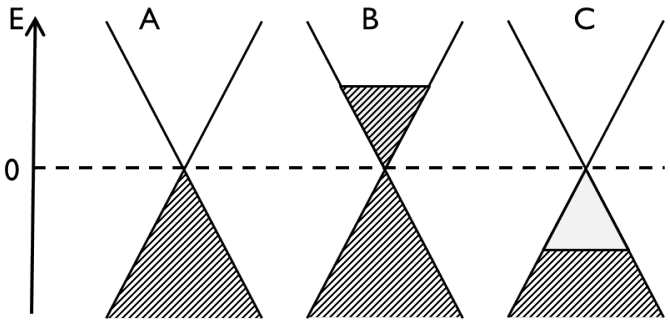

Figure 3: Dirac cones for graphene at varying amounts of doping. Shading shows occupied states. A shows undoped graphene. Here the Fermi energy, E_f, is at 0, such that the lower band is completely filled and the higher energy band is completely empty. As such, there are no charge carriers available in this material (neglecting thermal excitations). In B the graphene is n-doped and so the upper energy band is partially filled. Electrons are available as charge carriers. Finally, C shows p-doped graphene. The Fermi energy is negative and the lower energy band is partially filled. As such, holes are available as charge carriers.

We can see from Figure 3 that graphene appears as a semi-conductor with zero band gap. In this experiment, graphene's Fermi energy is precisely altered by applying a gate voltage across a graphene monolayer on a silicon wafer, separated by a layer of silicon dioxide. This ensemble acts as a capacitor, with the silicon and graphene as the two plates and silicon dioxide as the dielectric. When graphene is held at a positive potential relative to the silicon sheet below it, electrons are forced onto the graphene sheet and it becomes effectively n-doped. Similarly graphene can be p-doped by applying a negative potential to the graphene and a positive potential to the silicon. This allows us to alter its charge carriers and thus electrical properties.

2.2 The van der Pauw method

In this experiment the resistivity and Hall-coefficient measurements were obtained using a method called the 'van der Pauw' method. This method was developed by L. J. van der Pauw in 1958 and provides an accurate way of obtaining these measurements for an approximately two-dimensional material free of cavities[7]. .

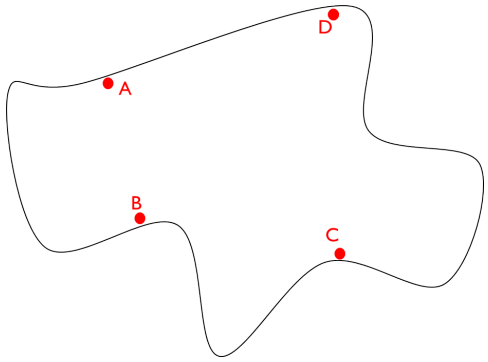

Figure 4: An arbitrary two dimensional lamella with four contacts on the periphery of the disc, marked A, B, C & D.

In order to determine the resistance of the arbitrary lamella shown in Figure 4 a current ,I_{AB}, is passed from A to B and the voltage across contacts C and D, V_{CD}, is measured. A current I_{BC} is then passed from B to C and the voltage across contacts D and A, V_{DA} is measured. The resisitivity of the material of the lamella, ρ, is then given by

$$\rho = \frac{\pi}{\ln 2} \frac{R_{ABCD} + R_{BCDA}}{2} f. \tag{2}$$

Here

$$R_{LMNO} = \frac{V_{NO}}{I_{LM}} \tag{3}$$

for any four contants labelled L, M, N and O. f is a function which can be calculated implicitly from

$$\cosh\left(\frac{R_{ABCD}/R_{BCDA} - 1}{R_{ABCD}/R_{BCDA} + 1} \frac{\ln 2}{f}\right) = \frac{1}{2} \exp\left(\frac{\ln 2}{f}\right). \tag{4}$$

It should be noted that because graphene is two dimensional, its resistivity is measured in Ω per square.

The van der Pauw method can also be used to measure the Hall coefficient for a material. This is done by passing a current from contact A to contact D in Figure 4 and measuring the voltage across contacts B and D. This measurement is taken with a magnetic field perpendicular to the plane of the graphene. The field is then removed and the measurement is re-done. The Hall coefficient, R_H is then given by

$$R_H = \frac{\Delta R_{ACBD}}{B}. \tag{5}$$

Here ΔR_{ACBD} is the difference in resistance R_{ACBD} (as defined in Equation 3) between the two measurements and B is the change in magnetic field at right angles to the graphene.

3 Method

A monolayer of graphene was planted on a silicon dioxide layer on top of a silicon wafer. Electrical contacts were painted onto the graphene using silver conductive paint. A precise gate voltage could then be applied across the graphene-silicon ensemble using a precise voltage source (approximately sensitive to 1 nV).

Van der Pauw measurements for resistivity were then taken. The apparatus was set up as shown in Figure 5. An AC 1 μA current was passed across the graphene from a lock-in amplifier, which also measured the potential. This removed signals of frequencies different to the input current, reducing noise and making an accurate measurement of voltage to be made.

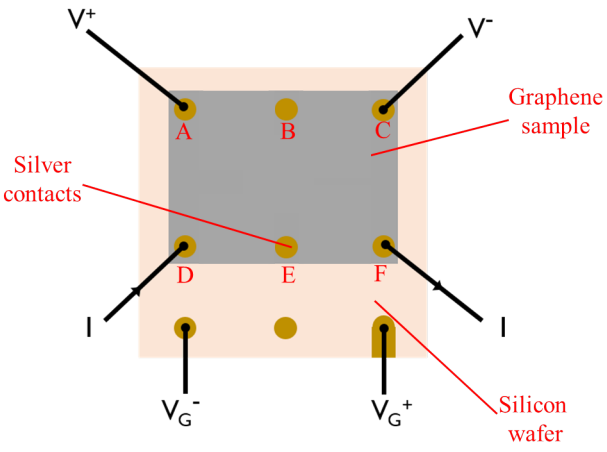

Figure 5: A schematic showing a configuration of the apparatus used to measure the resistivity of graphene. A current was passed from contact D to contact F and the potential from contact C to A is measured. This is combined with a measurement of the potential across C and F when the current is passed from A to D to calculate resistivity according to Equation 2.

It was found that the graphene was heavily n-doped, which was attributed to water molecules doping the graphene. In order to observe the Dirac peak without subjecting the graphene to such a high voltage that the silicon dioxide would break-down, the graphene was doped with ammonia. This is a p-dopant for graphene and caused its Fermi energy to be reduced

so that the Dirac peak could be observed. Once doped by ammonia, the graphene was placed in a vacuum chamber to prevent further doping.

The measurements for resistivity were then taken again with the Dirac peak in the observable range of gate voltages. Once these had been obtained an attempt was made to measure the Hall coefficient of graphene with changing gate voltages. The graphene was then shaped into a Hall bar and the apparatus was configured as shown in Figure 6.

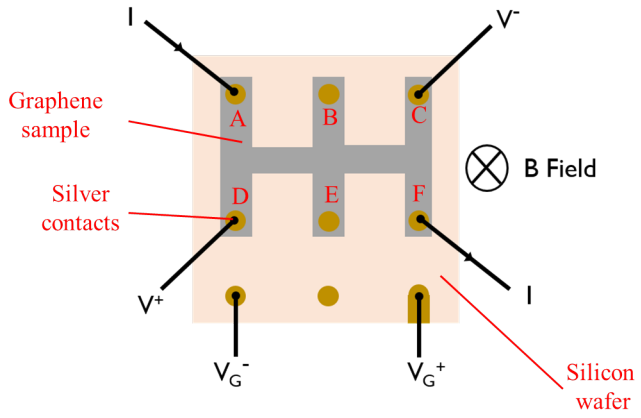

Figure 6: The configuration of the apparatus used to measure the Hall coefficient of graphene. A current is passed from contact A to contact F and the voltage across contacts C and D is measured.

With the apparatus in the configuration shown in Figure 6 two measurements were made; with and without the magnetic field applied perpendicular to the material. This field was applied by placing a small magnet below the graphene sample and the resulting field was measured using a Hall probe. The two measurements were then used to calculate the Hall coefficient of the graphene at varying gate voltage using Equation 5.

As graphene dopant concentration varied for each Hall measurement, the maximum for both measurements occurred at different voltages. To determine the Hall coefficient the gate voltages of each set of data were effectively shifted by a constant amount so that the maxima of each set of measurements coincided at 0 V.

4 Results and discussion

4.1 Resistivity

Figure 7 shows the results obtained for the resistivity of graphene as obtained by the van der Pauw method.

A clear peak in resistivity can be seen at V_G = 3.2 V, believed to be the Dirac point (A in Figure 3). This occurred at a resistivity of (10.7 ± 0.2) kΩ. Here the only charge carriers available to the graphene are due to thermal excitations as the Fermi energy is at 0 eV. The peak occurred at a resistivity value of (10.7 ± 0.2) kΩ per square. This varies significantly from the result obtained by Geim and Novoselov who found graphene's resistivity to peak

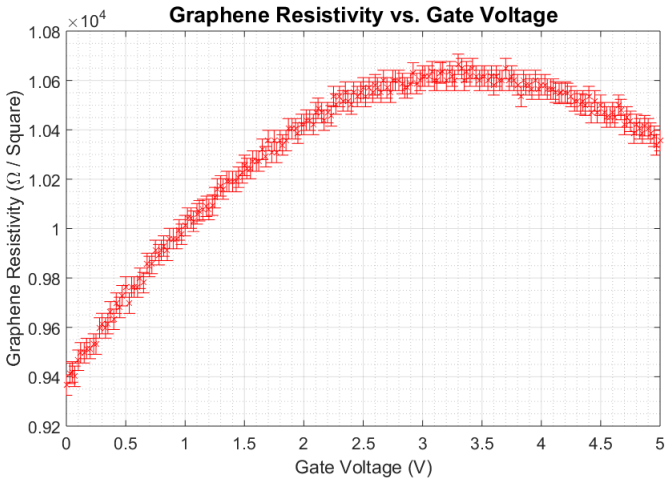

Figure 7: The resistivity of the graphene sample as a function of gate voltage applied.

at 5-10 kΩ per square. It should be noted that in the 2004 experiment, the measurements were made at a temperature of 4 K as opposed to at room temperature. However, this does not explain differences observed as we would expect that as temperature increases the resistivity of the graphene would decrease.

Other potential reasons for the differences in resistivity values include the Dirac peak shifting during the measurement, or impurities within the graphene changing its maximum resistivity. There are also uncertainties unaccounted for as the van der Pauw method assumes point-like contacts. This is unphysical, and the contacts used were of finite size (approximately 3 mm in diameter), introducing further uncertainty. Also during the experiment a small current was found to pass through the graphene to the silicon wafer due to the gate voltage. This resulted in potentially inaccurate measurements of the gate voltage applied.

4.2 Hall effect and charge carrier density

The Hall coefficient measurements are shown in Figure 8. Once again we observe a local maximum, at 0 V with a value of (-65 ± 15) kΩT^{-1}. These results vary significantly from those in 'Electric Field Effect in Atomically Thin Carbon Films' where a minima was observed in the negative range of R_H and a maxima in the positive range. Here a local maxima is observed at negative R_H. Unfortunately, the silicon dioxide layer would frequently breakdown at gate voltages above $\pm$ 5 V and as such the other stationary point was not observed. As well as observing a maxima where a minima was expected, the value at this point is around 100 times larger than the results recorded in the paper.

The uncertainties of this measurement are very similar to those for the resistivity measurement. However, there is an additional uncertainty due to the magnetic field being non-uniform across the graphene sheet. As such there was a high uncertainty in the field measurement, found to be 90 ± 10 mT. A Helmholtz coil could be used to provide a more uniform magnetic field.

Due to the significant difference between the observed and expected results for the Hall

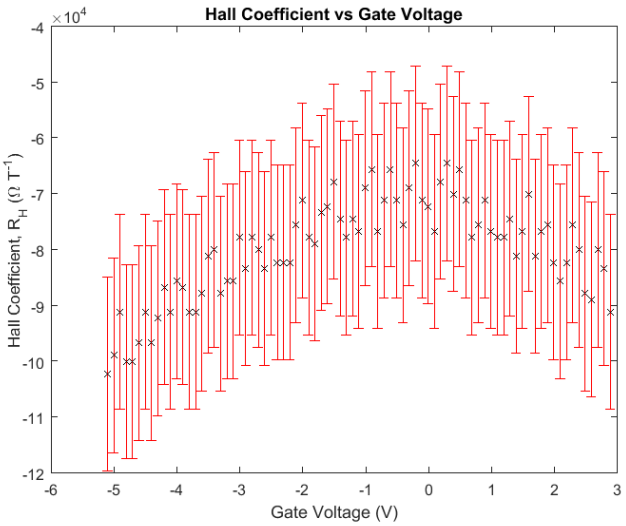

Figure 8: The Hall coefficient of graphene as a function of gate voltage applied across it.

coefficient, it is unlikely that the Hall effect has been observed here. This is likely due to the setup of the apparatus in Figure 6. By measuring the voltage across contacts B and E instead of across C and D, the potential difference would be measured perpendicular to current flow and Hall effect would be much stronger and hence easier to detect. Due to time constraints this theory unfortunately could not be explored any further.

5 Conclusion

Measurements were made of monolayer graphene's resistivity and Hall coefficient with varying gate voltages applied. The resistivity was found to peak at (10.7 ± 0.2) kΩ similar to that found by Geim and Novoselov in 2004.

The Hall coefficient measurements deviated significantly from those found by Geim and Novoselov. This is likely because of an inefficient configuration of the apparatus.

References

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