Platform for Graphene Sensors Using Printed Circuit Boards and Single Board Computers

by

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Abstract

A platform was designed to allow electrical measurements to be taken from graphene sensors without the need for a probing bench or other lab equipment. Research began with the characterization of a range of different sensors, including various types of graphene field-effect transistors (GFET), interdigitated electrodes (IDE), and Hall sensors. Out of all the dropcast FETs that were tested, 23.6% were within a 20% margin of the expected resistance. Testing for Hall sensors involved measuring resistivity and hall coefficient on a set of two bars that were perpendicular to the direction of the current. 9 out of the 64 hall sensors tested had resistivity and hall coefficients that were within 10% of each other on each bar. A selection of sensors, namely the hall, dropcast GFET (or "droplet"), and infrared sensors then had circuit boards designed to house them. The PCBs were designed to be connected to the GPIO of a Raspberry Pi, which could then supply voltage and read measurements using a MATLAB script. The hall and droplet sensors had two variants designed for them, one with fewer components to be used in conjunction with an ADC expansion board for the Raspberry Pi, and a more complex board with an on-board ADC. ADC variants for the boards were simulated in LTspice, while testing of the platform was done with a Graphenea S20 GFET chip mounted on one of the IR boards and included a breadboard and resistor to create a voltage divider. After initial calibration, resistance measurements from the Raspberry pi were accurate within 1% to those taken with a semiconductor parameter analyzer.
A method was developed to successfully refresh the graphene with acetone without damaging the PCB, raising the resistance of the GFETs by 701Ω on average. Results from using wax encapsulation to slow or stop resistance drift are inconclusive, the chip with wax had average resistance that shifted $-40.1\Omega$ to $+25.5\Omega$ per day, while the resistance drift on the chip without wax was $-75.4\Omega$ to $+52.2\Omega$ per day.
Acknowledgements

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I would like to thank Brian Kennedy for supplying the graphene sensors used in this project, as well as funding for the research. Wenyu Zhou for designing most of the sensors used in this research and providing the information needed to test them and integrate them with the larger system. As well as Daniel Christakos for assistance in verifying the hardware and software.

Waqar Ahmad and Otto Benedeczky for helping me learn how to use Altium Designer and giving tips on reducing board costs. Nagui Mikhail for getting me set up in the lab at Carleton, and supplying me with the equipment I needed for sensor characterization. Robert Vandusen for helping to develop and perform the acetone wash and wax encapsulation/removal.

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Chapter 1

Introduction

1.1 Motivation

In recent years there has been a growing amount of research done on graphene-based sensors. Graphene can offer a range of benefits compared to other types of transducers, such as silicon or carbon nanotubes, due to its high surface-to-volume ratio which allows for easy conjugation with biomolecules such as enzymes and receptors. This leads to a low detection limit for the concentration of target molecules. Furthermore, graphene’s high electron transfer rates allow for high sensitivity biosensing [1]. Potential uses for graphene sensors include biosensing[2], optical sensing[3], gas detection[4], and heavy metals[5]. The most common form of graphene sensors, and the ones used in this thesis, feature a flat graphene structure on a silicon substrate with metal contacts.

Production and use of graphene sensors are not without their challenges, graphene production is immature, and new advancements are being made in the field with each passing year. Process variations can cause a large amount of variance in resistance from graphene-metal contacts[6]. The most common technique used for
creating graphene is chemical vapour deposition (CVD) which can create grain boundaries and regions with varying thickness [7], leading to a difference in resistance and performance between sensors. There is also the issue of doping from environmental sources, mainly water, causing a drift in graphene resistance over time [8].

If a customer receives a silicon die with a graphene sensor, it can only be used to take measurements with a probing bench and other expensive lab equipment. For an end-user to have an operable product out of the box, there needs to be a support platform for the sensor. A platform for graphene sensors would need to house the sensor itself while still allowing access to the sensing area, along with a method of supplying voltage to the sensor, and a means of reading electrical measurements. The platform would require components that are used specifically for certain types of sensors while others could be universal, able to be used with a variety of sensor structures.

1.2 Proposed solution

While there has been research done on printing graphene sensors directly onto PCBs [9], this thesis will focus on combining pre-existing graphene on silicon chips with a larger platform. The graphene chips can be attached via epoxy to printed circuit boards, and gold bond wires will be used to connect the terminals of the sensors to exposed metal pads on the boards. On-board circuitry can be used to process the signal from the sensor, including analog to digital conversion that can
be done either on-board or off-board. Digital signals can then be read by a raspberry pi, and software can be used to calculate resistance, Hall coefficient, and other factors.

Encapsulation of the die while attached to a board is proposed as a solution to resistance drift in graphene samples. Wax can be poured on top of the chip after it is attached to the board, and heated acetone can be used to remove the wax once the sensor is ready to use.

1.3 Methodology

The first step of the solution was to test a variety of graphene sensors. A probing bench was used to take electrical measurements of resistance, transfer length, and hall mobility. Out of all the sensors that were tested, the Hall and Droplet sensors were chosen for further use.

A system for taking electrical measurements without the use of a probing bench was developed using PCBs paired with a Raspberry Pi. Variants of the circuit boards were designed for different scenarios and each sensor type. Simple boards meant to be used in conjunction with an analog to digital converter expansion were designed. These feature only the graphene sensor, headers, and a multiplexer is the number of sensor outputs exceeded the number of AD board inputs. Alternately, more complex boards meant to be used directly with a GPIO interface were created. These boards featured the same components as the basic boards but added current detection, amplification, digital to analog converters, and analog to
digital converters. Software used with this setup, created in MATLAB, allows for electrical readings to be taken from the sensors and control over bias voltage.

Testing to verify the functionality of the PCBs was done via simulation, alongside a comparison between resistance measurements from the Raspberry Pi setup and lab equipment. Testing was also done over time to track the change in graphene resistance, and methods were developed to refresh graphene chips without removing them from the boards. There was also an experiment in the use of wax to encapsulate the sensing area of the board to avoid graphene resistance drift. While there have been successful attempts at encapsulating graphene using Novec 1700 and PVP [10], paraffin wax may prove to be a low cost and easily removed substitute.

1.4 Contributions

Over the course of this thesis project, there were several contributions to the field of graphene-based sensors. Verification and testing were done on a range of new sensors from Kennedy Labs, and the results can be used to make improvements in the design and fabrication process.

A selection of sensors had a platform designed for them, utilizing a combination of printed circuit boards and a Raspberry Pi. The platform will allow for lower cost and user-friendly operation of the graphene sensors with or without lab equipment. Several versions and iterations of the boards were designed, with some containing more onboard components that eliminate the need for external
circuitry or analog to digital conversion. The software was written in MATLAB to operate the one of platforms, operating with the Graphenea S20 GFET chip.

A method for maintaining graphene chips while on the board was developed. A shallow pool of acetone was used to refresh chips while the board was suspended above, preventing it from being damaged. There were also experiments in the use of paraffin wax to encapsulate graphene chips while on-board, to protect the chip from damage and doping prior to use.

1.5 Thesis Organization

This thesis has been organized to explain the motivation behind the research, related theory, and provide a step-by-step overview of the testing and design work done.

Chapter 2 covers theoretical background and related work. There is a discussion on research done into the electrical properties of graphene, deposition techniques, and its use in biosensing applications. The chapter also covers hall sensors, biosensing FETs, graphene sheet resistance, and the transfer line method. There is then an overview of the graphene sensors that were used in this thesis.

Chapter 3 covers sensor testing. There is an explanation of the methodology used to test each type of sensor, and the equations used to extract the required device parameters from the measurements taken. There is an estimation of graphene resistance for most of the sensors using a theoretical model, followed by testing results binned in relation to the theoretical predictions.
Chapter 4 covers PCB design, moving from system diagrams to board schematics and layouts. There is also a discussion on the software that was written to operate the system.

Chapter 5 covers PCB testing. The first section shows LTspice simulations of the more complex boards, while also delving into a current sensing error that was discovered in the initial board design. There is then a comparison of test results between the raspberry pi system and a semiconductor parameter analyzer. There are also results from tests tracking resistance drift over time, as well as chip refreshes and encapsulation used to counteract the drift.

Chapter 6 is the conclusion, summarizing the work done and the results of the research. There is also a discussion on future work that can be pursued on this topic.

The Appendix contains the MATLAB code used for testing the circuit boards in chapter 5.
Chapter 2

Background and Related Work

2.1 Chapter Summary

This chapter gives a brief overview of graphene properties and deposition techniques, hall biosensors, biosensing FETs, sheet resistance, and the TLM method. It then goes on to discuss the different types of graphene sensors used in this thesis, their structure, and the type of readings that can be taken from them.

2.2 Graphene

Monolayer graphene can be created using a variety of techniques including micromechanical cleavage, liquid-phase exfoliation, thermal decomposition, and chemical vapour deposition (CVD). CVD allows for graphene layers with a large area [11] and was the method used to create the sensors tested in this thesis. CVD also has the advantage of growing the graphene directly on a silicon substrate as seen in figure 2.1. This helps avoid damage and expenses caused by transferring graphene films onto silicon using mechanical methods. There are some downsides
to CVD, low temperatures during deposition can leave holes in the layer, and the
growth process creates multilayer regions at the center and edges of graphene do-
mains [7]. Different CVD methods, such as atmospheric pressure (APCVD) and
plasma-enhanced (PECVD), can also affect sensor performance depending on the
application[12]. Graphene’s high conductivity along with its high surface area and
ability to bond with molecules used in biosensing make it an ideal material to cre-
ate a sensor from[11].

2.3 Hall Sensors

The hall effect creates a voltage across a conductive surface with a perpendicular
magnetic field, governed by the following equation [13]:

$$V_H = -\frac{RIH}{b}$$

(2.1)

Where b is the thickness of the conductor, I is current, H is the applied magnetic
field, and R is the hall constant of the conductor. Since there is a linear relationship
between magnetic field and Hall voltage, this effect can be used to measure the magnitude of magnetic fields using a setup like the one in figure 2.2. Hall-based biosensors work by bonding probe biomolecules to the surface of the hall device and introducing magnetic labels (usually ferromagnetic microbeads) which will bind to the target. The probe and target molecules will then bond to each other, effectively attaching the label to the sensor and creating a Hall voltage proportional to the concentration of target biomolecules [14].

Graphene hall sensors differ from standard metal ones in that they operate using a different version of the hall effect known as the quantum hall effect. The hall voltage is modelled by the following equation [15]:

\[ V_H = I \frac{h}{ve^2} \]  \hfill (2.2)

Where \( h \) is Plank’s constant and \( e \) is the electron charge. \( v \) is either an integer or fraction and is related to the magnetic flux through the graphene, and number of electrons in the area \( N \).

\[ v = \frac{N}{\Phi_0} \]  \hfill (2.3)

Where \( \Phi_0 = e/h \) is the magnetic flux quantum. Graphene hall sensors can also be used for label-free biosensing in certain applications such as DNA detection [16].
FIGURE 2.2: Setup for Measuring Hall Resistance, $V_X$ is used to determine resistivity while the hall voltage $V_Y$ is related to the magnetic field strength and hall coefficient[15]

2.4 Biosensing FETs

Biosensing FETs are structured similarly to a traditional MOSFET, with doping of a silicon substrate used to create the drain and source. Silicon dioxide is generally coupled with another material to create the gate [17] which is functionalized with the probe molecule. When the probe and target molecules bond, they alter the charge distribution on the gate, creating a gate voltage that alters the conductivity of the sensor. This type of sensor can be used in a broad range of biosensing applications, from proteins to full cells, and has the benefit of not requiring labels for the target molecules.

Graphene FETs feature a graphene channel on a silicon substrate, which may or may not have an insulating layer of silicon dioxide in between (see figure 2.3). Metal contacts create the source and drain regions and can be underneath or on
Chapter 2. Background and Related Work

top of the graphene channel [18] [17]. A top gate and dielectric may be added, or multiple contacts may be created along the length of a channel to create a four-point or transmission line structure. Probe molecules are bonded to the graphene channel[19], which creates a similar change in conductivity as seen in a standard BioFET. Graphene sports a number of benefits over silicon for biosensing applications including larger detection areas, ease of functionalization, and low electrical noise.

![Biosensing Graphene FET](image)

**Figure 2.3: Biosensing Graphene FET[19]**

### 2.5 Sheet Resistance

Sheet resistance is commonly used when discussing the impedance of materials used in ICs. Since monolayer graphene is a nearly flat material, it is useful to use sheet resistance in this case as well, particularly for GFET type sensors as they are resistance-based. Sheet resistance is presented in units of Ohms per square, where the square refers to a square unit of surface area. Total resistance can be calculated
from sheet resistance using the following equation [20]:

$$R = \frac{l}{w} R_S$$

(2.4)

Where \( l \) and \( w \) are the length and width of the material as seen in figure 2.4.

![Sheet Resistance Diagram](image)

**Figure 2.4: Sheet Resistance Diagram[20]**

### 2.6 Transmission Line Model

The transmission line model can be used to separate contact and sheet resistance for a conductive film. Figure 2.5 shows the typical TLM method. Contacts are placed along the channel at increasing intervals, with resistance measurements taken between each adjacent pair of contacts. This allows for a relationship to be found between channel length and resistance [21].

### 2.7 Overview of Graphene Sensors Tested

Testing was done on the following sensors to verify that the fabrication process at Kennedy Labs was producing usable graphene samples. While these sensors
were not selected to be used with PCBs due to time constraints and lower demand relative to other devices, the results from testing can be used to improve the design and fabrication process in the future.

### 2.7.1 Four Point

The four-point graphene FET, shown in figure 2.6, consists of a 60 by 10 micrometer graphene channel with four equally spaced contacts. The contacts are 5\( \mu m \) wide and 10\( \mu m \) apart. Resistance measurements can be taken using any combination of two points to vary the channel length or all four at once for greater accuracy. Using the full four contacts and reading the voltage across the middle two allows for the measurement of sheet resistance without contact resistance present.
2.7.2 Transmission Line

The transmission line FET, shown in figure 2.7, is another 60 by 10 micrometer graphene channel, with six contacts and variable spacing. The contacts are 5µm wide and spaced at 4, 6, 8, 10, and 12µm from each other. Like the four probe FET, pairs of contacts can be used to measure channel resistance at different lengths. The transfer length method can also be used to measure contact resistance [21].

2.7.3 IDE

The graphene inter-digited electrode (IDE), shown in figure 2.8, consists of two sets of fingers under a layer of graphene. Larger chips are ideal for liquid sensing, and using the devices in conjunction with a back gate allows for gas sensing. There are four types of IDE that were tested, with type A being the smallest and type D being the largest. IDE types and dimensions are listed in table 2.1.
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Figure 2.7: Graphene Transmission Line FET

<table>
<thead>
<tr>
<th>Type</th>
<th>Configuration</th>
<th>Fingers or Turns</th>
<th>Width(µm)</th>
<th>Row Length(µm) or Spiral GR size(mm)</th>
<th>Spacing(µm)</th>
</tr>
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<tr>
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<td>5/4/2/1</td>
<td>500</td>
<td>100</td>
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<tr>
<td>B</td>
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<td>9/11/13</td>
<td>5/4/2/1</td>
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<tr>
<td>C</td>
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<td>50</td>
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<td>250</td>
</tr>
<tr>
<td>D</td>
<td>Spiral</td>
<td>5.4</td>
<td>100</td>
<td>9x9</td>
<td>300</td>
</tr>
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Table 2.1: IDE Finger Dimensions

2.8 Overview of Graphene sensors Used with PCBs

The following sensors were chosen to be used with a PCB interface. The Droplet and Hall sensors were chosen from the lineup of devices from Kennedy Labs due to the broad range of possible applications, while the Graphenea chip was used to test the Raspberry Pi setup and software, due to supply issues with the Kennedy Labs sensors caused by the pandemic.
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2.8.1 Droplet

The four quadrant liquid sensor, or droplet sensor (see fig 2.9), features ten graphene pads per side in a square, with a space in the middle for dropping liquid samples. Each graphene pad has two contacts, operating as a basic GFET. On each side there are: two 100 x 100 µm pads, four 50 x 50 µm pads, two 25 x 25 µm pads, and two 10 x 10 µm pads. Each chip also includes four hall sensors, these are identical to the ones from the hall chip but have smaller metal pads.

2.8.2 Hall

The hall sensor, shown in figure 2.10, is a 1-2-2-1 hall bar of graphene with metal contacts on each terminal. The horizontal bar is 75µm across while the vertical bars are 50µm and spaced 25µm apart. The bars are all 10µm wide. In addition
to the resistance measurements that can be taken in a similar fashion to the GFET devices, the hall sensor can be used to detect magnetic fields using the hall voltage across the vertical bars.
2.8.3 Graphenea S-20

The Graphenea S-20 GFET chip, shown in figure 2.11, features 12 90µm by 90µm graphene pads that are separated into two rows of six. Each pad has a contact that is shared with the others in the row, and one contact that leads to a separate metal bonding pad. There is a metal gate electrode that runs in between the two rows of graphene that is used to apply a gate voltage to the chip. The spec sheet lists graphene resistance as varying from 1kΩ to 6kΩ depending on the gate voltage [22].

![Graphenea S-20](image)

**Figure 2.11:** Graphenea S-20 [22]

2.9 Conclusions

The high conductivity and chemical properties of monolayer graphene make it an ideal material to use in biosensing applications. Sheet resistance and other useful electrical properties can be analyzed through electrical measurements. The unique quantum hall effect present in graphene hall sensors allows for the detection of...
target molecules without the need for magnetic labels, while graphene BioFETs carry several benefits over those based on silicon. The graphene sensors used in this thesis are as follows:

- Four probe FET for sheet resistance measurements
- Transmission line FET for both sheet and contact resistance
- IDEs for large-area gas and liquid applications
- Droplet sensor featuring an array of basic GFETs
- Hall sensor for magnetic field detection
- S20 GFET featuring an array of basic GFETs along with a gate electrode for liquid gating
Chapter 3

Sensor Testing

3.1 Chapter Summary

This chapter reviews the testing methodology and results for each type of graphene sensor. The methodology section describes the equipment used, the test procedure, and the equations used to calculate resistance and other relevant properties from the initial voltage and current measurements. There is then a section containing theoretical predictions for test results based on ideal graphene sheet resistance. Next, is the results section, where calculated resistance/resistivity values are binned based on proximity to the theoretical predictions, and then discussed.

3.2 Methodology

Sensors were tested using a probing bench and HP4145B semiconductor parameter analyzer. For most sensors, a voltage sweep of 1 to 5 volts was performed while measuring the current to view the I-V curve of the device. Each device type had
different measurements taken, with the results binned to represent the quality of graphene in the sample.

### 3.2.1 Four Point

Voltage source of 5V was applied at terminal II while terminal III was grounded (see figure 2.6). Current was measured from terminal II while voltage was measured across terminals I and IV. Current and voltage measurements were then used to calculate the channel resistivity [23].

\[
\rho = \frac{V_{I-IV}}{I_{II}} \frac{d}{s} = \frac{V_{I-IV}}{I_{II}} \frac{\Omega}{\mu m} 
\]  

(3.1)

Where \( s = 10\mu m \) is the spacing between contacts and \( d=10\mu m \) is the channel width.

### 3.2.2 Transmission Line

For the transmission line FET, the source and sink were placed at pairs of adjacent terminals (see fig. 2.7), for a total of 5 pairs per device. The source was swept from 0-5V to create an IV curve, which had it’s slope taken by the semiconductor analyzer to measure resistance. Each resistance along with its respective channel length were fitted to a linear function \( f \). The function is then used to calculate transfer length, sheet resistance, and contact resistance [21].

\[
R_S = \frac{df}{dx} W 
\]  

(3.2)

\[
R_C = \frac{f(L = 0)}{2} 
\]  

(3.3)
3.2.3 IDE & Droplet

For both the IDE and Droplet chips Voltage sweeps from 0-5V were performed while measuring current, using the SPA to record the resistance slope of the I-V curve.

3.2.4 Hall

For the Hall sensor, the current was applied at terminal III (see fig. 2.10) while terminal IV was grounded. The remaining pads were probed to read voltage. Two different tests were run on each sensor, the first to measure resistivity, while the second measures the hall coefficient by introducing a magnetic field perpendicular to the sensor.

For the resistivity test, current is swept from negative to positive 40µA. At both ends of the sweep, the voltage across terminals I-II and V-VI are measured and used to calculate resistivity[24].

\[
\rho_A = \frac{V_{I-II}^- - V_{I-II}^+}{I^+ - I^-} \frac{wt}{a} = \frac{V_{I-II}^+ - V_{I-II}^-}{2|I|} \frac{wt}{a}
\]

(3.5)

\[
\rho_B = \frac{V_{V-VI}^- - V_{V-VI}^+}{I^+ - I^-} \frac{wt}{a}
\]

(3.6)

Where the + and - superscripts refer to the values with positive and negative current. \(w = 1e - 3\) cm is the width of the horizontal bar, \(t = 3.5e - 8\) cm is the estimated thickness of the graphene, and \(a = 2.5e - 3\) cm is the distance between
the vertical bars. If the two resistivity values agree within 10% of each other, the average can be used. If they do not agree, the graphene in the device cannot function as a hall bar.

For the hall coefficient test, a flat magnet was placed underneath the chip, creating a magnetic field of $B=1900\text{G}$ on the surface of the chip as measured by a Hall probe. Negative and positive field polarity tests were done by removing the chip, flipping the magnet, and placing the chip back on top. Current was swept from positive to negative $400\mu\text{A}$, a ten times increase in magnitude relative to the first test. This is due to voltage measurements being taken across $I-V$ and $II-VI$, which were too small to read at the lower current. The hall coefficient can then be calculated as:

$$R_{HA} = 10^8 \frac{t}{B} \frac{V_{I-V}(+B) - V_{I-V}(-B) + V_{I-V}(+B) - V_{I-V}(-B)}{I^+(+B) - I^-(+B) + I^-(+B) - I^+(+B)}$$

$$= 10^8 \frac{t}{B} \frac{V_{I-V}(+B) - V_{I-V}(-B) + V_{I-V}(-B) - V_{I-V}(-B)}{4|I|}$$

$$R_{HA} = 10^8 \frac{t}{B} \frac{V_{II-VI}(+B) + V_{II-VI}(-B) + V_{II-VI}(+B) - V_{II-VI}(-B)}{4|I|}$$

(3.7)

Where $(\pm B)$ denotes the value of voltage or current at a positive or negative field. Like the resistivity test, both coefficients must agree within 10% for the device to be usable. The average hall coefficient and resistivity can be used to calculate the Hall mobility.

$$\mu_H = \frac{|R_{Hav}|}{\rho_{av}}$$

(3.8)
3.3 Theoretical Model of Graphene Resistance

Using the contact resistance of $670 \ \Omega/\square$ and sheet resistance of $1870 \ \Omega/\square$ the resistance and resistivity of the devices being tested can be predicted [25].

3.3.1 Four Point

With the four-probe method only measuring sheet resistance, the measured value should be equal to $1870 \ \Omega/\square$.

3.3.2 Transmission Line

Sheet and contact resistance should be equal to $1870 \ \Omega/\square$ and $670 \ \Omega/\square$ respectively, using those values with equation 3.4 the transfer length should be $L_T = 3.58 \mu m$.

3.3.3 IDE

The structure of the IDE essentially creates a network of parallel resistors which is difficult to model analytically [26]. Simulations of graphene IDEs are possible using COMSOL [27], however, simulations for graphene devices are out of the scope of this thesis, as the focus is on design and simulation of the interface.

3.3.4 Droplet

The graphene pads on the droplet sensor are all square, giving a sheet resistance of $1870 \Omega$. The metal contacts all have a length of $5 \mu m$, but width varies with the
pad width, therefore:

\[ R = 1870 + 670 \times 5 \times 10^{-6} \times W \]  \hspace{1cm} (3.9)

<table>
<thead>
<tr>
<th>Size(µm)</th>
<th>R(Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2510</td>
</tr>
<tr>
<td>20</td>
<td>2175</td>
</tr>
<tr>
<td>50</td>
<td>1974</td>
</tr>
<tr>
<td>100</td>
<td>1907</td>
</tr>
</tbody>
</table>

Table 3.1: Estimates for Droplet Pad Resistance

3.3.5 Hall

The current in the hall sensor flows through the horizontal bar, with a 75x10µm graphene channel and two 5x10µm contacts. The resistance should therefore be 14.7kΩ

3.4 Results

3.4.1 Four Point

One full chip with 64 four point FETs was tested. Figure 3.1 shows a linear relationship between voltage and current when the graphene is not damaged. Figure 3.2 shows the current response of a device with an improperly formed graphene layer, which burnt out after the voltage reached 0.8V. Binning the testing results in groups of 40% relative to the expected value in figure 3.3, we see an uneven distribution. 30% of the FETs that were probed either had
Chapter 3. Sensor Testing

Figure 3.1: Four probe FET IV curve

Figure 3.2: Damaged four probe FET IV curve
Figure 3.3: Four probe FET Resistivity

no graphene or the graphene was too damaged to conduct current. Only 14% were within 20% of the expected value, while 27% were below that range, most likely due to the unintentional formation of multilayer islands in the production process, as multilayer graphene has a lower sheet resistance than monolayer graphene [28]. 30% were above 120% of the expected value, which can be attributed to breaks and holes in the graphene. The samples that had a lower resistivity than expected had the majority of their results closer to the expected value (within 60%), while the majority of the samples that had a higher sheet resistance were farther away.

3.4.2 Transmission Line

Figure 3.4 shows a graph of resistance versus channel length for the transmission line FETs with each line representing a separate device. While the relationship between resistance and channel length should be linear, there are huge amounts
of variance from one device to another, with shorter channels sometimes having higher resistance values than longer channels. Due to this inconsistency, testing was cut short after 29 devices, due to the likelihood that none of these devices will be usable as intended. MATLAB’s `polyfit` and `polyval` functions were used to fit linear functions to the results and calculate error. Figure 3.5 shows the large error in the fitted functions (only five are shown for ease of viewing) due to the inconsistency of the original results.

**FIGURE 3.4: Transmission Line Resistance**

Results for sheet resistance calculations (fig. 3.6) appear similar to those in the four-probe FET, with 24% of the FETs that were probed having no graphene. 21% were within 20% of the expected value, while 24% were below that range, and 31% were above that range. Like in the previous test, the samples that had a lower resistivity than expected had the majority of their results closer to the expected value (within 60%), while the majority of the samples that had a higher sheet resistance were farther away. Whether this is an accurate representation of these devices’ sheet resistance or merely a fluke of the fitting algorithm is unknown.
In figure 3.7, it can be seen that the plurality of contact resistance calculations yielded negative resistance values. While this is not physically possible, the appearance of negative contact resistance can occur due to unintentional doping of the graphene channel from the contacts [29]. This points to the contacts as being
the likely culprit behind the nonlinearity of resistance measurements. The transfer length calculations in figure 3.8 are similarly affected, due to the value being dependant on the contact resistance.

![Transmission Line Contact Resistance](image)

**Figure 3.7:** Transmission Line Contact Resistance

### 3.4.3 IDE

One full chip of 48 type A IDEs were tested. Figure 3.9 shows that the entire chip had functional graphene and produced usable results, with the majority of IDEs having a resistance of 20Ω to 30Ω.

No resistance measurements were able to be taken on the type B IDEs, this may have been from poor graphene quality on the chips, or because the pads on this type were very small and the probes were not connecting properly. Two containers of type C and D IDEs were tested, the chips in the first container all had no graphene, while the second container had six functional chips of each type. The
results for those tests will be displayed in a table, due to the small sample size. There is a great deal of overlap in the resistance values between these two types, and while type C tends to have lower resistance in these tests it may only appear that way due to the small sample size.
### Table 3.2: Resistance Measurements for Type C and D IDEs

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Type C R(Ω)</th>
<th>Type D R(Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50.7</td>
<td>50.8</td>
</tr>
<tr>
<td>2</td>
<td>60.8</td>
<td>67.2</td>
</tr>
<tr>
<td>3</td>
<td>53.8</td>
<td>88.9</td>
</tr>
<tr>
<td>4</td>
<td>53.9</td>
<td>58.4</td>
</tr>
<tr>
<td>5</td>
<td>61.2</td>
<td>57.9</td>
</tr>
<tr>
<td>6</td>
<td>86.2</td>
<td>138</td>
</tr>
</tbody>
</table>

3.4.4 Droplet

Testing results for the droplet sensors (fig. 3.10,3.11,3.12,3.13) show a majority of the smaller pads are nonfunctional. In all cases, most of the results are not within 20% of the expected values. The reasons for measured resistance being lower or higher than expected are the same as the four-probe FET; missing or damaged areas of graphene for higher resistance values, and multilayer islands for lower
Chapter 3. Sensor Testing

resistance values. Positive results that are out of the 20% range tend to be higher,

![Figure 3.11: Droplet 50µm Resistance](image)

except for the 100µm pads. The 50µm pads seem to have the best results, with

![Figure 3.12: Droplet 20µm Resistance](image)
the highest percentage of conductive pads and the most results within 20% of the expected value. It should be noted that the 50µm pads have a larger sample size, with twice the amount of pads per chip.

![10µm x 10µm Resistivity measurements on two chips (16 pads) chart]

**Figure 3.13: Droplet 10µm Resistance**

### 3.4.5 Hall

For the non-magnetic test, a full chip of 64 Hall sensors was tested. Equation 3.6 was used with the voltage measurements from testing to calculate hall resistivities for each device. The majority of sensors had functional graphene, with most of those also having resistivity measurements that agreed within 10%, passing the test as seen in figure 3.14. The next test was only performed on the 29 sensors that passed the first test. Figure 3.15 shows the majority of samples failed the magnetic test, with 10% no longer being able to conduct current while being tested, likely due to being damaged in the testing process. Out of an original sample size of 64,
only 9 sensors passed both tests and therefore are usable as hall sensors. Resistance measurements were taken across terminals III and IV on the usable sensors to find the lowest value, 4.56 kΩ, which will be used to represent the resistance of the sensor when designing the interface board.

**Figure 3.14: Hall Resistivity Test**

**Figure 3.15: Hall Coefficient Test**
3.5 Conclusions

Graphene sheet resistance was predicted to be $1870\,\Omega/\square$, while contact resistance should be $670\,\Omega/\square$. For the four point FETs, 14% of the sensors tested were in the range of $1496 - 2244\,\Omega/\square$, while 21% of the transmission line FETs tested had a sheet resistance within that range. Only 7% of TLM FETs tested were within 20% of the expected contact resistance.

The expected resistance values for the droplet pads are $2510\,\Omega$, $2175\,\Omega$, $1974\,\Omega$, and $1907\,\Omega$ for the 10, 20, 50, and 100 micrometer pads respectively. The portion of devices tested that fall within 20% of the expected resistance are 12% for $10\,\mu m$, 19% for $20\,\mu m$, 34% for $50\,\mu m$, and 19% for $100\,\mu m$.

Graphene resistance was fairly inconsistent across all devices, likely due to the age of the samples that were tested. In most cases, 20 – 30% of the samples did not conduct electricity, and less than a third had resistance values within 20% of what was expected. For the hall sensor, only 9 out of 64 samples passed both tests for usability as hall sensors, having resistivity and hall coefficients for each pair of arms that are within 10% of each other.
Chapter 4

Interface Design

4.1 Chapter Summary

This chapter contains system-level diagrams and descriptions of interfaces that were designed to take readings from the droplet and hall sensors. There is then an overview of the design of circuit boards used in the interface, including schematics and layouts for variants. Finally, there is a discussion on the software used to drive the boards.

4.2 System Outline

The hall and droplet sensors were chosen for the interface, as they were deemed to have the most potential use cases. The interface for the graphene sensors is a PCB that the sensor is attached to using epoxy and gold bond wires. The PCB is then connected to a raspberry pi to allow readings to be taken from the sensor without the need for a probing bench or lab equipment. Two types of boards were designed for each sensor, one with the minimum amount of components required
for readings to be taken with an off-board ADC such as the waveshare AD expansion board [30] for the raspberry pi, and another with an on-board ADC that can connect directly to the raspberry pi’s GPIO.

### 4.2.1 Droplet

The droplet chip will be diced into quarters before being attached to a board, and each will have a full side of 10 pads. Since the waveshare board only has 8 inputs and there are 10 pads, a multiplexer is needed as seen in figure 4.1. Either a single 16 input MUX or three four input MUXs can be used, and an analog multiplexer will need to be used to allow current to flow from the pad through the multiplexer. The 5V or 3.3V supply pin on the raspberry pi can be connected to all pads at once since the multiplexer will only allow current to flow through one at a time. I/O from the board can be done with male headers, which are connected to the pi by jumper cables.

The original concept for the ADC variant of the droplet board as seen in figure 4.2 included the same components as the non-ADC version, with a few additions. A hall-based current sensor is placed at the output of the MUX to detect the current flowing through the pad. The output of the sensor is then amplified with a non-inverting op-amp and passed into the ADC, which is then connected to the output. Based on the minimum recorded resistance from testing, the max current in the system will be roughly 5.6mA. Using a 45mV/A current detector, the amplification needed to bring this max value to the ADC’s supply voltage of 3.3V is 82.3dB. A 24-Bit ADC was used to match the resolution of the waveshare board, while the sampling rate is unimportant as the analog system operates at DC.
Figure 4.1: Basic Droplet Concept

Figure 4.2: ADC Droplet Concept
4.2.2 Hall

The basic hall board (fig. 4.3) is simply the hall sensor and some headers. No multiplexer is needed as there are enough inputs on the waveshare board to accommodate the three outputs, one current reading and two differential voltage readings.

For the ADC variant shown in figure 4.4, the same current detector as the droplet board will be connected to terminal IV and will need a 95.5dB amplifier to utilize the full range of the ADC. Variable gain amplifiers can be used with the hall voltage outputs from the chip to detect a wider range of magnetic fields. The VGAs will be voltage controlled by an 8-bit DAC. Since the hall voltages are differential, the VGA must have a differential input or a separate differential amplifier must be used before the variable amplifiers. A 24 bit ADC will be used and must have at least three inputs. As seen in figure 4.4 the ADC and DAC were originally going to use an SPI and I2C interface respectively, but it was later decided both
would use SPI, as the raspberry pi’s SPI channel can support up to three devices in parallel.

4.3 Resistance Measurement Methods

4.3.1 Voltage Divider

Resistance of GFETs on PCBs can be read using a voltage divider, which is done by placing a resistor with a known value in series with the graphene and ground. The resistor can either be on the PCB for the ADC variant or on a breadboard. The voltage between the resistor and graphene can be read and used to calculate the resistance of the GFET.

\[
R_1 = \left( \frac{V_{in}}{V_{out}} - 1 \right) \times R_2
\]  

(4.1)
Where $R_1$ is the resistance of the GFET, $R_2$ is the resistance of the series resistor, $V_{in}$ is the voltage across the whole voltage divider and $V_{out}$ is the voltage across $R_2$.

### 4.3.2 Transimpedance Amplifier

A transimpedance amplifier is created by placing a resistor between the negative input and output terminals of an op-amp while grounding the positive input terminal. The voltage at the output of the op-amp will be related to the current flowing through the resistor according to the following equation\[31\]:

$$-I = \frac{V_{out}}{R}$$  \hspace{1cm} (4.2)

When reading the output voltage with an ADC, this creates a response to changes in current that is more linear than the voltage divider, at the cost of a more complex circuit. The current, calculated from the read voltage, can then be used to calculate GFET resistance.

### 4.4 PCB Design

Circuit board design was done using Altium designer for both the schematic and layout. All components in the design were sourced from Digikey. Alterations were made from the initial concepts, with a DAC added to the ADC variants to supply a bias voltage to the sensors. Current detection was changed from a current sensor with a non-inverting op-amp to a current mirror with a transimpedance amplifier in order to reduce the board size.
4.4.1 Droplet

The basic droplet schematic (fig. 4.5) closely follows the original concept. There are three 3 pin headers for sensor supply voltage, bias voltage, and multiplexer output. All three pins in each header are shorted to each other to allow for the signal to be read by a raspberry pi and lab equipment simultaneously. A 7 pin header then supplies the other signals needed for the multiplexer: the source, ground, clear, and four-bit input selection. The layout uses two internal planes for ground and supply voltages, with the supply voltage plane split into 3.3V and 5V sections. An image of the fabricated board can be seen in figure 4.6.

![Figure 4.5: Basic Droplet Schematic](image)

The ADC variant keeps the three-pin headers in case the current sensing and conversion components on the board need to be bypassed. Multiplexer output
is passed through the reference end of an NPN BJT current mirror, with the mirror side pulling current through the transimpedance amplifier. Using the minimum resistance from testing results, a 5V supply voltage, and the current mirror’s threshold voltage of 0.7V, the max current flowing through the mirror should be about 4.8mA. Using the equation for transimpedance amplifier voltage to aim for a voltage of 3.15V at that current (to leave some space for potentially lower resistance) the resistance needed is 652.7Ω. A 649Ω resistor was chosen, as it is the closest to the calculated value available on Digikey. The ADC and DAC feature pairs of 1µF and 10µF coupling capacitors for their supply voltages, and share an SPI bus as can be seen in the schematic (fig. 4.7). A 20 pin header then handles the I/O for the SPI components, MUX, supply voltages, and grounds. The supply voltage plane is further split to allow a separate digital 3.3V source to be supplied to the ADC. The fabricated board can be seen in figure 4.8.
A revision of the ADC board (fig. 4.9) removes the current mirror, and reconfigures the amplifier to have a non inverting input. A 0.2Ω current sense resistor is used to create a voltage divider with the pad, while 1Ω and 1.6kΩ resistors
are used to amplify the voltage divider output by 1600V/V.

**Figure 4.9: Voltage Divider ADC Droplet Schematic**
4.4.2 Hall

The basic hall board has seven 3 pin headers for each terminal on the hall sensor. The schematic can be seen in figure 4.10 while figure 4.11 contains an image of the fabricated board.

**Figure 4.10: Basic Hall Schematic**
The ADC variant adds a pair of 12.5mV/dB variable gain amplifiers, which output the amplified signal as a differential voltage biased at 1.5V. The schematic in figure 4.12 shows the current detector and non-inverting op-amp have been replaced with a current mirror and transimpedance amplifier. With the minimum resistance found during testing, the maximum current will be 1.1mA so a 3kΩ resistor is used with the transimpedance amp. There are two DACs, one for bias voltage on the hall sensor, and one for the VGA gain voltage. The ADC that is used has four inputs to accommodate the two VGAs and TIA, with the fourth channel grounded. A 14 pin header handles the sources, grounds, and SPI signals. The fabricated board is visible in figure 4.13.
Similar to the droplet board, a revision was made to the hall board using the same current sense resistor and non-inverting amplifier setup as seen in figure 4.14. A 0.2Ω current sense resistor is used to create a voltage divider with the hall bar,
while $1\Omega$ and $6.04k\Omega$ resistors are used to amplify the voltage divider output by $6040V/V$.

![Voltage Divider ADC Hall Schematic](image)

**Figure 4.14: Voltage Divider ADC Hall Schematic**

### 4.4.3 Infrared Boards

Another set of boards was designed to accommodate infrared sensors from Kennedy Labs. The sensors come in four sizes and all have three terminals, a source, sink, and bias. Two boards were designed, one to fit 24 of the smallest sensors (fig. 4.15 and 4.16), and the other to fit 12 of the other sizes in any combination (fig. 4.17). The boards are both 1" by 1.2", and feature headers and wire bonding pads to create a common bias and source for all attached chips while leaving an individual sink connection for each. Since the boards feature bond pads that are evenly
Chapter 4. Interface Design

spaced throughout, they were also used for other sensors such as the GFET-S20 from Graphenea 4.18.

Figure 4.15: Small IR Schematic

Figure 4.16: Mixed IR Board
4.5 Software

MATLAB’s raspberry pi support package is used to read and write to the boards, with both the onboard ADC and the Waveshare board using the SPI channel. Code
developed by Austin Gosling [32] for waveshare board characterization was modified to take multiple voltage readings from the ADC, average the results, and perform resistance calculations. MATLAB Coder was then used to convert the MATLAB script into an executable that can be run on a raspberry pi without a connection to a PC running MATLAB.

4.6 Conclusions

PCBs were designed to interface the hall, droplet, and S20 graphene sensors to a Raspberry Pi with the Waveshare AD expansion. Variants for the hall and droplet with an onboard ADC were also designed to allow for taking measurements without the expansion board. There was also a redesign of the AD variants to address a current detection problem, which is discussed more in the following chapter. Finally, a MATLAB script was written to take measurements from the boards, as well as a standalone script that can run directly on the Raspberry Pi.
Chapter 5

Interface Testing

5.1 Chapter Summary

This section covers the simulation of the ADC boards using LTspice, including an investigation into the flawed current detection scheme of the initial design. There is then a description of the methodology used to test the IR board fitted with an S20 chip, including measurements of resistance drift, chip refresh, and wax encapsulation, followed by a discussion of the results.

5.2 Simulation

The simulation was done using LTspice, with the graphene chips modelled as variable resistors and voltage sources based on their characterization results and theoretical models. Models for other components were imported if available or approximated using models in the LTspice library. SPI functionality is not supported by LTspice, so instead, placeholder ADCs and DACs are used, with the digital input/output being represented by another analog signal.
5.2.1 Transimpedance Simulation

When board simulations began, it was discovered that the current detection method was not working. TIA output voltage was low, and the output of the CM did not mirror the input. Simulations of the isolated mirror and amplifier were done in an attempt to discover the source of the problem and fix the design error. The testbench schematic for the transimpedance amp can be seen in figure 5.1. The ideal operation of the transimpedance amp in these circuits is to have the current mirror acting as a current source, drawing current from the output to the negative input terminal. As seen in figure 5.2, the output voltage scales linearly with the current while the voltage at the negative input terminal stays at 0V. When adding a current mirror to the testbench (fig. 5.3), this causes the collector voltage on the output transistor to be lower than the bias voltage. As seen in figure 5.4, the output transistor is not able to turn on, and the TIA output voltage does not scale with the current mirror reference current. To fix this issue, the current sensing method has changed to a voltage divider scheme using a small resistor paired with a non-inverting op-amp. As seen in the next sections, this allows for functional current sensing while keeping the same board dimensions.

5.2.2 Droplet Board

The droplet board simulation schematic is shown in figure 5.5. The droplet sensor is modelled as a set of parallel resistors, with default values equal to the theoretical model in table 3.1. The analog multiplexer is modelled using a network of voltage-controlled switches with an on resistance of 22.5Ω. The spice model for
Chapter 5. Interface Testing

Figure 5.1: Transimpedance Amplifier Testbench

Figure 5.2: Transimpedance Voltage vs. Current

Figure 5.3: Current Mirror Testbench
the OPA189, the amplifier used in the board, was imported from the Texas Instruments website. A 16 bit ADC model from the LTspice library was used as a stand-in due to there being no spice model available for the ADC used on the board. Supply voltages and multiplexer selection signals were provided using basic voltage source models. Bypass capacitors were excluded from the simulation as there is no noise being modelled. A 0.2Ω resistor is used to create the voltage divider, with the non-inverting op-amp set up for a gain of 1600V/V using a 1.6kΩ and 1Ω resistor. The simulation was done by sweeping the resistance of one pad from 600 to 400 Ohms. One test was performed using the MUX to select the variable pad, while a second test was done selecting a fixed pad.
Figure 5.6 shows the voltage at the input and output of the ADC being almost identical. The curves showing output voltage and current through the pad have the same shape, which will allow the software to calculate pad current and therefore resistance from the output voltage. In figure 5.7 the current and ADC input voltage change slightly due to leakage from the MUX, but not enough to be registered by the ADC, as the output is constant.

5.2.3 Hall Board

The Hall board simulation schematic is shown in figure 5.8. The simulation for the hall board represents the hall sensor as a resistor and voltage source to model the current flowing through the device and hall voltage. Only one of the two sets of hall voltages and variable amps are included, as under ideal circumstances the hall
voltages and their respective outputs should be the same. A behavioural model was created for the variable gain amplifier, where the output voltage is generated by two behavioural voltage sources using the gain equation from the AD8338 datasheet [33]. The output is differential and biased around 1.5V, the max output voltage is 2.8V, and the gain stops scaling after the gain voltage is higher than 1.1V.

\[ V_O = V_I^{4(V_G-0.1)} \]  \hspace{1cm} (5.1)

Two 16-bit ADC models are used to represent the ADC on the board, while a 16-bit DAC from the LTspice library is used to represent the DAC. Like in the droplet board simulation, the OPA model is imported and a 0.2Ω resistor is used to create the voltage divider. 6kΩ and 1Ω resistors are used to set the gain of the op-amp. Three tests were run on the schematic, first, the current sensing was tested by sweeping the resistor value from 2000 to 6000 Ohms while measuring the current through the 0.2Ω resistor and comparing it to the input and output of the ADC. Figure 5.9 shows the current and output voltage following the same trend, like in the droplet simulation. The next test involved sweeping the hall voltage from 0.004V to 0.4V while keeping the gain voltage at 0.3V. The results in figure 5.10 show the ADC output in green and its inputs in blue and red, displaying a linear relationship between hall and output voltage with constant gain. The third test involved sweeping the gain voltage from 0 to 1.3V, with a constant hall voltage of 4.2mV. The results in figure 5.11 show an exponential increase in output with the differential amplifier hitting its maximum output around 0.8V.
Chapter 5. Interface Testing

**Figure 5.8**: Hall Board Testbench

**Figure 5.9**: Simulation Results Varying Resistance

**Figure 5.10**: Simulation Varying Hall Voltage
5.3 Methodology
Testing was done on the small IR board with a Graphenea S20 chip as seen in figure 5.12. Resistance measurements were taken using the semiconductor parameter analyzer, which was then used to calibrate the software for the raspberry pi measurements. Testing was focused on resistance of the channel alone without factoring in the bias voltage, this was because the full transfer curve of the S20 is visible in a bias sweep of 0-50V while the raspberry pi can only supply a maximum of 5V. The raspberry pi testing setup as seen in figure 5.13 uses the waveshare expansion board in conjunction with the PCB and a breadboard. The 5V supply from the pi is connected to a pad’s input, while the common sink terminal on the board is connected to the breadboard and AD0 via jumper wires. There is a 1kΩ resistor on the board between the row connected to the ADC and one that is connected to the ground. The resistance is then calculated using the following equation:

\[
R = \left( \frac{V_{CC}}{V_{AD}} - 1 \right) \times (R + r) = \left( \frac{5}{V_{AD}} - 1 \right) \times (1000 + 125) \tag{5.2}
\]

Where R is the value of the resistor used for the voltage divider and r is a calibration factor accounting for other sources of resistance in the setup, adjusting the readings to be more in line with those of the SPA. Testing was done on two boards, with the Raspberry Pi portion of the testing done in different locations. The first board was used to calibrate the software while the second was tested with a copy of the original setup and software. Testing using the SPA for both boards, and raspberry pi testing for board 1 were all done in June 2021, while raspberry pi testing for the second board was done in September 2021.

The chips were refreshed with acetone in October, and a few different methods were attempted. Normally, the chip is submerged in acetone overnight, this
method cannot be used in this case as the acetone can damage the board. First, a few drops of acetone were placed on the chip, but the acetone evaporated too quickly to complete the refresh. Second, a vial of acetone was placed upside down on the chip, but again evaporation occurred too quickly. Finally, a third method was used, which was successful:

1. A petri dish was filled with 2mm of acetone and the board was placed face down, with the soldered ends of the pins holding up the board.

2. The petri dish was refilled with acetone to keep it at 2mm over the course of 8 hours.

3. Board was removed from the petri dish and rinsed with IPA.


5. Placed in a vacuum oven at 60 deg C -20 to -25 inches/hg overnight.
Later the chips were encased in paraffin wax in an attempt to slow or stop changes in resistance. The wax was heated up using a heat gun before dropping onto and cooling on the chip. Later, the wax on one of the boards was removed using a heat gun again, heated acetone \((50 \circ C)\), and an IPA rinse, before being dried.

### 5.4 Results

<table>
<thead>
<tr>
<th>Pad#</th>
<th>(R_{SPA}(\Omega))</th>
<th>(R_{pi}(\Omega))</th>
<th>%Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>729</td>
<td>726.8979</td>
<td>0.2884</td>
</tr>
<tr>
<td>L2</td>
<td>698</td>
<td>693.6953</td>
<td>0.6167</td>
</tr>
<tr>
<td>L3</td>
<td>737</td>
<td>737.3987</td>
<td>0.0541</td>
</tr>
<tr>
<td>L4</td>
<td>703</td>
<td>698.5611</td>
<td>0.6314</td>
</tr>
<tr>
<td>L5</td>
<td>704</td>
<td>703.7088</td>
<td>0.0414</td>
</tr>
<tr>
<td>L6</td>
<td>727</td>
<td>727.8139</td>
<td>0.1120</td>
</tr>
<tr>
<td>R1</td>
<td>820</td>
<td>826.4855</td>
<td>0.7909</td>
</tr>
<tr>
<td>R2</td>
<td>756</td>
<td>758.8528</td>
<td>0.3774</td>
</tr>
<tr>
<td>R3</td>
<td>685</td>
<td>683.1139</td>
<td>0.2753</td>
</tr>
<tr>
<td>R4</td>
<td>721</td>
<td>723.4208</td>
<td>0.3358</td>
</tr>
<tr>
<td>R5</td>
<td>731</td>
<td>734.7256</td>
<td>0.5097</td>
</tr>
<tr>
<td>R6</td>
<td>682</td>
<td>682.5145</td>
<td>0.0754</td>
</tr>
</tbody>
</table>

*Table 5.1: Graphenea S20 Calibration Results*

Results from the SPA show resistance values that are generally lower than those from the datasheet [22], with only the left side of the second board having pads with a resistance of over 1\(k\Omega\). There is more deviation from the SPA results in the second round of testing than the first, with resistance values lower than expected. The difference in results is likely due to the time gap between when the calibration and testing of both boards were done, with pad resistance decreasing over time.
### Table 5.2: Test Results Before Refresh

<table>
<thead>
<tr>
<th>Pad#</th>
<th>$R_{SPA}(\Omega)$</th>
<th>$R_{pi}(\Omega)$</th>
<th>%Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1L1</td>
<td>729</td>
<td>672.0155</td>
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</tr>
<tr>
<td>1L2</td>
<td>698</td>
<td>652.3871</td>
<td>6.53480007517522</td>
</tr>
<tr>
<td>1L3</td>
<td>737</td>
<td>694.2015</td>
<td>5.807127576923345</td>
</tr>
<tr>
<td>1L4</td>
<td>703</td>
<td>670.6661</td>
<td>4.599415657286196</td>
</tr>
<tr>
<td>1L5</td>
<td>704</td>
<td>657.7273</td>
<td>6.572823725762931</td>
</tr>
<tr>
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<td>727</td>
<td>705.9245</td>
<td>2.898972573106464</td>
</tr>
<tr>
<td>1R1</td>
<td>820</td>
<td>789.7540</td>
<td>3.6885324520470735</td>
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<tr>
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<td>756</td>
<td>721.3510</td>
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<td>1R3</td>
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<td>685.3669</td>
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</tr>
<tr>
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</tr>
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<td>1R6</td>
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<tr>
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<td>622.1950</td>
<td>8.09523264401765</td>
</tr>
<tr>
<td>2L2</td>
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<td>1214.9220</td>
<td>3.5776190476190455</td>
</tr>
<tr>
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<td>1545.0876</td>
<td>5.787341463414631</td>
</tr>
<tr>
<td>2L4</td>
<td>1810</td>
<td>1778.0006</td>
<td>1.7679226519369755</td>
</tr>
<tr>
<td>2L5</td>
<td>1640</td>
<td>1609.6642</td>
<td>1.8497439024390283</td>
</tr>
<tr>
<td>2L6</td>
<td>1940</td>
<td>1919.7189</td>
<td>1.045417525773192</td>
</tr>
<tr>
<td>2R1</td>
<td>720</td>
<td>677.5733</td>
<td>5.892597222222222</td>
</tr>
<tr>
<td>2R2</td>
<td>681</td>
<td>637.6452</td>
<td>6.366343612334795</td>
</tr>
<tr>
<td>2R3</td>
<td>659</td>
<td>609.7224</td>
<td>7.477632776934751</td>
</tr>
<tr>
<td>2R4</td>
<td>636</td>
<td>591.3054</td>
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</tr>
<tr>
<td>2R5</td>
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<td>651.2707</td>
<td>6.694742120343834</td>
</tr>
<tr>
<td>2R6</td>
<td>647</td>
<td>600.1698</td>
<td>7.2380525502318385</td>
</tr>
</tbody>
</table>
[8], this could also explain why initial measurements with the SPA did not match the datasheet.

![Figure 5.14: Resistance drift over time, with refresh and encapsulation steps](image)

After being refreshed both boards have significantly higher resistance values, with resistance on individual pads rising by 50 to 95 percent. Figure 5.14 shows the average resistance on each board, measured over time, and indicates the refresh and encapsulation steps. For the first set of points, the first board had been refreshed, while the second had not. After the second board was refreshed, we can see a jump in average resistance while the resistance of the first board drifts downward. Applying wax increases the resistance of board 1 while decreasing the resistance of board 2. Both boards continue to fluctuate slightly with the wax applied, and once the wax is removed from board 2 it begins to sharply rise, then fall. Comparing the two boards when only the first had wax applied, it does appear that the wax has some sort of stabilizing effect on graphene resistance. Unfortunately, due to limited time and small sample size, it’s difficult to gauge the effectiveness of the wax, especially compared to other encapsulation methods. The raspberry pi is also not as accurate in its measurements as lab equipment, so error from the test setup itself could play a role in the fluctuations seen in the graph.
5.5 Conclusions

Simulation in LTspice demonstrated a problem with the current mirror and TIA method of current detection in the ADC boards. The redesigned boards featuring a voltage divider appear to function properly in simulation, with output voltage scaling with resistance changes. Electrical testing was done on the IR board with the S20, pairing the board with a voltage divider on a breadboard. Initial results were promising, matching up with measurements taken with the SPA within 1%, but resistance values were then observed dropping over time and were $1 - 8\%$ off of the original SPA measurements after three months. Acetone was used to refresh the graphene and restore its original resistance value, with average resistance rising from 688 to 1370 Ohms on board 1 and 1090 to 1810 Ohms on board 2. More measurements were then taken over time, with paraffin wax being used to encase the chips in an effort to slow resistance drift. The chip with wax had average resistance that shifted $-40.1\,\Omega$ to $+25.5\,\Omega$ per day, while the resistance drift on the chip without wax was $-75.4\,\Omega$ to $+52.2\,\Omega$ per day. Results show the encapsulated chip to fluctuate less over time than the unencapsulated chip, however, it’s difficult to draw conclusions due to the small sample size and limited time.
Chapter 6

Conclusions and Future Work

6.1 Summary

The goal of this thesis, to design an inexpensive and simple method of taking electrical measurements from graphene sensor chips, has been achieved through the use of software running on a raspberry pi, coupled with a line of custom PCBs. Research began with the electrical characterization of several graphene sensors, including a four-probe GFET, TLM GFET, Drop-casting GFET array, IDEs, and a Hall sensor. Testing showed a large failure rate and inconsistency between devices, likely due to the age of the sensors, and atmospheric doping.

After characterization, the Hall and Droplet sensors were chosen for interface design. The interface is driven by MATLAB code, which accesses the GPIO on a Raspberry Pi. The Pi’s SPI functionality is used to communicate with an ADC, either on the PCB or on an expansion board for the Pi. The Hall and Droplet sensor both had two PCBs designed for them, one with minimal components, and another featuring onboard amplification, current/resistance sensing, and an ADC. Boards were also designed to house an array of infrared sensors, but a large number of
header pins, bond pads, and the lack of any additional components allow them to be used for a variety of sensors.

The more complex boards were simulated in LTspice, which led to a redesign, as the current detection method was not working. Due to COVID, the production of new graphene chips to populate the boards was halted, so the Droplet and Hall boards were never able to be tested physically. Electrical testing with the Raspberry Pi was instead done on the IR board fitted with the S20 GFET from Graphenea. Resistance measurements from the board were initially taken using a SPA. Those results were then used to calibrate the software, and measurements from the board were then taken using the raspberry pi, along with a breadboard to create the voltage divider. Initial results from the Pi were very close (within 1%) to those from the SPA, confirming that this is a practical method of getting measurements from these chips.

Measurements on the board were then repeated over a 31 day period, tracking the resistance drift and the effects of acetone refreshes and encapsulation/removal of paraffin wax. The acetone raised the resistance of the GFETs to within the expected range, and the refresh was able to be completed without damaging the board. The wax was successfully applied and removed from the board. Test results, while inconclusive, do point to the wax reducing graphene resistance drift to some degree.
6.2 Future Work

Going forward, boards can be designed to house the other graphene sensors that were tested in chapter 3. The ADC boards with the voltage dividers need to be fabricated, and software needs to be written for the Droplet and Hall boards. Hopefully, with COVID restrictions loosening, the supply problems that prevented the completion of the boards will be resolved. Physical testing also still needs to be done on most boards, including the IR boards with infrared sensors installed on them, instead of the Graphenea chip. The software can be updated to provide a better user interface, as well as allow for remote access to the client’s boards from the supplier’s end.

Further study should be done on the effects of encapsulation methods over time. Ideally, a larger selection of boards can be tested with multiple different encapsulation methods, over a longer period of time. Testing surrounding refreshes, resistance drift, and encapsulation can also be done on the other types of graphene sensors, as the methods used here may prove to be more or less effective depending on sensor structure.
Appendix A

MATLAB Code for IR board with S20

dt = 0.01;
n = 20;
vref=5;
csdac = 23; csadc = 22; rstadc = 18; drdy = 17;
clear d; clear x; clear y; clear X;
%pkg load raspi

clear rpi; clear adc; clear dac;
rpi =raspi(‘192.168.2.247’,’pi’,‘********’);
%rpi=raspi();
fileID=fopen(‘ResMeas.txt’,’w’)
adc = rpi.spidev(’CE0’,1,2000000)
dac = rpi.spidev(’CE1’,1,2000000)

rpi.configurePin(csdac,’DigitalOutput’);
rpi.configurePin(rstadc,’DigitalOutput’);
Appendix A. MATLAB Code for IR board with S20

```
rpi.configurePin(drdy,'DigitalInput');
rpi.configurePin(csdac,'DigitalOutput');

rpi.writeDigitalPin(rstadc,1);
rpi.writeDigitalPin(rstadc,0); % hardware reset
rpi.writeDigitalPin(rstadc,1);

rpi.writeDigitalPin(csdac,1);
rpi.writeDigitalPin(csadc,1);

%fprintf('Startup registers: '); adcdumpregs(rpi,adc);

rpi.writeDigitalPin(csadc,0);
adc.writeRead([hex2dec('0f')]); % SDATAC
fprintf('SDATAC '); while (rpi.readDigitalPin(drdy) == 1); end;
adc.writeRead([hex2dec('50'),0,hex2dec('04')]); % status ACAL on no buffer
fprintf('STATUS '); while (rpi.readDigitalPin(drdy) == 1); end;
adc.writeRead([hex2dec('51'),0,hex2dec('08')]); % common ch 0
fprintf('MUX '); while (rpi.readDigitalPin(drdy) == 1); end;
adc.writeRead([hex2dec('52'),0,hex2dec('20')]); % CLK*1, SDCS off, PGA=1
fprintf('ADCON '); while (rpi.readDigitalPin(drdy) == 1); end;
adc.writeRead([hex2dec('53'),0,hex2dec('a1')]); % 1000 SPS
fprintf('DRATE '); while (rpi.readDigitalPin(drdy) == 1); end;
adc.writeRead([hex2dec('54'),0,hex2dec('01')]); % ? DRDY
```
fprintf('IO '); while (rpi.readDigitalPin(drdy) == 1); end;
adc.writeRead([hex2dec('f0')]); % self calibrate
fprintf('SELFCAL\n'); while (rpi.readDigitalPin(drdy) == 1); end;
rpi.writeDigitalPin(csadc,1);

%fprintf('After setup:    '); adcdumpregs(rpi,adc);

rpi.writeDigitalPin(csadc,0);
adc.writeRead([hex2dec('51'),0,hex2dec('08')]); % select channel 0 common
rpi.writeDigitalPin(csadc,1);

tic
R1=zeros(1,n+1);

%% Read
for i = 1:n+1
    rpi.writeDigitalPin(csadc,0);
adc.writeRead([hex2dec('fc')]); % SYNC
%while (rpi.readDigitalPin(drdy) == 0); end;
adc.writeRead([hex2dec('ff')]); % WAKEUP
rr = adc.writeRead([hex2dec('01'),0,0,0,0]); % Read data
%adc.writeRead([hex2dec('fd')]); % STANDBY
rpi.writeDigitalPin(csadc,1);
%d(i,2) = (100/167)*double(uint32(rr(3))*65536 + uint32(rr(4))*256 + uint32(rr(5)));
d2= (100/167)*double(uint32(rr(3))*65536 + uint32(rr(4))*256 + uint32(rr(5)));
V=d2/1e6;
R1(i)=(5/V-1)*(1125);
pause(dt/2);
end
R=mean(R1);
Appendix B

PCB Layouts

FIGURE B.1: Basic Droplet Layout
Appendix B. PCB Layouts

**Figure B.2: ADC Droplet Layout**

**Figure B.3: Voltage Divider ADC Droplet Layout**
Figure B.4: Basic Hall Layout

Figure B.5: ADC Hall Layout
Appendix B. PCB Layouts

FIGURE B.6: Voltage Divider ADC Hall Layout

FIGURE B.7: Small IR Layout
Appendix B. PCB Layouts

FIGURE B.8: Mixed IR Layout
Bibliography


