HIGH-MOBILITY GRAPHENE NANO-RECTIFIERS AND TRANSISTORS FOR HIGH FREQUENCY APPLICATIONS

A Thesis Submitted to the University of Manchester for the Degree of Doctor of Philosophy

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<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
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<tr>
<td>GNR</td>
<td>Graphene nano-ribbon</td>
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<tr>
<td>MFP</td>
<td>Mean free path</td>
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<tr>
<td>2DEG</td>
<td>2-dimensional material</td>
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<td>SSD</td>
<td>Self-switching diode</td>
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<tr>
<td>RF</td>
<td>Radio frequency</td>
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<tr>
<td>BR</td>
<td>Ballistic rectifier</td>
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<tr>
<td>TBR</td>
<td>Triangle ballistic rectifier</td>
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<tr>
<td>SGT</td>
<td>Side-gated transistor</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
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<tr>
<td>S</td>
<td>Source lead</td>
</tr>
<tr>
<td>D</td>
<td>Drain lead</td>
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<tr>
<td>U</td>
<td>Upper lead</td>
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<tr>
<td>L</td>
<td>Lower lead</td>
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<tr>
<td>BN</td>
<td>Hexagonal boron nitride</td>
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<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
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<tr>
<td>IPA</td>
<td>Isopropane alcohol</td>
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<tr>
<td>MIBK</td>
<td>Methylisobutane ketone</td>
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<tr>
<td>DI</td>
<td>Deionised water</td>
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<tr>
<td>DOS</td>
<td>Density of states</td>
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<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<td>HB</td>
<td>Hall bar</td>
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<td>DP</td>
<td>Dirac point</td>
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<td>NP</td>
<td>Neutrality point</td>
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<tr>
<td>TEP</td>
<td>Thermo-electric power</td>
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Abstract

High-Mobility Graphene Nano-Rectifiers and Transistors for High Frequency Applications

Gregory Hunter Auton
The University of Manchester

Graphene has the highest mobility of any material at room temperature; this property has attracted a great deal of interest for applications in high frequency electronics, specifically transistors and diodes. To date, there has been little success using graphene for these purposes because it lacks the bandgap necessary to create an efficient device. This work aims to approach this problem from a different angle; using device architecture that potentially does not need a bandgap. This could allow graphene’s excellent electrical properties to be exploited fully. The first example of this is the ballistic rectifier; a device that exploits the long mean free path of two dimensional electron gasses so that carriers can be treated like “billiard balls”. Here we demonstrate two different four-terminal ballistic rectifiers that redirect carriers from the two input leads to one of the two output leads; the effect of this is to rectify an AC signal into a DC signal. An extremely high voltage responsivity of 23,000 V/W and a very low noise equivalent power of 0.64 pW/Hz\(^{1/2}\) are achieved from a low-frequency AC signal at room temperature. This same device has been tested at 220GHz and showed no signs of a cut-off frequency.

Another rectifier tested here is the self-switching diode, a device that uses two side gates attached to its own source to locally gate its own conducting channel. This architecture demonstrates a modest peak responsivity of 690 V/W, a result of graphene’s missing bandgap. A side-gated transistor with a modest on/off ratio of ~2.33 is also fabricated in order to better understand the limited capabilities of the graphene self-switching diode.

Part of the novelty of this work is the introduction of a modified stamp transfer technique that allowed more flexibility creating hetero-structures. A dry etching recipe for hetero-structures is introduced that does not damage soft masks allowing for a new type of ultra-clean 1D contact. This new contact demonstrates considerably better contact resistance and reliability than previous generations; important for any high frequency application.
Declaration

I declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Gregory Hunter Auton

26th September 2015
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1. Introduction

Since the first experimental observations of graphene in 2004 [1] there has been a great deal of research into its properties and potential applications [2-9]. The simplicity and cost effectiveness of the mechanical exfoliation technique [1] has made it an ideal material to work with on the lab scale. Its compatibility with current micro fabrication techniques and the impressive rate of progress in large scale production have allowed the material to be fabricated with ease [10]. Most importantly, graphene’s unique set of mechanical properties have shown promise for commercial applications capturing the imagination of industrialists [9]. For example, graphene has one of the highest Young’s moduli of any material, is thermally stable in air up to 600°C and has high flexibility [11]. These properties combined with the liquid exfoliation production method have led to applications in polymer composites, coatings and printed electronics [12]. Many have envisaged chemical vapour deposition (CVD) graphene to be widely used in touch screen technology, transparent electronics and as the top electrode in photovoltaic cells. This is thanks to its high conductivity, high transparency and mechanical stability. Initially, many proposed that graphene could even rival silicon as the conductive channel in transistors. However, to date these hopes have not come to fruition since attempts to manipulate graphene to create a band gap have proved unsuccessful or impractical. The main attractions for the use of graphene in transistor technology were based on its high carrier concentration and being the highest mobility material known at room temperature. Both of these properties lead to electronic devices with low parasitic capacitance and hence high cut-off frequencies. Graphene transistors have been demonstrated at extremely high frequencies [13, 14] but unfortunately, they lack the on/off ratio to make them useful. Innovative solutions have been devised using tunnelling barriers and resonant tunnelling to improve this [15] but at the cost of introducing a fundamentally capacitive device architecture. Alternatively, by reducing the lateral size of the conductive channel it was shown [16] that graphene nano-ribbons (GNRs) do have a bandgap and it was possible to achieve high on/off ratios. However, this on/off ratio also came at a cost since the mobility of the conductive channel fell dramatically as the width of the channel decreased. If graphene was to be used in high frequency electronics a new approach was needed. By utilising novel device architecture and developing new fabrication techniques this work intends to integrate graphene into high frequency electronic devices.
Graphene was the first two dimensional material discovered. It can either be considered a semi-metal or a zero band gap semiconductor. It has a linear dispersion relation around its charge neutrality point; this led to the prediction [17] and observation [8] that its carriers can be thought of as massless Dirac fermions. The linear dispersion relation also describes the ambipolar nature of the charge carrier concentration under electrostatic gating. The same tight binding model used to predict its linear dispersion relation also predicted high carrier mobility. This mobility turned out to be sufficiently high that ballistic transport has been observed at room temperature [18]. The ballistic electron transport regime occurs when the mean free path of a carrier ($\lambda_{\text{MFP}}$) is longer than the characteristic length of the device. This regime of electron transport was first formally described by Landauer and Büttiker in 1985 where they consider the problem of metallic reservoirs connected by 1D channels to a ring (this will be discussed in more detail in chapter 2.2 and 4) [19, 20]. This formalism would go on to describe a range of ballistic effects such as quantum point contacts [21], bend resistance [22], electron focusing [23] and the ballistic rectifier [24]. The ballistic rectifier consists of a 4 terminal device with asymmetric cuts etched into the medium such that carriers arriving at either the source or the drain will specularly scatter to one of the two remaining contacts. Because the polarity of the output is the same irrespective of the input polarity, an AC input signal can be converted to a DC output (this will be described in more detail in the chapter 2). Previously, the ballistic rectifier has been fabricated from other high mobility two dimensional gasses (2DEGs). Although these devices show great promise their functionality is often limited to low temperatures due to the limitations of the materials they are made from. Other 2DEGs such as AlGaAs/GaAs may have a higher mobility at low temperature but their mobility is highly dependent on temperature. Graphene’s mobility is only weakly dependent on temperature. This means that graphene has the longest $\lambda_{\text{MFP}}$ of any material at room temperature, typically over 1μm in the best devices. Room temperature performance is important for any commercial application since cryogenic cooling is often expensive and bulky. Many ballistic rectifiers were fabricated during this work and the results will be shown in chapter 5.

The self-switching diode (SSD) has also been demonstrated to operate at a high frequency in other 2DEGs [25]. Consisting of a narrow conducting channel separated from side gates by an etched trench in the medium, the gates are left in contact with the medium at one side of the channel and cut off from the other. The resulting cuts look like back to back letter L’s with the conducting channel between them. The result is a device which
electrostatically gates itself creating asymmetric current-voltage characteristics (IVs). Similarly to the BR, the SSD has a planar structure which means it has low parasitic capacitance and should yield a high cut-off frequency. In AlGaAs/GaAs SSDs have been demonstrated at 1THz [26]. The SSD will be discussed in chapter 2.3 and 6. Following this logic, the side gated transistor has been demonstrated in graphene at high frequency [27]. Although previous studies have demonstrated graphene side-gated transistors [28, 29] they fail to achieve high mobility. A high mobility example will be discussed in chapter 6 and will be used to analyse the operation of the SSD since they rely on similar physical processes.

One possible application of these high frequency rectifiers is the rectenna, the result of combining an antenna with a rectifier [30-32]. The antenna acts to absorb an incident photon and convert it into an RF signal across the source and drain of the rectifier. The rectifier converts the unusable high frequency RF signal into a DC output compatible with traditional electronics. The rectenna relies on a rectifier that operates at the frequency of the incident photon. The principle was pioneered by W. Brown in the 1980s [33], he demonstrated the principle using wireless power transfer to a model helicopter. He was able to keep the helicopter in the air indefinitely. Although impressive, this work was limited by the cut-off frequency of the diodes available at the time. At higher frequencies the rectenna has a range of applications in communication, security and medical imaging.

Above the microwave portion of the spectrum (300MHz – 300GHz) there is a range of the spectrum known as the “THz gap” (300GHz – 10THz). It is known as a gap because current technologies for applications in this region are not as sensitive or efficient. It is challenging to detect these photons because many materials are transparent to them. It is this transparency that opens up this range of interesting applications. For example, THz imaging could be used to routinely image up to 10mm into flesh as a painless non-invasive method of finding epithelial cancer or as a way of imaging teeth in 3D. Crucially, it would be much safer than X-rays because THz radiation is not an ionizing radiation and does not damage DNA or cells. The penetrative nature of THz radiation is already being used in security as scanners at airports. Unfortunately, current THz imaging equipment is bulky, low resolution and limited sensitivity. There is a range of scientific applications in the THz frequency range from spectroscopy to sub millimetre astronomy.

Above the THz region there is the infrared part of the spectrum (300GHz-300THz). Objects at any temperature above absolute 0 will give off photons at this frequency; this is known as thermal radiation and is one of the fundamental methods of heat transfer. The
wavelength that an object will emit the most energy ($\lambda_{max}$) is dictated by Wien’s displacement law $\lambda_{max} = \frac{b}{T}$ where $T$ is the absolute temperature and $b$ is Wien’s displacement constant ($2.898 \times 10^{-3}$ mK). It follows that the corresponding frequency $\nu_{max} = \frac{c}{b} T \approx (1.03 \times 10^{11} \text{Hz/K}) T$. The frequency of this radiation at room temperature (296 K) is 30.6 THz, if a rectifier that operated at this frequency could be used in conjunction with an antenna this would be a major application in military or security technology.

Another major application of this technology lies in thermal energy harvesting, the current market for thermal energy harvesting is predicted to grow from $10$ million in 2015 to $225$ million in 2017 [34]. Thermoelectric power generation is still in its infancy. Commonly made from Bi$_2$Te$_3$, these devices are used to power watches and harvest energy from the exhaust manifold of cars [35]. However, these are expensive and inefficient because they have to be in contact with the entire surface of the warm object and cooled on the outward facing side. Rectennas could be fabricated on a chip and then the energy could be channelled by a wave guide. The chip does not need to be in physical contact with the hot object making it easier to keep cool, maintaining the temperature difference and efficiency.

The major obstacle for these devices getting to market is the lack of diode that operates sufficiently fast. Ballistic devices have been proposed as high frequency alternatives to Si electronics due to their planar nature and therefore low parasitic capacitance. However, the ballistic regime of carrier transport is still not completely understood and in graphene there is still much work to be done. For example, there is still debate whether the edge of graphene reflects carriers specularly or whether it simple diffusively scatters the carriers. In 2008 Du et al made the first suspended graphene devices, their initial work signalled that the carriers in suspended graphene may be able to achieve ballistic transport at room temperature [36]. It was later shown that room temperature ballistic transport in suspended graphene would be difficult because of flexural modes [37]. It was not until boron nitride was suggested as a substrate [3] that it would become possible in graphene. Negative bend resistance was observed in graphene by Mayorov et al in 2011 at room temperature [18], the graphene used in this study was encapsulated between two BN flakes. This encapsulation produces a “self-cleaning” effect on graphene because the pressure between the graphene and the BN squeezes any surface contaminants or add-atoms into bubbles. Then when devices are fabricated these bubbles
are avoided so that only the truly clean and pristine graphene is used. Although the results from this fabrication technique are impressive, they are often unreliable because in the self-cleaning process leaves behind small channels or folds (sub-wavelength so they may not be avoided during design). These channels are where the contamination moves from small bubbles into bigger ones. The best way to reduce this problem is to reduce the overall contamination.

It was well known that the contamination in these bubbles were hydrocarbons, presumably from residual resist used in the transfer process. In 2013 Wang et al demonstrated a transfer technique where the graphene itself does not come into contact with any resist [38]. Their stamp transfer technique made use of the strong Van Der Waal’s interaction between BN and graphene. By simply pressing a BN flake (that itself was in contact with resist) into graphene they were able to pick up the graphene flake. By the same process they were able to pick up a second BN flake and encapsulate the graphene. This method has been adapted for this work and will be discussed further in chapter 4.

Another large obstacle for any high frequency graphene application arises from its large and unpredictable contact resistances. At high frequencies any substantial resistance will result in large losses in power due to load mismatch. The same paper that introduced stamp transfer also discussed 1D contacts where carriers enter the graphene not through the Basel plane but through the edge of the graphene. Not only are these contacts considerably lower resistance, they are much less capacitive and almost completely ohmic. Chapter 4 will also discuss a new generation of 1D contact that improve on the previous technique by reducing hydrocarbon contamination between the graphene edge and the metal contact.

The aims of the project are to design and fabricate a range of graphene nano-diodes that have the potential for high cut-off frequencies. These diodes are to be tested at high frequency with an aim to discover their cut-off frequency. By measuring these devices at low temperature the fundamental processes by which these devices operate are to be understood. The diodes initially proposed for this work include the ballistic rectifier and the self-switching diode, both demonstrate cut off frequencies above 50GHz when fabricated from AlGaAs/GaAs 2DEGs [26, 39].
2. Background Theory

2.1 Graphene

Graphene is a zero band-gap semi-metal with incredible mechanical and electronic properties. It consists of a mono-layer of carbon atoms in a honeycomb lattice and was first shown to exist in its free state in 2004 by mechanical exfoliation[1]. Since its discovery there has been a great deal of interest in the material for a wide range of applications particularly in electronics [2, 14, 40-42].

![Diagram of the hexagonal structure of graphene](image)

Figure 1: shows a diagram of the hexagonal structure of graphene, showing both the unit cell and the lattice vectors. There are 2 sub lattices corresponding to the two atoms in the unit cell.

Figure 1 shows the molecular arrangement of graphene, with both its unit cell and its lattice vectors. The bond length in graphene $\delta = 1.42 \text{ Å}$. Each carbon atom is bonded to three other carbons by $\sigma$ bonds and the remaining bond is a $\pi$ bond which can be thought of as a pair of symmetric tear-shaped lobes in the z-plane of the lattice [7]. There are 2 sub lattices in graphene corresponding to the two atoms in the unit cell both contributing their own $\pi$ bonds. These $\pi$ bonds contribute to the unusual properties of graphene.
Figure 2: shows the crystal structure of graphene shown in k-space; showing the Brillouin zone, the K points and the reciprocal spacial vectors $\mathbf{b}_1$ and $\mathbf{b}_2$.

To describe the electrical properties of graphene we must first define the unit vectors in real space as $\mathbf{a}_1$ and $\mathbf{a}_2$ and the reciprocal space vectors as $\mathbf{b}_1$ and $\mathbf{b}_2$ shown in Figure 2:

$$\mathbf{a}_1 = \frac{\delta}{2} (3, \sqrt{3}), \mathbf{a}_2 = \frac{\delta}{2} (3, -\sqrt{3})$$  

$$\mathbf{b}_1 = \frac{2\pi}{3\delta} (1, \sqrt{3}), \mathbf{b}_2 = \frac{2\pi}{3\delta} (1, -\sqrt{3})$$

The tight binding model predicts a linear dispersion curve at low energies near the 6 K-points [7]; this fact means that graphene is a zero band gap semiconductor. A thorough calculation using the tight binding model gives the energy dispersion as follows:
\[ E(k) = \pm t\sqrt{3} + f(k) - t'f(k) \]  
\[ f(k) = 4\cos\left(\frac{3k_x\delta}{2}\right)\cos\left(\frac{\sqrt{3}k_y\delta}{2}\right) + 2\cos\left(\sqrt{3}k_y\delta\right) \]

Where \( t \) and \( t' \) are the nearest neighbour and next nearest neighbour hopping energies respectively; \( t \approx 2.7\text{eV} \) and \( t' \) is not well known, best estimates are near \( t' \approx -0.2t \) [8].

Equation (3) has both a positive and negative part; this physically represents the symmetric lobes of the \( \pi \) orbitals.

The point where the dispersion curves touch (and become degenerate) is called the Dirac point. At this point the electrons start behaving like massless chiral Dirac fermions. They move in the graphene at the Fermi velocity \( (v_f) \) which is 300 times less than the speed of light [43].

By taking the approximation that the dispersion relation is linear, the energy momentum relation becomes \( E_{\pm}(k) \approx \pm v_f|k| + O\left([k/K]^2\right) \), where \( k \) is the momentum relative to the Dirac point; this can be seen in the inset of Figure 3. This is one of the main reasons that both ballistic and self-switching devices, discussed in section 2.3, should work faster in graphene than in any other material. Previously, these diodes have been made in

Figure 3: a graph demonstrating the dispersion curve for graphene from equations (14) and (15), on the right is the region around the Dirac point expanded showing the linear behaviour. For this example \( t \) was taken to be 2.7eV and \( t' \) was assumed to be 0.2t.
InGaAs quantum wells; the alternative 2DEGs with the closest electrical properties to graphene. These 2DEGs consist of a highly doped, high mobility conductor (such as InGaAs) sandwiched between two wide band gap semiconductors (such as GaAs). When the thickness of the conducting region is of the same order as the de Broglie wavelength, lateral confinement effects can be seen in the transport properties such as energy quantisation in the dispersion relation [20]. Most importantly, these quantum well structures have high mobilities and high carrier velocities. However, the electron velocity in graphene is nearly 10 times faster [44]. One of the proposed limiting factors for the cut off frequency in these devices (ignoring any capacitive problems) is the distance the carriers can travel in the time before the electric potential switches.

At room temperature, the carrier mobilities for graphene can be more than 10 times larger than AlGaAs/InGaAs quantum wells [45]. This has important implications for making these devices in graphene because a high mobility will increase the efficiency of ballistic devices as more carriers will travel from the source to the desired channel without scattering.

One potential problem that may hinder the efficiency of the graphene BR is the effectiveness of the edge of graphene to scatter specularly. Early studies suggested that the edges of graphene would scatter purely diffusively [18, 46-48]. However, more recent unpublished work on electron focusing has shown this might not be the case. Part of the work here will be to discuss the scattering properties of the edge of graphene. The self-switching diode that will be discussed in section 2.3.2 normally relies on a depletion zone that expands with the local potential to block the conducting channel. However, graphene does not have a band gap so it will not have a depletion zone. Instead, the channel conductivity will change with the carrier concentration induced by the local side gate potential. This will mean there will be no off state for the SSD in graphene, merely a conductance minimum. Another potential problem graphene might present are edge traps, these will create variable local potentials and changes in local doping, both of which could lower efficiency. Variable local potentials may also be introduced by charge puddles in graphene; these puddles are particularly prevalent in graphene on SiO$_2$ substrate and are a result of charge donors from the substrate [49].
2.2 Rectenna

The rectenna is a very simple concept with a great deal of potential for commercial applications. When a photon is incident upon an antenna the photon is absorbed by oscillations of electrons in the antenna. These oscillations can be used to operate electrical devices, this is the principle that is used for inductive charging (coils are typically used as antennas in this case to increase efficiency). These oscillations are naturally at the same frequency as the incident photon. When the photon frequency is low most devices will be able to harness the energy but as the frequency is raised over 1MHz many will reach their cut-off frequency where most of the incident power will be lost due to capacitive effects. However, a rectifier that does operate at the necessary frequency can be used to turn this high frequency output into a DC output and electrical device can use. This amalgamation of an antenna and a rectifier is known as a rectenna. The rectenna has a range of advantages over conventional photovoltaics. Firstly, it is able to absorb a whole photon not just a quantum of energy from the photon corresponding to the bandgap of the semiconductor used to create the pn-junction (discussed in section 2.4.3.). This enables the rectenna to have a theoretical maximum efficiency of 100% and not the ~50% efficiency photovoltaics are predicted to have [50]. Secondly, rectennas could in principle operate over large ranges of the spectrum simultaneously, only limited by the antenna used to absorb the energy. Similarly, they can access areas of the spectrum quantum devices cannot like the THz and GHz range. Finally, they could be simple and cheap to fabricate and could potentially be made entirely from graphene to make flexible transparent sensors that could have a wide variety of applications.

2.3 Device Operational Principles

2.3.1 The Ballistic Rectifier

This work will consider three principles for rectifier design; all have been demonstrated to work above 1THz in InGaAs quantum well [25, 26, 32]. The first device is called the ballistic rectifier (BR); a rectifier’s primary purpose is to convert AC into DC power, a circuit diagram for a traditional rectifier is shown below in figure 4:
The ballistic rectifier relies on the ballistic regime of electron transport, the electrons travel far enough before scattering that they will hit an artificial geometrical inhomogeneity. By specifically designing these inhomogeneities so that no matter which direction carriers travel into the device they always leave by the same channel:

Figure 5 demonstrates the operating principle of the BR; through the narrow constrictions the electric field potential changes quickly accelerating the carriers in the
direction normal to the gap [24, 51], resulting in a change in the direction of the overall electron momentum at the gap.

Figure 6: Diagram of triangular ballistic rectifier, the faces of the triangle bounce the carriers to the lower contact no matter which direction they approach from.

Figure 6 shows the triangular ballistic rectifier (TBR) with its triangular anti-dot that will direct the electrons to the lower electrode. The formalism of the TBR electrical characteristics comes from [24] and will be discussed in further detail in section 5.2, the theory predicts that the voltage characteristics will be quadratic:

\[
V_{LU} \approx -\frac{\hbar}{e^2} \frac{3h}{4eE_FN_{SD}} \frac{\sin 2\vartheta_0 l_{SD}^2}{2N_{LU} - 3N_{SD}(1 - \sin \vartheta_0)^2}
\]  

(5)

Where \(E_F\) is the Fermi energy, \(V_{LU}\) is the voltage between the lower and upper contact, \(N_{SD}\) is the number of propagating modes between the source and the drain, \(N_{LU}\) is the number of propagating modes between the lower and upper contacts and \(\vartheta_0\) is the angle between the normal of the narrow channel and the point that it will just miss the triangle and go into the upper electrode.
Figure 7: Graph showing theoretical plots of typical features of both traditional rectifier and ballistic rectifier (note that data is only an example derived from formulas of Schottky diodes for the traditional rectifier case and from equation (5) in the case of the ballistic rectifier). Note the 0 A response region for the traditional rectifier corresponding to the 0 A response region in a normal pn-diode, this is important because the area under the graph corresponds to the power output from the device and there is no area under the traditional rectifier graph until it reaches the threshold input where as there is output near to 0 V for the ballistic rectifier.

Figure 7 demonstrates the advantage of using a ballistic device; the pn-diode based ballistic rectifier lacks the low voltage response. Since the power rectified is the integral of these graphs, for the region shown, the ballistic device will output a lot more useful DC power. For applications in direct solar energy harvesting a 100% efficiency antenna (without any gain) might generate a voltage around 3 mV and a standard silicon pn-diode has a $V_T$ of 0.7 V, one can see that 0 V response is essential.

However, there is still a problem with diffuse vs specular scattering; preferentially the ballistic devices need specular scattering at the boundaries of the graphene. However, it still remains unclear if scattering at the edge of graphene is specular or not [52], it is likely that the edges of the graphene will line up alternately with the armchair and zigzag crystal planes creating a very rough edge that creates diffuse scattering. However, the devices could still work in the diffuse scattering regime since the transmission probability to the lower contact will still be higher than the upper contact.
One of the primary reasons for adopting this design is its theoretically high cut-off frequency. Normally, the cut-off frequency \( f_c = \frac{1}{2\pi RC} \) where R is the resistance through the device and C is its capacitance. In these planar devices the only contributions to the capacitance will come from the cut trenches and the contacts. An alternative limit to the speed of these ballistic rectifiers may originate from causality because a carrier must be ejected from one of the two input leads, be redirected and reach the output lead before the instantaneous voltage of the RF source changes polarity. By assuming the carriers travel at the Fermi velocity \((10^6 \text{ m/s})\) and a device path length of 1 \(\mu\text{m}\) this presents an upper frequency limit of 1 THz. However, it remains to be seen what the important path length truly is, it could be the distance between the injection leads and the point the carriers are redirected since this is where their perpendicular momentum.

### 2.3.2. The Self-Switching Diode

The second diode is called the self-switching diode (SSD), it consists of a conducting channel with a trench cut either side, shown below in Figure 8:

![Figure 8: Schematic for SSD in an InGaAs 2-DEG, (a) is a diagrammatical representation of 5 SSDs in parallel with the equivalent circuit below. (b) shows when the electric field is higher on the right, holes gather in the wells either side of the channel creating a local potential. The local potential in the channel changes the](image-url)
depletion zone so the channel is open and the majority carrier can travel through the channel. (c) represents the alternate case were the left side has a higher potential, electrons now well either side of the channel increasing the size of the depletion zone so that the channel is blocked.

Figure 8 (b) shows a higher electric field on the right; holes gather in the wells either side of the channel creating a local potential. The local potential in the channel changes the depletion zone so the channel is open and the majority carrier can travel through the channel. Figure 8(c) represents the alternative case were the left side is a higher potential, electrons now gather either side of the channel increasing the size of the depletion zone so that the channel is blocked. An analogy for this principle is taking a standard MOSFET but connecting the source and the gate. By taking this analogy further we can expect these devices to follow a square law in their I-V characteristics. We can describe the MOSFET square law using the Shichman-Hodges model [53]:

\[
I = ZwJ = Zwnv = ZwQv
\]  
\[
Q = C\left(V_g - V_T - V(y)\right)
\]

Where \(J\) is current density, \(q\) is carrier charge, \(n\) is carrier density, \(Z\) is the thickness of the channel, \(w\) is the width of the channel, \(v\) is the drift velocity and \(Q\) is the charge induced by the gate. \(C\) is the capacitance of the gate per unit area, \(V_g\) is the gate voltage, \(V_T\) is the threshold voltage and \(V(y)\) is the potential in the channel as a function of \(y\) (along the channel). For a traditional semiconductor:

\[
v = -\mu \frac{dV(y)}{dy}
\]

Where \(\mu\) is the mobility, we will assume it is constant in this case, which leaves the current:

\[
I = \mu zwC \left(V_g - V_T - V(y)\right) \frac{dV(y)}{dy}
\]
Continuity implies \( \int I \, dy = IL \), where \( L \) is the channel length. This means one must integrate between 0 and the drain voltage on the \( V(y) \) side:

\[
I = \mu Z w C \left( (V_g - V_T)V_D - \frac{V_D^2}{2} \right)/L
\]  \hspace{1cm} (10)

However, for the case of mono-layer graphene in the intrinsically doped regime, \( V_T \) will be 0 since there is no band gap and the Fermi level is at the neutrality point. In graphene the mobility is described in two dimensions, therefore, \( Z \) can be left out since the sample has no thickness. For these devices \( V_G = V_D \) and the capacitance will be between the channel and the effective side gates, in the trench; leaving us with the square law:

\[
I = \frac{\mu w Z C_{\text{Trench}}} {L} \left( \frac{V_D^2}{2} \right)
\]  \hspace{1cm} (11)

Graphene has a minimum conductance that will add a linear term to the equation above. The magnitude of the linear signal will depend on the doping homogeneity of the sample. It is important to remember that graphene is ambipolar and that the differential conductance that the device relies upon will change polarity depending on the type of carrier. This does not mean that the linear term will change from positive resistance to negative depending on majority carrier type, instead only the quadratic term will change sign.
Figure 9: Graph showing diagrammatical examples of I-V characteristics for various diodes: the ideal diode is based on a finite resistance medium. The pn-diode shows reverse bias leakage, knee bend after a threshold voltage and exponential response after. The Self switching diode is based on a carefully tuned III-V semiconductor quantum well with a depletion region based on equation (7) [25]. The data for the graphene SSD shown is based on the model in equation (10) with values that accentuate the quadratic behaviour for clarity.

Figure 9 shows sample graphs for various devices, although the graphene SSD is very close to the ideal diode for positive bias it shows we should expect large leakage in the case of negative bias. This is a result of the lack of a depletion zone in graphene, in InGaAs quantum wells the depletion region blocks the channel but in graphene we rely on the field effect changing the number carriers. Even if the device is well tuned so that the negative bias brings the channel exactly to the Dirac point, single layer graphene (SLG) will still conduct. This means it will conduct even in the negative bias region but the overall effect will be a positive DC output when and AC signal is applied. However, if we were to use Few Layer Graphene (FLG) or graphene nano ribbons [7] we could reach lower conductivity in the off state in the case there is a band gap [7, 54].

In this model the conductance has been assumed to change linearly with $V_G$ by assuming $\mu_{eff}$ is constant for all densities. In section 5.4.4 devices with high mobility will be shown that demonstrate the change in mobility with carrier concentration. Electron-
electron interactions and shielding lower the differential conductance at higher carrier concentrations. Also, near the neutrality point there will be coexistence of both carrier types due to thermal excitation, making the minimum conductance much greater than zero. If the gate voltage is set to the conductance minimum at zero bias, when a voltage is applied the sign of the differential conductance will flip between positive and negative bias. This is because the relative voltage of $V_G$ will change compared to the average voltage in the device $(V_D - V_S)/2$. Therefore, there will be a narrow window of gate voltages where the device operates optimally. If such a device were going to be used in conjunction with an antenna field effect doping could not be used to control doping in the graphene. This is because a global backgate would couple capacitively with the antenna and all the power generated would be lost. The implications for this are common to almost all graphene high frequency applications, but there is much in the literature describing how it could be controlled in the future; for example: nitrogen ion bombardment, nitric acid doping, diazonium salts as hetero-atoms for doping, arc discharge and chemical modification by nitrous-oxide, ferric chloride and ammonium [55-59]. Another potential problem might be the effect of edge traps and narrow channels that effect conductance, well described in [47].

2.3.3. Side-Gated Transistor

Graphene has the highest mobility of any material at room temperature, putting it in a unique position to make some of the highest frequency transistors to date [13, 14, 60, 61]. The novel architecture of the Side-gated transistors (SGT) presents an opportunity to take advantage of graphene’s extremely high mobility. The low parasitic capacitance of the SGT could open up THz electronics. However, graphene lacks a bandgap which puts a fundamental limit on the on/off ratio of such devices. Graphene nano-ribbons (GNR), on the other hand, do have a bandgap [16]. It is conceivable to design a series of graphene SGT that use a GNR as the conductive channel. The fabrication of Side-gated transistors (SGT) involves very similar processes to the fabrication of SSDs. The operation of SSDs may be better understood by analysing the working principles of the SGT. SGTs can also be mass produced using stamp lithography which is cheap and easy thanks to the planar nature of the device. They also have the potential to operate at high frequencies due to the low parasitic capacitance in the device.
Early work on SGT resulted in very modest on/off ratios ranging from 1.3 [62] to 15 [27] that depended strongly on the quality of the graphene and the fabrication procedure. Molitor et al. noticed a flattening of their conductance curves due to the application of a large side gate voltage, a result of shielding on the central region of the channel by the edges of the channel [29]. The first work that demonstrated a large on/off ratio in a planar device with side gates was performed by Ponomarenko et al. in 2008, they were able to achieve an on/off ratio of $10^4$ [4]. However, the operation of this device relied on coulomb blockade; although not tested, it is likely that this device would not operate at high frequencies. A comprehensive study in 2010 performed by Han et al. showed that GNRs could achieve high on/off ratios and may still operate at high frequencies [16]. They observed that the bandgap scaled with the physical size of the GNR, meaning that the bandgap could be tuned to optimise the device. However, they only observed a bandgap when the sample was at cryogenic temperatures due to thermal excitations of carriers above and below the band gap. Unfortunately, it has also been observed that the mobility of the channels decreases as the width of the channels decreases presenting another potential obstacle for graphene high frequency GNR FETs [63].

The main purpose of investigating graphene SGTs in this work is to investigate the advantages of using the very latest fabrication techniques. One possible reason for the reduction of mobility of GNRs was that the etch used to shape the nanoribbon also damaged the conducting channel. By encapsulating the graphene channel before etching, we hope to preserve the mobility of the channel and promote high frequency applications. There has also not been a great deal of work investigating GNRs with side gates which presents an opportunity. Further, the operation of the graphene SSD has been theorised to work in a similar manner to the SGT, by looking at one of these we might hope to understand the other device better.

2.4. Competing Technologies

Competing technologies must be considered so that devices fabricated for the project can be evaluated for real world applications. The figures of merit for a sensing device are the responsivity and the noise equivalent power (NEP). The figures of merit for an energy harvesting device are the voltage and power efficiency. Both of these measurements will be discussed in this section.
2.4.1. Photovoltaics and Thermoelectrics

Photovoltaic (PV) and thermoelectric devices currently fill the role for both imaging and energy harvesting; they would represent the main competition for the devices proposed. In the simplest photovoltaic devices a pn-junction is created by artificially doping a semiconductor; the charge differential represents a built in electric field as in Figure 10.

Figure 10: photovoltaic with no incident light, showing built in potential and the depletion zone [specmat.com].

When a photon interacts in the semiconductor it creates an electron-hole pair, the built in electric field separates the electron and the hole stopping them from recombining, consequently creating a current as in Figure 11.

Figure 11: photovoltaic with incident light, showing photons interacting in the depletion region creating electron hole pairs, the electron- hole pairs are then pulled apart by the built in potential (adapted from specmat.com).
The efficiency of this process is fundamentally limited because only a discrete unit of energy can be taken from any photon. This discrete unit of energy is the same size as the energy necessary to create an electron hole pair in the semiconductor. Any extra energy the photon had is lost as heat in the device and if the photon does not have the required packet of energy then it is completely lost as heat. This principle describes most energy harvesting and some imaging devices in use today but many more complicated devices have been designed to increase efficiency for energy harvesting (e.g. Multi-layer solar cells) or sensitivity for imaging applications (e.g. Charge Coupled Devices(CCDs)). Multi-layer solar cells try to optimise the uptake of energy from the wide spectrum of photons that arrive from the sun. By having a narrow band gap semiconductor as the first layer that the photons impinge upon the easily absorbed lower energy photons are initially absorbed. The higher energy photons are more likely to pass through this layer into a second layer of semiconductor with a wider band gap. This layer is then thick enough so that all the remaining photons are absorbed; since its band gap is wider the photons are absorbed with less heat loss.

Thermoelectric devices rely on the Seebeck effect where carriers travel from a hot region to a cold region. In the steady state where there is no current loop, the voltage gradient in a conductor (\( \nabla V \)) is proportional to the temperature gradient (\( \nabla T \)) by the negative of the Seebeck coefficient (S) so that \( \nabla V = -S\nabla T \). Practical devices used as thermocouples or thermopiles are often made of semiconductors doped alternately as in Figure 12.
Figure 12: shows the schematic for a thermoelectric device where the hot object is placed at the top and the bottom side is cooled. In-between the metal pads that contact the temperature gradient there are a pair of semiconducting pillars. These pillars are doped differently so that an electro-motive force is formed between metal A and metal B.

Figure 12 demonstrates how thermo-electric devices work. A hot object is placed on top of the device and the bottom side is cooled. The device itself consists of a top metal contact that conducts heat from the hot object into the top of two semi-conducting pillars. At the bottom of the semi-conducting pillars there is a pair of metal contacts in contact with a cold surface in order to maintain the temperature differential across each pillar. The pillars are doped differently and the heat difference moves the carriers from the hot top of the device to the cold bottom (irrespective of carrier type). This creates an electro-motive force (EMF) between contact A and B.

Energy harvesting with PV devices has an estimated market value of $512 million and is growing 42.1% every year [64]; it is a major alternative to non-renewable energy but the price per Watt is still slightly more than non-renewable power plants [65]. In order to replace existing environmentally destructive infrastructure, the alternative will need to be
cheaper. One of the limiting features of solar energy harvesting using photovoltaics is the quantum nature of the absorption; only discrete units of energy are needed to create an electron hole pair. This means that any energy left after the electron hole pair has been created exists as kinetic energy in the electron and hole, which is not useful. If the photon does not have enough energy to create an electron hole pair no current is created. Multiple layers of different semiconductors with different band gaps can be used to create a higher efficiency device. Splitting the light into different wavelengths with optics[50] and absorbing with different band gap semiconductors to make the best use of the whole spectrum can create a higher efficiency device; both increase the cost of device manufacture making them commercially unviable.

Energy harvesting devices are characterised by their efficiency, this is calculated as the power developed by the device divided by the power in the light falling on the device. In order to characterise the devices proposed in this work in the same way we must assume all the incident light is absorbed by the antennas. Therefore, the efficiency of the rectifier is the power developed by the device in DC (P=IV) divided by the power put into the device. A crude approximation to the true power efficiency is the voltage efficiency; this can be useful for a rough estimate of the BR operation when the DC current voltage characteristics are taken. It is necessary because of the 4 terminal nature of the BR and is simply calculated by taking the ratio between the input voltage and the output voltage. It is only valid when \( R_{LU} \sim R_{SD} \). Typical values for efficiencies of photovoltaics are between 10% and 40% [50], thermo-voltaics have even lower efficiency.

2.4.2. Imaging and the THz Gap

The imaging market as a whole is worth over $11 billion but the market that the devices in this project would enter, the THz imaging market, is worth $83.7 million and is growing 32.7% a year [66]. The THz region spans from 0.1THz to 10THz and is commonly referred to as the THz gap. It is so called because at these frequencies the photons permeate through most non-metallic materials. This low absorption means that T-rays can be used to look inside objects or people, much like X-rays but without harmful ionisation, this could have applications in medical and security fields. The current devices filling this niche market are CCDs.

CCDs work by using a heavily doped semiconductor to gather electrons in a similar fashion to pn-junctions but instead of an inbuilt doped potential they have an array of
electro-static gates that attract the electrons and repel the holes. The gates are separated from the semiconductor by a dielectric allowing the electrons to gather, effectively integrating the signal. By activating each gate in series the signal can be pulled to the edge of the detecting area and converted into a current one pixel at a time. This process takes time slowing device operation and devices normally have to be cooled to reduce noise.

An alternative to the CCD is the bolometer; with both low noise and high sensitivity these devices are preferable to other types of devices in many cases. However, they often require cryogenic temperatures to operate and are very expensive to fabricate. They consist of a thermistor (often super conducting) attached to an absorber. Sometimes they are thermally insulated from any connected components in order to reduce noise. This reduces their response time which can be as low as 80Hz because the heat takes time to dissipate. They can be in contact with a large thermal well that ensures they respond quicker but this will result in higher noise equivalent power (NEP).

NEP is one of the figures of merit for any detector equipment. It is defined as the necessary input power to give a signal to noise ratio of one in a one hertz output bandwidth. It is normally extracted by dividing the noise spectral density ($NSD$) by the responsivity, both of which are figures of merit in their own right. The $NSD = \sqrt{4kTR}$ and the Current responsivity defined as the input/output gain or the electrical output per optical input power:

$$R = \frac{\text{electrical output current}}{\text{optical input power}}$$  \hspace{1cm} (12)

This figure of merit can be extended to diodes by changing the optical input power into electrical input power. By taking the Taylor expansion of the Schottky diode equation in the DC I-V curve case an expression for the current responsivity can be realised [67]:

$$R_I = \frac{\partial^2 I}{\partial V^2} \frac{\partial I}{\partial V}$$  \hspace{1cm} (13)

A typical pn-junction diode has a responsivity of between 0.3 and 1.2A/W at optical wavelengths [68]. Although valid for two terminal devices where we apply voltage and measure current (such as the SSD), problems arise when this same analysis is done for four
terminal devices. In this case a current is applied and a voltage is output between 2 separate terminals. Instead, voltage responsivity must be taken, changing current to voltage by multiplying by the resistance (R) of the device and rearranging equation (2):

\[
\mathcal{R}_V = R \mathcal{R}_I = \frac{\partial^2 V}{\partial I^2} \frac{\partial V}{\partial T} \tag{14}
\]

The Resistance used to calculate the *NSD* changes from the resistance between the source and drain contacts to the resistance between the two output contacts. A more practical way of extracting the responsivity from the device is to apply an AC power between the source and Drain and then measure the DC voltage output. Simply by dividing the DC voltage output by the RMS power input the responsivity can be extracted.

The principle aims of this work is to understand how these devices work in graphene and also how well they work. To achieve the latter they must be compared to current devices used in the sensing market and also other diodes or rectifiers that could be used in rectennas in their place. For that reason we must define the difference between intrinsic and extrinsic measurements. Specs given for devices used in THz imaging or energy harvesting are extrinsic because it quotes the output that would be important for the application in mind. Measurements made on the diodes are intrinsic because their eventual output depends on the antenna attached to the diode. In other words, a measurement of the responsivity of a diode will not be the same as the measurement of responsivity of a rectenna with this same diode used as the rectifying component. It is important not to confuse the two. The measurements of both current responsivity of a two terminal device and the voltage responsivity of a four terminal device are both intrinsic properties of rectifiers. The current responsivity of a photodiode or CCD is an extrinsic property of the device. The measurements shown in for the BR at high frequency in section 5.4.6 using the THz mesa will be representative of the extrinsic properties of a device since higher frequency measurements introduce signal loss due to load mismatch.

### 2.4.3. PN-junctions

In order to understand the advantages of the devices presented here one must consider what introduces the cut-off frequency in normal diodes. A traditional pn-diode is simply a region of n type doped semi-conductor followed by p type as shown in Figure 8 (a). This creates a region of built in potential where the two carrier types diffuse into the opposing
regions leaving behind a charge donor shown in Figure 13 (b). These charge donors make the interface region charged; this region is called the depletion region.

Figure 13: Diagrammatic representation of a pn-junction where no bias is applied, (a) shows the case before the carriers diffuse into the opposing doped regions (the case if saturation forward bias is reached where the depletion region is removed and then the bias is instantaneously removed). (b) shows the case after the recombination time $\tau_R$ where the diffusion has had a chance to take place.

The charge created by the static charge donors in the depletion region opposes the diffusion of carriers at the interface and the system ends up in equilibrium. When forward bias is applied, Figure 14 (a), the electrons in the n-type region push into the depletion region and the holes in the p-type region move the opposite direction. The net effect is to constrict the depletion region; eventually the voltage will reach a threshold voltage ($V_T$) where the depletion region is so thin that it cannot stop the carrier motion across the channel, this is the on state of the diode. In the case of reverse bias, the opposite will happen as in Figure 14 (b); the carriers will be pulled away from the depletion region making it larger and less conductive. Only when the voltage reaches the voltage breakdown point will current flow in this direction, which importantly is much larger than
The limiting factor for the speed in these diodes is the diffusion and annihilation of the carriers to form the depletion region after it has been destroyed by forward bias [69].

Figure 14: Diagrammatic representation of a pn-junction when different biases are applied. (a) shows the forward bias case where the potential decreases the size of the depletion region and the size of the potential barrier allowing current to pass easily. (b) is the negative bias case where both the depletion region and the potential step is extended by the bias, making it more difficult for current to pass.

The typical time for a carrier to diffuse back into the depletion region is about $10^{-6}$ s in an off-the-shelf diode, which corresponds to a cut-off frequency of 1 MHz. The BR will have no depletion region in graphene since there is no bandgap. Therefore, the cut-off frequency of the device must be limited by something else. There are several possibilities that point to different possible values for its maximum speed. It might be that it is simply like a traditional conductor in that although the carrier may move slowly, the message that the current is moving moves at the speed of light. In this case, if we assume the distance from S to L (or S to D for the SSD) is 1 μm, the cut-off frequency for a BR would be 300 THz. Alternatively, for causal reasons it might be important that the carriers have the
opportunity to travel from S to D before the polarity of the bias reverses; travelling at the Fermi velocity this would limit the device to 1 THz.

### 2.5. Landauer formalism

Although the simple “billiard ball” model for electron transmission through these devices is intuitive it is not entirely accurate. Onsager’s theorem dictates that if the current and voltage leads are reversed in any linear system (ie. no magnetic fields) the response will be the same. This means that if the BR displayed rectifying behaviour in the asymmetric arrangement where the current is passed from S to D it would need to display the same behaviour in the symmetric case when the current is passed from U to L. The simple “billiard ball” model suggests that the BRs will break Onsager’s theorem; therefore, a more in-depth model is needed. The Landauer formalism was proposed as a way of computing the current through a nanoscale device in the limit that $\lambda_{MFP}$ is longer than the device dimensions. This formalism has been used previously to describe the behaviour of BRs accurately [24], it will be introduced in this chapter and discussed with regard to each BR in chapter 5.

The original problem considered by Landauer was a 1D channel connecting two metallic reservoirs with an electrochemical potential $\mu_L$ and $\mu_R$. Figure 15 demonstrates the design of such a nanodevice. There are 5 main approximations made in this model. Firstly, the reservoirs connected adiabatically to the nano-junction are semi-infinite so that they can donate as many carriers as is needed without changing their internal state. Secondly, a steady state solution is assumed at long time limits for the Lindblad Equation. Although this does not limit how this model will work in our devices at low frequencies, it may introduce a frequency limit for which the model is valid. In the case we are considering it simply means that neither the chemical potential in the right lead ($\mu_R$) or in the left lead ($\mu_L$) change much in the time for the system to reach equilibrium. Thirdly, the electrons do not interact. This is a strong assumption because it has been proposed that in graphene electron-electron scattering may become the dominant scattering mechanism at certain densities and temperatures [70]. This could be included in the model using non-equilibrium Greens functions but this is beyond the scope of this project. Fourthly, both reservoirs are in equilibrium far from the channel so that we can fill their states using the Fermi-Dirac distribution function. This also gives us our boundary conditions that the voltage applied across the device $V = \frac{\mu_L - \mu_R}{e}$. Finally, any electron scattering event in the junction is elastic.
Figure 15: A diagrammatical representation of the 1D channel considered by Landauer.

The Pauli Exclusion Principle dictates that there can only be one conduction channel per energy state of carrier. Therefore, we must consider the energy levels that the carrier can take in graphene. This can be achieved by including the energy sub-bands of carriers in the dispersion relation for graphene:

\[ E_{i,k_x} = \varepsilon_i(x) + \hbar v_f k_x \]  

(15)

Where \( E_{i,k_x} \) is the total energy, \( \varepsilon_i(x) \) is the energy of the i-th sub-band, \( v_f \) is the Fermi velocity and \( k_x \) is the wavevector in \( x \). Considering the case where the contacts are reflectionless (ie. The transmission probability from L to R is 1) and let the temperature be 0 K; the current passing the positive x direction (\( I_i^+ \)) [71]:

\[ I_i^+ = \frac{q}{L} \sum_{k>0} v_x(k_x) f(E_{i,k_x} - \mu_L) \]  

(16)

where \( v_x \) is the velocity and \( f \) is the Fermi-Dirac distribution. We can then change the sum over \( k \) space into an integral using:

\[ \sum_{k>0} f(k) \rightarrow 2 \times \frac{L^d}{(2\pi)^d} \int f(k) dk \]  

(17)

where \( d \) is the dimensionality and spin has been taken into account, this gives:
\[
I_i^> = \frac{q}{\pi} \int_0^\infty v_x(k_x) f(E_{i,k_x} - \mu_L) dk_x
\]

By substituting the group velocity \( v_x = \frac{dE}{d\epsilon} \), we can express (8) as:

\[
I_i^> = \frac{q}{\pi h} \int_{\epsilon_i}^{\infty} f(E_{i,k_x} - \mu_L) dE
\]  \hspace{1cm} (19)

Equivalently, the expression for the current travelling left \((I_i^<)\) carried by the carriers with \(k_x < 0\):

\[
I_i^< = \frac{q}{\pi h} \int_{\epsilon_i}^{\infty} f(E_{i,k_x} - \mu_R) dE
\]  \hspace{1cm} (20)

We can then define a function \(N(E)\) as:

\[
N(E) = \sum_i u(E - \epsilon_i)
\]  \hspace{1cm} (21)

This equation simply counts the number of sub-bands in integer values and represents the number of conducting channels. Using (11) we can reduce (9) to:

\[
I^> = \sum_i I_i^> = \sum_i \frac{q}{\pi h} \int_{\epsilon_i}^{\infty} f(E_{i,k_x} - \mu_L) dE
\]  \hspace{1cm} (22)

\[
I^> = \frac{q}{\pi h} \int_{-\infty}^{\infty} f(E - \mu_L) N(E) dE
\]  \hspace{1cm} (23)

Finally, the overall current \((I)\):

\[
I = I^> - I^< = \frac{2q}{h} N(\mu_L - \mu_R)
\]  \hspace{1cm} (24)

So that,
\[ I = GV \]  

(25)

Where \( G \) is the conductance:

\[ G = \frac{2q^2}{\hbar}N \]  

(26)

This equation gives us the quantum of conductance \((2q^2/\hbar)\). We can then extend this for the case that the contacts are not perfect and do reflect. The probability \( T(E) \) that a carrier that originates at one contact arrives at the other contact travelling through the channel depends on the geometrical arrangement of the leads and channel. Let \( I_L^> \) be the current influx from the left reservoir, \( I_L^< \) be the current back-scattered and \( I_R^< \) be the flux of electrons that arrive at the right reservoir. In general \( T(E) \) does depend on energy weakly but if we take the assumption that it will be constant \((\tau)\) in the energy range \([\mu_L, \mu_R]\):

\[ I_L^> = \frac{2q}{\hbar}M(\mu_L - \mu_R) \]  

(27)

\[ I_L^< = \frac{2q}{\hbar}M(1 - \tau)(\mu_L - \mu_R) \]  

(28)

\[ I_R^< = \frac{2q}{\hbar}N\tau(\mu_L - \mu_R) \]  

(29)

This gives the total current to be:

\[ I = I_L^> - I_L^< = I_R^< = \frac{2q}{\hbar}N\tau(\mu_L - \mu_R) \]  

(30)

And the conductivity;

45
\[ G = \frac{2q^2}{h}N\tau \]  

This is the Landauer formula. \( N \) refers to the number of conducting channels in a very general way and includes the dispersion relation so that this formula holds when graphene’s dispersion relation is used instead. These channels are restricted by Pauli’s exclusion principle so that there can only be one electron from each energy mode in the channel. The number of modes is then limited by the Fermi energy because only the modes under the Fermi energy will fill. The boundary conditions for the wave function of the electron in the channel dictate that the wave function must be at 0 at the edges. This means that the width of the channel (\( W \)) is also important. According the particle in a box model:

\[ N = \frac{2W}{\lambda_F} \]
3. Introduction to Fabrication Techniques

3.1. Flake Preparation

In 1947 Wallace et al. used the tight binding model to analyse the band structure of graphite [17]. In his paper he discussed the possibility of a single layer of graphite and predicted the linear dispersion relation we now know to be true. However, the term graphene was not coined until later and it was later still that it was observed. In 2004 it was first isolated and tested by Andre Geim and Konstantin Novoselov using the scotch tape exfoliation method [1]. In 2010 they won the 2010 Nobel Prize in Physics for their ground-breaking work on graphene.

The exfoliation method first introduced in 2004 relied on the strong adhesive in sticky tape to mechanically cleave a naturally formed graphite crystal. To begin the process, a graphite crystal would be split and then exfoliated many times to clean off any contamination from one side of the graphite. The shiny side of the graphite crystal was then pressed into the tape firmly and evenly with a thumb. A clean piece of thin plastic was placed over the exposed graphite face to ensure the thumb did not touch the crystal and so that graphite powder was not spread onto areas of the tape that would soon be used. Once the crystal had been exfoliated onto the tape so that a large enough area had been covered a second piece of tape was pressed over the first to encapsulate the graphite. Next a substrate was cleaned for the graphite to be placed. Although 90nm SiO₂ on highly doped Si gave the best optical contrast when searching for flakes [72], 290nm SiO₂ was used for most of this work because the contrast was still good but the thicker dielectric layer allowed for stronger electrostatic gating and less risk of backgate shorts (electrical leaks between the backgate and the contacts). When splitting up the wafer a layer of Poly methyl methacrylate (PMMA) was used to protect the surface. In order to clean this off the substrate was placed in a beaker with acetone for 5 minutes in an ultrasonic bath and then in a fresh acetone for another 5 minutes. After this, the substrate was placed into isopropyl alcohol (IPA) in the ultrasonic bath for five minutes ensuring the surface did not dry while being transferred between beakers. The substrate was then dried with a nitrogen gun and cleaned with low powered oxygen plasma for 5 minutes. The oxygen plasma used during
this work was generated by an Advanced Energy RFX-600 inside a Moorefield MiniLab. It was operated at a pressure of $2.05 \times 10^{-2}$ mbar, a forward power of 10W and with flow rates of 8ccm of oxygen and 16ccm of argon. The purpose of the oxygen plasma was to clean the surface and change the surface profile so that flake adhesion increased. Once the substrate was clean the two pieces of tape were quickly separated and the graphite crystals pressed firmly onto the substrate. The less time spent in contact with air the lower the hydrocarbon contamination and the higher yield of graphene. The tape would be cut around the edge of the substrate to reduce the amount of adhesive that would need to be dissolved in later steps. This was then left for at least an hour to allow the graphene to relax and adhere better to the substrate.

During this resting time, 2 beakers of Methyl isobutyl ketone (MIBK) were heated up and one of IPA on a hot plate at 85 degrees in a fume hood. The sample was then placed into the first MIBK, this dissolved the tape adhesive so that the remaining tape would then role up and come off the substrate. Once the tape had been removed the sample would be placed into the second MIBK for five minutes and then into the final IPA. The sample surface had to remain wet while transferring between beakers. The IPA was then removed from the heat and allowed to cool for five minutes. The substrate was then dried and place on a hotplate for at least ten minutes at 130 degrees. In order to remove the thicker pieces of graphite from the surface and increase the yield of graphene a clean piece of tape was placed over the sample and pressed gently. While pressing it was important not to introduce any sheering motion which would have damaged and graphene on the surface. This tape was then peeled away and the sample was searched with an optical microscope.
Figure 16: An optical image of a number of flakes of different thicknesses on 290nm SiO₂. A is a mono-layer flake, B is bi-layer, C is 3 layers, D is ~10nm thick, E is ~30nm and F is 80nm+. The arrow points to one of many bubbles that get stuck between the graphene and its substrate.

Figure 16 is an optical micrograph of a region of 290nm SiO₂ with exfoliated graphene and graphite adhered to the surface. The various letters show regions of different thicknesses, the contrast was always the same provided the thickness of the SiO₂ was the same. A is a region of mono layer graphene, B is a small region of bi-layer graphene and C is a region of tri-layer graphene. Flakes thicker than tri-layer became more difficult to judge by optical contrast but D is roughly ~10nm, E is roughly 30nm and F is thicker than 80nm. All these flake thicknesses found uses within the lab, for example the thicker graphite like E and F where commonly used as gates and flakes such as D could be used as etch stops. The arrow points towards a bubble that formed between the graphite and the substrate. The bubbles are filled with hydrocarbon contamination and are undesirable for device fabrication.
3.2. Boron Nitride Substrate

Although SiO₂ was a good substrate for locating graphene and determining its thickness it was not a good substrate for achieving the very highest mobilities. The SiO₂ introduced charge puddles due to charge donating impurities and topographic corrugations [49]. Instead hexagonal BN made a better substrate because it had an atomically flat surface that was relatively free of charge impurities. BN had a very similar lattice constant to graphene meaning it would not introduce any lateral strain. It had a large band gap (5.2eV) and a large break down voltage making it an ideal gate dielectric. BN was exfoliated in much the same way as graphite but the crystals were made using a Ni solvent under high pressure by Watanabe and Taniguchi et al. [73]. The resulting man-made crystals are much smaller than the graphite mined from ground. Typically the crystals may have only been 1mm across and an entire crystal was used for one batch of substrates. BN was exfoliated by placing a single crystal in the middle of piece of tape and then using another piece of tape bifurcated ~ 10 times. This would give a 4cm² area of tape with BN crystals spread evenly over its surface. This area was pressed evenly onto a 290nm SiO₂ substrate cleaned in the same way as before. The sample was left for an hour so that the BN would adhere more strongly to the substrate and there would be a higher yield of flakes. Instead of removing the tape using MIBK, the tape was simply peeled off to allow for an atomically clean surface.

Figure 17: a) shows an optical image of a BN flake roughly 30nm thick, the straight lines arise due to the preference of the material to split along its crystal planes. On the right hand side of the image there are a series of thinner flakes that have been broken up. b) Shows a slightly thicker BN flake ~60nm with a large crack running across the flake.

Figure 17 a) and b) show two BN flakes on 290nm SiO₂ with thicknesses of ~30nm and ~60nm respectively. The colour was used to estimate the thickness of the flake. A dark
blue flake would typically be 10nm, a light sky blue (Figure 17 a)) would have been 20-30nm thick, whiter flakes would be 50-70nm (Figure 17 b)), yellow flakes would be 70-90nm and red flakes would have been 90-140nm. Anything thicker than 140nm colours started to repeat the colour spectrum. The thicker flakes would start to get a dark outline or look out of focus. Suitable substrate BN flakes were flat without terraces, had large areas without cracks and where typically 20-60nm thick. It was also important that there were no bubbles underneath the BN. All two dimensional crystals made by the exfoliation method could get contamination trapped between the crystal and its substrate. Investigations into these contaminations show that they are made up of hydro-carbons present in the atmosphere or highly compressed air [74, 75]. One feature evident in both Figure 17 a) and b) is that BN splits preferentially down its crystal plane, the long straight lines and 30° angles indicate this.

3.3. Wet Transfer

Once a suitable substrate BN flake was found, the graphene needed to be mechanically transferred on top. When fabricated on SiO$_2$, graphene could be lifted from the surface using the SiO$_2$ as a sacrificial layer and using a PMMA film for mechanical support. Since the process of dissolving the SiO$_2$ required the used of weak KOH, it became known as wet transfer.
Figure 18: Shows the steps necessary to transfer graphene by wet transfer. Initially, the graphene was made on SiO$_2$, PMMA was spun on top, a tape window was placed around the graphene, a scratch was made around the outside of the window and then the SiO$_2$ is dissolved away in a KOH solution.

Figure 18 demonstrates the steps that were necessary to perform a wet transfer. Firstly, 3% PMMA with a molecular mass of 950k was spun on top of the sample at 5krpm with a ramp speed of 5krpm$^2$ and then baked for 3 minutes at 130°C. A square of tape was cut 4mm by 4mm and then a hole 2mm diameter was punched in the middle of it. This tape window was placed around the flake on top of the PMMA film. The film was then scratched using a pair of sharp tweezers around the outside of the tape so that the window could be freed from the rest of the film. In order to dissolve the SiO$_2$ a 3% weight by volume solution of KOH was made up and the sample was placed inside the solution until the tape window floated off the surface. This could take between 3 hours and 12 hours. The window was then picked out of the KOH solution and re-floated in deionised (DI) water.
Once the membrane had been left for a 10 minutes it could be picked out of the water and dried carefully with a paper towel, ensuring that the PMMA did not get damaged. This could then be mounted onto a mechanical transfer machine.

![Transfer machine](image)

Figure 19: Is a picture of the transfer machine used in this work. The membrane supported by tape or washer would be stuck to the end of the transfer arm. The target flake on its substrate would be placed on the heated vacuum stage. The microscope would be used to align the flake on the membrane with the flake on the substrate below and then lowered into position.

The transfer machine shown in Figure 19 consisted of an arm fixed by a vacuum to a micro-manipulator with x, y and z control. It had a NIKON microscope with 5x, 10x, 20x and 50x magnification to allow for precise alignment between the flakes. The target Sample with the BN was placed on the vacuum stage. The stage had both x and y control so that the flake could be found. The stage was heated to allow for better adhesion of the membrane and less contamination between the flakes. Firstly, the tape window was stuck onto the arm using double sided sticky tape. Secondly, the arm with the tape window was lowered to within 1mm of the surface of the sample ensuring they did not touch yet. By moving the focal point between the flake on the surface and the flake on the membrane they could be lined up in both x and y. Then the membrane was lowered slowly as the alignment was checked more and more until the PMMA came into contact with the surface. Sometimes the membrane would not be flat enough for it to come into contact with the surface fully or at all. If this happened, a tweezer was used to press it down or stretch the membrane such that it would be in contact. Finally, a sharp tweezer was used to cut the membrane around the inside of the tape such that the tape could be removed leaving
the PMMA on the surface. Baking the sample for 10 minutes at 130°C reduced the risk of the flakes falling off the surface as the PMMA was removed. Once the sample was baked, it was allowed to cool and placed in acetone for five minutes. It was then placed into another 2 acetones for 5 minutes each and then into IPA for another 5 minutes. It was then dried with a nitrogen gun and the sample was ready for further processing.

3.4. Dry Transfer

The wet transfer technique was the first transfer technique introduced. It represented a step forward in graphene device fabrication techniques. It was still used after more advanced techniques where developed when very large flakes were required to be transferred onto BN or any other target substrate. This is because other exfoliation techniques did not result in graphene flakes larger than 100µm. However, when the quality of the flake was paramount wet transfer had some failings; during the wet transfer process the graphene came into contact with KOH and water which contaminated the surface. This limited mobility of wet transferred flakes to $\sim 30,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This was far from the theoretically predicted mobility of graphene ($\sim 1,000,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [7]. Wet transfer was also fraught with bubbles; often there would not be a larger area than 1µm$^2$ that did not have a bubble. A transfer technique was needed where the graphene did not come into contact with any liquid before it came into contact with the substrate. This would ensure that there was nearly no contamination between the graphene and the substrate. This transfer technique came to be known as dry transfer because the graphene surface would remain dry.
Figure 20: shows the process of dry transfer. First, a bi-layer resist of PMGI and PMMA was spun onto a silicon substrate, graphite was exfoliated onto the PMMA surface, graphene was identified using its optical contrast, a scratch was made around the graphene and MF319 was pipetted into the scratch. This MF319 then dissolved the PMGI leaving the PMMA film floating on the puddle of MF319, the substrate was lowered into DI water which pulled the PMMA layer onto the DI water by surface tension. The PMMA and graphene was pulled out of the water on a 2mm washer coated in dry PMMA and was ready for transfer.

Figure 20 demonstrates the steps necessary for the dry transfer technique. The first step was to prepare the membrane for the graphene to be exfoliated onto. A standard size piece of plain silicon was cleaned for 5 minutes in acetone and then 5 minutes in IPA. It was dried with a nitrogen gun and baked for 2 minutes at 130°C. Polymethylglutarimide SF6 (PMGI) from MicroChem was spun at 3000rpm with ramp 3000rpm$^2$ and then baked at 130°C for 3 minutes. This was allowed to cool and placed back on the spinner so that an 8% PMMA in anisole with molecular weight 950k could be spun on at the same speed and ramp. This was then baked at 130°C for a further 5 minutes. In the meantime graphite was exfoliated using the same method as before, leaving the thin pieces of graphite encapsulated in tape until the sample was ready to be removed from the hot plate. Once off the hot plate the two pieces of tape were separated and stuck onto the substrate while still warm. This was then allowed to rest for 10 minutes to allow the graphene to adhere better to the PMMA and then the tape was removed slowly and at a low angle.
The challenge during dry transfer was observing and finding the graphene flakes on the PMMA substrate because the contrast of the flakes changed with the thickness of the membrane[72]. The membrane changed thickness from sample to sample due to fluctuations in environmental humidity. The thickness would even vary across the same sample due to surface tension. However, the absorption was also wavelength dependent so a range of different filters could be used to view the graphene.

Figure 21: shows a series of images of the same graphene flake with a PMMA substrate under different wavelengths of light. a) was taken without a filter in white light. b), c), d), e), f) and g) where taken with 700, 640, 580, 530, 480, 440 nm filters respectively. h) is an image of the NIKON microscope used to “hunt” for flakes, on the table is the rack of filters used to make changing colours quick and easy.

Figure 21 demonstrates the importance of using filters while looking for flakes on the surface of PMMA. Although it was possible to see the graphene under white light as in Figure 21 a), it was very difficult and even more difficult at lower magnifications. Figure 21 a) to g) show the same image with a range of filters, some enhance the contracts of the
graphene and some make its nearly invisible. Figure 21 e) or f) would have been the filters of choice in this case since the graphene is easily visible. However, the correct filter would change from sample to sample and the only way to discover which filter to use was to compare the various filters on a graphene flake. This meant searching at high magnification using multiple filters to find a small flake to use a reference so that larger flake could be found. To speed up the process a rack of filters was made so that the user could slide between the different colours (as in Figure 21 h)).

Once a graphene flake had been identified a 3mm circle was scratched around the flake in the PMMA. MF319 was then put into this trench, this could be achieved using a closed tweezer to pick up a drop of the solution and then drop it out slowly into the gap. The aim was to keep the surface of the 2mm circle of PMMA dry and dissolve the PMGI underneath. Once the PMMA was free from the surface the substrate would be lowered into DI water such that the droplet of MF319 just touched the surface of the water. The droplet would be pulled into the water bringing the membrane with it. Next, a washer was prepared to fish the membrane out of the water. Firstly, the washer was dipped into 8% PMMA and then placed on a paper towel on a hotplate at 130°C for 5 minutes. This layer of PMMA allowed from better adhesion between the washer and the membrane. The washer was then allowed to cool and then used to fish the membrane out of the water. The aim was to pull the PMMA tightly across the hole in the washer and then dry it out with a paper towel. The washer was attached to the transfer machine arm using double sided sticky tape. Next, the flake was lowered over the substrate and aligned as described for wet transfer. The PMMA was then separated from the washer by scratching the membrane with a sharp tweezer. After, it was baked for 10 minutes at 130°C and the PMMA was washed off in 3 different acetones for 5 minutes each. Finally, the sample was put into IPA for 5 minutes before being dried with a nitrogen gun.

Dry transfer allows for a very clean interface between the BN and the graphene and this gave a much lower concentration of bubbles in samples. However, AFMs reveal a ~4nm layer of PMMA residue after it was washed off. Most samples are limited to ~60,000cm²V⁻¹s⁻¹ mobility for this reason. Further electrical testes showed that these samples are very sensitive to atmospheric effects. When transfer measurements were made on dry transferred samples open to air they showed considerable hysteresis, a result of contaminants and water being pulled onto the surface by the electric field. This layer of hydrocarbons and water acted to counteract the electric field creating the hysteresis. For any commercial application these devices would need to be used in atmospheric
conditions, so a solution had to be found. Other 2DEGs, such as InGaAs/GaAs heterostructures, do not suffer from strong hysteretic problems because they are buried up to 50nm below the surface limiting the effect of contaminants on the medium. This led to attempts to encapsulate graphene in BN to reduce air sensitivity. The first attempts where done with wet and dry transfer and there was a marked reduction in air sensitivity. However, the second interface between the graphene and the top layer of BN was already contaminated with PMMA residue; for this reason mobility did not improve when compared to encapsulated devices and bubbles became even more of a problem. It was necessary to fabricate contacts and etch the device geometry before encapsulation. Often bubbles would form on top of hall bars making them unavoidable. It became necessary to devise a new transfer method that would mean that the graphene flake itself would not touch any polymers. This new method was called stamp transfer and will be discussed in detail in section 4.1.

3.5. Microfabrication

Once a suitable stack of flakes had been made it was necessary to make electrical contacts to these flakes. Initial tests using photolithography showed that graphene was very susceptible to contamination from photo-resists. Often they would reduce mobility by up to an order of magnitude and dope by nearly $10^{13}$ cm$^{-2}$. The graphene used for this work needed to be high mobility so electron beam lithography (EBL) needed to be used instead. PMMA was used throughout this work because it did not dope the graphene and only left very small amounts of contamination when removed in acetone. The resist stack used whenever metallisation and lift-off were performed (even for the 1D contacts discussed in chapter 4) consisted of two layers. Initially, a layer of PMMA molecular weight 495k 3% (by weight) in anisole was spun onto the substrate at 5000rpm with a ramp of 5000rpm$^2$. This was baked at 150°C on a hot plate for 5 minutes before a second layer of PMMA molecular weight 950k 3% (by weight) in anisole is spun on top of the previous layer. This was placed back on the hot plate at 150°C for another 5 minutes. A scratch was made on the surface from 1mm bellow the target exposure region of the substrate to the bottom. This made it easy to locate both the bottom of the substrate and the flake or device. The scratch also made it easy to focus with the SEM near to the device without the need to rely on a carbon contamination to build a spot to focus on.
In the case that there was already a flake on the surface at an unknown coordinate the substrate would need to be placed on a microscope with flake tracking. The flake tracking system relied on a simple static webcam fixed to the back of a Nikon microscope looking up at a printed dot pattern attached to the back of the stage. The image from the webcam was fed into an image analysis program that gave a global coordinate system for the stage. The program then allowed the user to assign the coordinates of the bottom left and right of the substrate. This set up a local coordinate system for the sample that could be used to find the coordinate for the target flake. With this coordinate the sample could be placed in the SEM.

A Zeiss EVO and LEO were used during this work. Both SEMs had Gemini columns. The EVO had a Raith ELPHY Quantum lithography add-on and the LEO had a Raith ELPHY+ add-on. The LEO had a laser interferometer stage and a thermal emission tip. The EVO had a stepper motor stage with a LaB₆ tip. Before starting any exposure an acceleration voltage of 10kV would be set and the beam current would need to be measured using a Faraday cup. The write field (WF) could then be calibrated using a series of marks a known distance apart (known as the chessy). Then the coordinates of the bottom left and right corners of the substrate would be taken in the global stage coordinate system. The top of the scratch would then be found and the beam would be focussed. At this point the beam current would be re-measured, if it had changed a significant amount (>2%) time would be allowed for it to stabilise. Once the beam was stable, the coordinate from the stage tracking system would be used to move to the location of the flake. Typically, the first exposure would be a matrix of numbered crosses. These crosses would allow a second exposure to be more accurately aligned using manual marks. Often these crosses would only be exposed in the resist, developed and then used as alignment marks for contacts made in the same resist. Stamp transferred devices made use of pre-prepared substrates with metallised crosses on the surface at a known location. This reduced the risk that crosses would be exposed on top of an area of the flake that was intended to be used in a device.

During most exposures a nominal dose of 120µCm⁻² was used. Typically 2 different WFs would be used during one exposure, one small and one large. The small one (normally 200µm) allowed small features to be made where space was at a premium close to the flake. A small beam current (15pA) could be used while writing such small areas. The larger write field (normally 1500µm) allowed the contacts to be extended far enough from the device and far enough from each other that mechanical bonding could be used to
attach them to a chip carrier. A large beam current (600pA) would be needed to speed up the write speed when writing a large area. The step sizes used for the 200μm and 1500μm WFs were 8nm and 48nm, respectively.

A normal device design would have the area of the contacts within the small WF split from the rest of the contact and placed in another layer. The remaining large contacts would be manipulated to allow a 5μm overlap between the layers in case of misalignment between the WFs. In order to design a device, a series of pictures would be taken on the optical microscope once the flake and cross matrix were in place. Each picture had to have at least 2 crosses. A Matlab script was used that took the coordinate of each cross and used an affine transform to create a matrix that mapped the crosses onto their coordinate in the cross design. This matrix was then used to link the image into an SVG file so that it would appear when designing the contacts in Inkscape. This could be done for a range of different magnification images and a clear image of the flakes for the device could be built up. Importantly, other large flakes or contaminations around the useful flakes could be avoided. Often, pads would be included in the design where, after development, a diamond scribe could be used to intentionally create a short to the backgate to the pad. These contacts could then be mechanically bonded to the chip carrier as oppose to using silver paint to bond to the side of the chip.

During exposure there were certain exceptions to the nominal dose. If the exposure was on top of BN the nominal dose would be increased by 20%. If the lateral dimension of the contact fell below 500nm the dose would be increased by another 20%. If the same dimension decreased below 300nm the dose would be increased by 50% instead. If the exposed area was intended to make a Basel plane contact to graphene the dose would be increased by 20%, this ensured that a good contact was made to the graphene with no residual PMMA left after development. Development was performed in 1:3 MIBK:IPA for 30s followed by 40s in IPA. If two dimensional contacts were used it was important to develop with the beakers in the sonicating bath at very low power. The sonication ensured any residue left after development was minimised. Sonication was not necessary for devices that would use 1D contacts since the plasma etching would remove any residue and leave a clean dry line of graphene to contact. If 1D contacts were being used the sample would be etched, in CHF₃ and Ar in an Oxford RIE for 40s (further details about the etch can be found in section 4.2.).

For 2D contacts it was important to place the sample in a vacuum after development and evaporate the Cr/Au contacts as quickly as possible to reduce hydrocarbon
contamination. Similarly, when 1D contacts were being used it was important that the samples were moved quickly from the RIE to the electron beam evaporator. The evaporator used for metallisation consisted of a Moorefield minilab vacuum chamber with an electron gun. Throughout this work Cr was used as an initial contact layer with the graphene because Cr was a good adhesive layer with a similar work function to graphene. Matching the work functions was important because when a metal is in contact with a semiconductor with a different work function a Schottky diode forms. Contacts needed to be ohmic so that any non-linearity or rectification effect from the device could be detected without being drowned out by any non-linear effects from the contacts. 3nm of Cr was found to give the best contact resistances. Au was used for the remaining contact because it was an excellent conductor and it was inert whereas Cr oxidises. The thickness of Au evaporated changed from device to device. For devices with no BN substrate 30nm of Au was used. Devices with a BN substrate or a similar vertical step needed to have an Au layer 30 nm higher than the step height. This was found to be thin enough that lift-off worked properly. Also, this was thick enough that contacts were stable both mechanically and electrically.

Lift-off was performed by initially placing a beaker of acetone in a sonicating bath at very low power. The sample would be held in a pair of tweezers and dipped into the acetone for ten seconds. The acetone would be removed from the bath as the sample was dropped into the acetone. The water droplets on the bottom of the beaker would be dried on a paper towel and the beaker would be placed on a hotplate at 85°C in a fume hood. After 5 minutes the beaker would be removed and allowed to cool for another 2 minutes. A pipet would then be used to blow away the remaining Au film. The sample would be placed in another clean acetone for 5 minutes and then placed in a Petri-dish containing acetone. Using an optical microscope the sample could be viewed while still in the Petri-dish to check if all the unwanted Au had been removed. If lift-off had not been successful the process would be repeated.
Figure 22: Shows the etchmask of a device after development. This device has two BR on it: a TBR and a DBR. The arrows point to the three contacts that were not working due to misalignment, note that they have not been included at contacts to the Hall bar.

Once the contacts were finished they would be tested on a probe station. A SUSS Microtech PM5 probe station was used in conjunction with a Kiethley 2410 source meter to check the contact resistances and whether there were any shorts through to the back gate. With full knowledge of which contacts should and should not be used, an etchmask could be designed. Typically, a device would consist of a normal Hall bar region for transport measurements and a geometric device with sufficient contacts so that 4-point measurements could be made in all directions. Figure 22 shows a Hall bar device with a TBR and a DBR etched into the heterostructure. 3 of the contacts were found not to be working due to misalignment and were not used as contacts to the Hall bar. Often the feature sizes for the BR would approach ~100nm and the rules of thumb for dose correction did not help at this resolution. To combat this NanoPECS dose correction was used so that smaller elements would receive more current. The parameters selected for the dose correction were accuracy 3 with a PMMA thickness of 100nm on Si. Using these parameters on the nominal dose (without any corrections) with a typical heterostructure 100nm high would give good results. A resolution of ~100nm could be achieved on a stack 100nm high. The resist used for the etch mask was 3% 495k molecular weight PMMA.
spun on at 5000rpm with a ramp rate of 5000rpm\(^2\). The sample was placed in the EVO and the same procedure was performed to locate the device and create the local coordinate system as was performed when exposing the contacts. However, more care was taken when focusing the beam before exposing the resist. The samples were developed in the same way as before; they are waved gently in 1:3 MIBK:IPA for 30s and then in IPA for a further 40s. Figure 22 shows the result of such an exposure and development, the green coloured regions are where there was still PMMA and rest was exposed to the etch. The same etch procedure was used as before was used as before.

![Image](image_url)

**Figure 22**: The result of such an exposure and development, the green coloured regions are where there was still PMMA and rest was exposed to the etch.

![Image](image_url)

**Figure 23**: a) and b) show a typical device at 100x and 5x magnification, respectively, after the etch mask has been removed. The light blue contamination in b) near contact A and B is cross-linked PMMA that could not be removed with acetone.

**Figure 23** a) shows the same device at 100x magnification after it had been etched and the mask removed. The etch mask was removed by placing the sample in three different acetones for 5 minutes each. The arrow in the figure points to the remains of a bubble that formed between the graphene and one of the BN layers. The contents of these bubbles did not etch very quickly and would leave remains. Although it was very rare that these
remains would conduct, it was always worth avoiding them when designing the contacts. Figure 23 b) shows the whole device at 5x magnification. There are regions on the surface of the devices that have a blue hue, this was where the PMMA had cross-linked and left residue on the surface. The contamination could be avoided if the etch was done for 30s instead of 40s. However, the BN-graphene-BN stack in this case was 100nm thick and had to be etched for 40s to ensure all the possible conductive shorts were cut. In order to measure these Hall bar devices at low frequency they would need to be bonded onto a chip carrier. This bonding would be done using an Inseto mechanical wire bonder.
4. Modified Stamp Transfer and Device Design

4.1. Stamp Transfer

While preforming a dry transfer it was possible to put the graphene flake onto the BN and remove the membrane leaving the graphene on the surface. The Van Der Waal’s force between the BN and the graphene was stronger than the force between the graphene and the PMMA. In this case the force between the SiO$_2$ substrate and the BN was also stronger than the force between the graphene and the PMMA. This BN-SiO$_2$ force was increased by oxygen plasma in order to increase the yield of large flakes. Later, it was found that without this oxygen plasma clean a PMMA membrane could be used to pick up a BN flake. If the adhesion between a graphene and the substrate was low enough it could also be picked up. This process could be extrapolated to stack a series of flakes of arbitrary size and thickness. This became known as stamp transfer.

![Diagram of stamp transfer process](image)

Figure 24: demonstrates the steps taken to make a clean PMMA membrane used for stamp transfer. Initially, a bi layer resist of PMGI and PMMA was spun onto a silicon substrate a scratch was made with
3mm diameter and MF319 was pipetted into the scratch. This MF319 then dissolved the PMGI leaving the PMMA film floating on the puddle of MF319, the substrate was lowered into DI water which pulled the PMMA layer onto the DI water by surface tension. The PMMA and graphene was pulled out of the water on a 2mm washer coated in dry PMMA.

Figure 24 shows how a clean dry PMMA membrane is made for stamp transfer. Firstly, a clean flat area of the membrane would be chosen and a 3mm radius circle scratched into it. This would be lifted from the surface using MF319, put into water and fished onto a washer covered in dry PMMA. This membrane was baked on a hot plate at 130°C in a Petri dish while the flakes were prepared.

It was necessary not to oxygen plasma the surface of the SiO$_2$ since it increased the adhesion of the flakes past the point that the PMMA could pick them up. To ensure that the substrate was clean despite not using plasma cleaning a more rigorous wet cleaning procedure was used. 290nm SiO$_2$ substrates were first sonicated in 5 different acetones for 5 minutes each, jet cleaning with acetone between each beaker. They were placed in IPA for a final 5 minutes before being dried with a nitrogen gun and placed on a hotplate for at least 15 minutes at 130°C. During this time, BN and graphite was exfoliated onto separate pieces of tape. As the substrates were removed from the hot plate, the crystals were exfoliated one last time before they were pressed evenly onto the surface. The substrates were left for up to an hour to increase the yield of graphene. If they were left for more than an hour there would sometimes be large regions of the substrate contaminated with tape adhesive. This was likely to be due to its degradation in air. The tape was then removed from the surface slowly at a low angle. The graphene was found by optical contrast and both the substrate and top layers of BN were found as described 3.2. Typically, both the substrate and top layer of BN would be ~30nm thick. It normally increased transfer success if the top layer was laterally larger than the bottom layer, a flake 100µm in its longest dimension would make a good top layer.
Figure 25: Shows a typical process for stamp transfer, in this case a graphene flake was laminated between 2 BN flakes. The membrane was initially loaded onto the transfer arm and lowered onto the top layer of BN. This was slowly retracted until the flake is peeled from the SiO₂. The SiO₂ with the graphene was then placed on the transfer stage and the BN flake was lowered onto the graphene. These flakes were then peeled away from the surface as before and the substrate BN flake was placed on the transfer stage. Again the membrane was lowered so that the graphene was encapsulated between the BN flakes. The whole stack was then lifted up and placed onto a final SiO₂ substrate with Au alignment marks on the surface.

After finding the flakes, the membrane would be loaded onto the transfer arm as before. Figure 25 shows how the clean membrane was used to stack the flakes. The membrane was lowered onto the top layer of BN. Once in contact with the flake it would be removed slowly ensuring there was as little strain in the membrane as possible to reduce plastic deformation, hence, reducing the risk that the PMMA would eventually split. This did not always work first time, it was sometimes necessary to peel the membrane from different directions across the flake in order to lift it from the substrate. This top BN was then used as a stamp to pick up the graphene and the final substrate BN. The final step was
to place the stack of flakes onto a pre-prepared substrate with gold crosses so that contacts can be designed and aligned easily.

4.2. Exposing the Edge

Stamp transfer had a wide range of advantages over dry transfer such as higher mobility graphene flakes, lower device production time and there was a lower density of bubbles. However, it required a new approach to make electrical contacts to the flake. In the wet and dry transfer methods, contact could be made to the basal plane of the flake but in stamp transfer both basal planes are covered with BN. Instead, the side of the stack would need to be contacted after etching all the way through the 2D crystals.

Figure 26: a) and b) are diagrams of the cross-section through at traditional 2D contact and a quasi-1D contact respectively.

Figure 26 demonstrates the how the two contact types differed. Figure 26 a) shows a traditional 2D contact where current would pass through the basal plane of the graphene. Figure 26 b) shows the quasi-1D contact where most of the current would enter the graphene through the edge. The 2D contact had an edge as long laterally as in the 1D case. However, the metal atoms in contact with the graphene between its edges and where the contact ended acted as scattering centres. These scattering centres lowered the mobility and increased the resistance of the graphene underneath the contact. Carriers that had entered the graphene at the edge also had the opportunity to scatter back into the metal. Whereas, 1D contacts had no metal in contact with the graphene after the edge allowing for more efficient movement of carriers from the metal into the conducting channel. Nagashio et al. showed that it was the width of the contact that was important for contact resistance not the area of the contact[76]. This emphasises that carriers injected into the graphene far from the end of the metal contact do not make it into the conducting channel. The importance of
the edge for conduction was highlighted by Smith et al. [77]. By varying the number of etched cuts in the graphene before adding contacts they changed the length of the 1D contact and the area of the 2D contact. They found that the resistance of the contact reduced initially as the length of the 1D contact increased. Then the area through which the carriers could be transported decreased to the point that it became the dominant contribution to the contact resistance and the contact resistance increased. This culminated in the development of 1D contacts in 2013 by Wang et al. [38]. These contacts have been demonstrated to be consistently low resistance and have linear I-V characteristics.

The etch procedure used to expose the graphene edges and remove unmasked graphene was a CHF₃ Reactive ion Etch (RIE). To perform this procedure an Oxford Instruments Plasma Lab 100 was first put through a “2 step clean”. The first step used flow rates of 30 ccm SF₆ and 40 ccm O₂ with an RF power of 100 W and an ICP power input of 300 W at a pressure of 50 mTorr for 10 minutes. The second step used a flow rate of 45 ccm of O₂ with an RF power of 100W and an ICP power of 300W for 15 minutes. The sample was then loaded into the main chamber and the main etch procedure was started. Flowrates of 17.5 ccm of CHF₃ and 8 ccm of O₂ were used with RF power 5W and ICP 50W at a pressure of 10 mTorr. The time used for the main etch would vary depending on the thickness of the BN-graphene-BN stack, the etch rate for BN was 4nm/s but bubbles and graphene took longer to etch. Typically a 40s etch would be used for both contacts and etchmask on a stack 80nm high to ensure any shorts would be destroyed. If the etch was any longer than 1 minute there was a risk that the PMMA used as the etch mask would cross-link. Cross-linked PMMA could not be removed easily. If cross-linked PMMA was used for lift-off it would invariably fail. Once the etch was finished the system would be cleaned again using the same “2 step clean”.

Figure 26 b) shows that the edge of the stack had an angular profile. This was because the etch procedure used was isotropic. The angle was measured with an AFM to be 45°; this was be limited by the slope of the side of the AFM tip. TEM images suggest that the angle of the slope is close to 60°.
Figure 27: a) is an SEM micrograph of a device with two Hall bars from the top down. b) Shows a close up tilted image of a single contact from the same device with finger like extensions to increase the length of the contact. c) Shows an image of the same contact after a FIB has made an incision in the contact to show the cross section. d) Is an EELS TEM image of the edge of one these contacts (shown by the red box in c). The map shows boron in red, carbon in green and Chromium in blue. (SEM and TEM images courtesy of AP Rooney and SJ Haigh)

Figure 27 a) shows a scanning electron microscope (SEM) image of a typical device (in this case a pair of ballistic rectifiers). Both the contacts and the BN graphene BN stack have been labelled for clarity. The length of the linear contact between the graphene and the metal was increased by etching the graphene stack into finger like structures. Figure 27 b) is a tilted SEM picture of a single contact. Figure 27 c) shows the same contact after an FEI Nova 600i focused ion beam (FIB) had been used to make a cut perpendicularly to show a cross-section through the device. Figure 27 d) shows a transmission electron microscope image of a section through a contact made using the FIB. To achieve this thin cross-section of contact[78], a 50nm layer of Au-Pd was sputtered on top of the whole
device and then a 1µm Pt strap was deposited *in situ* using a gas injection system to protect the region of interest from damage by the FIB. Two wedges were cut out of the device so that a thin section through the device remained. The lamella was soldered to a micromanipulator using the same Al deposition technique and the remaining sides connecting the thin slice of contact to the substrate were cut so that the sample could be removed. This was then placed on an Omniprobe copper half grid and put into an FEI Titan G2.80-200 equipped with an electron energy loss spectrometer (EELS).

Figure 27 d) Is an EELS TEM image of the edge of one these contacts. The map shows boron in red, carbon in green and Chromium in blue. It was evident that the graphene resisted the etch more than the BN because it created a 2nm step where the graphene masked the lower BN flake. This step allowed contact to be made to the graphene. There was also a carbon lip sticking up from the step, this was amorphous and was directly touching both the chromium and the graphene. It was possible that this amorphous carbon aided with good contact because it was likely to have a large density of states (DOS) so charge could be passed easily into the carbon.

Figure 28: a) is an AFM of a DBR. b) Is a phase image from the same DBR, the step can be seen clearly in the phase image due to the high contrast in adhesion between the BN and the graphene.

Figure 28 a) shows an AFM height map for a BR. In this figure it is difficult to see the step seen in Figure 27 d), unfortunately the AFM tip was not sharp enough to resolve the step clearly. Figure 28 b) shows a phase image of the same area shown in Figure 28 a). The edge of the graphene is easy to see in this image. At the point where the graphene ends there is clearly a spike in the phase map. The graphene edge must have been more adhesive.
with the AFM than the clean slopes of the BN or the step itself was damping the tips movement. This maybe a result of the amorphous carbon lip seen in Figure 27 d), if this stuck up from the edge of the BN it could have interacted with the tip.

4.3. 1D Contacts

Now that edges of the graphene had been exposed metal contacts could be evaporated so that electrical measurements could be made. In the original work on 1D contacts by Wang et al. the etch mask was PMMA and hydrogen-silsesquioxane (HSQ), a similar resist stack to the one used in this work. However, the etch used in the previous work only etched BN at 0.5 nm/s meaning that the stack of flakes had to be thin and the exposure to the plasma had to be longer. The etch developed for this work worked 8 times faster at a much lower pressure and input power. It is likely that the work done previously could not use their etchmask to preform lift-off after it had been used as a mask. This would have meant that they had to apply a fresh layer of PMMA, expose and develop to define contacts. The interface between the graphene and the evaporated contacts would be contaminated with hydrocarbons and solvent left over after the development. In the work presented here the etch mask did not need to be exposed to the plasma for as long because the reactive ion etch was nearly an order of magnitude faster. Therefore, the etch mask remained undamaged and could be used for lift-off. Therefore, the contacts could be to be applied to the flake before the etchmask.
Figure 29: a) and b) are AFMs of HB devices with 1D contacts. a) example of a device with undesirable bunny ears. b) example device without bunny ears.

Figure 29 a) shows an example device where the contacts have been placed before the etchmask, unlike the device that featured in Figure 27 where the etchmask was done first. Figure 29 is a bad example of these contacts because you can clearly see there is a problem with ~30nm “bunny ears”. These are sharp pieces of Au at the edge of the designed pattern that rise higher than the majority of the Au. They are normally a result of using a single layer of resist when preforming lift-off since the Au builds up against the sides of the resist. “Bunny ears” are undesirable because they can create static discharges and make the device more susceptible to electrostatic damage. If two layers of resist are used, where the bottom layer dissolves quicker in the developing solvent, an undercut is formed so that there is no resist for the metal to stick too. However, while making these 1D contacts a bi-layer resist set-up was used as described in 3.5. Instead it was likely that the “bunny ears” were forming due to the slope of the stack elevating the edges. Figure 29 is an example device where there are no “bunny ears”. After a series of trails it was found that the “bunny ears” would be smaller when the thickness of the metal contact matched the thickness of the flake stack. The thickness of the flake stake also played a role in the size of the “bunny ears”, a thinner stack would always make them smaller. However, if the thickness of the BN was less than ~20nm there would be hysteresis in the transport properties when $V_G$ was changed. It is likely that the hysteresis came from ion transport in the SiO$_2$, a thicker substrate BN crystal shielded the graphene from this effect (this is why 30nm substrate BN flakes were chosen).
Figure 30 is a box chart detailing the 2-probe measurements for twelve different devices. The first four devices shown used 2D contacts to the Basel plane of the graphene. The next four used stamp transfer but followed the fabrication method described in [38]. The final four devices were made using stamp transfer and then the contacts were made as described here.

2-probe measurements are not a true measure of contact resistance since they will contain the resistance of the graphene between the two contacts. Naturally, 2-probe measurements will vary dramatically with backgate voltage due to the changing carrier concentration in the graphene. All the measurements shown were performed while no gate voltage was applied. One would assume the devices with high intrinsic doping will appear lower resistance since they would have a lower contribution to the resistance from the graphene. However, quite the opposite is observed; the stamp transferred devices show much lower resistances and these devices were measured very near to their DP.
Figure 30 is very clearly and demonstrates how well these new contacts work. Not only do they have considerably lower resistances, they also have far better consistency than any previous generation of contact. The failure-rate for contacts while being fabricated, during annealing and during thermo-cycling also fell considerably. All the measurements shown are from regions of devices without BRs since the high resistances of travelling through the BRs would skew the data.

4.4. Device Geometry

Each of the planar devices investigated fundamentally relied on their geometry to give them their novel electrical properties. Likewise, the electrical properties of each device could be tuned by altering the geometry. This section will discuss the geometry of each device in turn.

4.5. Triangular Ballistic Rectifier

The TBR is a four terminal cross junction with an asymmetric triangular anti-dot that preferentially scatters carriers from either of the two input terminals to only one of the two output channels. When an AC electric current is applied to the two input carriers there is then a build-up of carriers at L when compared to U. A DC current will then pass from one output lead to the other through an external circuit.
Figure 31: A diagram showing the important geometrical features of the TBR, the black regions represent where the graphene was removed so that only the white regions are where graphene remains.

Figure 31 is a diagram of a TBR with the important geometrical features labelled. The angle of the side for the triangle is chosen to be 45° to the normal of S and D leads. This angle ensures that carriers that specularly scatter from the edge of the graphene gain the most momentum towards L. The width of both the S and D channels is designed to be the same ($W_{SD}$). However, due to inaccuracies in the fabrication procedure the width of the S channel ($W_S$) would always be different to the width of D ($W_D$) and to the width they were designed to be. In all the TBRs shown in this work $W_T = \frac{2}{3} W_{LU}$ or at least this is how they were designed to be.

4.5.1. Ballistic Rectifier

The BR is an asymmetric cross junction that uses the high field density of two narrow input leads to redirect carriers to one of the two output leads. This meant that when an AC field is applied to the input leads a DC output would be generated. The electric field falls linearly across the narrow channel; the electric field density then falls rapidly as the edges of the channel recede. Therefore, the carriers are accelerated in the narrowest parts of each
channel in the direction of the normal to the channel. The side of the L channel are then used to reflect the carriers towards L.

Figure 32: demonstrates how carriers that arrive at D are redirected to L. The black regions represent were the graphene was removed so that only the white regions are where graphene remains. The dependence of the angles $\phi$ and $\theta$ are shown so that the carriers receive the largest component of momentum towards L.

Figure 32 is a diagram of the active region of a BR showing how carriers that arrive at D (symmetrically S) are directed to L and not U. One important geometrical factor that ensured the carriers received the most momentum towards L is the angle between the line from S to D and the normal of the narrow channels ($\theta$). It is important that the sides of L are at an angle $\phi = 90 - \theta$ so that the final trajectories of the carriers are in the negative y-axis direction.

4.5.2. Side Gated Transistor

The side gated transistor uses capacitive coupling from a pair of side gates to change the number of carriers in a narrow conductive channel. This enables the device to change from a high resistance off state to a low resistance on state.
4.5.3. Self-Switching Diode

The design of the SSD is similar to the side gated transistor except that the source electrode is shorted to the gates. When a voltage is applied between the source and the...
drain, the gate would be at the same potential as the source and a different potential to the channel. The gates then capacitively couple to the channel and effectively self-gate the channel. Depending on the Fermi level of the graphene in the channel it could either increase conductivity or decrease conductivity. To optimise the operation of the SSD the Fermi level of the channel could be tuned such that the channel is in its off state when the current passed in one direction and then in its on state when the current was passed in the other direction.

Figure 34: a diagram of an SSD with channel length $L_{Ch}$, channel width $W_{Ch}$ and trench width $W_{Tr}$. The dark regions are where the graphene is removed so that the white region is where the graphene remains.

Figure 34 is a diagram showing an SSD with channel length $L_{Ch}$, channel width $W_{Ch}$ and trench width $W_{Tr}$. The geometrical features of both the SSD and the side-gated transistor have similar effects on their electrical properties. A narrow trench allows the gates to couple more efficiently with the channel and therefore have a larger difference in resistance between a positive current and a negative current. Like the side-gated transistor a thin channel allows the conducting region to more evenly gated and opens up the
possibility of inducing a bandgap. The length of the channel simply changes the on/off ratio as there is a larger voltage drop through the channel and therefore a larger voltage difference between the channel and the side gates.

5. Ballistic Rectifiers

5.1. Four Terminal Landauer Theory

The ballistic rectifier is a novel four terminal device that relies on the ballistic regime of electron transport to convert an AC input into a DC output. The four terminals are connected via an asymmetric cross junction that either reflects or collimates the carriers to one of the two output leads. The important feature of these devices is that they redirect the carriers to the same contact irrespective of which lead they arrived in. This means there will be a net increase in chemical potential at one of the output leads compared to the other. The difference in chemical potentials between the output contacts results in a DC output. In section 2.5 the Landauer formalism was used to describe the current through a nanoscale junction connecting two semi-infinite metallic reservoirs. In order to get a better understanding of the ballistic rectifiers that will be discussed in this chapter the Landauer theory must be extended to the case that there are more than two reservoirs. There is a full description of this formalism in [24] and a more general description of four terminal ballistic devices in [79]. In the general case the conductance between lead $\beta$ and $\alpha$ ($G_{\alpha\beta}$):

\[ G_{\beta\alpha} = \frac{2e^2}{h} T_{[\beta,\alpha]}(I_{[\beta,\alpha]}) \]

\[ T_{[\beta,\alpha]}(I_{[\beta,\alpha]}) \] is equal to the transmission probability from contact $\alpha$ to $\beta$; $T_{\alpha\rightarrow\beta}(I_{\alpha})$ if $\mu_\alpha > \mu_\beta$ or $T_{\beta\rightarrow\alpha}(I_{\beta})$ if $\mu_\alpha < \mu_\beta$. It is important to note that the transmission probabilities depend on the local potential at every point in the device; it would take a full self-consistent calculation to model this properly and is outside the scope of this work. In order to model the rectification effect for both the TBR and the BR we must use the boundary conditions: $I_S = -I_{SD}$, $I_L = I_U = 0$ and $V_D = 0$. The second condition means that $T_{D\rightarrow\alpha}(I_U)$ and $T_{D\rightarrow\lambda}(I_L)$ can be treated as constants. The third constraint limits the 4x4 matrix defined by equation (1) to a 3x3 conductance matrix ($G$):

80
\[
\begin{pmatrix}
I_S \\
I_U \\
I_L
\end{pmatrix} = G
\begin{pmatrix}
V_S \\
V_U \\
V_L
\end{pmatrix} = 
\begin{pmatrix}
G_{SU} + G_{SL} + G_{SD} & -G_{SU} & -G_{SL} \\
-G_{US} & G_{US} + G_{UL} + G_{UD} & -G_{UL} \\
-G_{LS} & -G_{LU} & G_{LS} + G_{LU} + G_{LD}
\end{pmatrix}
\begin{pmatrix}
V_S \\
V_U \\
V_L
\end{pmatrix}
\]

(34)

By this logic a 3x3 matrix of resistances \( R = G^{-1} \) can be built:

\[
R = D^{-1}\begin{pmatrix}
G_{SU}G_{SL} + G_{SU}G_{UL} + G_{SU}G_{UL} + G_{SU}G_{LD} & G_{SU}G_{SL} + G_{SU}G_{UL} + G_{SU}G_{UL} + G_{SU}G_{LD} & G_{SU}G_{SL} + G_{SU}G_{UL} + G_{SU}G_{UL} + G_{SU}G_{LD} \\
G_{US}G_{SU} + G_{US}G_{UL} + G_{US}G_{UL} + G_{US}G_{LD} & G_{US}G_{SU} + G_{US}G_{UL} + G_{US}G_{UL} + G_{US}G_{LD} & G_{US}G_{SU} + G_{US}G_{UL} + G_{US}G_{UL} + G_{US}G_{LD} \\
G_{LS}G_{SU} + G_{LS}G_{UL} + G_{LS}G_{UL} + G_{LS}G_{LD} & G_{LS}G_{SU} + G_{LS}G_{UL} + G_{LS}G_{UL} + G_{LS}G_{LD} & G_{LS}G_{SU} + G_{LS}G_{UL} + G_{LS}G_{UL} + G_{LS}G_{LD}
\end{pmatrix}
\]

The diagonal has been left out because they are not needed in the next set of calculations.

\[
D_t = \det(G) = G_{SU}(G_{UL} + G_{UL} + G_{UL} + G_{UL}) + G_{US}(G_{SU} + G_{SU} + G_{SU} + G_{SU}) + G_{LS}(G_{SU} + G_{SU} + G_{SU} + G_{SU})
\]

The \( V_{LU} \) vs \( I_{SD} \) characteristics can be characterised by \( R_{SD,LU} \equiv V_{LU}/I_{SD} \) and using (34):

\[
R_{SD,LU} = -\frac{e(\mu_L - \mu_U)}{I_S} = R_{21} - R_{31}
\]

(35)

Luckily lots of the terms cancel:

\[
R_{SD,LU} = D_t^{-1}(G_{US}G_{LD} - G_{UD}G_{LS})
\]

(36)

This result is the common theoretical basis for both the TBR and the DBR, it only remains to analyse the transmission coefficients at equilibrium and how this changes as a current is applied.

### 5.2. Triangle Ballistic Rectifier Theory

When an AC current is applied the TBR relies on a triangular anti-dot to redirect carriers from the narrow input leads to the L output lead and not the U output lead. Figure 35 is a schematic of a TBR. The difference in the number of charge carriers between L and U in the short term is what creates the EMF that moves the electrons from L to U over the time scale of a measurement. When L and U are not connected externally the carriers still travel internally from L to U in order to preserve charge neutrality. The process of evening out the charge within the device is very quick, on the order of ~3fs, the time it took for the EM wave to travel the length of the device (~1μm). However, over the time scale of an electrical measurement (~1s) or the time for a 1THz AC current to change polarity (~1ps) the device achieves electrostatic equilibrium. The movement of carriers on the shortest times scales represents a “charge pump” [80] or electro-motive force (EMF) on the longer time scales. When the L and U terminals are connected by a circuit with a finite resistance
a current loop forms. In practice, the output from the device comes from the current passing from L to U ($I_{LU}$) through an external circuit.

Figure 35: Is a schematic diagram of a TBR highlighting the angle $\theta_0$. Electrons whose $\theta$ is larger $\theta_0$ end up at U. Electrons whose $\theta$ is less than $\theta_0$ end up at U.

Figure 35 shows the angle $\theta_0$ that dictated whether a carrier emitted from D would end up at L or U. Due to the symmetry of the device through its centre the S and D leads are equivalent so $\theta_0$ will be the same for positive current and negative current. $W_{LU}$ is the width of the L and U channels, $W_{SD}$ is the width of the S and D channels and $W_t$ is the length of the top side of the triangle as shown. The parameters defining the geometry of the device are important to understand the output of the device, as discussed in section 2.3.1:

$$N = \frac{2W}{\lambda_F} \quad (37)$$

To predict the electrical properties of the device we must firstly consider the transmission coefficients between the terminals at equilibrium when $I_{SD} = 0$. The angular distribution of the carriers leaving the S and D leads is $P(\theta) = \frac{1}{2} \cos \theta$. Where $\theta$ is the angle between the ejected electron and the normal of the channel ($n$) and lies between $-\pi/2$ and $\pi/2$. By integrating over the range of angles that the carriers can be ejected, the proportion of carriers transmitted to the different channels can be found. In other words the
Transmission coefficients are a result of the geometry of the device. The transmission probabilities can therefore be described as:

\[ T_{S \rightarrow L}(0) = T_{D \rightarrow L}(0) = \int_{-\pi/2}^{\theta_0} (N_{SD}/2) \cos \theta \, d\theta \]  

(38)  

\[ T_{S \rightarrow U}(0) = T_{D \rightarrow U}(0) = \int_{\theta_0}^{\pi/2} (N_{SD}/2) \cos \theta \, d\theta \]  

(39)  

Where \( N_{SD} = \frac{k_f W_{SD}}{\pi} \) is the number of propagating modes through the S and D leads of width \( W_{SD} \) and carrier wavenumber \( k_f \). As shown in Figure 35, carriers with emission angle \( \theta < \theta_0 \) will be transmitted to \( L \) and carriers with emission angle \( \theta > \theta_0 \) will be transmitted to \( U \).

However, at any finite current there will be an electric field between S and D in the direction of the x axis. This field will have an effect on the emission trajectories of the carriers. In the case of a positive current from source to drain while holes are the dominant carrier the holes will have an excess velocity \( (\Delta \nu) \) from S to D. The holes gain \( \Delta \nu \) from the self-consistent electric field. The effect of \( \Delta \nu \) on the transmission coefficients is a change in transmission coefficients defined by:

\[ T_{S \rightarrow L}(I_S) - T_{S \rightarrow L}(0) = \frac{N_{SD} \sin \theta_e - \sin \theta_0}{2} \]  

(40)  

\[ T_{S \rightarrow U}(I_S) - T_{S \rightarrow U}(0) = -\frac{N_{SD} \sin \theta_e - \sin \theta_0}{2} \]  

(41)  

Where:

\[ \theta_e = \theta_0 + \arcsin \left( \frac{\Delta \nu}{v_f} \sin \theta_0 \right) \]  

(42)  

Represents the cut-off angle between carriers travelling to \( U \) rather than \( L \) when a current is applied. Due to time reversal invariance \( T_{L \rightarrow D}(0) = T_{D \rightarrow L}(0) \) and \( T_{U \rightarrow D}(0) = T_{D \rightarrow U}(0) \).[79]

In order to calculate \( R_{SD,LU} \) we need to know \( D_t \) which can be simplified by making use of \( T_{S \rightarrow D} = T_{D \rightarrow S} = 0 \) because the path from S to D is blocked by the triangle anti-dot. Therefore, it simplifies to:

\[ D_t = G_{SU}(G_{UL}G_{LD} + G_{UD}(G_{LS} + G_{LU} + G_{LD})) \]

\[ + G_{SL}(G_{LD}(G_{US} + G_{UL}) + G_{UD}(G_{LU} + G_{LD})) \]  

(43)  

Making use of the time reversal invariance in conjunction with equations 1, 7 and 8:

\[ D_t = \frac{e^6 N_{SD}^2}{h^3} \left( N_{LU} \left( 1 - \frac{W_L}{W_{LU}} \right) - \frac{N_{SD}(1 - \sin \theta_0)^2}{2} \right) \]  

(44)
The ratio $\frac{W_L}{W_{LU}}$ was typically $\frac{2}{3}$ for the devices conceived in this work. The conductance in the L and U channels has been attenuated by this ratio because any modes propagating between the two will have a $\frac{2}{3}$ chance of reflecting back the way they came or towards S or D. Therefore, $R_{SD,LU}$ can be written as:

$$R_{SD,LU} = \frac{3}{2} \frac{h}{e^2} \frac{\sin \theta_e - \sin \theta_0}{2N_{LU} - 3N_{SD}(1 - \sin \theta_0)^2}$$  \hspace{1cm} (45)$$

In order to model this function we must take a closer look at $\theta_e$ and how it varies with not just current but also Fermi energy. Its change with current will reveal the quadratic IV curves that characterise the device output. The net velocity ($\Delta v$) of the carriers can simply be derived from the current as:

$$\Delta v = \frac{I_{SD}}{neW_{SD}}$$  \hspace{1cm} (46)$$

Using 11:

$$\sin \theta_e = \sin \left( \theta_0 + \arcsin \left( \frac{\Delta v}{v_f} \sin \theta_0 \right) \right) = \sin \theta_0 \cos \left( \arcsin \left( \frac{\Delta v}{v_f} \sin \theta_0 \right) \right) + \frac{\Delta v}{v_f} \sin \theta_0 \cos \theta_0$$  \hspace{1cm} (47)$$

This becomes:

$$\sin \theta_e = \sqrt{1 - \left( \frac{\Delta v}{v_f} \sin \theta_0 \right)^2} \sin \theta_0 + \frac{\Delta v}{2v_f} \sin 2\theta_0$$  \hspace{1cm} (48)$$

When the current is small so that $\Delta v \ll v_f$:

$$R_{SD,LU} = \frac{3}{2} \frac{h}{e^2} \frac{\Delta v}{2v_f} \sin \frac{2\theta_0}{v_f}$$  \hspace{1cm} (49)$$

Using 6:

$$\frac{\Delta v}{v_f} = \frac{I_{SD} \hbar}{E_F e N_{SD}}$$  \hspace{1cm} (50)$$

Therefore:

$$\frac{V_{LU}}{I_{SD}} \approx - \frac{\hbar}{e^2} \frac{3h}{4eE_F N_{SD}} \frac{\sin 2\theta_0}{2N_{LU} - 3N_{SD}(1 - \sin \theta_0)^2} I_{SD}$$  \hspace{1cm} (51)$$

Not only does this equation predict the TBR will have quadratic behaviour in $I_{SD}$ vs $V_{LU}$ but it also predicts how the devices will behave as the fermi energy is changed with a backgate. It predicts that as the fermi energy rises and the number of conduction modes increases, the output will fall.
Figure 36: a) Shows $R_{SD,LU}$ against backgate voltage from equation 19, the model assumes a 290nm SiO$_2$ dielectric layer between the gate and the device. 5 μA has been used as an example input.

Figure 36 a) and b) both show the theoretical response from a device with realistic input values. Figure 36 a) shows $V_{LU}$ against the backgate voltage for a hypothetical sample with a 290nm SiO$_2$ dielectric layer, $W_{LU} = 200$ nm and $W_{SD} = 100$ nm. A positive 5 μA fixed DC $I_{SD}$ has been applied to demonstrate a realistic input current. Figure 36 b) shows how the device would respond with different applied currents; clearly there is quadratic behaviour around 0mA. The asymptotic behaviour in Figure 36 a) at low backgate voltages is a result of the fermi energy falling to 0 eV. In real samples there are charge inhomogeneities that smear out the charge neutrality point [80, 81]. Also, at any finite temperature there would also be coexistence of electrons and holes near the Dirac point due to thermal excitations [80]. This would result in a linear change of output between the peaks for holes and electrons. The steps are a direct result of the discrete nature of $N_{SD}$ and $N_{LU}$. At any finite temperature these steps would start to round off as the Fermi-Dirac distribution softens.
The model neglects several key issues that will affect its correlation with real data. Firstly, the transmission coefficients will also depend on the chance that a carrier will scatter off a phonon or lattice defect. This will scale with \( \left( \frac{1}{2} \right)^{1/\lambda_{\text{MFP}}} \) where \( l \) is the characteristic length of the device. This is true because half the carriers will scatter every \( \lambda_{\text{MFP}} \). Again, this emphasises the importance that the samples are high quality with extremely high mobility. Secondly, the model assumes that the carriers scatter specularly from the edges of the graphene. There is still a great deal of debate in the literature as to whether the edges of graphene scatter diffusively. Most of the early work concludes (or at least assumes) that the edges of graphene will scatter diffusively \([4, 18]\), recently there have been some experiments that have observed specular scattering \([82, 83]\). It is likely that only a proportion of incident carriers reflect specularly from the edge of the graphene; this proportion likely depends on the edge profile, edge defects and chemical make-up \([47, 84]\). Thirdly, the model neglects that the width of the S and D channels may not be the same, this will introduce more softening to the lateral quantisation steps. The model ignores thermal rectification effects; these will be discussed in more detail in section 5.4. Edge conduction may have also played a role in the properties of the device particularly near the NP. Edge conduction has been suggested as a limiting factor in approaching the Dirac point \([52]\). Finally, the Landauer formalism assumes the contacts are reflectionless which will not be the case; this will decrease the output of the device.

### 5.3. Thermal rectification

One other possible explanation for output from these devices comes from locally heating regions of the device, a result of the large currents passing through the asymmetric structures. Both the TBR and the DBR have an easier current path from S to D through L since the channels from S and D to U are narrower than the channels from S and D to L. This means that more current passes through the region of graphene close to L, locally heating the contact and creating a chemical potential difference between L and U. Zuev et al. demonstrated that a heat difference across graphene will create thermoelectric power (TEP) output as it does in other materials via the Seaman effect \([80]\).
Figure 37: (from [80]) a) demonstrates how conductivity changed across a graphene flake as $V_g$ was changed for five different temperatures. b) shows how TEP changed with $V_g$ for the same five temperatures. The SEM image shows how the device was laid out with the heater at the top, two thermometers to detect the temperature difference and four electrical contacts to detect TEP. The dark region shows where the graphene was left after plasma etching. The graphical inset shows the linear dependence of TEP on the temperature of the sample at $V_g$ of -5V and -30V.

Figure 37 comes from [80] and shows the remarkably similar output characteristics of a thermal device. Since the same part of the device will heat up irrespective of which direction the current is passing we can expect that any geometrically asymmetric device will show similar properties to the ones shown in this figure. Figure 37 a) and b) show how the conductivity and TEP change while $V_G$ is changed at different temperatures, respectively. Importantly, the conductivity does not change considerably with temperature but as the average temperature of the device is changed the TEP reduces dramatically. This means that any thermal rectification effects would have been less prevalent at low
temperatures. Therefore, if the device relied on thermal rectification effects the efficiency would become lower at lower temperatures. Whereas, if the device was ballistic it was expected that at lower temperatures the device would be more efficient since there would be less phonons to scatter the carriers.

The Seaman effect means that the carriers move from the hot region to the cold region, in this case the carriers are moving from the top contacts to the bottom contacts. In both the DBR and the TBR the carriers would move from L to U which means that the thermal rectification effect would be in the opposite direction to that of the ballistic effect.

5.4. Results

A major part of this work was learning and developing skills in order to create high mobility devices. A high mobility was essential to enter ballistic regime of electron transport and demonstrate how these devices operate. To show this progression, each generation of fabrication technique will be demonstrated in this section.

5.4.1. SiO₂ Substrate Devices

The first devices that were fabricated for this work used SiO₂ as a substrate because it was easy to find graphene on SiO₂. However, this substrate created charge puddles in the graphene and doped the graphene. The charge puddles reduced the mobility of the device by introducing scattering centres. When it was not likely that the carrier could travel from the injection lead all the way to the output contact the device performance was severely diminished.
Figure 38: a) Shows an optical image of a Hall bar device fabricated from graphene on SiO$_2$ with Au contacts. b) Is an AFM of a DBR located at one of the intersections of the Hall crosses in a). Similarly, c) is an AFM of a TBR at a different intersection. The device geometry has been overlaid on c) because the amount of PMMA residue makes it hard to see.

Figure 38 a) is an optical picture of a Hall bar made from graphene with SiO$_2$ as a substrate. A Hall bar arrangement was chosen so that transport measurements could be made in parallel with device measurements. Figure 38 b) is an AFM of a DBR located at one of the intersections of the Hall bar. It is clear that the edges of the graphene were rough and there was a considerable amount of polymer residue left by the etch mask. When the PMMA etch mask was exposed to the O$_2$ plasma the exposed regions would be damaged creating much longer length polymer chains. This process was known as cross-linking. Cross-linked PMMA was hard to remove and was often left on top of samples. Although this did affect device performance PMMA was chosen because it does not dope or reduce mobility as much as other resists. The S lead width measured from this image is $W_S = 106$nm, likewise $W_D = 98$nm and $W_U = 178$nm. Figure 38 shows an AFM of a TBR, there is a considerable amount of PMMA residue on the surface of the graphene. For this reason the device geometry has been overlaid to make it easier to see where the graphene ends. It was likely there were shorts across the narrow trenches due to incomplete exposure of the
PMMA with the electron beam. This added a linear component to the quadratic response expected and decreased device rectification efficiency. The geometric parameters measured from the AFMs were $W_D = 102\text{nm}$, $W_{LU} = 280\text{nm}$ and $W_S \sim 120\text{nm}$. $W_S$ was difficult to determine since the edge of the etched region were difficult to make out.

![Graphene Conductance vs. Gate Voltage](image)

Figure 39: Shows a measurement of the conductance of a device on SiO$_2$ using a four probe setup (shown in the diagram) as the gate voltage ($V_G$) is swept. The field effect mobility can be taken from this graph as the slope divided by the capacitance of the dielectric layer separating the graphene from the gate.

The first step in measuring any device was to explore the transport properties of the carriers by making a measurement of the conductance of the device while the Fermi energy was changed. In order to change the Fermi energy the backgate voltage ($V_G$) was swept from positive to negative. The charge in the backgate induced carriers in the graphene capacitively so that when a positive gate voltage was applied electrons gather in the graphene. Figure 39 demonstrates how the conductance of graphene changed as the gate was swept. The ambipolar nature of graphene meant that both holes and electrons could be induced depending on the gate voltage. At the Dirac point there should have been no carriers at all. However, at any finite temperature thermal excitations induced an equal number of electrons and holes; this was where the sample was at its least conductive and was sometimes referred to as the neutrality point (NP). The mobility of each type of carrier
can be estimated from this measurement as \( d\sigma_{xx}/dV_G \) divided by the capacitance of the SiO\(_2\) layer. This was measured to be 1810cm\(^2\)/Vs for electrons and 1572cm\(^2\)/Vs for holes corresponding to \( \lambda_{MFP} \) 31nm and 27nm, respectively. Since the characteristic length of this device was \( ~500\) nm we should have been in the diffusive regime. The field effect mobility is not as accurate as the Hall mobility since the density of carriers is approximated as a linear function of gate voltage which may not be true. However, a full Hall measurement requires a magnetic field which was not used during these initial measurements.

Figure 40: Shows how \( V_{LU} \) changed as \( V_G \) was changed while a constant AC current of 20\( \mu \)A was applied between S and D of a DBR. In the top right corner there is a circuit diagram of the measurement setup.

Figure 40 shows how \( V_{LU} \) responds as \( V_G \) was changed from negative to positive while a constant AC current of 20 \( \mu \)A was applied. This measurement was performed with a Stanford Research Instruments SR830 lock-in amplifier at 190 Hz to match the sampling speed of the DC Kiethley 2182 nano-voltmeter used to measure \( V_{LU} \). This ensured there was not a beating effect in the \( V_{LU} \) output that appeared as an oscillation in the data. 190 Hz was not an ideal measurement frequency since it did not perfectly match the coaxial cables used. However, the out-of-phase voltage measurement over the device was always at least an order of magnitude smaller than the in-phase voltage. \( V_G \) was swept with a Kiethley 2410 source meter from positive to negative and back again to look for hysteretic effects. When the device was measured in a vacuum there were no hysteretic
effects for this device. The results showed that the device operated mostly as expected. Initially, at high hole densities the output was minimal due to the large number of conducting channels in the input leads reducing the output. Then as the Fermi energy approached the Dirac point the output rose until inhomogeneities and thermal effects in the sample meant that both carriers contributed to the output equally. There was a linear change of carrier type as expected for graphene before the number of conduction channels for holes then increased to the point that the output fell again.

The peaks in the output represent the maximums in responsivity; here the maximum responsivity for electrons was 110V/W and 67V/W for holes. $R_{LU}$ was measured to be 55kΩ and 47kΩ at these backgate voltage respectively. This means the measured NEP for this device was 274 pW/Hz$^{1/2}$ and 416 pW/Hz$^{1/2}$ respectively. There was a disparity between holes and electrons, the peak in the output when electrons were the majority carrier was larger than the peak in the output when holes were the majority carrier. This was consistent with the measurement of mobility since it indicated that electrons should have given a higher output. The results were also quite noisy this was because the contact resistances for this first generation of devices were very high. The output of the device was surprisingly high since the mobility of the graphene used was relatively low. Since the output was expected to scale linearly with the transmission coefficients and the transmission coefficients scale with $\left(\frac{1}{2}\right)^{1/\lambda_{MFP}}$ the device was not expected to operate very well or at all. This suggests that the local mobility in the device may have been higher. The large currents passed through the device may have effectively current annealed the most important parts of the device, removing charge inhomogeneities from the injection leads at the thinnest parts where the current density was at its highest.
Figure 41: Shows $V_{LU}$ against $I_{SD}$ for four different gate voltages, in the top right there is a circuit diagram of the measurement setup. -13V and -3V curves have been fitted with polynomials to show the device gives the quadratic response expected.

To understand the results in Figure 40 we looked at how $V_{LU}$ changed with $I_{SD}$. Figure 41 demonstrates this at four different gate voltages. +20V and -30V characterise how the device behaved at high electron and hole densities respectively. Both showed a linear response with a small non linearity between positive and negative current. The linear response was likely to be due to a misalignment horizontally between the L and U contacts adding a $R_{XX}$ component to the resistance. -3V and -13V represent how the device behaved near the maximums of the output and have been fitted with polynomials to show that the DBR measured responds quadratically with input current as expected from equation (51).
Figure 42: Shows how $V_{LU}$ changed with back gate voltage while a constant AC current of 20μA was applied between S and D of a TBR. In the top right corner there is a circuit diagram of the measurement setup.

Figure 42 demonstrates the rectified DC output $V_{LU}$ for a TBR while $V_G$ was swept from negative to positive while a constant AC current of 20μA is applied between S and D. There is a diagram of the circuit used to measure the response in the top right of the figure. This device showed a much more symmetric response between holes and electrons than the DBR. The size of the response was similar in both ballistic rectifiers; this is not surprising since the dimensions of the devices were similar. The peak responsivities were 86 V/W and 110 V/W for electrons and holes respectively.
Figure 43: A graph showing $V_{LU}$ against $I_{SD}$ for a TBR at two different $V_G$. A large linear component can be seen due to leaks between the contacts.

Figure 43 is a graph showing how the output $V_{LU}$ changed as $I_{SD}$ was swept from negative to positive for a TBR at two different $V_G$. The gate voltages shown correspond to the peaks in output from Figure 42. There was a large linear DC component to the output due to shorts between the various input and output contacts allowing the current to pass directly from S and D to L and U without passing through the device itself. The shorts were a result of the cuts used to separate the contacts not being wide enough and in future devices they would be made wider. In order to eliminate this linear component we could take the asymmetry such that $Asymmetry = (V_{LU}(I_{SD}) + V_{LU}(-I_{SD}))/2$. This effectively removes any first order polynomial components and highlights the second order terms that are expected.
Figure 44: Shows the Asymmetry of the DC IVs shown in Figure 43. It can be seen that there was both positive and negative quadratic response at different input currents.

Figure 44 demonstrates how the asymmetry varied with input current. In the case that electrons were the majority carriers (-8V) initially there was a negative output as expected. However, at 30μA the output plateaus and starts to reverse. This could have been the result of thermal rectification [79, 80] discussed in section 5.3. In the case that holes were the majority carriers the polarity of the output started negative as expected and then a similar thermal rectification effect was observed at higher currents.

5.4.2. Wet Transferred Devices

The first set of devices proved to be encouraging; despite lacking the mobility to be truly in the ballistic regime they still produced a reasonably adequate output voltage. The limiting factor for the device efficiency and output was the substrate so the second generation of devices were wet transferred onto BN as discussed in section 3.3. Wet transferred devices often showed hysteretic properties transport properties when measured because water and ions got trapped between the graphene its substrate.
Figure 45: Shows the dependence of conductance on gate voltage for a wet transferred device. The coloured linear fits show the slope that was used to calculate the mobilities shown.

Figure 45 shows the conductance of a wet transferred device, the linear regions shown in red and blue show were the slope was measured to calculate the mobility of the bulk graphene sample. The resulting mobilities were nearly an order of magnitude higher now BN was being used as the substrate. Note the shape of the curve near the Dirac point; the two minima represent two differently doped regions of the bulk graphene, a signature of localised contamination.

Figure 46: is a graph showing how $V_{LU}$ changed for a wet transferred BR while a DC current was passed from S to D at different gate voltages.
Figure 46 shows how $V_{LU}$ changed for a wet transferred device while a DC current was passed from S to D at different gate voltages. While $V_G = -2V$ the output showed the characteristic quadratic behaviour expected for a BR with electrons as majority carriers. The device had a strong linear dependence at high carrier concentrations due to misalignment of L and U. However, the device was still able to demonstrate both negative and positive curvature.

![Graph showing $V_{LU}$ as a DC current $I_{SD}$ was passed through a wet transferred TBR for 4 different values of $V_G$.](image)

Figure 47 demonstrates how $V_{LU}$ changed with $I_{SD}$ for four different gate voltages. Again, both negative and positive curvature could be seen above and below the Dirac point respectively. Also, the linear component to the output was opposite to the wet transferred BR shown in Figure 46.
Figure 48: shows how the DC voltage output $V_{LU}$ depended on $V_G$ for both a wet transferred BR and TBR while a constant 190Hz AC current of 10 μA is applied between S and D.

Figure 48 demonstrates the dependence of $V_{LU}$ on $V_G$ for both a wet transferred BR and TBR while a constant 190Hz AC current was applied between S and D. The data shows that the device was doped inhomogeneously because the point where both carriers exist in equal numbers was different for each device despite the two devices being fabricated on the same Hall bar structure. Clearly the BR operated considerably better than the TBR in this case; this was likely due to the fact that it was on a more homogeneously doped region of graphene. In a region where the doping was lower there would be less scattering centres and therefore the mean free path of the carriers would be higher. This also emphasises the point that the measurement for the mobility in the bulk graphene may not be valid for the graphene in the active regions of the device. Both the BR and the TBR curves seem to have anomalous shapes. The BR has a lump on the hole side that protrudes as a positive feature to the expected data. However, when $V_G$ was swept in the opposite direction it protruded as a negative feature. This lump was simply the movement of ions near the device that counteracted the effect of the changing gate voltage. Similar effects were seen for the TBR but were less pronounced and less predictable.

Overall, the wet transferred devices were considerably better than the first generation of devices. The mobility measured for these devices estimates that $\lambda_{MFP} \sim 200 \text{ nm}$, putting these devices close to the ballistic regime. Devices made by this method were air sensitive and highly unpredictable. Large amounts of noise on DC voltage measurements
were common due to high (~20 kΩ) contact resistances, often as large as $R_{SD}$ for the ballistic rectifier. The responsivity measured for the BR was 1270 V/W and 1190 V/W for holes and electrons respectively. However, the TBR only managed to achieve responsivities of 168 V/W and 56 V/W for holes and electrons respectively. This could have been because there were a large number of scatterers in the active region of the TBR as previously discussed.

5.4.3. Dry Transferred Devices

The wet transferred BR demonstrated an order of magnitude improvement in sensitivity when compared to the devices fabricated on SiO$_2$. The next logical step was to fabricate an even higher mobility device to see if the trend continued.

![Figure 49: a) and b) are optical images of a dry transferred BR device at 5x and 100x magnification respectively.](image)

Figure 49 a) and b) are optical images of a pair of dry transferred BR devices at 5x and 100x magnification respectively. The device was encapsulated with a top layer of BN 15nm thick by dry transfer after the etch mask had been washed away. It is clear that the graphene device was not visible after the top layer of BN had been transferred on top. The top layer of BN clearly conformed to the contacts and most of the contamination gathered underneath these regions. However, there were still small bubbles between the top layer of BN and the HB, most of these gathered near the edges on the HB.
Figure 50: a graph of conductance $\sigma_{XX}$ in a Hall bar device as shown in the circuit diagram while $V_G$ was changed for a dry transferred sample.

Figure 50 is a graph of conductance $\sigma_{XX}$ measured in a Hall bar device as shown in the circuit diagram while $V_G$ was changed. It illustrates that the mobility of the dry transferred devices was better than the wet transferred devices and considerably better than the devices fabricated on SiO$_2$. However, there was a small puncture between one of the contacts and the back gate through the SiO$_2$ that was likely to have happened during the mechanical bonding process. This meant that $|V_G| > 10$ V leaked by more than 1 nA, all gate sweeps had to be kept below 10V. For this reason the conductance curve did not allow us to make an estimate for the mobility of holes because the gate was not able to move the Fermi energy into this range without leaking.
Figure 51: a graph showing the dependence of $V_{LU}$ on input current $I_{SD}$ for a range of different $V_G$ for a dry transferred BR.

Figure 51 demonstrates the dependence of $V_{LU}$ on $I_{SD}$ for a range of different $V_G$. The device showed strong quadratic behaviour, as expected, with both positive and negative curvature depending on the type of majority carrier. The output was much larger for electrons than it was for holes. The reason for this is unclear, without information on the mobility of the holes it is difficult to know whether their mobility was simply lower or if the data was hinting at an asymmetry between the properties of electrons and holes. If one type of carrier interacted differently with the edges used to reflect carriers this feature might be seen. Likewise, if the mobility was lower the number of carriers able to reach L without scattering would be less ensuring there would be a smaller output.
Figure 52: A graph showing how $V_{LU}$ varied while a 190Hz 20 μA $I_{SD}$ was applied as the gate voltage was changed. The circuit diagram shows how the device was measured. The output for the holes was considerably lower than the electrons. The data features both a positive and negative sweep of backgate voltage demonstrating the lack of hysteretic behaviour for these encapsulated devices.

Figure 52 demonstrates how $V_{LU}$ changes with $V_G$ while a constant 190Hz 20 μA AC $I_{SD}$ is applied. Both a positive and negative gate sweep have been included to demonstrate how little hysteresis occurred when these devices were encapsulated. Both Figure 51 and Figure 52 demonstrate that this device showed considerable asymmetry between the two carrier types. This was not common to all devices and sometimes the devices would work better when holes were the majority carrier. This implies that the asymmetry was not a fundamental property of the carriers; instead it must be a property of the devices themselves. For example, the chemical composition of the edges of the graphene in the active region may have created strong localised doping [47, 52]. It could have been possible that in the case that the edges were doped in the opposite direction to the bulk of the graphene a np-junction could form. Although carriers Klien tunnel through np-junctions in graphene when they impinge on the barrier in the normal direction, when they impinge at any other angle they can scatter specularly [42, 85]. Consequently, the n-p junction would only form for one majority carrier type and not the other since the doping at the edge would be fixed. The peak responsivity measured while electrons were the majority carrier was 6,980 V/W.
5.4.4. Stamp Transferred Devices

The advent of stamp transfer resulted in devices that were both reliably higher mobility and featured almost no intrinsic doping. With the introduction of 1D contacts as described in section 4.3 the contact resistances were considerably lower. The devices that will feature in this section were fabricated with both of these techniques.

Figure 53: a) and b) show optical micrographs of two HB devices at 5x and 100x magnification respectively. One HB features a BR and the other features a TBR. c) is an atomic force micrograph of a stamp transferred BR where the channels were measured to be 122 nm and 137 nm wide on the left and right respectively. d) is an atomic force micrograph of a stamp transfer TBR where the channels were measured to be 149 nm and 117 nm on the left and right respectively.

Figure 53 shows the stamp transferred BR and TBR that will be discussed in this section. Figure 53 a) and b) show optical micrographs of the two HB devices at 5x and 100x magnification respectively. Figure 53 c) is an atomic force micrograph of a stamp transferred BR where the channels were measured to be 122 nm and 137 nm wide on the left and right respectively. Figure 53 d) is an atomic force micrograph of a stamp transfer
TBR where the channels were measured to be 149 nm and 117 nm on the left and right respectively.

Figure 54: graph showing longitudinal conductance of the bulk graphene against $V_G$ measured from the BR HB.

Figure 54 demonstrates the conductivity of stamp transferred graphene against $V_G$ measured from the BR HB. A mobility of 197,600 cm$^2$/Vs and 106,000 cm$^2$/Vs was measured for electrons and holes respectively. The behaviour of the carriers in the TBR HB was almost identical showing the long range uniformity and high quality of the sample. The corresponding $\lambda_{MFP}$ for these mobilities is longer than the characteristic length of the HB used to measure this mobility. Therefore, the electrostatic gating method used for measuring mobility is only a lower estimate. A more accurate approach was be to use a magnetic field to make Hall measurements:
Figure 55: a) hall resistance and linear conductance as a function of gate voltage with an applied magnetic field of 0.1 T at 250 K. b) the corresponding mobility from the hall measurements as a function of density at 250, 200 and 50 K. c) $\lambda_{MFP}$ as a function of carrier density at 250, 200 and 50 K.

Figure 55 a) shows hall resistance and linear conductance as a function of gate voltage with an applied magnetic field of 0.1 T at 250 K. Figure 55 b) demonstrates the corresponding mobility from the hall measurements as a function of density at 250, 200 and 50 K. Figure 55 c) shows an estimate for $\lambda_{MFP}$ as a function of carrier density at 250, 200 and 50 K. The cryostat used to make these measurements and apply the magnetic field was unable to sustain room temperature for long due to the rapid loss of He. For this reason room temperature measurements were not made with a magnetic field. However, the change in mobility and $\lambda_{MFP}$ with temperature was small and matched well with the electrostatic measurements for these values at room temperature. The measured $\lambda_{MFP}$ verifies that this device functioned exclusively in the ballistic regime of electron transport.

Figure 56: a) and b) are plots showing the dependence of $V_{LU}$ on $V_G$ for fixed 190Hz input currents of 1, 2.5, 5, 10 $\mu$A at 300 K for a BR and a TBR respectively.

Figure 56 a) and b) are plots showing the dependence of $V_{LU}$ on $V_G$ for fixed 190Hz input currents of 1, 2.5, 5 and 10 $\mu$A at 300 K for a BR and a TBR respectively. Both
stamp transferred devices demonstrated ambipolar output. The peaks of responsivity for electrons and holes in the BR were 23,100 and 8,100 V/W respectively. Correspondingly the peaks of responsivity for electrons and holes in the TBR were 2,400 and 1,400 V/W for electrons and holes respectively.

Figure 57: a) and b) feature $V_{LU}$ as a function of DC $I_{SD}$ for a range of gate voltages at room temperature for a BR and a TBR respectively.

Figure 57 a) and b) show how $V_{LU}$ depended on DC $I_{SD}$ for a range of different gate voltages at room temperature for both a BR and a TBR respectively. Both graphs demonstrate the quadratic behaviour that was expected at low densities. However, it was easier to observe this behaviour in the BR than the TBR, this could relate to the fact that the responsivity measured for the DBR was much higher. The curve in Figure 57 a) when $V_G = 1$ V demonstrates strange behaviour, there seems to be both positive and negative curvature. This was simply the bias voltage altering the relative voltage of the backgate, effectively the device swaps carrier type between positive and negative bias. The process of changing carrier types over such a narrow voltage range ($\pm 0.1$V) is only possible due to the exceptional quality of the sample.
Figure 58: a) and b) show $V_{LU}$ as a function of $V_G$ while a fixed $I_{SD}$ of 5 μA was applied at 50, 150, 200 and 250 K for both a BR and a TBR respectively.

Figure 58 a) and b) show $V_{LU}$ as a function of $V_G$ while a fixed $I_{SD}$ of 5 μA was applied at 50, 150, 200 and 250 K for both a BR and a TBR respectively. The peak of output increased at lower temperatures for both devices as expected for a ballistic effect. The location of the peaks also got closer to the Dirac point since the region that both carriers existed was smaller. The output from the DBR shown in Figure 58 a) (and to some extent the TBR in Figure 58 b)) at low temperature seemed to oscillate with gate voltage. These oscillations resemble mesoscopic conductance fluctuations due to coherent carriers but typically this type of feature is washed out by 5 K [86], in these samples the oscillations were seen at 150 K. Shubnikov–de Haas oscillations are observed at room temperature but only in a relatively high magnetic field and there is no field in this case. They could have been the result of surface traps and edge states that change the emission profile from the narrow injection leads. However, it is unlikely that these maxima and minima in output would be as regular and reproducible if this was the case. Instead, we propose that oscillations could be the result of the lateral confinement modes discussed in section 5.2. To investigate this further this data was manipulated to enhance the periodic behaviour:
Figure 59: The differential of $V_{LU}$ with respect to $V_G$ as a function of the Fermi energy for both electrons and holes at 50 K for the BR.

Figure 59 shows the differential of $V_{LU}$ at 50 K with respect to $V_G$ from Figure 58 a) plotted against Fermi energy for both holes and electrons. The Fermi energy was determined using $E_F = \hbar v_F \sqrt{n}$, where the carrier concentration $n$ was found using the Hall resistance. This plot allowed us to look at the oscillations as a function of carrier energy. The functionality of the device moved the peaks around since the output also changed with carrier energy when there were no oscillations and thus had to be taken into consideration. It also had to be remembered that since holes and electrons had opposite output polarities the phase of the peaks would be opposite. The position of the peaks was quite striking particularly at higher Fermi energies where the output from the device was changing less and there was only one type of carrier present. The separation of these peaks ($\Delta E$) ranged from 7.6 meV to 17.9 meV with a mean value of 15.1 meV. The number of conducting modes ($M$) from the Landauer formalism $M = \frac{2E_F D}{v_F \Delta E}$ where $D$ is the width of the narrow lead and $v_F$ is the Fermi velocity [19]. The degeneracy must be removed since both spins and valleys will contribute at the same energy only affecting the amplitude of the oscillation. Considering that $M$ changes by 1 between each peak $D = \frac{v_F h}{2\Delta E}$, giving a range of values for $D$ between 133nm and 57nm with an average of 71nm. Comparing well with the width measured with AFM, 122nm for the source lead and 137nm for the drain lead. The discrepancy between the AFM measurements and the electrical measurements could be explained by considering that the ballistically conducting region of the graphene does not extend all the way to the edge due to surface states and defects. Also, the carrier...
transport measurements used to determine the Fermi energy were made in the bulk graphene which may not have applied to carriers found in the narrow injection leads. The variation in peak separation may have been a result of the differing widths between $W_S$ and $W_D$. The S and D leads were different widths, resulting in different periods of oscillation and in the complicated oscillatory pattern seen.

Figure 60: Shows the resistance from S to D measured with DC in a 4-point set up as the device is measured. Clear non-linear resistance can be seen. Near the Dirac point the graphene is behaving as a semiconductor since the resistance decreases with higher current. At higher densities the graphene acts more like a metal and the resistance rises with higher current.

Figure 60 demonstrates the non-linear IV characteristics of the device at different gate voltages at 50K. The 50K data has been shown because the non-linear characteristics are emphasised at low temperature. Near the Dirac point the resistance of the device decreases at higher currents indicative of electron-hole pair generation, typically observed in semiconductors. At higher carrier concentrations, the resistance through the device increases with current indicative of lattice heating and phonons scattering carriers, a phenomenon observed in metals. Therefore, unsurprisingly this indicates that graphene, the
semi-metal, behaves more like a semi-conductor at low density and more like a metal at high density.

5.4.5. BR Noise Measurements

Another potential advantage of the ballistic rectifier over typical diodes or bridge rectifiers is that its low and upper terminals are distinct from its source and drain terminals. When a current is applied to a traditional diode the sensing contacts must be either side of device, so the thermal noise from the large resistance across the diode becomes the limiting factor at high frequencies. Whereas, both BR designs could be tailored such that the resistance $R_{LU}$ could be small and therefore the noise can be low. Previous work has shown that $1/f$ noise limits the low frequency noise levels [81], its origin lies in the mobility fluctuation that can be expressed using Hooge’s relation [87]. However, the high frequency noise is limited by the thermal noise through the device.

Figure 61: A graph showing both $R_{SD}$ and $R_{LU}$ as a function of $V_G$ for the stamp transferred device that featured in section 5.4.4.
Figure 61 shows $R_{LU}$ and $R_{SD}$ as a function of $V_G$ for the stamp transferred device that featured in section 5.4.4. From the figure it is evident that the resistance through the device was higher than the resistance between the two sensing electrodes.

Another advantage of having the sensing electrodes distinct from the source and drain electrodes is that any non ohmic feature of the contacts can be ignored. The four terminal architecture allows L and U to be used purely as voltage sensing probes, simplifying both the output from the device and how we understand how it works (see section 5.2).

![Diagram](image)

Figure 62: a) Voltage noise spectra of the stamp transferred BR with different input currents. The inset shows the voltage noise over the square of the applied bias, $S_V/V^2$, from 0.1 μA to 2.0 μA at 10 Hz. b) shows a schematic diagram of the low frequency noise measurement setup. The current was applied by a Keithley 2400 power source through a 0.05 Hz low pass filter. The noise of the rectifier was amplified and measured by two independent channels.

Figure 62 a) shows voltage noise spectra of the same stamp transferred device at different input currents. The inset shows the voltage noise over the square of the applied bias, $S_V/V^2$, from 0.1 to 2.0 μA at 10 Hz. Figure 62 b) is a schematic diagram of the setup used to measure the voltage noise spectra. The current was applied by a Keithley 2400 power source through a 0.05 Hz low pass filter. The noise of the rectifier was amplified and measured by two independent channels.

The cross-correlation technique was used to minimize the noise from the measurement setup [83]. At zero bias, the BR generated a white noise which was around 13.3 nVHz$^{1/2}$. From Figure 62, $R_{LU}$ is around 17 kΩ while no gate was applied, this result is in good agreement with the theoretical thermal noise, $\sqrt{4kT R_{LU}} = 15.7$ nVHz$^{1/2}$. Any discrepancy could be attributed to the resistance measurements being made in a vacuum and the noise measurements being made in atmospheric conditions. In air graphene can become slightly
doped due to polar molecules like water aligning on the surface. Although this device was encapsulated the surface contamination on the BN did have an effect on the doping of the device, this was clear from the hysteretic properties of the device with $V_G$ that were only present in atmosphere. The abrupt increase at frequencies lower than 10 Hz is generated by the power source. As expected, after applying a DC current signal from drain to source, the low frequency noise became dominated by the flicker noise (sometimes also called 1/f noise). It is found that the flicker noise increases with the applied current. The inset in Fig. 3 b) shows that $S_V/V^2$ remains almost the same from 0.1 µA to 2 µA at 10 Hz. It suggests that the flicker noise at low frequencies attributes to the mobility fluctuation according to Hooge’s empirical equation [81, 87]. At high frequencies, the flicker noise will eventually become negligible compared with the thermal noise [81]. Thus, the minimum power that the ballistic device can detect is determined by the measured thermal noise over the responsivity, this is the noise equivalent power (NEP).

Figure 63: a) a graph showing voltage responsivity against $V_G$ for the stamp transferred BR featured in section 5.4.4. b) NEP against $V_G$ for the same ballistic rectifier calculated from $\text{NEP} = \frac{4kT R_{LU}}{\text{Responsivity}}$

Figure 633 a) demonstrates how the responsivity of the stamp transferred BR changes with $V_G$. This was simply calculated from $V_{LU}$ divided by the power between S and D ($V_{SD}$ was measured in 4-point). Figure 633 b) shows how the NEP varied with $V_G$, NEP was calculated from $\text{NEP} = \frac{4kT R_{LU}}{\text{Responsivity}}$. The peak value measured for responsivity was 23,000 V/W and the minima measured for the NEP was 0.64 pW/Hz$^{1/2}$. These values were impressive and mean that the BR matched values for sensitivity and noise that superconducting bolometers can achieve without the need to be cooled.
5.4.6. High Frequency Measurements

In order to test the BR at high frequency it was necessary to fabricate devices with specifically designed contacts. The contacts were designed in such a way that they matched a $50 \, \Omega$ load. Matching the load of the device to the supply was important so that the maximum amount of power was transmitted from the vector network analyser to the device itself.

![Image](image.png)

Figure 64: a) is an optical micrograph of a set of contacts specifically designed to operate at high frequency. b) is an AFM of the device at the very centre of the contacts.

Figure 644 a) is an optical micrograph showing how the contacts were arranged in the THz mesa. The large drain pad acts as a strip line ground for the other 3 contacts, shielding them from external fields and capacitive effects. Next, a shielded probe station with SUSS MicroTec PH100 probes were used in conjunction with an Agilent PNA 5224A network analyser and a Kiethley 2182A nanovoltmeter to measure the DC output as an RF signal was applied.
The frequency dependence of the data is a result of the non-uniform input power and losses within the cables used to transfer the input signal. b) is a graph showing $V_{LU}$ dependence on input power, a line has been added to indicate the region over which the device operates within the square law region as expected.

Figure 65 a) is the result of these measurements; the voltage responsivity is shown against frequency. The model predicts that the output from the device should not change as the frequency is changed. It is clear that there was some variation in output as the frequency was changed, later it was shown that this was in fact a result of the input signal changing with frequency. Unfortunately, the cables used to transfer the signal from the network analyser to the probes were not perfect and had frequency dependent absorption properties. There was also a large discrepancy between the responsivity measured at high frequency and the responsivity measured at low frequency in section 5.4.4. The low responsivity measured here was the result of two problems. Firstly, there was no backgate making it impossible to change the Fermi energy, it is clear from Figure 633 a) that when intrinsically doped the device would be far from its optimal operation. Secondly, the device itself had a resistance of 20 kΩ and the RF equipment was designed for a 50 Ω load. The general form of the reflection coefficient $R_{12} = \frac{Z_2 - Z_1}{Z_2 + Z_1}$ results in 99.5% of the power being reflected so that only 0.5% of the power reaches the device. By taking the power reflected from the device into account and the lack of control of the Fermi energy the responsivity fits well with similar devices tested at low frequency.
5.4.7. Two-Layer devices

The high frequency measurements in the previous section highlight the problem of impedance matching. The properties of the BR are excellent; the responsivity measured at low frequency was one of the highest reported in the literature [67, 68]. However, if the device resistance cannot be matched to an antenna then any advantage the BR might have over a traditional device would be lost. For this reason a device was fabricated that would have a lower resistance without sacrificing its rectifying properties. By stacking 2 layers on top of each other with a thin BN spacer the conductivity of the medium could be improved without sacrificing mobility. However, if the edges of the graphene touched each other it was hard to imagine how the carriers could specularly scatter. To test this both layers of the device would need to be individually contacted. Initially, it was necessary to test that such a device could be fabricated and whether there would be current leaks between the two layers. One problem faced while fabricating this device was that in order to contact the top flake without simultaneously contacting the bottom flake only the top layer of BN could be etched through. Although problematic, it was found that a 12 s etch could achieve this for a 20 nm top layer BN.
Figure 66: a), b), c) and d) are pictures of the double layer BR on a HB at each stage of fabrication. In a) stamp transfer has been used to create the stack of BN/graphene/BN/graphene/BN where the layers of BN are roughly 20, 10, 20 nm respectively. The bottom layer of graphene was considerably larger than the top layer so that it could be contacted from the outside of the top graphene flake. In b) one etch mask was applied to create 200 nm wide holes to access the top layer of graphene and then another etch mask was applied to create both the device, 1D contacts for the bottom layer and the long BN struts. The long struts allow the contacts for the top layer to go over the edge of the BN where there was no graphene. In c) the contacts have been added and in d) a top layer of BN has been added so that a top gate could be fabricated.

Initially, there was a small leak between the layers but after a short burst of O₂ plasma this was fixed. The result when both devices were used in series was 500 Ω at high carrier concentrations and 2 kΩ near the maximum in output for electrons and 3.6 kΩ for holes. The mobility of the bottom graphene flake was measured to be 106,000 and 77,800 cm²/Vs for holes and electrons respectively. The mobility of the top layer was measured to be 80,000 and 70,000 cm²/Vs for holes and electrons respectively. However, the contacts to the top layer of graphene were high resistance due to residual BN left after making the 200 nm holes. These top contacts contributed a considerable amount of noise. In a practical device of this type the top contact would not be necessary since contacts to the top and bottom layers would be made simultaneously using normal 1D contacts.
Figure 67: a) graph showing the $V_{LU}/I_{SD}$ characteristics of both the top and bottom layer of a double layer BR in parallel with both $V_L$ and $V_S$ fed into the same nanovoltmeter terminal. Similarly, b) is a graph showing the same DC $V_{LU}$ output when a 20 $\mu$A 190 Hz AC current is passed from S to D.

Figure 677 a) is a graph showing the DC $V_{LU}/I_{SD}$ characteristics with the two layers of BR in parallel and both outputs tied together into the same nanovoltmeter input. Similarly, Figure 677 b) shows the rectifying properties of a double layer BR; a 20 $\mu$A current was applied between both sources and drains, both lower and upper outputs were tied together so that the voltage between them could be measured. The voltage output was modest compared to previous devices. However, the resistance was considerably lower and the peak responsivity was therefore 5,500 V/W and 2,200 V/W for holes and electrons respectively.

Looking at the individual layers it was clear that the electrostatic gating method was not suitable for such a system because the bottom layer partially shielded the top layer from the electric field. Luckily, the neutrality point for this device was close to 0 V for both layers which allowed both layers to work well at the same gate voltages. If either layer had been intrinsically doped differently to the other there would have been two maximums for each carrier. The current would have preferentially passed through the device with the highest carrier concentration, since the devices do not operate well at high concentration, there would have been a considerable drop in efficiency. The resistance of each layer was lower than the single layer device presented in section 5.4.4, this was a result of the larger geometry used for this double layer device. The individual layers had a lower responsivity than the single layer device presented before; this again was a result of the larger geometry.
5.4.8. Comparing the Devices

Learning the techniques and increasing the mobility of the devices required a great deal of practice and optimisation this led to a lot of devices being fabricated. In total 94 devices were fabricated over the three and a half years of research, about two thirds of these devices were ballistic rectifiers. Of these 94 devices only 33 where successfully measured from initial conception. However, This yield was not continuous throughout the research, as one would expect when the techniques were being learnt and then the new techniques being developed more mistakes were made. In the first year, 27 devices attempts were made but only 4 devices were finished and measured successfully. In the second year and third years, 32 and 24 devices were started but only 8 and 12 devices were completed respectively. In the final 6 months 11 devices were fabricated and 9 were measured, this is more representative of the true device yield. Of the 33 devices successfully fabricated 12 were fabricated on quartz to be measured at high frequency, 8 of these used a THz strip-line mesa so that a vector network analyser could be used in conjunction with high frequency probe station to take the measurements observed in section 5.4.6. Of these 8 devices with THz mesas on quartz only 2 where measured at high frequency without being destroyed by static discharge. The problem with static discharge originates from the lack of back gate when the devices are fabricated on quartz, normally the Si back gate allows any build-up of charge in the contacts to drain away slowly before contact is made with the probes. However, when there is no gate the charge will build up in the metal contacts and discharge to the probes when they are connected through the ~100nm graphene channels. The other 4 devices fabricated successfully on quartz were contacted with log-tooth antennas to test the operational principle of the rectenna. However, the static discharge problem proved to be even worse for these devices because the size of the metal antenna was so much larger than the THz mesa. Unfortunately, none of the rectenna devices were measured successfully.

The BR theory predicts that a high mobility device will operate more efficiently than a lower mobility device. Fortunately, each generation of device that was fabricated for this work had higher mobility than the last.
Figure 68: a) a graph showing voltage asymmetry as a function of $P_{SD}$ for a range of different devices. b) is a scatter plot showing the responsivity of a range of devices as a function of their mobility. Each device had a slightly different geometry and was fabricated using a different method, despite this there is a clear positive correlation. The fitted lines correspond to the equation $y = A \left( \frac{1}{2} \right)^{B/x}$ referring to the linear relation between the transmission coefficient and the output voltage.

Figure 688 a) is a graph showing the voltage asymmetry as a function of $P_{SD}$ for a range of different devices with similar geometry. Figure 688 b) is a scatter plot showing the responsivity of a range of devices as a function of their mobility. Each device had a slightly different geometry and was fabricated using a different method, despite this there is a clear positive correlation. The fitted lines correspond to the equation $y = A \left( \frac{1}{2} \right)^{B/x}$ referring to the linear relation between the transmission coefficient and the output voltage.

The transmission coefficient of carriers through the device will vary with $\left( \frac{1}{2} \right)^{1/\lambda_{MFP}}$ and $\lambda_{MFP}$ goes as $\frac{\hbar}{2e\mu} \left( \frac{n}{\pi} \right)^{1/2}$ [7]. Here $\frac{B}{x} = \frac{l}{\lambda_{MFP}}$ and $A$ corresponds to a maximum achievable responsivity (if the device were to be purely ballistic. The result of this was that for electrons the maximum responsivity is 57,700 V/W and that the actual path length $l$ predicted from this fits was ~2.7 μm, longer than was expected but not unreasonable. However, throughout this chapter we have discussed the validity of the mobility measurement in a HB near to the device compared to that of the active region of the device. If the constrictions in the device do decrease the mobility due to local doping of the graphene due to edge defects, the mobility measurements would be inherently inaccurate. The maximum responsivity predicted for holes was 39,900 V/W.
6. Self-Switching Diodes and Side Gated Transistors

6.1. Self-Switching Diodes

The SSD is not only one of the simplest diode concepts but also has one of the highest operational speeds measured. J. Mateos et al. demonstrated that SSDs operate in excess of 1 THz [26], when the work was published this was the fastest electronic device ever measured. In this previous work InGaAs/AlGaAs quantum wells were used to fabricate the device. Fabricated in a single lithography step, the SSD is a planar device with two narrow insulating trenches.

Figure 69: Adapted from [88] a) an AFM of an SSD with a conducting channel and etched insulating trenches. b), c) and d) are schematic representations of a traditional 2DEG SSD under 0V bias, positive bias and negative bias respectively. The grey regions represent the depletion created by the etched trenches and the positive and negative symbols represent the built up of charge. e) a graph showing the I-V characteristics of an InGaAs/GaAs quantum well SSD.

Figure 699 a) is an AFM of an SSD with a conducting channel and etched insulating trenches. b), c) and d) are schematic representations of a traditional 2DEG SSD under 0V bias, positive bias and negative bias respectively. The grey regions represent the depletion created by the etched trenches and the positive and negative symbols represent the built up of charge. c) and d) demonstrate how the width of the channel changes with applied bias. e) a graph showing the I-V characteristics of an InGaAs/GaAs quantum well SSD. The
side gates can be considered to be at the same potential as the source. The potential will fall nearly linearly along the conducting channel. These facts mean that there will always be a difference in potential between the side gates and the drain end of the channel. Since the side gates and the channel are capacitively coupled the size of the depletion zone will change according to the size of the potential difference. Importantly, the depletion will increase or decrease depending on the polarity of the charge difference. In traditional 2DEG semiconductors this can close off the channel completely in one polarity and open it up further in the other.

However, graphene does not have a bandgap. Instead, the conductivity of the channel will change as the bias is applied. In section 2.3.2 the implications of using a semi-metal instead of a semiconductor were considered. The conclusion was that we can expect not only a quadratic non-linear response from the device but a large linear response since the channel will not “pinch off” as it does in a semiconductor.

6.1.1. Single Layer Graphene SSD

The SSDs fabricated during this work used SiO₂ as a substrate and were fabricated on the same HB as the BRs that featured in section 5.4.1. The limited mobility of this sample would impact on the operation of the device directly. This is because the change in $\sigma_{XX}$ with $V_G$ divided by the capacitance is both a measure of mobility and the proportionality constant in the quadratic term for the output of the SSD.

Figure 70: a) and b) are 5x and 100x magnification optical images of a graphene HB on a SiO₂ substrate with an SSD etched into one section of the HB, respectively. c) is an SEM image of an SSD with channel width 92.7nm and length 878.2nm; the trenches were measured to be on average 58.6nm wide.

Figure 70: a) and b) are 5x and 100x magnification optical images of a graphene HB on a SiO₂ substrate with an SSD etched into one section of the HB, respectively. Figure 70 c) is an SEM image of an SSD with channel width 92.7nm and length 878.2nm; the
trenches were measured to be on average 58.6nm wide. The mobility was measured to be 1810 cm$^2$/Vs for electrons and 1572 cm$^2$/Vs for holes.

Figure 71: a) a graph showing how the DC voltage $V_{SD,DC}$ changed with $V_G$ for an SSD fabricated on SiO$_2$ while a 20 $\mu$A 190Hz AC $I_{SD}$ was applied. b) a graph showing $d\sigma_{xx}/dV_G$ as a function of $V_G$ from a HB on the same device. There is a schematic diagram in both a) and b) showing how they were measured in a four terminal configuration. Both measurements were made on the same device shown in Figure 70 b).

Figure 711 a) shows how DC $V_{SD,DC}$ from the SSD changed with $V_G$ while a constant AC $I_{SD}$ of 20 $\mu$A at 190 Hz was applied. There is a schematic diagram of the measurement setup showing how it was measured in a four terminal configuration. The model predicted that the voltage output from the device should be proportional to the differential of the conductance as long as the current was constant (as discussed in section 2.3.2). The differential conductance is shown in Figure 711 b). The device operated as expected when electrons were the majority carriers. However, when holes were the majority carriers the device operated unexpectedly. There is a feature around -5 V, a minimum and a maximum in the negative output that does not match the theoretical model for the device. This could be because the neutrality point measured for the sample on a nearby HB was found to be -5 V and the voltage that the device had the highest resistance was at +10 V. The implication of this was that the conducting channel in the SSD was doped differently to the bulk graphene. If it was doped differently there could be a point where the channel was using one type of carrier and the bulk was using another. At the point where the carriers change type an np-junction could have formed. In graphene an np-junction does not create depletion as it does in other semiconductors since there is no bandgap [89]. Instead, Klein tunnelling occurs which allows carriers to change type at the barrier with some probability, a probability that depends on the angle of the incident carrier. The effect of this in a
practical device was that the resistance would increase. This increase in resistance would not have contributed to the DC output if the junction itself was static. If the np-junction was being created and destroyed at one end of the channel and then at the other by the action of the self-gating mechanism then the output observed might be better understood. An alternate explanation for the observed fluctuation in output could be variation in doping through the channel. If one section of the channel was doped differently to another then there would be two superimposed outputs. The difference in average intrinsic doping between the channel and the bulk could have been because of current annealing in the channel due to high current densities.

![Graph showing how the DC voltage $V_{SD,DC}$ changed with $I_{SD}$ at different gate voltages for an SSD fabricated on SiO$_2$. There is a schematic diagram of the measurement setup showing and how it was measured in a four terminal configuration.](image)

Figure 72: a graph showing how the DC voltage $V_{SD,DC}$ changed with $I_{SD}$ at different gate voltages for an SSD fabricated on SiO$_2$. There is a schematic diagram of the measurement setup showing how it was measured in a four terminal configuration.

Figure 722 demonstrates how the DC $I_{SD}$ depended on DC $V_{SD}$ at different gate voltages. There was a very large linear component in the output, so large that it was difficult to determine if there was any asymmetric behaviour at all. In order to enhance any asymmetric behaviour the symmetric term could be removed by taking the average of the data and its inverse about the y-axis such that the current asymmetry $I_{SD\ Asymmetry}(V_{SD}) = (I_{SD}(V_{SD}) + I_{SD}(-V_{SD}))/2$. 

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Figure 73: demonstrates how the current asymmetry varied with $V_{SD}$ for different $V_G$ for an SSD fabricated on SiO$_2$.

The results in Figure 73 demonstrate the asymmetric IV-characteristics of the SSD. The measurements were made at room temperature in a vacuum. The asymmetry is shown for $V_G$ 20, 10, 0, -10 and -20 V. There is clear evidence of quadratic behaviour at low bias as predicted by the theory discussed in section 2.3.2. However, at higher bias the current asymmetry often diverges from the quadratic behaviour and in some cases changes polarity. The strongest response was observed at a $V_G$ of 0 V, this was expected from the AC measurements in Figure 711. However, the same curve shows a step like feature at higher bias. This could be a result of the previously discussed np-junction being pushed in and out of the conducting channel of the SSD due to the high bias voltage. The responsivity measured using the DC curves were 690 V/W and 162 V/W at gate voltages of 0 V and 20 V respectively.

### 6.1.2. Four Layer Graphene on SiO$_2$ SSD

In order to achieve better responsivity using the same SSD design while maintaining the high mobility, a bandgap would need to be introduced. The best way to do this was to use multi-layer graphene instead of single layer. The band structure of multi-layer
graphene is more complicated than the simple linear dispersion of graphene. When an electric field is applied to an even number of layers of graphene a small band gap can form [6]. By using four layer graphene to fabricate SSDs we hoped to be able to improve their performance.

![Graph showing I_S D vs V_S D](image)

Figure 74: a) shows how $I_{SD}$ varied with $V_{SD}$ for a 4 layer graphene SSD on SiO$_2$ at a range of $V_g$ from -60 V to +60 V. b) shows the asymmetry of $I_{SD}$ from a).

Figure 74 a) shows the $I_{SD}/V_{SD}$ characteristics for a four layer graphene SSD at a range of $V_G$ from -60 V to + 60 V. It was possible to apply much larger current to the device without damaging it due to the higher conductivity of multilayer graphene. The device was very heavily intrinsically doped making it impossible to find the neutrality point. The resulting output was visually impressive but the responsivity measured at +60 V was only 217 V/W. The reason for this was that the graphene was so heavily doped that the neutrality point could not be reached and therefore the bandgap could not be opened or used. Despite this, the resistance of the device was less than half that of the mono-layer device. A lower resistance device would allow for better impedance matching to an antenna in the proposed applications.

### 6.2. Side-Gated Transistors

Like the other planar devices presented in this work, the SGT is easy to fabricate and has the potential to operate at high frequency due to the low parasitic capacitance between its parallel components. Work previously done on graphene SGTs has made use of traditional fabrication techniques where the graphene is not encapsulated. The device that was fabricated for this work used stamp transfer and 1D contacts as described in chapter 4.
It was fabricated on a HB with a SiO$_2$ substrate and Si backgate so that the channel’s transport properties could be accurately measured.

Figure 75: a) and b) are optical pictures of a graphene SGT on a HB with SiO$_2$ substrate at magnifications 5x and 100x respectively. c) is an AFM of the same SGT, the conductive channel is ~60nm wide, ~400nm long and the trench separating the gates from the channel is ~30nm wide.

Figure 75 a) and b) are optical pictures of a graphene SGT on a HB with SiO$_2$ substrate at magnifications 5x and 100x respectively. Figure 75 c) is an AFM of the same SGT, the conductive channel was ~60 nm wide, ~400 nm long and the trench separating the gates from the channel was ~30 nm wide. The graphene used was single layer. The substrate BN was 5 nm thick and the encapsulating layer of BN was also 5 nm. The BN was deliberately chosen to be thin since the profile of the sides of the BN/G/BN stacks would present the limiting factor in reducing the size of the features.
Figure 76: shows conductivity of the graphene featured in Figure 755 from a clear HB using only the backgate to change the number of carriers. Despite the thinness of the substrate BN, high mobilities of 144,000 and 88,500 cm$^2$/Vs were recorded for electrons and holes respectively.

Figure 766 demonstrates that despite only using ~5nm substrate BN the resulting mobilities were high. The electrons were measured to have a mobility of 144,000 cm$^2$/Vs and the holes were measured to have a mobility of 88,500 cm$^2$/Vs at room temperature. The longitudinal conductance was measured on a HB near to the SGT but may not represent the mobility of the graphene in the channel because defect sites at the edge of graphene can introduce doping and scattering centres.
Figure 77: a) and b) show the longitudinal conductance and resistance, respectively, of the graphene SGT using the backgate to change the Fermi energy.

Figure 77 a) and b) show the longitudinal conductance and resistance, respectively, of the graphene SGT using the backgate to change the Fermi energy. Mobilities of 876 and 934 cm$^2$/Vs were measured for electrons and holes respectively. The conductance minimum of the SGT was 3 V more than the bulk graphene, this could be a result of local doping from edge defects in the channel [52, 90, 91]. Over the narrow range of voltage tested the on/off ratio using the backgate was 2.33. The measurements were made at room temperature using a 4-point measurement setup so that contact resistances could be ignored.
Figure 78: shows the resistance of a SGT as the side gate voltage is swept up and down two times. The arrows indicate the direction of the sweep.

Figure 78 shows the resistance of a SGT as the side gate voltage is swept up and down two times. The data demonstrates a very modest on/off ratio of ~2.5. The arrows indicate the direction of the sweep. It was clear there was a lot of hysteresis while measuring these devices with the side-gate.

The SGT demonstrated here would not serve well in typical digital logic applications, it’s on/off ratio was far too small. However, it could still be used in analogue electronics. For example, it might be used as a modulator in telecommunications applications. When considering the operation of the SSD in relation to the SGT it was clear that the SSD was never going to be efficient since graphene has no bandgap. In fact, since the SSD only had an on/off ratio of 7% the relative voltage between the gate and the channel could not have been very high.
7. Conclusions and Future Work

This work has looked at the possibility of harnessing graphene’s unique electrical properties for high frequency applications. One such application was the BR that demonstrated a responsivity of 23,000 V/W and an NEP of 0.64 pW/Hz$^{1/2}$ at room temperature; comparable to superconducting bolometers at cryogenic temperatures. By taking measurements at cryogenic temperatures we were able to better understand the nature of operation of the BR, even observing lateral confinement modes through the narrow regions of graphene. A graphene TBR was measured to have a peak responsivity of 2,400 V/W; although this was not as high as the BR, this quality factor matches or betters other rectifiers that have the potential to operate at THz frequencies [26, 31, 32]. A double layer BR was fabricated to demonstrate a potential solution to the problem of matching the devices to an antenna. This acted to increase the conductivity of the medium lowering the resistance of the device considerably. This same device demonstrated that the geometry could be changed to decrease the resistance of the device but this would come at the cost of responsivity. A series of devices with similar geometry but different mobilities were compared to highlight the clear positive correlation between mean free path and device sensitivity. A graphene BR was tested up to 220 GHz and showed no signs of a cut-off frequency. By combining the BR with an antenna a rectenna could be produced that might be a disruptive technology with a wide range of applications in science, imaging, energy harvesting, heat management, wireless energy transport, and communications. By combining a graphene BR with a graphene antenna one might envisage a transparent sensor for using mobile phones or automotive transport.

The BR devices presented here compare well with previous examples in the literature measured at room temperature. One such rectifier that might be used instead of the BR is the Schottky diode, a good example of one of these diodes was fabricated by Ito et al.[92], they achieved a sensitivity of 1460 V/W at 350 GHz with a matching circuit. The metal-insulator-semiconductor (MIS) diode could also be used at the rectifying element in a rectenna; to the best of the author’s knowledge the state-of-the-art for this area is 7,800 V/W derived from DC measurements [93]. Similarly, the metal-insulator-metal (MIM) diode has shown a great deal of promise for such applications. Gadalla et al. fabricated an Au/CuO/Cu diode with responsivity 2000 V/W measured from DC IV characteristics [94], although the sensitivity of this example was lower than other devices it
had a bias resistance of 500 $\Omega$ allowing it to be matched easily to an antenna. However, all these layered devices are fundamentally capacitive limiting their cut-off frequency, there are very few examples of Schottky diodes or the various types of tunnelling diodes with a cut-off frequency above 1 THz. One of the fastest rectifiers demonstrated was a planar graphene geometric diode [95]; demonstrated to operate up to 10 THz with a responsivity of 21.3 V/W.

A new etch procedure was tested and optimised to allow for a new generation of contacts to be fabricated. These contacts were characterised using various imaging techniques to better understand their excellent electrical properties. A clean interphase between the conductive metal and graphene edge allowed them to demonstrate a considerable improvement on traditional contacts and a marked improvement on other 1D contacts. This is important for all devices because contacts are a major source of power loss in high frequency devices. These contacts were particularly important for the devices presented here because they required reliably ohmic contacts to demonstrate their non-ohmic behaviour.

The potential of graphene as the conductive channel in an SSD was investigated. This architecture demonstrated a modest peak responsivity of 690 V/W, a result of graphene’s missing bandgap. A side-gated transistor with a modest on/off ratio of $\sim 2.33$ was also fabricated in order to better understand the limited capabilities of the graphene self-switching diode.

Although I was able to fabricate some BR devices attached to antennas, I did not manage to measure any of them due to issues with static discharge. Future work within this project would be to fabricate similar devices but with small leakage diodes to stop electrostatic damage. Such devices could be tested up to very high frequencies using a blackbody radiator; this could in principle discover the operational limit of the BR. It would also be interesting to look at how the geometry of the devices alters their electrical performance. A future student might also develop these same devices for use on a larger scale by making the same devices from CVD. This would of course require the improvement of mobility through the testing of different substrates for CVD graphene. Another potential extension to this project might be to use different 2D crystals with a bandgap (such as MoS$_2$ or black phosphorous) to fabricate SSDs. Such crystals might demonstrate good performance while still taking advantage of their 2D nature for simple fabrication and low capacitance.
References

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**Publications**

**Submitted**


2015


2014


2013


Conferences

Graphene Week 2015 presenting a poster and a talk at the business partners satellite symposium

Graphene NOWNANO DTC Summer School 2015 presenting a poster

CAPS15 gave a presentation and assisted in organisation (invited speakers)

ISCNN 2014 giving 2 talks:

- Graphene Based Ballistic Nanostructures for Rectification
- 20 MHz Operation of Organic Nano-Diodes
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