On the Fabrication of a Graphene Resonator and Detection of the Resonance via Electrical Read-out towards a graphene permeability measurement

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Report number: MNE 2013.009
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Specialization: Micro & Nano Engineering
Date: March 11, 2013
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MASTER OF SCIENCE THESIS

For the degree of Master of Science in Mechanical Engineering at Delft University of Technology

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March 11, 2013

Faculty of Mechanical, Maritime and Materials Engineering (3mE) · Delft University of Technology
Abstract

Since 2004 a new material is discovered which can contribute to a sustainable future. It consists of ordinary carbon atoms, but it has unique properties: graphene. It is a single layer of carbon atoms structured in a honeycomb. This material possesses extremely high mechanical strength and electrical conductivity. It is also the thinnest material and therefore it has a great potential for usage as a gas separation membrane. Currently development in that area is underway. People are working on methods to tune the permeability of graphene by making pores or using strain engineering. A permeability assessment is essential for the characterization of membrane performance. Researchers have been working on methods to measure the permeability of graphene and the most sensitive solution is tracking its resonance frequency. The resonance frequency of graphene shifts as a function of partial pressure over a membrane, so by measuring the resonance, the pressure can be derived. The leak rate is then determined via the ideal gas law. This thesis focuses on designing and fabricating a graphene resonator and building and testing an electrical resonance read-out scheme as a first step towards a permeability measurement. The design of the graphene resonator enables electrical read-out of the resonance frequency and it has a back inlet. Via the back inlet gases can be sealed in the cavity for future permeability measurements. The sealing method is already designed, but not yet applied. A read-out of the resonance of a graphene membrane at vacuum is the first milestone. The chip has a suspended graphene membrane above a gate which can be driven into resonance by electrical actuation. The electrical actuation technique uses the electrostatic field-effect to bring the graphene into vibration. It is possible to monitor the conductance change in graphene by measuring a current through the graphene itself. The resonance frequency of a graphene membrane is in the order of 10 MHz to 100 MHz, therefore the frequencies are mixed down to a reference frequency before read-out takes place. Two chips are measured in the setup, but only one resonator generates an output signal. The output of the chip shows a parabolic relation between output and the driving frequency. At a high frequency in the order of 90 MHz a discontinuity is present in the signal. This discontinuity arises from an input overload at the lock-in amplifier which might indicate a resonance. It is necessary to perform more measurements around this frequency with varying driving voltages to determine if it is indeed a resonance frequency. If so, it would correspond to a strain of 0.1% in the graphene. This is well within the range specified in literature. It in unclear
why the other resonator does not work since fabrication wise no problems were encountered. It is suspected that there is something wrong in the electrical connections to the graphene. Another Raman measurement is necessary to assess the graphene quality. The read-out setup is very accurate, but also sensitive for disturbances. For example the current amplifier starts oscillating when it sees a high capacitance at the input, or it shows an electrical resonance which was only eliminated by applying an extra low pass filter. If the system is stable however, the read-out signal is very smooth. The circuit can be improved by performing the experiments inside a noise box. It is also beneficial to shield the current amplifier from DC power sources and other electronics. Another step is improving the resonator by increasing its sensitivity, because compared to other resonators mentioned in literature its sensitivity is poor. This is mainly caused by the large gate-graphene distance. There is a plan ready to fabricate more sensitive resonators without the need of new masks. This research has contributed in the field of design and fabrication of graphene resonators and also brought high frequency electronics in the attention. With some improvements this method could lead to a fully automated graphene permeability measurement setup.
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Acknowledgements

The last 12 months I have been working on this thesis project and now the project has come to an end. It is a good time to look back on the past year. It has been a year where I gained a lot of in depth knowledge about micro- and nano engineering, where I learned to love research, where I experienced how difficult high frequency electronics are in practice and just as important: where I met some many inspirational people. Without the help of so many intelligent and kind people I wouldn’t have been able to complete this thesis in such a short timeframe and I wouldn’t have accomplished all this. I want to thank my team of mentors for always being available for difficult questions, fruitful discussions, and practical assistance: Professor Urs Stauffer, Associate professor Merlijn van Spengen, and my daily supervisor Doctor of Philosophy (PhD) researcher Hugo Perez Garza. Their input was crucial for my project. During my research project I encountered a lot of practical difficulties: gathering all components of the electrical and vacuum setup, nanofabrication issues, graphene transferring and disturbances in the read-out signals. Therefore I would like to thank Rob Lutjebroer and Harry Jansen and Patrick from the Precision & Microsystems Engineering (PME) lab support, who where always available to help me building my setup and being so kind and patient. From the Kavli Institute of Nanoscience Delft (Kavli) team I want to thank Anja van Langen for training Hugo and myself on the electron beam lithography machine. Also special thanks to Hugo Schellevis and Wim van der Vlist from Dimes and the guys from Electronic and Mechanical Support Division (DEMO) who let me borrow some of there equipment( a lot of people at 3mE are jealous of ‘my’ high frequency signal generator!). Also many thanks to Jos van Driel from the Measurement shop for helping out with my Labview file and borrowing equipment. Then there is someone I want to thank for collaborating with us. Without the knowledge and experience of Gergory Schneider of the Applied Physics department the graphene transfer onto the chip would be a bottleneck in the project. So I am very grateful for that! Besides all the people who contributed to the content of the project, I would also like to thank the people who made it such a fun and ‘gezellig’ year. During the project my office mates were always around for a chat and coffee breaks. Thank you Paula, Richard, Siamand, Martijn, Oncu en Jeroen! My lunches were always a pleasure with many thanks to the Delmes team, Erik Molenaar, Laurens Pluimers, Oncu Atar and Eric Kievit who I started this adventure with. Special thanks to Eric for his courage to start Delmes and his trust in a succesfull completion of the project. At times when I experienced experimental difficulties, Eric and Hugo were always there to support me and generate new ideas and solutions. Many thanks to you guys! On a personal level I want to thank a lot of
people who I know for years and make me such a happy person. First of all I want to thank my family for always supporting me. For triggering me to get the best out of myself and giving me the freedom to explore life. I also want to mention my grandparents for always creating a very safe, loving atmosphere. My friends from Twente weren’t around all the time, but they distracted me from time to time with great parties and lively discussions: I am very glad to enjoy your friendship guys! But my studies wouldn’t have been so awesome without my room mates and my dear ‘clubgenoten van Watt’. I want to thank you Mik, Dion, Didi, Mik, Sjors, Rox for the lovely dinners, the evenings that we watched tv and all the times that we chatted with tea and cookies. Liefste Dan, Charlie, Boef, Flap, Simoon, Lies, Ilhame, Prees, El, Steef, KJ, Willie, Siets, Syl and Adje thank you for always being around for parties, holidays, dinners and support if needed ;-) Last but certainly not least I want to thank my dearest Willem for making me so happy!

Delft, University of Technology

March 11, 2013

L. M. Willems

Acknowledgements
Chapter 1

Introduction

In this chapter the introduction of my Master thesis project on resonance measurements of a graphene resonator is given. This thesis project is part of a national research project into efficient energy utilization where a graphene membrane can play a role as an energy efficient gas separation membrane. Graphene is a purely two dimensional material: carbon atoms structured in hexagons. Graphene has a great potential for use as a gas separation membrane because of its material properties. For the performance of a gas membrane, permeability is an important measure. The permeability of graphene can be determined by tracking the resonance frequency of a suspended graphene membrane as a function of pressure. Since time limitations do not allow the realization of actual permeability measurements, this thesis focuses on fabricating a graphene resonator and a read-out setup to detect the resonance frequency of the graphene membrane. After completing the graphene resonator and electrical read-out circuit, resonance measurements are carried out. This chapter start with the motivation in Section 1-1 where the contribution of this project to society and science is described and the relation to the national research project is defined. Here, graphene’s qualifications for a gas separation membrane are given as well. In the Section 1-2 the principle behind the permeability measurement of graphene is explained. Then an outline is given of the experiments carried out during the project where the read-out circuit is validated and the mechanical resonance of graphene is detected. The objectives of the project are defined in Section 1-4, where also the problem statement is given and the deliverables are listed. Then Section 1-5 summerized the main results from the project. Finally a thesis outline is given in section 1-6.

1-1 Motivation

1-1-1 NAMECOSH project

In the summer of 2011 a fellow student, Eric Kievit, and two professors of the department Precision & Microsystems Engineering (PME) from the Delft University of Technology, Urs Staufer and Fred van Keulen, founded DELMES B.V., a company that bridges
the gap between academic invention and industrial product in the field of Nanoscience. DELMES B.V. strives to develop micro and nanoscale solutions from the department into business. In the spring of 2012 I joined the nanomechanically controlled separation of hydrogen from a carrier stream (NAMECOSH) project of DELMES to start my final Master project. The NAMECOSH project is initiated by Delft University of Technology (TU Delft) and Delmes and is supported by the Dutch Economic Structure Enhancing Fund (FES) program NanoNextNL. The project contributes to the theme Efficient Energy Utilization by secondary conversion and separation, where methods for converting one energy form into another are studied. Conversion of energy carrier becomes increasingly important as the global energy consumption keeps increasing. For instance, Hydrogen is very good energy source for end users in for instance fuel cells, but it is difficult to capture and transport hydrogen in a safe and cost-effective manner. The NAMECOSH project contributes to research in this particular field. The goal of the NAMECOSH project is the development of nanomechanical elements which can efficiently separate gases out of a carrier gas stream with an internal driving force. Graphene offers possibilities for such a self-controlled membrane. If a membrane can internally regulate the diffusion rate of atoms, an external force like a large partial pressure over the membrane would be superfluous. The absence of such an external driving force enables energy efficient gas separation. Another advantage of active membrane technology is the possibility to separate gases against the concentration gradient. This would create possibilities to filter gases out of air, where a low concentration of hydrogen or carbon dioxide gas is present. These are dreams for the future, Imagine the opportunities that this technique offers for carbon dioxide filters and hydrogen storage... It would be a big step forward towards a more sustainable society.

1-1-2 Graphene gas filter

The goal of Namecosh is realizing an energy efficient, active gas separation membrane from graphene. Graphene is a single layer of carbon atoms in a honeycomb lattice which was isolated for the first time in 2004 by professor Geim and professor Novoselov at the University of Manchester [26]. Before, only other forms of graphene were realized. Graphene is actually the building block for fullerenes as zero dimensional bucky balls and one dimensional carbon
nanotubes, see 1-1. And stacked layers of graphene on top of each other form the three-dimensional material graphite. Since the first exfoliation of graphene, worldwide research into this new material is booming. Graphene has drawn so much interest due to its extraordinary mechanical, chemical and electrical properties like superconductivity and ultrahigh mechanical strength. The potential of graphene as a filter material originates from the fact that this is a purely two-dimensional material with a single atom thickness [1]. Since the permeance of a membrane scales inversely proportional to the thickness [27], a membrane with atomic thickness would be the ultimate limit. However, it is proven both experimentally and theoretically that single layer graphene is impermeable for all gases, including the smallest gas helium [25, 28]. The impermeability is caused by a high diffusion barrier, since diffusing atoms are repelled by the high electron density of the aromatic rings. Multiple calculations and simulations have shown that even defects and small pores are not sufficient to increase the permeance to an industrially acceptable level [28–30]. To use the graphene as a gas separation filter, the material must be tailored, for example by creating pores or applying high strains. Up to know porous graphene is modeled [29, 31, 32] and some attempts to create and shape pores have been undertaken [19–21]. However no feasible method to create the desired pores is known yet. Theoretical research has predicted that the permeability of graphene can also be increased by strain engineering which reduces the out-of-plane diffusion barrier for hydrogen atoms [3]. In the development phase of a permeable graphene membrane, it is essential to evaluate its permeability. Therefore a permeability measurement setup is needed. Currently, measuring the permeability of graphene sheets is a challenge due to scale issues. First of all the in-house fabrication method of graphene, mechanical exfoliation, limits the flake size to approximately 10 µm. So only very small membranes can be evaluated. Such a membrane can enclose only a small gas volume and thus confines a limited number of molecules. So a very sensitive device is required to determine the gas permeability. Direct measurement of the permeability is ruled out because for example helium mass spectrometers are not sensitive enough to detect the gas flow typical for graphene membranes with micrometer sizes.

1-2 Permeability measurement principle

In 2008 the impermeability of graphene was shown by applying a partial pressure over a graphene membrane and detecting the leak rate of gases [25]. The idea is to deduct the leak rate from the change in partial pressure over the graphene membrane, by the ideal gas law:

\[
\frac{dN}{dt} = \frac{V}{k_B T} \frac{dp_{in}}{dt},
\]

where \(N\) is the number of molecules or atoms in the chamber, \(V\) is the cavity volume, \(k_B\) is the Boltzmann constant and \(p_{in}\) is the pressure inside the cavity. So the change of pressure inside the cavity of the graphene resonator is needed to calculate the leak rate. It is expected that in time the gas inside the cavity will diffuse to the vacuum environment until an equilibrium is reached, so the pressure shifts in time. It is important to notice that perfect graphene is impermeable, so the gas will not diffuse through the graphene, but the gas is expected to diffuse through the walls. So independent of the membrane material the pressure decreases to zero, but depending on the permeability of the membrane the time constant to reach equilibrium varies. The pressure in the cavity is not measured directly, but the effect of the pressure on the tension in the membrane is measured. There is a relation between partial
pressure over a membrane and the tension in the membrane. If the partial pressure is bigger, the tension is also bigger. That shift in tension, and thus in pressure, can be measured as a shift in resonance frequency:

\[ f_{\text{res}} \propto \sqrt{\frac{T}{\alpha \rho}}, \]  

(1-2)

where \( T \) is tension, \( \alpha \) is mass adsorption coefficient and \( \rho \) is mass density. If the tension increases, the frequency shift upwards. So by tracking the shift in resonance frequency, the partial pressure over the membrane can be derived. For these measurements a graphene resonator is needed which can be actuated at its resonance frequency, and read-out. Various research groups have built nanomechanical resonators of graphene and detected the resonance frequency of suspended membranes \([7, 13, 25, 33, 34]\), mostly under vacuum conditions. The resonance frequency can be excited and detected either optically or electrically. In this research the focus is on electrical actuation and observation of the graphene resonance. Electrical detection schemes are preferred since they do not require expensive lasers and they are more compatible with microelectronic applications than optical detection methods. The need for a permeability measurement of graphene has led to this thesis where a graphene resonator is designed and built and an electrical read-out technique of a mechanical resonance is presented. During this project a paper is published \([35]\), where selective molecular sieving of porous graphene is proven by a leak rate measurement via resonance tracking.

1-3 Project outline

In this thesis a start is made for the described permeability measurement setup. First a graphene resonator is designed and fabricated according to the specifications arising from graphene membranes, the permeability test and the electrical read-out method. My daily supervisor, Hugo Perez Garza and I worked together during the design phase of the resonator. We combined his expertise on the field on nanofabrication with my knowledge about the requirements of the resonator for this specific application. Another aspect of this project was handling graphene. In the department there was no experience with fabricating, identifying and transferring (single layer) graphene. I, Hugo and Eric Kievit, who was graduating at the same time as I, have developed that experience. For transferring the graphene to a precise location on the chips a collaboration is setup with Gregory Schneider, a former Post-doctoral researcher at the faculty of Applied Sciences. His group is very experienced with graphene transfer and they were interested in a collaboration. In the meantime I immersed myself in the electrical read-out circuit. The electronics for the read-out setup are quite challenging since the signal we want to measure is in the order of tens of pA and high frequency signals (in the order of graphene’s resonance frequency) are involved. Assistant professor Merlijn van Spengen is the expert in the field of high precision measurements and he was very important during the experimental phase of the project. First a test setup is built where the chip in the electrical read-out circuit is replaced by a field effect transistor (FET). This experiment is used for testing and validating the read-out setup. In this phase problems in the circuit could be detected and tackled before implementing the resonator chip in the electrical scheme. In the second experiment the resonator chip is inserted in a revised electrical scheme and resonance measurements are performed. The goal of the second experiment is detection of a mechanical...
vibration of the graphene membrane in the output current. Professor Urs Stauffer, who is also chairman of my graduation committee, was involved during all phases of the project. Every couple of weeks, and sometimes more often, Hugo and I sought his advice in practical problems concerning nanofabrication and electronics. He also guided the direction of the overall project. Urs Stauffer, Merlijn van Spengen, Hugo Perez Garza and Lina Sarro form my graduation committee. Lina Sarro is the external member of the committee. She is a professor at Delft Institute of Microsystems and Nanoelectronics (DIMES), the cleanroom facility at the faculty of Electrical Engineering, Mathematics and Computer Science (EWI).

1-4 Objectives

The goal of this thesis project is: Design, construct and validate an experimental setup to measure the resonance frequency of a suspended graphene membrane which can be used for future permeability measurements. For this experiment also a graphene resonator was designed and fabricated. The following research questions are formulated:

- Is the material graphene promising for gas separation membrane applications?
- How does graphene interact with its environment?
- How do we arrange graphene fabrication, transfer and single layer identification?
- What is the best method to read-out a mechanical resonance of a graphene membrane?
- What is the mechanical and electrical response of a driven graphene membrane?
- What should the electronic circuit look like for the resonance read-out?
- Is it possible to design and fabricate a graphene resonator compatible with electrical read-out with a back inlet?
- Is a mechanical resonance of graphene detected with the selected read-out method?

The scope of the project is narrow, because I want to advance the project as much as possible in the available time. The project focuses on two subsequent steps. The first step is design and fabrication of a graphene resonator specifically for the selected electrical actuation and read-out and with a possibility for future permeability measurements. The second step is building and verifying one specific electrical setup. Then it is time to start measuring the resonator in the electrical read-out setup. The project is limited to electrically driven resonators with mechanically exfoliated graphene flakes. The application of the permeability measurement setup is very wide: the permeability measurement could be used for any type of gas and any type of porous, strained, or chemically grown graphene. It can also be used to detect the permeability of other pure 2 dimensional membranes.

The goals for the this thesis project are:

1. Design and fabrication of a graphene resonator
(a) Chip fabrication  
b) Graphene handling

2. Design and building of an electrical setup for resonance read-out  
(a) Design and procurement of a printed circuit board  
b) Design, building and testing of the electrical interface

3. Measurement of mechanical resonance of graphene membrane  
(a) Model the chip response  
b) Measuring a resonance

1-5 Summary results

A design is made for graphene resonators with a back inlet for gases and a support membrane. The design is fabricated and three chips have survived the fabrication process. The graphene flakes are suspended on a hole in the support membrane above an electrical back gate. The transfer of graphene was successful for at least one chip. The presence of graphene is proven with Raman spectrum measurements. In a dummy setup, the electrical resonance read-out circuit is validated for currents of mA. An electrical resonance at a high frequency was artificially generated and detected by the setup. The results of the dummy measurement have contributed to the final design of the printed circuit board (PCB) for the chip with the graphene resonator. After embedding the chip in the electrical circuit, noise problems are identified. Noise troubles the electrical resonance measurements, because the signal we try to detect in the graphene is in the order of nA. Since the signal is so small, the signal to noise ratio is very small as well and it becomes increasingly difficult to distinguish signal from noise. By placing extra electronic filters and shielding, the noise in the output is decreased. Two chips are tested in the setup. Unfortunately at only one chip a signal is detected. The measurements of the graphene resonance show a possible resonance, but this is not validated yet. Furthermore the circuit is proven to generate an output signal as expected from the model. Therefore it is well possible that the chip is too insensitive and not the read-out setup. Compared to other resonators the sensitivity is one- to two orders lower. By changing some steps in the fabrication process the sensitivity can be improved one order without need for extra masks. If that is not enough, it is also possible to add a top gate.

1-6 Thesis outline

In chapter 2 the material properties of graphene are discussed, with special attention for the performance of graphene as a gas separation membrane. Then the interaction of graphene with its environment is investigated. The chapter on graphene is closed by the description of suitable graphene fabrication, transfer and single layer identification methods. Chapter 3 contains the graphene resonance detection methods and information about the mechanical and electrical response of a graphene membrane to a mechanical vibration. The resonance frequency is modeled, influences the quality factor and line response are treated. Then the experimental
setup is described in chapter 4, where the design and analysis of the electrical read-out circuit is presented. The critical points for practical measurements of very small, high frequency signals are identified and the output signal of the chip is modeled. The next chapter 5, is dedicated to the fabrication of the graphene resonator. This chapter contains the chip design and fabrication steps, the graphene-to-chip transfer method an evaluation of the fabrication process. In the following chapter, 6 the electrical circuit validation experiment is described and the results of the test are shown. This leads to recommendations for improvement of the setup and the PCB used in the next experiment where the resonance frequency of graphene is detected. The chapter 7 describes the setup of the experiment and the difficulties that are encountered and how they are solved. The output signal of the chip is shown as a function of frequency and voltages. It also contains the results of the current and frequency modeling so that a comparison to the empirical obtained values can be made. In the final chapter 8 the conclusions of the project and recommendations for future work can be found. At the end of the thesis the appendices and the bibliography are present.
In this chapter relevant information about graphene is gathered. Of course a lot more information is available, but I restricted myself to properties of graphene which are important for graphene resonator application. The unique material properties of graphene are treated but we also take a look at the potential of the material for gas separation applications. Since this project if funded for research into future application of graphene as a gas separation membrane, it is important to know: What is the potential of graphene for gas separation membrane applications? Graphene interacts easily with its environment, what could alter its properties and change the resonator behavior. Therefore these interactions, but also quality treatments to restore the original properties are investigated. The second research question that will be addressed in this chapter has a more practical nature. How do we arrange graphene fabrication, transfer and single layer identification? In Section 2-1 graphene’s material properties which are relevant for this particular application as resonator membrane are summarized. The Section 2-2 looks into the membrane performance of graphene. Than in Section 2-4 the most feasible preparation techniques of graphene are discussed. And finally in the last section single layer identification is treated. The conclusions section at the end of the chapter summarizes the findings of the research questions.

2-1 Material properties

2-1-1 Introduction

The unique features of graphene are its 2 dimensionality and lattice symmetry. These are responsible for graphene’s ultrahigh electron mobility, high thermal conductance and high mechanical strength [1,10,26,36–38]. It is important to realize that since graphene has an atomic layer thickness, there is interaction between the mechanical, electrical and chemical properties. For example, at the nanoscale the behavior of electrons influences the chemical interactions and its conductivity but also bond strength and thus mechanical strength. This interaction will become clear in the next sections.
2-1-2 Mechanical structure

Graphene is the first known strictly 2 dimensional material: it is a single layer of carbon atoms structured in hexagons, see Figure 2-1(a) [1,39–42]. The bond length between two atoms is 1.42 Å and the C-C-C bond angle is 120°. The thickness of a monolayer graphene sheet equals carbons van der Waals diameter, which is 0.34 nm. The two dimensional mass density of graphene is $7.4 \cdot 10^{-7}$ kg/m². Graphene has two crystallographic edge directions, zigzag and armchair, see Figure 2-1(a). Graphene has a different chemical reactivity and varying electronic and mechanical properties in the two edge directions [37,43]. Graphene can withstand higher tensile loads in the zigzag direction (the longitudinal mode) than in the armchair direction (transverse mode). The Young’s modulus in the zigzag direction is slightly larger than that for the arm chair direction, respectively 1.13 TPa and 1.05 TPa [44]. So graphene is an anisotropic material. However for the modeling of graphene it is treated as isotropic, with a Young’s modulus of 1 TPa [45,46]. Also graphene can sustain approximately 20 – 25% strain before permanent deformation occurs. The breaking strength of graphene is 42 N/m [45]. The extraordinary bending properties of graphene arise from the existence of out-of-plane oscillations of atoms. This is expressed as almost zero bending stiffness [45]. Research showed that suspended graphene membranes show complicated conformational structure including small scale ripples, with an amplitude of $\sim 10$ nm, and large scale buckling of the membrane along the length and width of $\sim 100$ nm [13]. Ripples and buckling have been observed in exfoliated, chemical vapor deposition induced growth and epitaxial graphene membranes, see Figure 2-1(b).

2-1-3 Electronic structure

In graphene the carbon atoms are sp²-hybridized, see Figure 2-1(c) and each carbon atom supplies three out of their four valence electrons to form in-plane covalent bonds. The overlapping sp²-orbitals of two neighboring carbon atoms form a double covalent $\sigma$-bond by sharing one electron pair. According to the Pauli principle, the $\sigma$-bands have a filled shell, and thus form a deep valence band. The electrons in the deep valence band do not participate in electronic transitions, which makes the lattice structure very robust. The robustness is reflected in graphene’s extremely high in-plane Young’s modulus, which is at least six times
higher than for silicon. Perpendicular to the plane the p_z-orbitals of neighboring carbon atoms form π-bonds by sharing the last valence electron. A bonding π-band and a antibonding π*-band are created. The energy level up to which electrons occupy states is called the Fermi level. Only excitations close to the Fermi energy are considered for graphene’s transport properties because at energies much higher or far lower than \( k_B T \), where \( k_B \) is the Boltzmann energy and \( T \) is the room temperature, the states are either completely filled, or completely empty, and hence unable to participate in transitions between states required for the spatial movement of electrons. In the case of graphene all electronic transitions occur in the π-band. In neutral graphene the π-band is completely filled and forms the valence band, the empty π-band forms the conduction band. The bandstructure of graphene shows that the conduction and valence band meet at six points of the Brillouin zone, at the so called Dirac points, see Figure 2-1(d). The fact that the conduction and the valence band meet classifies graphene as a zero bandgap semiconductor or a semimetal. It can be called a semiconductor since it can reach a zero density of states, but also metal since is has no bandgap.

**Massless Dirac fermions**

In graphene, the interaction between electrons and the periodic potential of the two dimensional honeycomb lattice makes electrons behave like they have no mass. They behave as relativistic particles, and therefore they have a lineair dispersion relation, see Figure 2-1(d). The lineair dispersion relation is described by the Dirac equation [49], which formulates the relativistical motion of electrons from a quantum mechanical point of view. Therefore the electrons in graphene are called Dirac fermions. They exhibit the relativistic effects (like photons) at a speed threehundred times smaller than the speed of light.
Klein tunneling

It is remarkable that graphene shows ballistic transport at room temperature: electrons can travel long distances, in the order of micrometers, without being scattered. Klein tunneling is responsible for this effect [50]. Klein tunneling is transmission of Dirac fermions through a classically forbidden region with probability 1. So they can tunnel without reflection through potential barriers for normal incidence. The electron mobility of graphene before annealing is in the order of 15000 cm²/(V s) at room temperature [26], when impurities induce electron scattering. The highest carrier mobility measured exceeds 200000 cm²/(V s) for an ultraclean suspended single layer of mechanically exfoliated graphene [10]. This mobility was measured at 5 K in a vacuum environment. Compared to commonly used semiconductor materials, like InSb which has an electron mobility of 77000 cm²/(V s) [1] this is almost a factor 3 higher.

Ambipolar electric field effect

One of the unique electrical features of graphene is the ambipolar field effect [2], see Figure 2-2. Due to the linear dispersion relation of Dirac fermions in graphene, it is possible to change the amount and type of charge carriers between electrons and holes by applying a homogeneous electric field effect perpendicular to the graphene sheet. In practice, this effect can be explored if a transistor is build from a graphene flake on a substrate with patterned electrodes and a gate, where an applied gate voltage induces capacitively a net charge in the graphene sheet. When a negative voltage is applied to the gate, the Fermi level is shifted down and electrons are depleted from the graphene. When the Fermi level drops below the Dirac point, a significant population of holes is introduced into the valence band. However, when a voltage is swept from negative to positive values, the charge carriers change from holes to electrons. Under positive gate bias, when the Fermi level rises above the Dirac point a significant population of electrons is promoted into the conduction band. The conductivity of graphene depends linearly on the charge carrier density. So by varying the gate voltage, the conductivity of the graphene can be manipulated. The conductivity of graphene is given by the Drude-Boltzmann expression at zero magnetic field [2]:

\[ \sigma = n|e|\mu \]  \hspace{1cm} (2-1)

where \( n \) is the charge carrier density, \( e \) the charge and \( \mu \) the electron mobility [2]. The charge carrier density is:

\[ n = \frac{\kappa}{ed}\Delta V_{BG} \]  \hspace{1cm} (2-2)

where, \( \kappa \) is the electrical permittivity (to prevent confusion with \( \epsilon \) strain), \( \Delta V_{BG} \) is the back gate voltage while taking into account the offset from the conductivity minimum. For a perfectly clean graphene sheet the conductivity minimum (neutral point or Dirac point) is located at zero gate voltage, but in practice this point is shifted due to charge transfer with environmental particles. In theory, when the Fermi level is at the Dirac point, the conductivity should be zero, since the density of charge carriers is zero there. However, a minimum conductivity is proven experimentally [49], probably because electrons remain present due to randomly distributed electron-hole puddles, caused by inhomogeneities in the...
environment of the sample. And due to Klein tunneling there is always charge transfer in the sample [42]. The conductivity minimum is shown to be independent of the impurity concentration [51]. Figure 2-2 shows a resistance peak at zero gate voltage for ultraclean graphene.

2-1-4 Thermal properties

Besides all remarkable electronic properties of graphene, also its thermal properties are quite impressive. The room temperature thermal conductivity is $5000 \, \text{W/(m K)}$ [52]. Also graphene is proven to have a negative linear thermal expansion coefficient of $-7 \, \mu\text{K}$ at $300 \, \text{K}$ [14]. The nature of the negative thermal expansion is domination of membrane phonons in two dimensions. As temperature increases the phonons make the graphene ripple more and thus a contraction occurs.

2-2 Membrane performance

2-2-1 Introduction

In principle, perfect graphene is proven to be impermeable both experimental and by simulations [25,28]. If a gas separation membrane of graphene is to be built, it is important to understand gas transport through graphene and what opportunities are available for maximizing productivity and selectivity. Membrane productivity is expressed as gas flux through the membrane and selectivity is expressed by the retention or separation factor. The combination of productivity and selectivity together with the stability determines the membrane performance. First gas transport in a graphene sheet is discussed and second methods to increase the performance are mentioned.
Gas transport in graphene is based on tunneling where the gas molecule or atom must overcome a potential barrier to diffuse through graphene. The potential barrier arises from the Pauli exclusion principle: the diameter of the hexagonal ring is so small (0.246 nm [30]) that the orbitals of a diffusing atom interfere with the orbitals of carbon and thus experience a repellant force. The tunneling probability is given by:

\[ P = e^{-\frac{2x\sqrt{2m(V-E)}}{\hbar}} \]  

(2-3)

where \( x \) is the length of the barrier (0.34 nm for graphene), \( m \) is the mass of the particle, \( V \) is the potential barrier, \( E \) is the energy of the particle and \( \hbar \) is Planck’s constant. The higher the tunneling probability is, the higher is the flux of gases through the membrane. For a filter with an industrially acceptable permeance, the maximum potential barrier is 0.5 eV [29]. For hydrogen and helium, the smallest gas molecules, the potential diffusion barrier is calculated for two diffusion paths. The first path \( (O_1) \) is via a covalent bond which undergoes a process of bond breaking and forming and a second path \( (O_2) \) is through the center of the hexagonal ring while the \( \sigma \)-bonds remain intact, see 2-3 [3]. For a helium molecule tunneling via path 2 a potential barrier is calculated of 11.7 eV and for path 1 a potential barrier of 3.5 eV [25]. This makes penetration by helium impossible at any temperature at which the graphene remains stable. A hydrogen atom experiences a potential barrier of 2.46 eV via path 2 and a barrier of 3.85 eV diffusing through path 1 [3]. It is clear that these potential barriers are above the industrially acceptable level. Even diffusion through graphene with defects is taken into account. For aromatic rings with up to 9 carbons instead of 6, the potential barrier remains too high, varying from 1.04 eV to 1.20 eV depending on the simulation method [28]. It is concluded that for small defects, graphene remains impermeable. Furthermore the penetration barrier height is found to decrease exponentially with increasing size of defects.
2-3 Interaction with surroundings

2-2-3 Enhance membrane performance

It may be clear that manipulation of graphene is necessary to enhance the membrane performance. Diffusion can be enhanced by strain engineering [3] or by creating pores. The selectivity of a porous membrane is influenced by the size of the pores and the chemical interaction between the pore passivating atoms and the diffusing atoms. The productivity is determined by the pore density. So when evaluating pore creation techniques the key functional requirements are: control of shape and size of the pores, choice and composition of passivating atoms and achievable pore density. Possible methods are shooting pores in a perfect graphene sheet by means of an electron or ion beam [19,21], or by bottom up synthesis of graphitic building blocks [22]. Describing and evaluating the different techniques is out of the scope of this thesis, but with the overall goal of the project in mind, in Appendix B the various techniques to enhance the permeability of graphene are briefly described.

2-3 Interaction with surroundings

2-3-1 Introduction

Graphene is a chemically stable material, but it reacts easily with the environment, especially when there are defects present with dangling bonds. Chemical interaction severely influences the behavior of graphene because the high surface area to volume ratio maximizes surface effects. Both physical and electrical properties of graphene are influenced. For practical work some basic understanding of the chemical interaction between graphene and its environment is important. The first section deals with the structure of single layer graphene, where clamping to the substrate is discussed. The second part is about how adsorbates influence the electrical properties and mass of graphene. And finally methods to increase the graphene quality are given.

2-3-2 Clamping

A graphene membrane is clamped to the substrate by Van der Waals forces [53]. But the van der Waals interaction is so significant that is also causes tensioning of a suspended graphene sheet because the membrane partially adheres to the sidewalls of the cavity. For this thesis
the adhesion of graphene to silicon nitride and silicon oxide is important. In the literature, experimental examples of graphene adhered to both silicon oxide [25] and silicon nitride [13] can be found. For monolayer graphene an adhesion energy of 0.4 J m\(^{-2}\) of graphene sheets with an silicon oxide substrate is measured [46]. Compared to typical micromechanical structures the energies are higher, they are in the order of solid-liquid adhesion energies [46]. This solid-liquid interaction is attributed to the extreme out-of-plane flexibility of graphene, which allows the graphene to precisely follow the topography of substrates. When a high pressure difference is applied over a graphene membrane, at some point slipping occurs. At a partial pressure higher than a few atmosphere graphene is released from the substrate [25].

### 2-3-3 Adsorption

Variations in the nature of the substrate or atmosphere lead to a wide variety of electronic properties of the graphene sample. For example the type of charge carriers in graphene, electrons or holes, depends strongly on the environment. When adsorption occurs, the amount of electrons available for electron transport changes. Donors locally increase the electron density of graphene while acceptors reduce it. Adsorption is not only shifting the Fermi level, but also changes the band structure of graphene. For example hydrogenation of graphene into graphane, see Figure 2-4(b), leads to the opening of a bandgap between the valence and conduction band, see Figure 2-4(b). The hydrogen attaches to the graphene by changing the sp\(^2\)-hybridization into sp\(^3\)-hybridization, which removes the conducting \(\pi\)-bands [54,55]. The hydrogenation process is reversible by annealling the graphene [56]. A possible application of this effect is hydrogen storage. Other researchers are looking into chemical functionalization of graphene to form novel materials which can be tailored for specific electronic behavior [31,55,57,58]. The most important effect of impurities in graphene is scattering of electrons, which reduces the free mean path and thus the electron mobility. During the preparation of the experiment, the samples are being exposed to ambient conditions. Therefore it is expected that adsorption of molecules from the air takes place. Under atmospheric conditions at room temperature the adsorbate concentration of hydrogen is estimated at 0.3% of the carbon atoms [59], which relates to about one impurity per 10 nm\(^2\). By annealing the adsorption reaction can be reversed and the electronic properties of pristine graphene can be recovered. The annealing process is described in Section 2-3-4.

### 2-3-4 Quality treatment

As previously stated graphene’s conductivity and mass can be influenced by adsorbates. The amount and type of adsorbates depend heavily on fabrication methods and experimental conditions. When for example polymethylmethacrylate (PMMA) is used for graphene transfer, PMMA residues can remain on the graphene [4]. It is not possible to remove these residues completely with standard removers as acetone due to the strong van der Waals interaction [61]. For some applications it is critical to remove these adatoms and molecules. The idea is to add energy to the graphene so that the binding energy of adsorbates is overcome and they diffuse into the environment. For suspended graphene this works quite well, but when graphene lays on a substrate impurities get trapped between the layers. Even after quality treatments, the highest electron mobilities are measured in suspended graphene [10] or on special substrates as boron nitride [62,63]. The most frequently applied methods are thermal
and current annealing. The advantage of current annealing over thermal annealing is that it can be carried out in the vacuum where also the final experiment is performed. If thermal annealing is chosen, the sample must be transferred from the oven to the vacuum chamber through the air and thus unwanted doping occurs. Therefore only current annealing is discussed. The quality of graphene flakes is checked by measuring the electronic properties like electron mobility, location of conductivity minimum, visibility of the half integer Quantum Hall Effect and roughness measurements with atomic force microscope (AFM) and tunneling electron microscope (TEM) [48].

**Current annealing**

Current annealing is based on power dissipation in graphene samples which causes the desorption of contaminants and enhances the electron mobility [4]. In a few μm² sample, a few mA is applied, which causes an extremely high current density of $J \sim 10 \cdot 10^8$ A/cm². Remarkably, the graphene can sustain such high current densities. The effects of a large current in a mesoscopic, conducting device are electromigration and joule heating in the order of mW. After annealing the conductivity minimum is located at zero gate voltage as in pristine graphene, see Figure 2-5, and AFM results show a roughness equal to the roughness of freshly cleaved graphene. During current annealing special care has to be taken to preserve the integrity of the graphene sheet upon applying large source-drain biases. First the gate voltage is set to zero, then the source-drain voltage is slowly increased. Regularly the voltage is kept constant to monitor the time dependence of the current. If the current stays constant, the drain-source voltage is increased. This is repeated until the current suddenly decreases
as a function of time. If a too high voltage is applied, an acceleration of the current decay usually precedes the rupture of graphene. It is very important to perform current annealing under ultra high vacuum condition at a pressure of $10 \cdot 10^{-7}$ mbar, otherwise the graphene breaks down [64,65]. The exact reason for breakdown is unknown, but interaction with gas molecules or ignition of local plasma are mentioned.

2-4 Graphene synthesis

When Andre Geim and Kostya Novoselov and their fellow researchers at the University of Manchester discovered graphene in 2004 [26], the world was amazed that this novel material was cleaved with only adhesive tape. No expensive, elaborated machine was used to cleave graphite until mono layer graphene is achieved. The method they have found, the so called scotch-tape method, is described in subsection 2-4-1. The scotch-tape technique however, has some disadvantages as limited flake size, no control over position and low throughput. Other chemical growth methods to obtain graphene are chemical vapor deposition [66] and epitaxial growth [23]. The advantage of chemically grown graphene is that it is possible to make much bigger flakes, but the quality is worse. The biggest chemical vapor induced flakes reported are maximal 76.2 cm with an electron mobility of 7350 cm$^2$/V s [67]. However, at the moment a lot of researchers are improving the technique to make chemically grown graphene flakes even bigger and improve the quality by creating less grain boundaries. In the future, when the technique is fully developed, chemically graphene can be used for upscaling of permeability measurements and gas filters.

2-4-1 Mechanical exfoliation

The scotch-tape method [68] is very cheap, simple and fast, and produces the highest quality flakes so therefore this method is selected for producing graphene for our resonator devices. The exfoliation process is as follows: highly ordered pyrolytic graphite (HOPG) is pressed gently against a piece of scotch tape. Then the excess graphite is removed from the scotch tape until only a few graphite flakes remain. Next, the scotch tape is closed gently at new
sites of the tape and opened slowly again some 5 to 10 times in a row. Then the scotch tape is pressed against a thoroughly cleaned wafer with 285 nm ~ 300 nm Silicon dioxide on top. Upon removing the scotch tape from the wafer, single- and multi layer graphene flakes remain attached to the substrate via VanderWaals forces. It is very important that the substrate is very clean, otherwise transfer fails. The graphene flakes are now randomly deposited on the substrate and they are visible through an optical microscope, see section 2-5-1. With this method the nominal flake size is about 10 µm [69].

### 2-5 Single layer identification

#### 2-5-1 Optical identification

Single layer graphene absorbs only 2.3% of the white light [70], ruling out direct visual observation. However, graphene can be made visible for the human eye when placed on top of a silicon oxide substrate with a specific thickness by interference effects. Its visibility depends strongly on both thickness of SiO\textsubscript{2} and the light wavelength. The combination of a oxide thickness of 90 nm or 280 nm with green light gives the best contrast between few layer graphene and the naked substrate [5]. However, most people use 300 nm oxide thickness and white light to observe single and few layer graphene. Monolayer and multilayer graphene appear as a specific color depending on the flake thickness. The interference of light creates this colorspectrum. By optical means thin graphene flakes can be identified, but it is not possible to ensure that a certain flake is monolayer. Further characterization is necessary, for instance by Raman spectroscopy, see section 2-5-2 [71].
2-5-2 Raman spectroscopy

Raman spectroscopy is an analytical tool which uses the interaction between light and a sample for several purposes as chemical identification, characterization of molecular structures, effects of bonding, environment and stress on a sample. Raman uses only the inelastic scatter of electromagnetic radiation to identify molecules, the so called Raman scatter. The frequency of the Raman scatter and the incident radiation wavelength is compared and the change of wavelength provides chemical and structural information of the sample. Different molecules show a unique combination of electron transitions, which are used as fingerprints. The Raman fingerprints for single- bi- and few-layer graphene reflect changes in the electronic structure and allow high throughput, unambiguous, non destructive identification of graphene layers [71]. The major features of the graphene fingerprint are the G peak at 1580 cm\(^{-1}\) and a band at 2700 cm\(^{-1}\), which is called 2D band. Compared to bulk graphite, graphene shows a different shape and higher intensity of the 2D peak, see Figure 2-8(a). The identification of single- and few-layer graphene is done by evaluating the 2D peak in Figure 2-8(b). It is possible to distinguish between graphene with a thickness up to 5 layers, above 5 layers bulk graphite and multilayer graphene exhibits a comparable Raman spectrum. Bilayer graphene has much broader and up-shofted 2D band with respect to graphene. Evolution of electronic bands from single to multilayer graphene is responsible for single 2D peak in graphene and why it splits in multiple components in bi-layer graphene, what causes the peak to broaden. Another band, the D band at 1350 cm\(^{-1}\), indicates the quality of the atomic crystal. The D band is visible in defected graphite. When D peak is absent, this proves the absence of significant number of defects of the structure. At the edge of the graphene flake a D peak is expected. So Raman analysis does not only identifies the number of layers, but also assesses the quality.
2-6 Conclusions

The truly two-dimensional nature and lattice symmetry of graphene leads to an exceptionally high Young’s modulus and conductivity, but also causes the impermeability for gases. The tightness of the carbon crystal is responsible for the repulsive force that gas atoms experience when approaching the graphene. Eventhough graphene is impermeable in its natural state, and thus useless as a gas membrane, there is hope. Because a lot of research is going on in enhancing the permeability of graphene by creating pores or strain engineering. Simulations of graphene membranes show promising results for productivity and selectivity. For hydrogen separation for example, graphene would be a very good solution since it can be made selective for hydrogen, in contrast to many other membrane materials. Ans since the productivity of a membrane scales inversely to its thickness graphene could become a very efficient filter. So research into permeability measurement setups for graphene become increasingly important for the characterization of all these to be developed gas membranes. For the development of such an experimental setup is is necessary to work on graphene fabrication, transfer and identification. With the current possibilities at the university it is easiest to use mechanically exfoliated graphene. However, this limits the membrane size so in the future hopefully also Chemical vapor deposition grown graphene can be used. Transfer and alignment was a bottleneck in the development of the graphene resonator, but that is solved in collaboration with applied physics who do the transfer procedure for us. Identification of single layer graphene can be done relatively easy in an optical microscope, however that requires some experience. A Raman spectrometer can distinguish between single and bilayer graphene.
Detection of resonance of a graphene membrane is a challenge due to scale issues. Therefore it is important to figure out the best method to read-out a mechanical resonance of a graphene membrane. The most common methods, optical and electrical, are reviewed. For the interpretation of resonance measurements results, a model of the resonance frequency brings clarity. The membrane model is suited for a graphene membrane and the derivation of an equation for the fundamental frequency of circular and rectangular membranes is shown. The mechanical vibration causes an electrical response when inserted into the electrical measurement setup, therefore also the lineshape and quality factor that response is discussed. After this chapter the answer is formulated to the question: What is the mechanical and electrical response of a driven graphene membrane? First, an introduction is given into graphene resonator research. Second, the optical and electrical readout methods are discussed. Then the mechanical resonance of graphene membranes is explored in Section 3-3. Finally, the electrical response of nanomechanical resonators is addressed in Section 3-4. In the Conclusions a summary is given and the research questions are answered.

3-1 Introduction

Graphene is a very interesting membrane material for resonators, because capacitive coupling between the suspended membrane and the gate changes the tension in the membrane and thus the frequency of the resonator is tunable. And thanks to the single atomic layer thickness, very high frequencies can be reached. Currently operation in the order of 100 MHz is achieved [33,34]. In principle a resonator consists of graphene suspended over a trench in a insulating layer where the conducting substrate underneath, the bulk, acts as a back gate, see Figure 3-1. The graphene membrane can be actuated by applying an alternating back gate voltage. At the resonance frequency the graphene starts mechanically vibrating and this can be measured electrically or optically. The frequency at which the membrane resonates depends on different factors like: dimensions of the membrane and tension induced by temperature, adsorbates, partial pressure over the membrane and DC back gate voltage. Most of the studied resonators
Figure 3-1: Schematic drawing of double clamped resonator suspended above back gate [6].

are used to investigate the mechanical resonance properties of graphene [13], but in the future they are suitable for ultra sensitive mass [72], position [73] and force sensing [74], transducing high frequencies and leak rate determination [25,35].

3-2 Actuation and readout of resonance

There are two main readout and actuation techniques for graphene resonators: electrical and optical. Both methods are explained in this section.

3-2-1 Optical drive and readout

Optical techniques are employed to detect and actuate graphene resonators [13,23,35,75]. For optical actuation the temperature on or near a resonator is modulated locally using a focused laser [76]. The first method is modulating the intensity of a diode laser focused on the graphene sheet at frequency \( f \), causing a periodic photothermal contraction/ expansion of the layer that leads to motion. The second option is focusing the laser on the graphene-substrate interface and by a difference in thermal expansion coefficient of the substrate and the graphene thermal stresses arise which set the graphene sheet in motion. The motion can be detected optically by using an atomic force microscope (AFM) beam deflection technique or interferometric setup. The interferometric method is more sensitive and therefore more commonly used [13,23,76]. The motion is detected by monitoring the interference patterns of a reference laser beam and a laser beam reflected from the graphene sheet on a photodetector. As the membrane vibrates, the interference patterns change and the varying intensity is used to extract the movement of the graphene. In Figure 3-2, a schematic of the experimental setup to actuate and detect vibrations is shown. Mechanical vibration is detected in a vacuum environment of \( p = 5 \cdot 10^{-5} \) mbar at room temperature to minimize gas damping. Damping and quality factor of the resonance is discussed in section 3-4-2.

3-2-2 Electrical drive and readout

Carbon Nanotube resonator

In 2004 an all electrical actuation and detection method for the resonance of doubly clamped carbon nanotube carbon nanotube (CNT) oscillators is reported [8]. The motion of the carbon nanotube is detected and actuated using the electrostatic interaction with a gate underneath, see Figure 3-3. First, by applying a gate voltage, an additional charge on the nanotube is induced as in a capacitor. The attraction between the charge on the nanotube and the
opposite charge in the gate causes an electrostatic force downwards. This electrostatic force has a static and a periodic component. The direct current (DC) gate voltage introduces a static force which can be used to control its tension and the conductivity of the graphene, while an alternating current (AC) gate voltage produces a periodic electrostatic force which sets the nanotube into motion. As the driving frequency of the AC signal approaches the resonance frequency, the displacement of the nanotube becomes large. This displacement causes a conductance change which is reflected in the current through the carbon nanotube:

\[ I = \frac{dQ}{dt} = GV, \]  

(3-1)

where \( Q \) is charge, \( G \) is conductance and \( V \) is voltage. The change of induced charge in a resonator has two contributions:

\[ \delta Q = \delta(CV_{BG}) = C\delta V_{BG} + V_{BG}\delta C. \]  

(3-2)

The first term is the transistor gating effect: modulation of the charge due to modulation of the gate voltage. This effect is observed at all driving frequencies. The second term however, is only present when the distance between the CNT and the gate changes, that is when the driving frequency approaches the resonance frequency.

**Graphene membrane resonator**

Based on CNT resonance readout [8], an all electrical high frequency mixing approach is implemented for the actuation and readout of graphene mechanical resonators [33]. The electrical scheme proposed is shown in Figure 3-4. A direct voltage \( V_{BG} \) induces a static tension
in the graphene, while an alternating radio frequency signal $V_{RF}$ drives the motion and another alternating signal with a small frequency offset, $V_{RF \pm \Delta f}$, is applied to the gate. In the graphene resonator $V_{RF}$ and $V_{RF \pm \Delta f}$ are mixed so that the output signal contains a component at the difference frequency $f_{\Delta f}$, among other frequencies. The higher frequencies are then rejected by a low pass filter and the mixed down current $I_{\Delta f}$ is converted into a voltage which is measured in the lock-in amplifier. It is important to realize that the resonance frequency of graphene membranes with lengths of approximately 1 to 5 $\mu$m is in the order of 10 to 100 MHz. Since it is difficult to readout the signal at such high frequencies, the signal is mixed to a lower frequency, which can be detected by a lock-in amplifier. In this experiment the graphene membranes act as a frequency mixer. For electrical readout of the mechanical vibration of a graphene membrane, monolayer graphene is preferred over multilayer graphene because the gate response of the conductivity of multilayer graphene is weaker.

**Gate-graphene interaction**

The back gate voltage manipulates the conductivity and tension in the graphene in two ways:

1. The DC part of the back gate signal, $V_{DC}$ shifts the conductivity of graphene by the ambipolar field effect. In the experiment the influence of the DC part of the gate voltage on the conductivity is visible in the mixed down current at all frequencies. Next to a change in conductivity, $V_{DC}$ also causes a strain in the graphene. The opposite charge of the graphene membrane and the back gate create an electrostatic force downwards. Coulomb’s law for a parallel plate capacitor describes the relation between electrostatic force $F_{el}$, charge $Q$ and electric field $E$:

$$F_{el} = QE = \frac{CV^2}{2} = \frac{C(V_{DC}^2 + 2V_{DC}V_{RF} + V_{RF}^2)}{2}, \quad (3-3)$$

where $C$ is the capacitance of the graphene resonator and $L$ is the membrane length. The formula shows that the DC voltage is the dominant term in the electrostatic force and
thus determines the tension in the graphene membrane. The factor $\frac{1}{2}$ originates from the fact that the charge on only 1 plate (the graphene) is considered. The assumption that graphene can be modeled as a parallel plate capacitor is a rough approximation since in reality the membrane describes a parabolic deflection in x- and y-direction due to the electrostatic pressure. The parabolic deflection is taken into account in the models to describe the behavior of the graphene membrane in Section 3-3. For unclamped graphene, the electrostatic force results in higher deformation of the membrane, than for the clamped situation [6]. This is explained by graphene slipping into the trench. It is shown that this slipping process is reversible and elastic.

2. The AC part of the signal, $V_{RF}$ can bring the membrane in resonance when the eigen-frequency is applied. The formula for electrostatic force, Equation 3-3, shows a contribution from $V_{RF}$. So a period force is applied to the graphene membrane, which only causes a large displacement when the drive frequency approaches the resonance frequency of the membrane. At resonance a capacitance change is present in the output and this is the signal component of interest. The capacitance change depends on the amplitude of the mechanical vibration and so the quality factor should be high enough so that the resonance is visible in the output current. More information about the quality factor can be found in 3-4-2. The derivation of the output signal including the resonance part, is given in 4.

Graphene exhibits piezooconductive behavior because the conductivity of the graphene membrane is not only influenced by the Fermi level shift, but also by the strain [77,78]. The effect of the deformation is twofold: due to lattice distortion pseudovector potentials arise in the Dirac formalism and inhomogeneous density redistribution occurs due to the gate [77]. By reflections of electrons due to the pseudovector potentials the conductivity is reduced while the charge redistribution enhances the conductivity. The first effect dominates when strong deformation is induced, while the second effect dominates for small deformations and not too high initial strains.
3-3 Resonance frequency

The eigenfrequency of a suspended graphene membrane can be estimated by modeling it as a membrane with zero bending stiffness under tension [25, 33, 45]. The model of a membrane is a perfectly flexible thin plate subjected to tension. It has negligible resistance to shear or bending forces, and the restoring forces arise exclusively from the in-plane stretching or tensile forces. A graphene drumhead is an example of such a membrane.

3-3-1 Nonlinear membrane model

The vibration of graphene is described by a nonlinear equation, which is derived from the membrane element in Figure 3-6 [11]. For the resultant force in z-direction two expressions based on tension in the membrane and Newton’s second law are combined to form the equation of motion for the vibrating membrane:

$$\frac{\partial^2 z}{\partial t^2} = \frac{1}{\rho h} \left( \frac{\partial T_x}{\partial x} \sin \theta \cos \phi + T_x \cos^2 \theta \cos \phi \frac{\partial \theta}{\partial x} + \frac{\partial T_y}{\partial y} \sin \phi \cos \theta \cos \phi + T_y \cos \theta \cos^2 \phi \frac{\partial \phi}{\partial y} \right).$$ (3-4)

where the parameters are used from Figure 3-6: $z$ is displacement, $T$ s tension, $\theta$ and $\phi$ are angles, $h$ is membrane thickness and $x$ and $y$ are directions. This equation in its general form is valid for large amplitudes and large rotations. For small rotations however, the following simplifications can be made: $\cos \theta \approx 1$, $\cos \phi \approx 1$, $\sin \theta \approx 0$ and $\sin \phi \approx 0$. If the thickness is assumed constant, the Equation 3-4 simplifies to:

$$\frac{\partial^2 z}{\partial t^2} = \frac{1}{\rho h} \left( T_x \frac{\partial \theta}{\partial x} + T_y \frac{\partial \phi}{\partial y} \right).$$ (3-5)

From Figure 3-6, the following geometric relations are obtained: $\tan \theta = \frac{\partial z}{\partial x}$ and $\tan \phi = \frac{\partial z}{\partial y}$, by substituting these into Equation 3-5, the final equation is obtained:

$$\frac{\partial^2 z}{\partial t^2} = \frac{1}{\rho h} \left( T_x \frac{\partial^2 z}{\partial x^2} + T_y \frac{\partial^2 z}{\partial y^2} \right).$$ (3-6)

from which parameters $T_x$ and $T_y$ are derived. By inserting the expressions $T_x$ and $T_y$ into Equation 3-6, the equation of motion for large vibrations and small rotations is derived. Unfortunately this equation has no analytical closed form solution so a numerical approach is necessary where the tension in x- and y-direction is assumed uniaxial so $T_x = T_y = T$.

3-3-2 Rectangular membrane

Vibration of rectangular membranes clamped on all sides is considered [79, 80]. In that case the Equation 3-6 can be solved analytically via the method of separation of variables [79]. The first eigenfrequency in Hz is given by:
3-3 Resonance frequency

Figure 3-6: Schematic drawing of membrane element used to obtain nonlinear equation of large amplitude vibration [11].

\[
f_{\text{res}} = \frac{1}{2} \sqrt{\frac{T}{\alpha \rho}} \sqrt{\left(\frac{1}{W}\right)^2 + \left(\frac{1}{L}\right)^2},
\]

(3-7)

where \(W\) and \(L\) are respectively the width and length of the sides of the drumhead, \(T\) the tension per unit length, \(\rho\) is mass density per unit area and \(\alpha\) is the adsorbed mass coefficient \(\rho_{\text{total}} / \rho_0\). Equation 3-7 shows that the natural frequency scales proportional to the inverse of the membrane dimensions, so bigger membranes show lower resonance frequencies. It is also clear that higher tension in the membrane increases the resonance frequency. It was shown that the model successfully predicted the resonance frequency for more than 20 studied resonators with sides up to 2 µm [33].

3-3-3 Circular membrane

For circular membranes the Equation 3-6 can be rewritten in polar coordinates. Then with separation of variables the Bessel’s equation is derived. The only boundary condition is zero deformation at the edge and the solutions of Bessel’s function are tabulated in literature. Then the fundamental frequency of clamped circular membranes under tension is described in the following equation [12, 13, 80]:

\[
f_{\text{res}} = \frac{4.808}{2\pi D} \sqrt{\frac{T}{\alpha \rho}}
\]

(3-8)

where \(D\) is the diameter, \(T\) the tension per unit length, \(\rho\) is mass density per unit area and \(\alpha\) is the adsorbed mass coefficient \(\rho_{\text{total}} / \rho_0\). In Figure 3-7 the predicted and measured resonance frequencies are plotted, which show good agreement [12]. The Equation 3-8 shows that the resonance frequency of circular membranes scales with the inverse of the radius and the square root of the tension over the mass adsorption coefficient. The tension in a graphene membrane is discussed in Section 3-3-4.

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3.3.4 Tension

The tension in a graphene membrane is approximated as isotropic elastic response under uniaxial extension [45]:

\[ T = E^{2D} \epsilon + D^{2D} \epsilon^2, \]  

(3-9)

where \( E^{2D} \) is the Young’s modulus, \( \epsilon \) is the strain and \( D^{2D} \) is the third-order elastic modulus. Thus the tension in a membrane depends on its material properties \( E^{2D} = 340 \text{ N/m} \) and \( D^{2D} = -690 \text{ N/m} \) [45] and the strain. In this model a change in elastic material properties by for instance adsorption of particles is not taken into account. In further modeling the negative term is neglected because it is only important when more than 10% strain is applied [45].

The strain values in the resonator are not expected to exceed 2%. The strain in a graphene membrane is the sum of five components: \( \epsilon = \epsilon_0 + \epsilon_p + \epsilon_{V_{BG}} + \epsilon_m + \epsilon_T \) where \( \epsilon_0 \) is the initial strain along the boundary, \( \epsilon_p \) is the pressure induced strain and \( \epsilon_{V_{BG}} \) is the strain induced by the electrostatic force of the back gate [13, 25]. Only the contributions of \( \epsilon_{V_{BG}} \) and \( \epsilon_p \) are considered individually, the other factors are considered at once as built-in strain where \( \epsilon_{built-in} = \epsilon_0 + \epsilon_m + \epsilon_T \).

Built-in strain

Graphene resonators show higher resonance frequencies at zero gate voltage than modeled when zero built-in tension is assumed [13, 23, 25, 33]. It is shown that the expected resonance frequency for a square graphene resonator with sides of 4.75 µm, modeled as a square plate under zero tension, is only 0.3 MHz. But the assured resonance frequency is 38 MHz when no external tension is induced [25]. This is significantly higher than expected. In most publications this increase in resonance frequency is attributed to initial tension and mass adsorbates. For instance [13] systematically studied 38 identical resonators. In Figure 3-8 the fundamental frequencies and quality factors are shown. The most common resonance frequency is around 15 MHz with a spread of 8 MHz. Since all these resonators have equal dimensions, the variation in frequency and quality factors can only be explained due to adsorbed mass, strain and conformational structure of membranes. Because the built-in
strain varies per resonator, it is difficult to give an estimation of $\epsilon_0$. From a best fit analysis with the results of [12, 13], a value for $\frac{\epsilon}{\alpha} \sim 1 \cdot 10^{-5}$ is extracted. Previous papers have shown a value of $\alpha$ between 2 and 11 [25, 33]. After the experiments it is possible to extract a value for $\frac{\epsilon}{\alpha}$ from our devices and compare the obtained values. Previous research shows strains values of $0.002 - 0.2\%$ [14, 23, 33, 75].

**Initial strain** Initial strain in mechanically exfoliated graphene is likely to result from the fabrication process, where the friction between graphite and the oxide surface stretches the graphene sheets across the well or trench [75]. Another cause of strain is self-tensioning by adhesion between the membrane and the substrate due to VanderWaals interaction [13, 77, 78]. Sometimes graphene resonators show slack, which means that the graphene membrane is longer and/or wider than the sides of the well. Slack is an elongation of the membrane which causes a negative initial strain and reduced the resonance frequency [45]. For an undeformed graphene membrane its length is given by $L + \Delta L$ where $\Delta L$ can be positive or negative. The reported values for slack of graphene sheets are 15 nm for a graphene sheet of 3 $\mu$m length and 17 nm for a sheet of 4.75 $\mu$m length. [6, 81].

**Temperature** Upon cooling graphene resonator devices, the resonance frequency shifts upwards, see Figure 3-9 [13, 14, 33]. This indicates a temperature dependent strain in the devices. The strain changes due to interplay between shrinkage of the electrodes and/or substrate that clamp the graphene and the expansion of the graphene itself [14, 33]. So the equation for total thermal strain becomes [14] $\epsilon_{\text{clamped graphene}}(T) = \epsilon_{\text{graphene}}(T) + \epsilon_{\text{substrate}}(T)$. This property of graphene would enable designing a positive, zero or negative temperature induced frequency shift [6, 82]. By performing the resonance experiments at a constant temperature the temperature influence can be modeled as part of the built-in strain. At other temperatures the thermal strain in unconstrained graphene is given by [14]:

$$\epsilon_{\text{graphene}} = \int_{T}^{300} \epsilon_{\text{graphene}}(t)dt,$$

where $\epsilon$ is the thermal expansion coefficient.

---

**Figure 3-8:** Quality factors and fundamental frequency of 38 identical doubly clamped graphene resonators [13].
Figure 3-9: The resonance frequency versus gate voltage is given for varying temperatures [14].

Figure 3-10: Removal of mass by ohmic heating, a) Conductance versus gate voltage before (black curve) and after ohmic-heating cycles (red-green-blue-pink curve) b-e) Resonant response with derived strain and density values which confirm mass removal [33].

**Mass**  From the continuum model, it is expected that added mass decreases the resonant frequency. When it is assumed that mass loading doesn’t affect the mechanics of a membrane, the relative change in resonant frequency scales with the relative change in mass: \( \frac{\Delta f}{f} \sim \frac{\Delta m}{m} \) [33]. This equation shows that the resonance frequency of a resonator with a low mass is highly affected by mass adsorbates. In practice however, the decrease in resonance frequency is only visible when high tension is induced in the membrane. At low gate voltages, the resonant frequency shifts upwards, indicating that the added mass increases the built-in strain. Also other experiments have shown this resonance increase, upon removal of mass by ohmic heating, see 3-10 indicating that adsorbates impart tension [33]. For different types of adsorbates their influence on the tension in graphene varies, which makes it hard to predict the tension. In the continuum model the added mass is taken into account by the factor \( \alpha \) and the strain induced by adsorbates is considered to be part of the built-in strain.
Electrostatic interaction

3-2-2 Next to built-in strain which is assumed to stay constant during experiments, also a variable strain by exerting electrostatic force can be applied. The electrostatic force induces a static and periodic tension in the graphene [8]. By describing the electrostatic and pressure induced deformation of the membrane, the strain can be approximated. This approximation is valid for clamped graphene membranes with a maximal deformation up to 200 nm [6]. The total tension in a graphene membrane where a force is applied can be approximated by [6]:

\[
T = T_0 + T_{el} = T_0 + E_{2D} \frac{\Delta L}{L} = T_0 + E_{2D} \epsilon_{el},
\]

(3-11)

where \( T \) is the tension, \( E_{2D} \) is the Young’s modulus, \( L \) is the length of the membrane and \( \epsilon \) the strain. The electrostatic tension is induced by the electrostatic force and is a result of elastic elongation of the membrane. The graphene membrane shows a parabolic deflection when subjected to a uniform force [6,83]. Therefore the elongation of the membrane is given by the arc length of the parabola minus the initial length:

\[
\epsilon_{el} = \int_0^L \sqrt{1 + (z'(x))^2} - L,
\]

(3-12)

where \( z \) is the displacement and \( L \) the length of the membrane. The maximum deflection depends on the amount of force applied. Figure 3-11 shows the maximum deflection of the membrane for 3 different values of initial tension. By solving the following equation, for a certain pressure the maximum deflection can be extracted [6]:

\[
PL^2 = 8 T_0 h z_0 + \frac{64}{3} \frac{E_{2D} z_0^3}{L^2},
\]

(3-13)

where \( P \) is the electrostatic pressure, \( T_0 \) the initial tension, \( h \) the membrane thickness, \( E_{2D} \) the Young’s modulus, \( z \) the displacement and \( L \) the membrane length. The electrostatic pressure is derived from the following equation:

\[
P = \frac{F_{el}}{A} = \frac{CV^2}{2A},
\]

(3-14)

where \( C \) is the capacitance between the graphene membrane and the gate, \( V \) is the potential and \( A \) is the capacitor area. The capacitance is given by:

\[
C = \frac{\kappa A}{d},
\]

(3-15)

where \( \kappa \) is the electrical permittivity, \( A \) is the area of the capacitor and \( d \) is the distance between the gate and the graphene. The Equation 3-14 can be used for both electrostatic induced force and pressure induced force. A comparison between the model and experimental
Figure 3-11: The maximum deflection of the graphene membrane due to electrostatic forces, shown for zero initial tension (red), 0.03% initial tension (green) and 0.03% slack (blue) [6].

Figure 3-12: The deformation of single layer graphene is shown as a function of gate voltage. Eq. (2) refers to predicted deformation based on the parallel plate model and Eq. (3) to the situation where parabolic shape of the membrane is taken into account [6].

results for the deflection of a graphene membrane where a gate voltage of 30 V is applied is shown in Figure 3-12. It is seen that the modeled deformation, when taken into account parabolic deformation of the graphene membrane and clamping, nicely coincides with the measured deflections. The deformation is then used as input for Equation 3-12 to derive the induced strain. The strain is on its turn used to determine the total tension in Equation 3-11 which serves as input for the modeling of the resonance frequencies for circular or rectangular membranes. In Section 7-2 the model is expanded for the fabricated graphene resonators to estimate the resonance frequency.

**Partial pressure**

Similar to electrostatic pressure, a partial gas pressure over the membrane induces a tension in the membrane. Using Equation 3-13, the maximum deflection of the membrane is approximated and the strain is calculated. The model is verified for a pressure induced force of $F_p = \Delta pA = 93\,\text{kPa} \cdot (4.75\,\mu\text{m})^2 = 2.1\,\mu\text{N}$, which creates a maximum deflection of 175 nm in a membrane of 4.75 µm by 4.75 µm measured with an AFM tip [25]. The maximum deflection estimated by the Equation 3-13 is 185 nm, which is less than 6% higher than measured.
3-4 Electrical response

The electrical response of a graphene resonator is seen in Figure 3-13(a). In its general form the output current $I$ is given by:

$$I = GV$$

where $G$ is conductance and $V$ the voltage. The conductance of the graphene sheet depends on the resonator geometry, the conductivity of the graphene and the amplitude of the input voltages. In Section 4-2, a model for the output current is derived. The mechanical vibration causes a resonance in the output current by a resonance in the graphene conductance.

3-4-1 Line shape

At low driving amplitudes, this resonance has a Lorentzian lineshape when the incoming signals from the gate and the source are in phase. When the signals are out of phase, the graphene resonator response shows that, see Figure 3-13(b). It is possible to adjust the phase of the signal by varying the cable length, see Section 4-1-1. Nonlinear dynamics are commonly encountered in nanomechanical resonators. The two main origins of observed nonlinear effects are: nonlinear external potentials and nonlinear restoring forces due to the elongation during vibration [15, 84]. In the equation of motion a force is introduced that is proportional to the cube of the displacement $\alpha x^3$. This force component turns a simple harmonic resonator with a linear restoring force into a so-called Duffing resonator. Without additional driving or damping the equation of motion takes the form:

$$m\ddot{a} + kx + \beta x^2 + \alpha x^3 = 0$$

with $\beta > 0$, $\alpha < 0$ and where $m$ is the effective mass of the resonator, $k$ is the effective stiffness, $\beta$ a positive elastic constant and $\alpha$ is the Duffing constant. For small driving amplitudes the resonance has a Lorentzian lineshape, but as the amplitude is increased above the critical
amplitude, the peak falls over towards higher frequencies, see Figure 3-13. A typical value for critical amplitude is 1 to 3 nm [33, 75]. The change in line shape occurs because the equation of motion has two stable and one unstable solution above the critical amplitude. So the response develops a hysteretic switching as the frequency is swept up and down, see Figure 3-14. The effect that a resonance becomes non-linear from high driving voltages can be exploited to investigate if a resonance is mechanical or electrical from origin by measuring the resonance sweeping up and down in frequency.

3-4-2 Quality factor

For the visibility of the resonance it is important that the quality factor is high because it increases the sensitivity to external perturbation. This is wanted for the visibility of the mechanical resonance. Unfortunately graphene has a relatively low quality factor compared to Micro electro Mechanical Systems (MEMS) [12]. Quality factors of graphene membranes under high vacuum conditions and at room temperature are found in the range of 25 – 400 [13, 23–25, 33]. Eventough at temperatures of 90 mK quality factors have been measured up to $10^5$ [16] for graphene resonators, it is more practical to work at room temperature. Therefore...
it is important to understand how the quality factor changes as a function of pressure, surface effects, temperature and driving force [24]. The various damping mechanisms in graphene are not completely understood [12,13], but in general there are two types of losses: intrinsic and extrinsic [15]. Intrinsic losses arise from imperfections or interactions within the structure or from fundamental processes within the lattice, while extrinsic losses are caused by interactions with the surrounding media such as gas friction, clamping and measurement scheme. In the linear regime, the quality factor can be obtained from the full width half maximum Lorentzian line shape [75]:

\[
Q_f = \frac{f}{\Delta f}, \quad (3-18)
\]

where \( f \) is the frequency.

**Frequency** In previous research identical graphene resonators were tested and their quality factors ranged from 25 to 250 with a peak at 70 [13]. A correlation is found between high frequencies and high quality factors. Since the geometry of the resonators is identical to one eachother, the increase in resonance frequency is caused by higher tension in the graphene. Also other research shows that tension enhances the mechanical quality factor [24]. However, a decrease of the quality factor with increasing frequency is found as well [12]. But in this case the lower resonance frequency is caused by bigger membrane sizes. Therefore it is concluded that higher strains increase the quality factor. The origin of the temperature dependence on the quality factor is unknown [33].

**Gas pressure** The most prominent cause of quality factor reduction is gas damping. At higher pressures the molecules in the gas collide with the graphene and this causes kinetic energy to be transferred to the gas. This occurs in the viscous regime [15], where the quality factor scales as:

\[
Q_f \propto \frac{1}{\sqrt{p}}, \quad (3-19)
\]

The viscous damping for micron sized devices is insignificant below a pressure \( 1 \cdot 10^{-3} \) mbar [12]. At pressures where the mean free path of a single molecule is much larger than the length scale of the device, the flow type is molecular. Here the losses are due to individual collisions with the gas atoms [15]. The quality factor in the molecular regime scales as:

\[
Q_{f,\text{gas}} = \frac{\alpha \rho 2\pi f_{\text{res}} v}{p}, \quad (3-20)
\]

where \( \alpha \) is the mass adsorption coefficient, \( \rho \) is the 2D mass density, \( f_{\text{res}} \) is the resonance frequency, \( v \) is the thermal velocity of the gas molecules and \( p \) is the pressure in the vacuum system [15].
Surface effects  A high size dependency is found for the quality factor of circular graphene resonators, see Figure 3-15(a) [12]. The following relation is found from a best fit to the results:

\[ Q_f \propto D^{1.1 \pm 0.1}, \quad (3-21) \]

where \( D \) is the diameter. The underlying dissipation mechanism which causes the size dependency of the quality factor is probably related to surface effects [12]. Surface treatment experiments in ultrahigh vacuum on nano- and micromechanical devices have shown that surface oxides, defects, and adsorbates augment the energy dissipation [85]. These two results contradict each other, because it is expected that increased dissipation reduces the quality factor. Further investigation into this size dependency is needed.

Driving force  Damping strongly depends on amplitude of motion, which is determined by the driving force, see Figure 3-15(b) [16]. As the resonance frequency shifts upwards due to increased driving force, the resonance peak broadens, and thus the quality factor decreases [33]. The effect is clear for graphene sheets under tensile stress, but it is less prominent when slack is observed.

Temperature  The quality factor is strongly improved by decreasing the temperature [13,33, 75]. Upon cooling, quality factors of 9000 at 10 K are reached [2010]. Also this behavior is still not understood.

\[ \frac{1}{Q_f} \propto T^\gamma \quad (3-22) \]

Where \( \gamma \) is 2.3 ± 0.1 from 40 K to room temperature and \( \gamma \) is 0.35 ± 0.05 from 9 K to 40 K.
3-5 Conclusions

It is shown that electrical actuation and read-out of a graphene resonance is preferred. The electrical circuit is presented and the interaction between the graphene and the gate is explained. Then the nonlinear equation of motion is solved analytically for a membrane. Under the assumption that rotations are small and uniaxial tension the resonance frequency is derived. The model can incorporate changes in tension due to electrostatic fields and gas pressures. The electrical response of the mechanical vibration in the output of the read-out setup will lead to a Lorentzian line shape for a linear response. For higher driving amplitudes a non-linear lineshape is obtained. The signal to noise ratio of the resonance depends on the quality factor. The quality factor can be maximized by working at low pressures in the molecular regime, increasing the tension, increasing membrane diameter, and driving the resonance at low temperatures.

Figure 3-15: The inverse quality factor versus temperature. The red and magenta lines show data scales as $T^2$ and $T^{2.3}$, respectively [13].

3-5 Conclusions

It is shown that electrical actuation and read-out of a graphene resonance is preferred. The electrical circuit is presented and the interaction between the graphene and the gate is explained. Then the nonlinear equation of motion is solved analytically for a membrane. Under the assumption that rotations are small and uniaxial tension the resonance frequency is derived. The model can incorporate changes in tension due to electrostatic fields and gas pressures. The electrical response of the mechanical vibration in the output of the read-out setup will lead to a Lorentzian line shape for a linear response. For higher driving amplitudes a non-linear lineshape is obtained. The signal to noise ratio of the resonance depends on the quality factor. The quality factor can be maximized by working at low pressures in the molecular regime, increasing the tension, increasing membrane diameter, and driving the resonance at low temperatures.
In the previous chapter it was shown that the resonance frequencies of graphene membranes are in the order of 10 to 100 MHz. Therefore the electrical circuit has to be designed specifically for high frequencies. Working at high frequencies is quite challenging, because components start behaving differently: at high frequencies in fact every component has a resistance, capacitance and inductance. In this chapter is is described what the circuit should look like to allow graphene resonance measurements. Also the behavior of the electrical components in the setup such as the lock-in amplifier, current amplifier, frequency mixers, etc. Also a model of the output is given, which improves the understanding of the circuit. And it is also identified how different input influence the output. In Section 4-1 the electrical read-out setup is presented. The principle of the resonance measurement and the individual components of the circuit are explained. In Section 4-2 the analytical model is described which described the output signal of the read-out circuit.

4-1 Design circuit

For the graphene resonance measurement a chip is designed where a graphene membrane is suspended above a gate see Chapter 5. In this section the design of the total system is explained, so a graphene resonator embedded in an electrical read-out and actuation circuit.

The resonance read-out circuit [8,13,14,33], is shown in Figure 4-1. The circuit operates at drain and gate voltages with very high frequencies in the range of 10 MHz to 100 MHz because this is the range where the mechanical resonance of graphene is located. A high frequency signal generator supplies a signal to both the source and the gate of the graphene resonator, $V_{RF}$. But before entering the gate, the alternating current (AC) signal is mixed with the lock-in signal $V_{LI}$ in a frequency mixer. The output of the frequency mixer is a voltage with the sum and difference frequency of the inputs. The mixer output is then added to a DC voltage in a bias tee before it reaches the gate, this is an AC signal with a direct current (DC) offset. The AC signal to the gate drives the graphene membrane via the electrostatic force. When the frequencies of the AC voltage equals the fundamental resonance frequency of the graphene
membrane, it will start to resonate. The DC bias voltage creates a static tension in the membrane, and changes the conductivity of the membrane via the gating effect. Remember that $V_{RF}$ was also applied to the graphene via the drain terminal. A current starts flowing to the graphene. The circuit is designed such that these high frequencies signals from the gate and the drain are mixed down in the graphene chip, to the frequency of the lock-in amplifier. The output of the graphene source is the actual measurement signal. After pre-amplification in a current amplifier the output current is converted into a voltage which is detected by a lock-in amplifier. Preamplification is necessary because the output current is in the order of nA. A digital to analogue converter (DAC), transmits the signal to a laptop where it is filed. A list of all the electronic devices including brand name, type and location where to find them within the Delft University of Technology is given in the Appendix A.

4-1-1 Electronics

Because the signal that we try to detect is in the order of nano Amperes and the high frequencies in the circuit are in the range of 10 to 100 MHz, special measures have to be taken to readout the source-drain current and limit the noise. In this section the different components of the read-out circuit will be discussed.
**Current amplifier**  A current amplifier is used to amplify the output current into a voltage that can be read out by the lock-in amplifier. The gain of the current amplifier is variable between $10^3$ and $10^{11}$. The current amplifier is easily overloaded by spiking or oscillations in the input signal. Therefore proper filtering is essential.

**Signal generators**  Two separate power sources are present in the circuit. A DC voltage is supplied to the bias tee by a switching mode power supply and the high frequency function generator provides an AC signal to the drain. The switching mode power supply causes a high frequency line distortion at the input of the current amplifier, therefore it is located as far away as possible from the current amplifier. So limiting crosstalk between the electrical components is important.

**Lock-in amplifier**  The output signal of the graphene resonator is measured with a Lock-in amplifier. With a lock-in amplifier accurate measurements may be made even when the nV signal is obscured by noise sources many thousands of times larger. Lock-in amplifiers use a technique known as phase-sensitive detection to single out the component of the signal at a specific reference frequency and phase. A block diagram of a lock-in amplifier is shown in Figure 4-2. The read-out signal $V_{in}$ is amplified with a gain $G$ in the AC amplifier:

$$V_{AC} = G_{AC} \cdot V_{in} \cos(2\pi f_{in} t). \quad (4-1)$$

The read-out signal should contain a frequency component at the frequency of the reference signal. Therefore the output of the internal oscillator is used as the reference signal which is fed into the circuit. In the phase sensitive detector the signal $V_{AC}$ is multiplied with an internal reference signal $V_{VCO} \cos(2\pi f_{VCO} \pm \phi)$ with a fixed frequency and phase:

$$V_{PSD} = G_{AC} \cdot V_{in} \cos(2\pi f_{in}) \cdot V_{VCO} \cos(2\pi f_{VCO} \pm \phi) = \frac{V_{ac} V_{vco}}{2} \cos(2\pi (f_{in} \pm f_{vco})). \quad (4-2)$$

It is assumed that $\phi = 0$, that the reference is in phase with the signal being measured. In practice $\phi$ can be adjusted at the lock-in amplifier to maximize the output. The frequency of interest in the read-out signal is $f_{VCO}$, so the output of the phase sensitive detector is:

$$V_{PSD} = \frac{V_{ac} V_{vco}}{2} (1 + \cos(4\pi f_{VCO})). \quad (4-3)$$

Since the signal passes a low pass filter, only the low frequency component arrives at the DC amplifier with gain $G_{DC}$. Therefore the time constant of the filter is chosen so that the signal at the frequency $2f_{vco}$ is strongly attenuated. Another purpose of the amplifier is integration of noise, which will integrate to zero and therefore its contribution to the output is negligible. The final output signal is a DC signal proportional to the input voltage:

$$V_{out} = \frac{G_{DC} \cdot G_{AC} \cdot V_{in} \cdot V_{VCO}}{2}. \quad (4-4)$$
In the ideal case noise signals, at frequencies other than the reference frequency, are rejected and do not affect the measurement \[86\]. In practice however the performance of the electronics is not perfect. The high frequency noise is very well attenuated in the phase sensitive detector (PSD) output by the low pass filter. But noise at frequencies very close to the reference frequency will result in very low frequency outputs from the PSD. Their attenuation depends upon the low pass filter bandwidth and rolloff. A narrower bandwidth will remove noise sources very close to the reference frequency; a wider bandwidth allows these signals to pass. So the low pass filter bandwidth determines the bandwidth of detection. Only the signal at reference frequency results in a true DC signal which is unaffected by the low pass filter.

**Frequency mixer**  Frequency mixers enable frequency conversion, or heterodyning. In the mixer the reference signal of the lock-in amplifier is mixed with the signal from the high frequency signal generator. The ideal frequency mixer generates a signal with only the sum and difference frequency of the inputs:

\[
f_{\text{mix}} = f_1 \pm f_2. \tag{4-5}
\]

Mixing is based on the trigonometric identity:

\[
\cos \alpha \cos \beta = \frac{\cos \alpha - \beta}{2} + \frac{\cos \alpha + \beta}{2} \tag{4-6}
\]

In a real mixer however, the sum and difference frequency of the higher harmonics of the input signal are also generated. These unwanted frequencies must be filtered out, which is done in the mixer. Higher order signals are attenuated and the rate of decrease versus the order depends on the quality of the mixing circuit. The mixer is a nonlinear device, in this case a double balanced passive diode mixer. A passive mixer is chosen because it outperforms a active mixer when high amplitude radio frequency (RF) signal is supplied. However, in
stead of insertion gain as active mixers generate, passive mixers have an insertion loss. The passive mixer conversion losses are caused by the mixing diode’s internal resistance, port impedance mismatches, mixer product generation, and the inevitable 3 dB that is wasted in the undesired sum or difference frequency. In the reasonance read-out setup the local oscillator signal is $V_{LI} \cos(2\pi f_{LI})$, the radio frequency signal is $V_{RF} \cos(2\pi f_{RF})$ and the intermediate frequency signal is $V_{FM} \cos(2\pi f_{RF} \pm f_{LI})$.

**Bias tee** A DC voltage passes a resistor $10\, \text{M}\Omega$ before entering the bias tee where the bias is added to the AC signal from the mixer. The resistor has a double function, the most important is the protection of the chip against burning it with a really high voltage ($P = UI$) and it also protects the bias tee of exceeding its maximum ratings. A bias tee consists of a capacitor at the AC input and an inductor at the DC input. The impedance of the capacitor in the bias tee, see 4-3, blocks the DC voltage from entering the frequency mixer and the inductor does not allow high frequency signals to pass.

**Loads and characteristic impedance** The complete system must have a constant characteristic impedance to minimize reflection. Therefore the drain and gate of the chip are each terminated with a matching load consisting of two parallel capacitors ($100\, \text{nF}$ and $100\, \text{pF}$) in series with a $50\, \Omega$ resistor to ground. The load at the drain ensures that the frequency mixer sees $50\, \Omega$ at its input ports to minimize reflections. The reflection coefficient $\Gamma$ is defined as:

$$\Gamma = \frac{Z_L - Z_0}{Z_L + Z_0},$$  \hspace{1cm} (4-7)

where $Z_L$ is the input impedance of the mixer and $Z_0$ is the characteristic impedance of the total system. So to achieve minimum reflection $Z_L = Z_0$, which is realized by the load at the drain. The load at the gate ensures an overall characteristic impedance of $50\, \Omega$ which is important for simultaneous DC and RF biasing in the bias tee, because the capacitor and inductor values are chosen for that characteristic impedance. Also for the bias tee, the load helps minimizing RF reflections.

**Parallel capacitors** The reason behind the parallel capacitors in the loads and the low pass filter at the source is the high frequency behavior of capacitors. Essentially all passive components exhibit frequency dependent behavior [87]. At high frequencies all components are $L, C$ and $R$. For a capacitor the most important parasitic effects are dielectric loss resistance and
series inductance. Inductance and capacitance are both frequency dependent impedances:

\[ Z_L = j\omega L \quad \text{and} \quad Z_C = \frac{1}{j\omega C}, \]  

(4-8)

where \( j \) is the imaginary unit, \( \omega \) is the frequency, \( L \) is the inductance and \( C \) is the capacitance. The inductive impedance increases with higher frequencies, while the capacitive impedance decreases. However, a crossover point exists where the inductive and capacitive impedances are equal. This point, also called effective series resonant point, causes problems if a source of harmonics exist at the frequency where impedances match. This is called harmonic resonance which can result in very high harmonic currents and voltages at the resonant frequency. If you add two capacitors with the right values, you never enter the resonance frequency region. Such an electrical resonance can occur between any two inductive and capacitive impedances, so the interplay between cables and components should be kept in mind while designing and connecting the circuit.

**Guarding and shielding** All components which carry electrical signals should be shielded from electromagnetic radiation. All standards electronic devices are therefore built in a Faraday cage for electric field shielding, and the self made printed circuit board (PCB) including the chip is placed in a grounded Faraday cage as well. The Faraday cage causes the electric charges induced by external electrical fields to go to ground. All components are connected via coax cables through Bayonet-Neill-Concelman (BNC) connectors. The high frequency limit of BNC connectors and RG-58C/U coax cables is 4 GHz. The output current with the measurement signal from the drain electrode to the current amplifier is secured by a guard ring. Because this signal is not yet amplified, guarding is important to keep the signal to noise ratio as big as possible. The guard wire will guide away leakage currents. It is applied when surface currents are a potential problem.

**Printed Circuit Board** The circuit is printed onto a circuit board because we are dealing with very high frequencies and small signals. On a PCB the wires are as short as possible, to minimize the influence capacitive and magnetic interference. It is important on a PCB to separate the grounds of DC and RF signals. Furthermore it is advice to place high frequency components nearest to the connectors. The most critical components, as the wire who carrier the measurement signal and RF components should be located first to minimize their route.

**Filtering** The read-out signal passes a passive low pass filter, so that only the low frequency component, which is used in the lock-in amplifier, will be amplified in the current amplifier. Problems as ringing arise when high frequencies are supplied to the current amplifier, so filtering is necessary. The low pass filter consists of a in-line resistor and a double capacitor to ground, see Figure 4-4. The values of the resistor and capacitor are chosen based on the desired cut-off frequency of the filter. For an effective low pass filter which attenuates frequencies above the lock-in frequency, of 1 kHz, a relatively high capacitance is wanted. However, it is important to keep the capacitor value as low as possible, because otherwise the current amplifier output shows a resonance and thus creates an overload in the desired frequency range. It is still possible to create the desired bandwidth by increasing the resistor value, but a high resistance is also unwanted since it decreases the output current. So a trade-off between cut-off frequency of the filter and resistor and capacitor values is necessary.
Cabling Coax cable with a characteristic impedance of 50Ω of type RG58C/U are used in the experiment. This value is chosen because all components have a characteristic impedance of 50Ω. The cables itself influence the output signal. It is wanted to keep the cable length as short as possible for three reasons: minimize attenuation, capacitive and inductive interference. The attenuation depends on the length and varies for different frequencies. The attenuation of the signal increases with frequency from $1 \cdot 10^{-2}$ dB/m for 1 MHz to $12.5 \cdot 10^{-2}$ dB/m for 100 MHz. So the signal shape changes with cable length because the high frequencies are more attenuated than the lower frequencies. The attenuation in a cable is caused by heat dissipation from electrical resistance and dielectric loss. The nominal capacitance of a RG58C/U coax cable is $95.1$ pF/m and nominal inductance is $0.26$ µH/m. This is important to keep in mind for electric resonances. The mixing in the chip should take place when the gate and source signal are in phase, to achieve the highest resonance vibration. The phase of the signal can be adjusted by changing the cable length connecting the source or gate electrode. The wavelength of the frequency is:

$$\lambda = \frac{V F \cdot c}{f},$$

where $V F$ is the velocity factor, typically 0.66, $c$ is speed of light $3 \cdot 10^8$ m/s and $f$ is the frequency. For the example of $f = 50$ MHz, $\lambda$ is 3.96 m.

### 4-2 Modeling output signal

This set of derivations applies to a graphene resonator with no partial pressure applied over the membrane. For the mathematical description of the electrical circuit, it is chosen to approach the circuit as if it were ideal. That means that we assume ideal processing by all components in Figure ???. A high frequency signal $V_{RF}$ is generated by the function generator, which is supplied to the drain of the graphene resonator and the frequency mixer.

$$V_{RF} = |V_{RF}|\cos(\omega_{RF}t)$$

(4-10)

The lock-in amplifier generates a low frequency reference signal $V_{LI}$ which will be mixed with the signal $V_{RF}$.

$$V_{LI} = |V_{LI}|\cos(\omega_{LI}t)$$

(4-11)
Both signals $V_{RF}$ and $V_{LI}$ are supplied to the frequency mixer which generates a mixed signal with the sum and difference frequency $f_{RF} \pm f_{LI}$:

$$V_{FM} = |V_{RF}| \cos(\omega_{RF}t) \ast |V_{LI}| \cos(\omega_{LI}t) = |V_{FM}| \cos((\omega_{RF} \pm \omega_{LI})t)$$  (4-12)

where $V_{FM} = \frac{1}{2}|V_{RF}| \ast |V_{LI}|$. The biased gate voltage $V_{FM}$ is added to a DC voltage $V_{DC}$ which creates static tension and a charge density shift in the membrane by the electric field effect, see ???. The voltage addition occurs in a bias tee. The total back gate voltage $V_{BG}$ is then:

$$V_{BG} = V_{DC} + |V_{FM}| \cos((\omega_{RF} \pm \omega_{LI})t).$$  (4-13)

The gate of the chip is supplied with $V_{BG}$. The signal $V_{FM}$ contains multiple frequencies of which one drives the motion of the graphene membrane. For this derivation I assume that the sum frequency drives the motion. By the capacitive interplay between membrane and gate, the conductance of the graphene changes. This is derived from the formula for the change in charge in a capacitor:

$$\delta Q = \delta(C \cdot V) = C \cdot \delta V + V \cdot \delta C,$$  (4-14)

where $Q$ is the charge, $C$ is the capacitance and $V$ is the voltage over the capacitor. The change in charge in a capacitor has thus two contributions:

1. Gating effect ($C \cdot \delta V$)
2. Varying membrane-to-gate distance ($V \cdot \delta C$)

The first term describes the gating effect, where the capacitance stays constant, but a change in voltage creates a change in the amount of charge on the capacitor. This effect is present at all frequencies. The second term, where the number of charge carriers changes due to a change in capacitance, is present when the membrane-to-gate distance varies. These distance variations occur on two time scales. At the resonance frequency a small deflection, in the order of nm occurs through the mechanical resonance of the membrane. The capacitance of the resonator is derived from the parallel plate model, where the parabolic shape of the graphene membrane due to electrostatic forces, is accounted for by subtracting the root mean square value of the maximal deflection of the parabola from the gate-graphene distance. The expression for the capacitance of the graphene resonator where the graphene flake is supended above a serial dielectric (vacuum and oxide) is given by:

$$C = \frac{\kappa_{ox} \kappa_{vac} A}{\kappa_{ox}(d_{vac} - \frac{1}{\sqrt{2}}z_0) + d_{ox}},$$  (4-15)

where $\kappa_{ox}$ and $\kappa_{vac}$ are the permittivities of respectively oxide and vacuum, where $d_{ox}$ and $d_{vac}$ are the thickness of respectively oxide and vacuum dielectric. The maximum displacement $z_0$ has two contributions, a large (semi)static component due to an applied DC gate voltage, and an AC component which drives the resonance motion. The factor $\frac{1}{\sqrt{2}}$ originates from the parabolic deflection of the membrane. By taking the mean square root value of the deflection,
the parabolic shape of the gate-graphene distance is accounted for. The total displacement of the membrane $z_0$ is given by:

$$z_0 = z_{DC} + z_{FM} = z_{DC} + z_{FM} \cos((\omega_{RF} \pm \omega_{LI})t).$$ \hfill (4-16)

Taken into account that the charge neutrality point (CNP) could be shifted due to doping, the conductance in graphene is described by:

$$G = \frac{\sigma W}{L} = n|e|\mu W = \frac{C W}{A}$

$$= \frac{C W}{\mu} [V_{DC} - V_{CNP} + V_{FM} \cos((\omega_{RF} \pm \omega_{LI})t)]$$ \hfill (4-17)

where $\sigma$ is the conductivity, $W$ and $L$ are respectively width and length of the membrane, $\mu$ is the charge carrier mobility, $C$ is the capacitance, $A$ is the area, $V$ are the voltages and $n$ is the induced charge density estimated with the parallel plate capacitor model \cite{2}. The induced charge density is given by:

$$n = \frac{\delta Q}{A} = \frac{\delta (C \cdot V)}{A} \cdot [V_{DC} - V_{CNP} + V_{FM} \cos((\omega_{RF} \pm \omega_{LI})t)]$$ \hfill (4-18)

where $V_{CNP}$ compensates the offset to the CNP in back gate voltage. The visibility of the resonance in the output current depends on the capacitance change and thus on the deformation caused by the mechanical vibration and the gate-graphene distance.

### 4-2-1 Background current

The current in the graphene has a component which is present at all driving frequencies, the so called back ground current. To determine this current, the deformation in the membrane at resonance frequency is left out of the equation:

$$I_{mix} = \delta V_{RF} \cdot G = |V_{RF}| \cos(\omega_{RF}t) \frac{\kappa_{ox}(d_{vac} - \frac{1}{2}(V_{DC} + z_{res} \cos((\omega_{RF} \pm \omega_{LI})t))+d_{az}}{W\mu [V_{DC} + V_{FM} \cos((\omega_{RF} \pm \omega_{LI})t)]}$$

$$= \frac{V_{RF}V_{FM}}{2} \frac{\kappa_{ox}(d_{vac} - \frac{1}{2}(V_{DC} + z_{res} \cos((\omega_{RF} \pm \omega_{LI})t))+d_{az}}{W\mu} \cos(\omega_{LI}t)$$ \hfill (4-19)

where only the frequency term is noted which remains after the signal passes a low pass filter.

### 4-2-2 Resonance current

The current in a graphene membrane which vibrates at resonance frequency is described by implementing the membrane deflection in the equation for the back ground current:

$$I_{mix,res} = \delta V_{RF} \cdot G = |V_{RF}| \cos(\omega_{RF}t) \frac{\kappa_{ox}(d_{vac} - \frac{1}{2}(z_{DC} + z_{res} \cos((\omega_{RF} \pm \omega_{LI})t))+d_{az}}{W\mu [V_{DC} + |V_{FM}| \cos((\omega_{RF} \pm \omega_{LI})t)]}$$

$$= \frac{V_{RF}V_{LI}}{4} \frac{\kappa_{ox}(d_{vac} - \frac{1}{2}(z_{DC} + z_{res} \cos((\omega_{RF} \pm \omega_{LI})t))+d_{az}}{W\mu} \cos(\omega_{LI}t)$$ \hfill (4-20)
4-3 Conclusions

It is seen that it is quite challenging to read-out a graphene resonance via an electrical setup. The frequencies are high and the output signals are very low. The signal can be easily disturbed by noise. Therefore it is crucial to understand all components in the electrical scheme, so that if troubleshooting is necessary, you know on which components to focus. The most important signal is from the chip to the current amplifier, because that signal contains the information about the resonance. Unfortunately the model predicts an output current in the order of pA and nA. So therefore it is very important that this signal is shielded from noise and amplified as soon as possible. Shielding the measurement signal is achieved by proper design of the PCB, connectors, cables and Faraday cage. Since the signal is amplified in the current amplifier and the output is read-out by the lock-in amplifier, a good performance of both components is required. The model shows that the output current scales with the high frequency amplitude squared and that the resonator design, and thus the capacitance between graphene and the gate, modifies the output signal. When the ratio of the graphene deflection induced by the resonance and the graphene-to-gate distance becomes smaller, the resonance shows a bigger peak in the output current. Since it is hard to estimate the electron mobility of graphene, it is hard to give an absolute value to the expected current.
Chapter 5

Resonator fabrication

In this chapter the design and fabrication of the graphene resonator is discussed. The research question of this chapter is: Is it possible to design and fabricate a graphene resonator compatible with electrical read-out with a back inlet? The design requirements arise from the permeability test and electrical read-out circuit and both must be incorporated in the chip. The processing is done in three stages: initial fabrication in Delft Institute of Microsystems and Nanoelectronics (DIMES), graphene transfer in Kavli Institute of Nanoscience Delft (Kavli), and secondary fabrication and packaging and wire bonding in DIMES again. All these steps are described. First the functionality and design requirements of the chip are presented in the Section Chip design 5-1. Then the process flow is discussed in Section 5-2 and the results of the fabrication are presented in Section 5-3. Finally in Section 5-4, the fabrication process is evaluated and recommendations for future fabrication work are given.

5-1 Chip design

In microfabrication the available fabrication processes limit the design freedom. The interplay between design and fabrication leads to an iterative design process. Therefore knowledge of the available fabrication processes is very helpful when designing a device. By sharing ideas with colleagues in the Micro&Nano Engineering group and DIMES the final design is achieved. My daily supervisor and I worked together on the design and fabrication of the resonator chip. Hugo made the drawings for the masks in L-Edit, he wrote the flow chart and he did the fabrication in DIMES and Kavli. Together we arranged the graphene transfer and the final fabrication phase of the resonator. For further inquiries you should contact him via mail (H.H.PerezGarza@tudelft.nl) or phone (tel: +31 (0)15 27 81092).

5-1-1 Chip functionality and requirements

The basic idea of the design is to create a drumhead with suspended graphene, a nanomechanical resonator. Underneath the membrane an electrode is located which serves as a back
The resonator is actuated electrically by the electrostatic force from this gate. On the topside of the chip, the graphene flake is connected to two electrodes necessary for the electrical readout, a source and a drain. For the permeability measurement a back gate access is needed for the supply of different gases to the drumhead. Those gases must be confined inside the chip, so the hole must be sealed from the top side and the back side. Furthermore, the chip must be mechanically robust to survive the fabrication process, graphene transfer and usage of the chip. From the chip functionality, a list of design constraints emerges. In this section the underlying ideas of the various requirements are discussed.

1. **Gate-graphene distance**
   In the electrical readout the part of the signal that contains the information about the resonance frequency is proportional to \( \frac{\delta C}{C} = \frac{\delta z}{z} \) where \( C \) is the capacitance, \( z \) is the gate-graphene distance. The bigger \( z \) is, the smaller the resonance signal is, therefore \( z \) should be minimized. Another reason for minimizing \( z \) is that the field lines from the gate are more homogeneous when located close to the graphene.

2. **Back gas inlet**
   A back access for gases is requested, because it makes it easier to supply the volume with gases. With a back access it is possible to first transfer the graphene onto the chip and then seal the chip from the back while capturing a certain gas inside. The diameter of the back gate access is determined by the limited aspect ratio of the etch process. Since the back gate access is almost a through-the-wafer-hole, the hole has a relatively big diameter. In section ?? the sealing method of this back access is discussed.

3. **Electrode size**
   An insulation layer is necessary to separate the source and drain electrodes from the substrate, which is supplied with a gate voltage. There are limitations on the electrode size because of their capacitance with the underlying silicon. Together with the impedance of the electrical circuit, a low pass filter is created, which is unwanted since the high frequency signal should enter the graphene and not the gate. The cutoff frequency of such a filter depends on the capacitance of the electrodes since the resistor value is not adjustable. The formula for the cutoff frequency is
   \[
   f_c = \frac{1}{2\pi RC}
   \]
   where
   \[
   C = \frac{\kappa_{\text{vac}} \cdot \kappa_{\text{ox}} \cdot A}{z}.
   \]
   The cutoff frequency of the filter should be significantly higher than the maximal signal frequency of 100 MHz. Since the thickness of the insulation layer of 500 nm is chosen for reasons of mechanical integrity, the only variable is the electrode area \( A \).

4. **Chip size**
   The final chip size is also something to consider, since the smaller the chips are, the more chips can be fabricated at once. However, the bigger the chips are, the easier it is to handle them during experiments. For the final application in the vacuum chamber however, small chips are preferable since the working area for the printed circuit board
is limited. And the smaller the chips are, the more space is left for the electronics. When determining the size of the chip also the packaging and wire bonding process should be taken into account. The size of the available chip carriers at dimes and the length of the wire bonds limits the die size to squares with sides of 10 mm.

5. **Bondpad location and connections**
The graphene must be connected to 3 electrodes: a source, a drain and a back gate. The connections of the source and drain bondpads to the graphene should be located on top of the graphene. Therefore these connections can be made only after graphene transfer. The gate electrode should be positioned underneath the graphene, close to the graphene membrane, for homogeneous field lines and high sensitivity for mechanical vibration in the output current. The bondpad of the gate must be positioned on top of the chip so that it is easy to incorporate the chip onto a printed circuit board (PCB).

6. **Suspended graphene area**
The drum head size is restricted by the dimensions of the available graphene flakes because the flakes must completely seal off the drumhead so that gas is confined. It is very unusual to create flakes of $>100 \, \mu m$ with the scotch-tape method, it is more common that flakes are $<10 \, \mu m$.

7. **Suspended membrane**
The graphene membrane must be supported by another suspended membrane which can bridge the through-the-wafer-hole (back gas inlet). The thickness of the membrane is limited by the gate-to-graphene distance. The membrane material must be chosen such that the membrane is mechanically robust, but as thin as possible. The membrane should insulate the graphene membrane electrically from the back gate, so it must be an insulator.

5-1-2 Design

Every die contains two resonator designs. A resonator consists of a suspended oxide membrane with a hole where graphene is suspended and connected to a drain and source electrode. The two resonators share a bondpad for the back gate. In the Figure 5-1(a), a detail of the chip shows the drain and source electrode and the membrane with the hole on which the graphene will be suspended. The cross section in Figure 5-1(b) shows the back gate access and the gas channel, the back gate electrode and the suspended support membrane. From a fabrication point of view the challenge was to suspend the $10 \, \mu m$ graphene flake as close as possible to the back gate while a back access for the gases exists. Finally it was chosen to create a membrane which spans the back gate inlet and which is used as a support for the suspended graphene flake.

5-2 Chip fabrication

5-2-1 Process flow

The main idea is to first etch the structures in the base wafer. Then a sacrificial wafer in bonded on top so that a cavity is created. The walls of the cavity will be oxidizes to form a
Figure 5-1: The numbers in the drawings correspond to:

1. Support membrane
2. Source electrode
3. Drain electrode
4. Bondpad back gate
5. Suspended graphene flake
6. Alignment mark
7. Insulation layer
8. Back inlet
9. Flow channel
10. Back gate
11. Hole in membrane
membrane. Then the sacrificial wafer will be etched away so that only the base wafer with the support membrane remains. Another oxidation step will oxidize the bare silicon surface so that an insulator is formed. On top of the insulation layer the golden electrodes are deposited. The wafer will be diced and then a hole will be opened in the support membrane of individual dies at the site where the graphene will be suspended. After graphene transfer the electrodes are connected to the graphene via a E-beam lithography and a lift-off procedure. Then the chip is glued inside a package and wire bonds are made to connect the chip to the carrier. These fabrication steps are explained in this section, but cleaning and measurements steps, etc. are left out of the thesis. Fabrication is done at different locations: DIMES, Kavli and the focused ion beam (FIB) machine at the faculty of Applied Physics.

**Alignment marks in base wafer** A 100 mm, n-type Silicon wafer with a thickness of 300 µm is used as substrate material. First, the alignment marks for the wafer stepper are patterned and etched on the front and back side of the wafer. These alignment marks are very important to obtain a good alignment of all the reticles which are used in the fabrication process. Then a first wet oxidation is performed, after which the wafer bonder alignment marks are patterned and etched on the front side. A second wet oxidation step is performed to protect the wafer bonder marks. The wafer bonder marks are applied to the bottom of the base and the top of the sacrificial wafer to minimize the alignment error in the bonding process. The result after two oxidation and etch steps is shown in Figure 5-2(a), where the alignment marks are covered with a 500 nm oxide layer.

**Structuring base wafer** Then resist is coated on the frontside of the wafer and the first mask is exposed. This mask defines the back gate, the E-beam alignment marks and the well to contact the silicon substrate, see Figure 5-2(b). After the development of the resist a 500 nm plasma etch into the oxide is performed. Then the gate-oxide membrane distance is defined by a plasma etch in the Silicon base wafer, see Figure 5-2(c). The gate-oxide membrane distance is 1 µm. Then an oxidation step is performed to grow 2 µm oxide all over the wafer. The next structure which has to be created is the flow channel which connects the back inlet and the (yet to fabricated) hole in the support membrane. The frontside is patterned with the mask which defines the flow channel, see Figure 5-2(d). Then another plasma etch defines the depth of the flow channel, 50 µm, see Figure 5-2(e). Then the chip is flipped and the back side of the chip is patterned with the back gate inlet, see Figure 5-2(f). The plasma etch of the back gate inlet meets the etch of the flowchannel so that a through the wafer hole is created, see Figure 5-2(g). Then all remaining oxide on the base wafer is etched away with Buffered Hydrofluoric acid (BHF)), see Figure 5-2(h). A wet etch is performed to ensure a low surface roughness, which is required for the subsequent bonding process. Then the wafer is ready for the wafer bonding process to form the support membrane.

**Alignment marks sacrificial wafer** A 100 mm, p-type Silicon wafer with a thickness of 300 µm is used as sacrificial wafer for the wafer bonding process. The wafer is prepared for the bonding process by etching alignment marks for the wafer stepper and wafer bonder as described for the base wafer in Section 5-2-1. Before bonding the oxide on the sacrificial wafer is removed by a wet etch to make the surface as smooth as possible.
Resonator fabrication

(a) After etching alignment marks and oxidation.

(b) Exposure of mask for alignment marks, back gate and gate bondpad

(c) Cross section after etching alignment marks, back gate and gate bondpad

(d) Exposure of mask for gas channel

(e) Result after etch of gas channel

(f) Exposure of mask for back inlet

(g) Result after etch of back inlet

(h) Cross section after HF etch

Figure 5-2: Fabrication of base wafer (H.H. Perez Garza Private Communications).
**Bonding the wafers**  Alignment is done on the wafer bonder machine using the bonding holders for Silicon direct bonding, see Figure 5-3(a). With a force of 3 kN the wafers are pre-bonded during 5 min. In an annealing step the silicon wafers are fused for 1 h at 500 °C. Since the direct bonding principle is based on intramolecular interaction the surface requirements are strict. To form a strong bond it is important that the surfaces are as clean, smooth and flat as possible. After annealing the bonded wafer is placed in a furnace for 500 nm oxide deposition, see Figure 5-3(b). The oxide forms in a chemical reaction of oxygen with the silicon wafers, where 40% of the thickness is consumed from the Silicon. The oxide membrane is then released by plasma etching the top oxide layer and a two step etching process to remove the sacrificial silicon wafer. The silicon wafer is etched in two steps because only a wet etch process with Potassium Hydroxide (KOH) would take too long and is difficult to time. This gives problems when the wet etch reaches the oxide membrane, because the KOH will not only etch the silicon, but also attack the oxide. Therefore first a (fast) dry etching technique, deep reactive-ion etching (DRIE) is employed. The drawback of DRIE is that it results in a non homogeneous substrate, while wet etching creates a very smooth substrate. The latter is wanted for the quality of the support membrane and is thus used to fully release the oxide membrane. Then a freeze drying procedure is performed to dry the chip without breaking the membrane. In a furnace the final 500 nm oxide layer is grown where silicon is available for consumption. The oxide membrane will grow negligibly in thickness because no silicon is directly available for oxidation. The results is a fairly homogeneous insulation layer. Then the wafer is coated again with resist to pattern the back gate bondpad, since that part of the insulation layer must be removed, see Figure 5-3(c). A dry method created the well into the oxide layer until the silicon is reached. Then on the front side a negative resist is applied to pattern the electrodes. A negative resist is chosen because a negative slope is necessary for the following lift-off procedure. After resist stripping first a 5 nm chromium adhesion layer and then a 200 nm gold layer is deposited via evaporation. The final lift-off procedure removes the excess metallic material. Before further processing is done, the wafer is diced into chips. These chips contain two support membranes above a back gate. The next step is milling a hole in the membrane.

**Open hole in oxide membrane**  A hole in the oxide membrane is created where the graphene sheet will be suspended. The FIB mills the holes. The membrane thickness is 500 nm, so a mill depth of 550 nm is chosen to make sure that an open hole is created. The shape and the size of the hole are chosen for individual chips because the FIB pattern is written directly from the computer. It is decided to make relatively small holes so that it is easier to suspend a graphene flake which fully covers the hole. In the FIB the location of the hole cannot be precisely controlled, because the ion beam cannot distinguish the membrane from the bulk. The hole is therefore located with respect to the electrodes.

**Graphene transfer method**  The next step is precisely locating the graphene on top of the hole, so that the gas volume inside the chip is sealed. Different transfer method have been reviewed [13, 18, 63, 88]. Finally, the transfer method employed to place a graphene flake on the hole in the membrane, is wedge transfer [18]. This choice originates from the fact that a group at the faculty of Applied Physics of the Delft University of Technology is experienced with this type of graphene transfer and was willing to collaborate with us. The group of Gregory Schneider performed the graphene fabrication and transfer.
Resonator fabrication

(a) Two silicon wafers are bonded via direct bonding. (b) An oxide membrane is grown overall on the wafer pair.

(c) The nitride membrane is released. (d) Electrodes are deposited

Figure 5-3: Schematics of the wafer bonding and membrane release (H.H. Perez Garza Private Communications).

Wedge transfer In the wedge transfer [18] method first graphene and graphite is deposited on a 300 nm silicon oxide substrate. Then a search for big, few-layer flakes, is performed by optical means. After identification, a polymer film is dip-coated on the substrate. Next, the chip with graphene and polymer layer on top is placed in a water basin underneath an optical microscope. By intercalation of water, the hydrophobic graphene flake on a hydrophobic polymer film is seperated from the hydrophilic susbstrate. The result is a polymer film with graphene and graphite flakes floating on the air-water interface. Then the resonator chip with the hole in the membrane is positioned in the liquid bath underneath the floating polymer film. With the microscope the alignment of the chip with respect to the graphene flake is checked. The position of the graphene flake is determined with respect to thicker, so visible, graphite flakes. The polymer film is positioned with a probe needle connected to a x- y- and z-stage. Then the chip and polymer surfaces are brought in contact by slowly pumping out the liquid while checking the alignment. The final step after contact is dissolving the polymer so that the only the graphene flake remains. The Van der Waals forces between graphene and silicon oxide keep the graphene flake in place. The process steps are schematically shown in Figure 5-4.

Electrical connections After the graphene is transferred onto the hole in the membrane, the connection between the deposited drain and source electrodes and the graphene can be made. In L-Edit for each chip a custom mask for the electrode connection is designed which takes into account the position, shape and size of the hole with respect to the deposited electrodes. E-beam lithography is used to pattern the resist layer. The pattern is checked with an optical microscope. Then subsequent chromium and gold evaporation is performed to make the connections. After a lift-off procedure the connections between the graphene and the source and drain electrodes remain.
Figure 5-4: The successive steps of the wedge transfer technique are shown [18].
Packaging and wire bonding  The chip is glued inside the cavity of the chip carrier with a non-conducting epoxy. For the resonance resonance measurements it is important that pressure over the membrane is equal, therefore the back side of the chip is only partly covered with epoxy so that a gas channel connects the chip cavity to the environment. Then the electrical connections from the chip to chip carrier are created via wedge-wedge wire bonding. In total three wires are connected to the carrier: the drain, source and gate electrode. A dual in-line package (DIP) chip carrier with 40 pins is used. After packaging and wire bonding the chip is ready to be inbedded in the measurement setup.

5-3 Results fabrication

5-3-1 Etch dummy wafer

A dummy wafer is used to check the etch rates in the silicon. After etching the back gate, gate bond pad, flow channel and back inlet with DRIE, scanning electron microscope (SEM) pictures are taken see Figure 5-5.

5-3-2 Membranes

During cleanroom processing, the wafer was taped to the wafer holder. Unfortunately the tape was very sticky and while trying to remove the the wafer from the holder, it broke. Only three chips with an complete oxide membranes survived. The intactness of the membrane is checked by optical microscopy, see Figure 5-6.

5-3-3 Misalignment

The pictures of the membrane 5-7 reveal a misalignment of the electrodes with respect to the oxide membrane. This misalignment is caused by the wafer stepper having difficulties finding all 14 alignment marks. After the membrane is released a 500 nm oxide layer is grown all over. This oxide layers covers the alignement marks which are 1 µm deep and the resulting depth of 500 nm is not enough for the wafer stepper to clearly distinguish them. A possible solution for this problem is etching deeper alignment marks. The misalignment of the electrodes causes no severe problems for further processing. However, when drawing the masks for electron beam (E-beam) lithography the real location of the electrodes accounted for.
(a) Oxide membrane, electrodes and alignment marks (chip 3)

(b) Broken oxide membrane where back gate is visible on the right (chip 3)

**Figure 5-6:** Pictures of membrane after fabrication

(a) Close up membrane and electrodes (chip 1)

(b) Close up membrane and electrodes (chip 2)

**Figure 5-7:** Position of electrodes with respect to membrane reveal misalignment
5-3-4 Missing oxide flakes

One chip has a disconnected electrode because a part of the underlying oxide layer is gone, see Figure 5-8. Some oxide flakes probably bursted off the substrate because of some voids and cracks that are formed during wafer bonding. When the etch to remove the sacrificial layer is not totally homogeneous, some thin flakes of the upper wafer remain on the interface. The flakes which are not bonded well to surface due to voids and cracks may burst off during the fabrication process and thus also the above lying oxide layer is removed. This causes a problem only at the site where an electrode is disconnected. It is possible to reconnect the electrode via ion beam deposition of platinum, but that creates a bad connection. Better would be using a conductive silver glue to create a connection through the air.

5-3-5 Milling holes FIB

In the FIB the holes are milled in the membranes. It is chosen to create three different holes: a circular hole with 4 mm diameter, a rectangular hole with sides of $W = 2 \mu m$ by $L = 3 \mu m$ and another rectangular hole with sides of $W = 3 \mu m$ by $L = 4 \mu m$. The pictures are shown in Figure 5-9.
5-3 Results fabrication

5-3-6 Graphene transfer

Optical inspection

The graphene flake on chip two is very clearly visible on pictures taken with the optical microscope, see Figure 5-10.

Raman single layer check

In the Raman spectrometer at DIMES the Raman spectrum of chip #2 is obtained. The used wavelength is 488 nm and the power was low to prevent excessive heating and thus damage of graphene. In Figure 5-11(a) the locations where the laser measured a Raman spectrum are indicated. The results of these Raman measurements are shown in Figure 5-11(d) and 5-11(c). The results are compared to the Raman spectra of few layer graphene taken with the same wavelengths [89]. When the obtained spectra are evaluated based on peak position, shape and height, it is concluded that at location 1 single or bi layer graphene is present and at location 2, 5 layer graphene. This result proves the successful transfer of few-layer graphene onto the membrane.

5-3-7 Electrodes connecting graphene

With E-beam lithography the pattern for the electrodes which connect the source and drain to the graphene is created. The location and geometry of these connections is determined with help of optical microscopy. The results of the patterning are shown in Figure 5-12. After confirmation through optical microscopy that the pattern would indeed connect the graphene to the source and drain (and not cover the graphene), the golden layer is deposited. We have forgotten to deposit first a chromium adhesion layer underneath the gold, but since the gold remained after the ultrasonic bath for lift-off, it was assumed that the electrodes would remain during the measurements as well. The golden contacts (shown in Figure 5-13) are patterned close to the edges of the hole and will thus provide good clamping. In all chips the golden contacts connect the graphene to the source and drain electrodes.
Resonator fabrication

(a) Laser spot shows locations of obtained Raman spectra.

(b) The color contrast indicates the presence of few layer graphene (chip #2).

(c) Single layer graphene spectrum obtained from chip #2 at location 1.

(d) Bilayer graphene spectrum obtained from chip #2 at location 2.

(e) Published Raman spectra for few layer graphene [89].

**Figure 5-11:** Results of Raman spectroscopy for layer thickness identification.
5-3 Results fabrication

Figure 5.12: E-beam patterns for graphene-to-electrode connecting gold wires

Figure 5.13: Golden wires after lift-off procedure

5-3-8 Replace Backgate

Chip #1 and Chip #2 are broken during fabrication. The membrane survived, but the back gate bond pad was broken off. New bondpads to connect the back gates are made with Focused Ion Beam technology. A square area of membrane material with the size of the bondpad, 100 µm by 100 µm is milled with a voltage of 20 kV. The oxide layer that has to be removed has a thickness of 500 nm so the material is removed to a depth of 600 nm. Then the hole is filled with 750 nm platinum so that the bondpads extend approximately 150 nm above the surface. This material is conductive so by wire bonding onto the platinum bond pad the connection to the back gate electrode is restored.

5-3-9 Cut electrodes FIB

The large area of the drain and source electrodes in the original mask creates an unwanted low pass filter with a cut-off frequency below the signal frequencies, so the high frequency signal would be lost. Therefore the electrode area is reduced by cutting the electrodes with the Focused Ion Beam. A trench is milled in the gold and oxide layer to separate a small area of the electrode which can be used for wire bonding. This method is applied to chip #1 and #3, see Figure 5.15. For chip #2 cutting the electrodes was unnecessary, because when the die broke, also the electrodes broke, leaving small bond pads behind.
Figure 5-14: Overview of structures including gate bond pad.

Figure 5-15: Electrodes are cut by FIB
5-3 Results fabrication

5-3-10 Die size

Initially the die size was 20 by 20 mm, but it was decided to re-dice the chips into 10 mm dies, because a 20 mm die package was not standard available. Also the the wire bonds would become very long connecting the electrodes to such a big carrier. However, the graphene was already placed on top of the membrane, so this part had to be protected during the dicing procedure. There are two risks present during dicing: released particles can damage the device and a high pressure water jet is used to remove those particles. The vulnerable part of the devices, the oxide membrane with the graphene and the connections to the electrodes is protected by covering the target area with non sticky foil and then protecting the device with blue tape. In Figure 5-16, pictures of chip #1 are shown after the dicing step. Since Chip #1 is contaminated after the dicing step it is assumed that the foil was not covering the resonator and that the contamination are tape residues. Pictures of chip #2 show no contamination of tape residues, so the foil protected the device.

5-3-11 Packaging and wire bonding

Chips #1 and #2 are packaged into a chip carrier and wire bonds between bond pads and the carrier are created. Figure 5-17(a) shows chip #1 and #2 in their package. A schematic representation of the resonator on chip #2 and the wires connecting the electrodes is given in Figure 5-17(b). Since the resonator of chip #2 is located on the edge, the wire bonds are very short. The resonator of chip #1 is located more in the middle of the chip and thus the wires are longer. Shorter wires are preferred to limit capacitive coupling in the read-out signal. The actual pictures of the wire bonds on chip #1 (Figure 5-17(d)) and chip #2 (Figure 5-17(c)) show a varying quality of the golden source and drain electrodes. The electrodes on chip #1 are in perfect condition, while the electrodes on chip #2 are damaged severely by the wedge bonding process. On both the bond pad on the chip carrier and the chip itself it is seen that various bonding attempts have been undertaken before the bond succeeded. It is unclear why it was so difficult to perform the bonding. It could be a problem on the adhesion layer, but according to other experienced clean room users, 5 nm should be sufficient. It could also be a problem of the parameters of the bonding machine. It is however strange that the bonds on

Figure 5-16: Residues on resonator after dicing (Chip #1)
chip #1 look perfectly normal. I cannot explain why this happened.

5-4 Conclusions and Recommendations

5-4-1 Devices

Per chip the final results are assessed and it is identified which chip is most likely to generate nice results in the resonance measurement. In total three chips have survived the fabrication process.

Chip #1

The membrane of chip #1 has survived the fabrication process. During a SEM session however the bond pad for the back gate broke off, but a new bond pad is created with the FIB. The deposition of gold wires to connect the graphene to the electrodes has succeeded. And the electrodes are cut to an appropriate size. So the functionality of chip #1 is complete: membrane, back gate bond pad and electrodes are present. The presence of graphene however is not validated by Raman spectroscopy. Even if a graphene flake is present, the results of the resonance measurements are uncertain. Chip #1 might show a resonance, but the influence of the sticky tape residues and the tension of the sticky tape on the graphene membrane is unclear.

Chip #2

Chip #2 also broke during the SEM session. The edge of the chip is now located very close to the membrane with the graphene. This is a nice coincidence because the wires connecting the electrodes can now be very short and the electrodes broke off to an appropriate size. Also on chip #2 a new back gate is created. The functionality of chip #2 is complete: membrane, back gate bond pad and electrodes are present, see Figure ???. The pictures after graphene transfer show the presence of graphene, the flake is visible with optical microscopy. Also single or bi layer verification is performed with the Raman. The presence of graphene combined with the short wires makes chip #2 most suitable for resonance measurements.

Chip #3

Chip #3 is the only chip with a membrane that didn’t break. Unfortunately oxide flakes have come loose, disconnecting the source electrode. It is possible to reconnect the electrode via platinum deposition with the FIB or using conductive glue. Due to time limitations however, it is chosen to proceed the resonance measurements with chip #1 and #2. Graphene is transferred onto the hole, but the presence is not confirmed with Raman and optical microscopy image doesn’t give a decisive answer.
(a) Chips glued and wirebonded in carrier

(b) Schematic of chip #2 after wire bonding - edited picture.

(c) Picture wire bond (chip #2)

(d) Picture wire bond (chip #1)

(e) Bond pads on the carrier after wire bonding

Figure 5-17: Results wirebonding
5-4-2 Design evaluation

This resonator design has combined the requirements of the electrical read-out with a back gate inlet, as requested in the research question. The fabricated back inlet for gases has a diameter of 100 µm. For future permeability measurements this inlet must be closed off hermetically. In the future outlook a method is described to perform the closure. In the design of future graphene resonators three improvements are identified: reducing membrane thickness, fabricating electrodes via E-beam lithography area and cuts smaller dies. The next improvement is a new method for electrode fabrication. For future resonator fabrication I would recommend to integrate the pattern of the new bond pads with the wires contacting the graphene. This would make one photolithography step superfluous. These new bond pads of the source and gate electrode can directly contact the graphene. The advantage of E-beam lithography is that you don’t need a reticle and you can place the bond pads for every chip individually. The drawback of using E-beam is the patterning time. But since the minimal bond pad size for wire bonding is 100 by 100 µm that will not take too long via E-beam.

5-4-3 Fabrication evaluation

In this paragraph the critical steps in the fabrication process are identified and improvements are suggested. First of all the alignment marks for the wafer stepper should be etched deeper into the silicon to prevent alignment problems with subsequent masks. Second, more attention should be given to the bonding process of the base and sacrificial wafer and the previous etch steps, to ensure a very smooth surface. If the number of voids and cracks is reduced, the wafer is stronger bonded and less oxide flakes will burst off during processing. Furthermore it was seen that milling holes in graphene with the FIB is a good solution for individual chips, but for full wafers it is not suited due to the duration of the process. The transfer of graphene is difficult to evaluate since only two chips are left for assessment. For sure the graphene is present at chip #2. Patterning the gold wires to connect the graphene to the electrodes showed good results. The pattern was nicely defined. The only critical point here is drawing the masks. Since the location of the FIB milled hole is undefined with relation to the membrane and the misaligned electrodes, individual mask are drawn based on measurements in pictures. This is not ideal, a solution could be to create the holes at a known position in the membranes before dicing.
Chapter 6

Electrical circuit verification with JFET

This chapter deals with the electrical circuit verification. The high frequency signals in the resonance measurement require that the components are soldered onto a printed circuit board (PCB). PCBs are customized for their application. The disadvantage of using a PCB is that it is not so easy to add or remove components. In contrast to a bread board where you can plug and unplug as many components as you like in every configuration, a PCB doesn’t have that flexibility. Therefore it is important to design the PCB ‘right’ at once. The experiments that are executed in this chapter are used to verify the performance of the electrical circuit for the final application of graphene resonance measurements. Designing a PCB for the experiments in this chapter is a preparation for the final PCB design for the chip. It is chosen to first test the electrical circuit without the chip, but with a field effect transistor (FET). In the introduction the analogy between a graphene resonator and a field effect transistor is explained. It is also shown how certain properties of a graphene resonator, as showing an resonance are artificially introduced in the circuit with the FET. Since the behavior of the field effect transistor is specified by the producer, the behavior of the circuit can be analyzed. It is also important to model the relation between the current and voltage in a FET. By comparing the current response of the circuit to the model and the specifications, you start understanding the electrical setup. For the future resonance measurement with the chip, it is important to identify what problems can occur in the circuit and how to deal with those issues. So that is what we will do in this experiment. The chapter starts with an introduction into field effect transistors in Section 6-1 and its analogy with a graphene resonator. Then in Section 6-1-2 the model for the electrical behavior of the FET is derived. In Section 6-2 the testplan is presented which is divided into direct current (DC) voltage test and alternating current (AC) voltage test. In the testplan also the circuits and the PCB design are shown. Then the final measurement results and matlab simulations are shown in the Section 6-3. In the last Section 6-4, the conclusions of the experiment are given.
Electrical circuit verification with JFET

<table>
<thead>
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<th>Property</th>
<th>Symbol</th>
<th>Value</th>
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<tbody>
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<td>n-channel JFET</td>
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<tr>
<td>Breakdown voltage</td>
<td>(V_{(BR)GSS})</td>
<td>-30 V</td>
</tr>
<tr>
<td>Zero gate voltage drain current</td>
<td>(I_{DSS})</td>
<td>2 µA (\sim) 6.5 µA</td>
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<tr>
<td>Gate-source Max cutoff voltage</td>
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<td>Gate cut-off current</td>
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<tr>
<td>Drain source voltage</td>
<td>(V_{DS})</td>
<td>30 V</td>
</tr>
</tbody>
</table>

Table 6-1: Specifications of BF245A JFET

6-1 junction gate field-effect transistor (JFET)

A field effect transistor is a device where the input voltage of the gate controls the current. The type of FET used in this experiment is a n-type JFET BF245A. Its specifications can be found in Table 6-1. A schematic representation of a n-type JFET is shown in Figure 6-1(a). A FET has three terminals: a gate, source and drain. Between the source and drain is a channel of semiconducting material. For a n-type JFET, the charge carriers are electrons and the bias voltage is always negative. When a voltage is applied between source and drain, \(V_{DS}\), a current will flow. By applying a bias voltage at the gate terminal \(V_{GS}\), the electric-field effect determines the shape and the width of the channel and thus controls the electric current which flows between the source and drain terminals. The source terminal is where the electrons enter the channel and they leave via the drain. When no gate voltage is applied, the current is not increasing linear with the drain-source voltage, but reaches a constant value when the drain-source voltage is higher than a threshold value \(V_P\). By applying a gate voltage larger than the pinch-off voltage \(V_P\), it is possible to fully close off the channel so that no current is flowing, therefore a FET is essentially a switch. A FET operates in three different regimes depending on the applied input voltage, see Figure 6-1(b):

- **Triode, linear or ohmic regime** \(|V_{GS}| > |V_P|\) and \(V_{DS} \leq V_{GS} - V_P\); here the channel is formed, but not pinched-off. In this mode the JFET behaves as a variable, ‘voltage controlled’ resistor.

- **Saturation, active or pinch-off regime** \(|V_{GS}| \geq |V_P|\) and \(|V_{DS}| \leq V_{GS} - |V_P|\); here the channel is pinched-off, so \(I_{DS}\) only varies with \(V_{GS}\).

- **Cut-off regime** \(V_{GS} < V_P\) and all \(V_{DS}\); In the cut-off regime no current flows because there is no conductive path between source to drain due to a high gate voltage. So \(I_{DS} = 0\).

6-1-1 Analogy between JFET and graphene resonator

It is chosen to replace the graphene resonator in this test by a JFET. A JFET is chosen because of its analogies with a graphene resonator. First of all, both devices have a gate, source and drain terminal. And in both, a current which flows from drain to source is influenced by the electric-field effect. Depending on sign of the gate voltage, graphene behaves as a n- or a p-type FET. This property of graphene originates from the ambipolar field effect. The
(a) Schematic representation of n-type JFET

(b) N-type JFET operation

(c) Source-drain voltage current relation JFET

(d) Gate voltage current relation JFET
difference between a FET and a graphene resonator is the relation between gate voltage and conductivity. In graphene the relation is linear, while in a FET the relation is quadratic. The difference is caused by a different physical configuration. The equation that describes the current in a JFET in the saturation regime is Shockley’s equation:

\[ I_D = I_{DSS}(1 - \frac{V_{GS}}{V_P}), \]  

(6-1)

where \( I_D \) is the output current, \( I_{DSS} \) is the drain current at zero gate voltage, \( V_{GS} \) is the gate voltage and \( V_P \) is the pinch-off gate voltage. One aspect of the graphene resonator that the JFET cannot duplicate is the mechanical resonance at the resonance frequency. Therefore in the second test, an electronic resonance is generated by inserting a LC-resonance circuit at the or drain of the JFET.

**Electrical resonance circuit**

An electrical resonance can be generated by placing an inductor and a capacitor in parallel to each other. Such a circuit acts as an harmonic oscillator for current and will resonate when supplied with a signal at the resonance frequency. A capacitor stores energy in an electric field between its plates, depending on the voltage across it. And the inductor can store energy in a magnetic field depending on the current through it. If a charged capacitor is now connected across a inductor, charge will start to flow through the inductor, building up a magnetic field and reducing the potential over the capacitor. This continues until the voltage across the capacitor reaches zero. The inductor however, keeps the current flowing while extracting energy from the magnetic field, which starts to decline. The current then charges the capacitor plate with the opposite voltage sign and an electric field builds up. Then the cycle repeats itself, and current starts to flow in the opposite direction through the inductor again. When the inductive and capacitive reactances are equal in magnitude, the charge starts flowing back and forth through the circuit. The resonance frequency of the LC circuit is:

\[ f_{res} = \frac{1}{\sqrt{LC}2\pi} = \frac{1}{\sqrt{390 \text{nH} \cdot 10 \text{pF}^2}2\pi} \approx 80 \text{ MHz}, \]  

(6-2)

where the values for \( L \) and \( C \) in the circuit are used to determine the resonance frequency. Ideally, the resonance would continue forever, but in reality resistance makes the oscillations die out. If a resistance is placed parallel to the LC circuit, damping is added. The Quality factor of a RLC circuit is then given by:

\[ Q = R\sqrt{\frac{C}{L}} = 3.3 \text{k} \Omega \sqrt{\frac{10 \text{pF}}{390 \text{nH}}} \approx 16.7, \]  

(6-3)

where the values for \( L \) and \( C \) in the circuit are used to determine the resonance frequency.
6-1-2 Model output current JFET

Shockley’s equation 6-1 is used to derive an expression for the current $I_d$ as a function of $V_{GS}$ valid for the saturation region. In the experimental setup not the gate-source voltage $V_{GS}$ is defined but the potential between gate and ground $V_{BG}$. This is not equal since the current $I_d$ passes a 50 Ω resistor before it is at ground potential, see Figure 6-2.

$$I_D = I_{DSS}(1 - \frac{V_{GS}}{V_P})^2,$$

(6-4)

where $V_{GS} = V_{BG} - RI_d$. Therefore the current $I_d$ is described in an implicit function:

$$I_D = I_{DSS}(1 - \frac{V_{BG} - RI_d}{V_P})^2.$$

(6-5)

This approximation is generally good to within about ten percent and is the accepted equation for all JFET calculations. An even better approximation for the current $I_d$ is given in [?]:

$$I_D = I_{DSS}(1 - 3\frac{V_{GS}}{V_P} + 2\frac{V_{GS}^3}{V_P^3})$$

$$= I_{DSS}(1 - 3\frac{V_{BG} - RI_d}{V_P} + 2\frac{V_{BG} - RI_d^3}{V_P^3}).$$

(6-6)

These implicit functions are solved with Matlab. Both models are used for comparison with the measured result.

6-2 Testplan JFET

Two separate circuits will be tested in this experiment. First the DC characteristics of the JFET are measured, to compare the results to the transfer and output specifications of the
producer, shown in Figure 6-1(d) and 6-1(c). If necessary this can lead to modifications of the electrical measurement setup. When the results are satisfactory, an AC measurement will be performed where an electrical resonance is generated and measured. It is expected that the resonance is shown in the output signal. If the resonance is not visible, the circuit must be adjusted.

6-2-1 DC experiment

In the DC experiment the following questions are answered:

1. What is the relation between the output current $I_d$ and the voltages $V_{SD}$ and $V_{GS}$?

2. Does the measured relation agree with the specified relation from the producer and the model?

The electrical circuit for the DC measurements is shown in Figure 6-3. The idea is to keep as many of the components which are also present in the future resonance measurements. The specifications of the JFET are given by the producer for static voltages, therefore the high frequency signal generator is replaced by a DC voltage source. The drain-source voltage passes a load before it is applied to the drain. It is assumed that the presence of the load makes no difference for the output signal since capacitors have very high impedances for DC voltages. Another DC voltage source supplies a negative voltage to the gate via a 10 MΩ resistor. The gate voltage also passes a load and an extra resistor, which is placed to prevent high currents through the FET, which can break the junction and thus kill the FET. The output current of the JFET passes a first order passive low-pass filter, but again since only DC voltages are present they should not contribute. A coax cable connects the current output to the current amplifier which amplifies the current to a voltage. The current has a variable gain, so the same current amplifier can be used for this experiment, at mA as the resonance measurements at nA. Via a digital to analogue converter (DAC) the signal is read-out on the computer with a Labview programme.

6-2-2 AC experiment

Then the high frequency signals are introduced in the setup. The final goal is detecting the frequency and quality factor of the electrical resonance. This is analogous to the graphene resonance measurements, so these results are very important. However, the success of the AC test depends on the ability of the JFET to mix high and low frequency signals. That is important because the lock-in detects only the signal at the reference frequency, 1 kHz. That frequency is only generated when the JFET acts as a frequency mixer. After the AC test the following questions should be answered:

1. Is the JFET capable of mixing frequencies in the order of 100 MHz?

2. Do we see a resonance in the MHz range?

3. Is the measured resonance close to the predicted value?
4. Does the quality factor match with the estimations?

The AC circuit is shown in Figure 6-4. A high frequency signal, \( V_{RF} \) is applied to both the drain and the mixer. The high frequency signal is added to an AC voltage in a bias tee. The addition of a second bias tee is necessary for proper JFET operation. The JFET should always see a gate negative gate voltage with a lower value than the source-drain voltage, otherwise the junction breaks. Applying a bias to the drain source prevents that this problem occurs. In the mixer the gate voltage is generated at the sum and difference frequency of the incoming voltages, \( V_{LI} \) and \( V_{RF} \) with an amplitude \( \frac{V_{RF}V_{LI}}{2} \), is added to a DC voltage in the bias tee and supplied to the gate. In the JFET the voltages at the gate and the drain are mixed down to the frequency of the lock-in amplifier. The high frequencies are attenuated by the low-pass filter and the frequencies below the cut-off frequency of the filter are applied to the current amplifier. The current amplifier converts the current into a voltage which is amplified with a gain factor and read-out by the lock-in amplifier. The first question, 'Does the JFET mix frequencies?', is answered by looking at the relation between the output current and the amplitudes of the lock-in and high frequency voltage. The second question is tested by applying a frequency sweep and analyzing the output current. The lineshape and quality factor of the resonance are determined and compared with the estimated values.

6-2-3 PCB design

For the DC and AC experiments only one PCB is designed and ordered. The basis of the design is the electrical circuit design for the resonance measurements. For the measurements with
Figure 6-4: Electrical circuit for AC test

the JFET the size of the PCB and the connectors is not critical, as the currents are relatively high in order of mA and the PCB will be built in a Faraday cage that we order ourselves. Therefore it is decided to connect the coax cables directly to the PCB. The connectors are placed along the edges. The FET is located close to the edge, in the neighborhood of the connector which will carry the measurement signal. A quad wire is added around the signal line to protect it from surface currents. The capacitors and resistors are located closely to the FET to minimize interference. There is a lot of empty space on the PCB because the connectors are relatively big compared to the components. The ground plane of the DC signal through the 10 MΩ is separated from the radio frequency (RF) signal part on the PCB. The ground plane is connected via screws to the Faraday cage and thus to ground via the shields of the coax cables. The components for the PCB are ordered at Farnell. The soldered PCB and its box are shown in 6-6.

6-3 Results

6-3-1 DC characteristics

The output current is measured as a function of gate voltage for a drain-source voltage of 15 V. It is expected that at zero gate voltage the current is between 2 and 6.5 mA, as specified by the producer. The first results are shown in Figure 6-7. It is seen that $I_{DSS} = 4.32$ mA, which is within specifications. When $V_G$ is stepwise varied from 0 V to negative values, the current decreases, but 0 mA cannot be measured. Because at $V_G = -0.9$ V, the output current starts
Figure 6-5: Design of the PCB by Merlijn van Spengen.

(a) Schematic representation of circuit on PCB
(b) 3 Dimensional view of the PCB

Figure 6-6: Faraday cage and PCB FET tests

(a) Faraday cage which contains PCB with BNC connectors
(b) Fully soldered PCB
The output decreases as a function of gate voltage.

Figure 6-8: The voltage step response of the output current is visible and the oscillations start when $V_{GS} = -0.9$ V is reached.

oscillating and at $V_{GS} = -1.0$ V, the current amplifier shows an overload error. The oscillations are a time dependent phenomenon therefore the output current is also plotted as a function of time in Figure 6-8. The gate voltage is applied in steps and the step response is visible in the output. These oscillations disturb the measurement and their cause should be removed. It is certain that the overload error is not caused by a very high current in the FET, because increasing the gate voltage has the opposite effect: the current is reduced. When $V_{GS}$ is set back to 0 V, the oscillations diminish and the measurements show the expected behavior. So the oscillations are most likely a problem caused by the combination of the current amplifier and the rest of the circuit. After troubleshooting it was found that the current amplifier start showing strange behavior when it has a large capacitance at its input. That capacitor is important for filtering the output signal in the resonance measurements, so the capacitance is decreased from 100 nF to 10 nF, but not removed. There is also a back-up plan if the capacitance cannot be reduced: placing a large resistance at the input of the current amplifier.

After the capacitance at the input of the current amplifier is reduced, again the output current is measured as a function of gate voltage. The modeled output and the measured output are...
plotted in one Figure, ??, where the output relation given by the producer is plotted as well. The results show that it is possible to close the channel in the JFET completely, since the current declines to zero for \( V_{GS} = -1.8 \) V, which is called gate-source cut-off voltage. This value is specified between \(-0.25\) V and \(-8\) V, so the measured result is well within specs. Comparing the measured and modeled results to the specified output relation, it is seen that the measured results fit better to the specifications than the modeled current. This was expected since the model has only 10% accuracy. The output is also measured as a function of source-drain voltage for zero back gate voltage. These results are presented in Figure 6-9(c) and 6-9(d). The current slope obtained from the measurements is a little steeper for low voltages than the relation from the producer. It is also seen that the JFET does not reach a constant value for \( I_{DSS} \) but it keeps increasing a little as the source-drain voltage increases. These results show that the FET is behaving not perfect, but keeping in mind that it interacts with the system these results are acceptable.

### 6-3-2 AC test

In the AC test two circuit configurations are used. First the \( LC \) resonance circuit is shortcircuited by a \( 0 \) Ω resistor. This configuration is used to check if the FET is able to mix-down the high frequency signal to the reference frequency of the lock-in amplifier. For the resonance test the \( 0 \) Ω is replaced by a higher value of \( 1 \) kΩ.

**Frequency mixing in JFET**

The first test is measuring the output current as a function of lock-in voltage for:

- \( V_{RF} = 200^{-3} \sin(50 \text{ MHz}2\pi t) \) V
- \( V_{BT1} = 3.5 \) V
- \( V_{LI} = \sqrt{21} \) V\( \sin(1 \text{ kHz}2\pi t) \)
- \( V_{BG} = 0 \) V

The \( RLC \) circuit does not contribute to the circuit because a \( 0 \) Ω resistor is placed, which behaves as a wire and thus the current will not flow through the capacitor and inductor. In an ideal mixer the output would be linearly proportional to the lock-in voltage. The results of the measurement and the model are shown in Figure 6-9. The mixing behavior of a FET is not investigated in this thesis. It is assumed that since the output changes as a function of lock-in voltage, for low voltages below \( 0.5 \) V, mixing occurs.

**Resonance measurement**

The second test is applying a frequency sweep to check if a resonance is present. The first measurement is done with a \( 1 \) kΩ resistor in the RLC circuit. The expected resonance frequency is \( 80 \) MHz, therefore the frequency was swept from \( 32 \) MHz to \( 100 \) MHz. In the output no resonance was visible. For \( R = 1 \) kΩ, the calculated quality factor is \( Q = 5 \). It was decided...
(a) Plot of 2 models and measured results

(b) Output current as function of gate voltage from producer

(c) Plot of measured results

(d) Output current as function of source-drain voltage from producer
to replace the resistor for a 3.3 kΩ resistor, which has a calculated quality factor of $Q = 16.7$. The frequency sweep was applied again. Figure 6-10 shows the results of the measurements with the two resistor values. At $R = 1 \, \text{kΩ}$, no resonance is seen, but at $R = 3.3 \, \text{kΩ}$, a clear resonance peak is visible in the output signal. The resonance frequency is observed at 67 MHz. The observed frequency at which the resonance occurs is lower than the expected 80 MHz. Taken into account 5% and 10% variation of specified values for the inductor (L) and the capacitor (C), the lowest obtained resonance frequency is $f_{\text{res}} = 75$ MHz. The difference between expected and observed frequency can be explained by the presence of other capacitances and inductances in the circuit, besides the $LCR$ circuit. If by interfering capacitances the capacitor value is increased from 10 pF to 14 pF, the resonance frequency shifts to 68 MHz. For instance the internal capacitance of the current amplifier might cause the interference.

The quality factor of a resonance is defined as:

$$Q_f = \frac{f_{\text{res}}}{\Delta f},$$

where $\Delta f$, is the full width-half maximum value of the resonance peak. The measured resonance peak has a quality factor of 9.6. This result indicates that the damping is higher than only from the resistor in the $RLC$ circuit. Probably the resistance of the JFET or the current amplifier contributes to the damping.

### 6-4 Conclusions

It can be concluded that the current amplifier cannot cope with high input capacitances. When high input capacitances are applied, the amplifier start oscillating and an overload error occurs. The initial value of 100 nF has to be decreased. When the capacitor is replaced by 10 nF, the current amplifier does not show any oscillations when the gate voltage becomes more negative. The drawback however, is that the cut-off frequency of the low pass filter...
increases and that more high frequency signals, which are noise in the output signal, enter the current amplifier. Furthermore the measured DC characteristics of the JFET are within specifications of the producer, which shows that for DC current in the order of mA, the circuit behaves as expected. The AC test shows that the JFET is indeed mixing the signals at the drain and gate input to the lock-in frequency, because the output varies as a function of lock-in voltage. The electrical resonance is visible in the output of the circuit, but only after inserting a higher resistor value 3.3 kΩ. The measured resonance frequency is a little lower than expected and also the quality factor is lower than expected. This indicated that inductance, impedance and resistance from other components in the circuit contribute to the resonance. These results show that indeed components at radio frequencies behave different from low frequency signals and that we have to deal with that. Something else that was discovered during measurements, was that the output of the high frequency signal generator is not constant with frequency. When an output is specified at 32 MHz it decreases with 30% until 70 MHz. This is measured with an analogue oscilloscope, which cannot show higher frequencies. It is also possible that the oscilloscope, which is specified to work up to 50 MHz cannot represent the high frequency signal and that the signal amplifier amplitude indeed stays constant.

**Figure 6-10:** The output current is measured as a function of frequency.
In this chapter the actual read-out of the graphene resonators is performed. First the resonance frequency is modeled. Second, a model of the output current, which is derived in 4-2, is compared to measured result to see if the model is correct and if the circuit behaves as expected. This measurement can give some information about the properties of the graphene resonator as electron mobility. Also the sensitivity of the resonators is assessed by looking at the capacitance change that the gate induces on the membrane when it is displaced. These values are compared to reported values and the sensitivity is evaluated. This gives an indication whether a resonance peak can be detected in the output of the setup. Then the actual resonance measurements are performed to see if a resonance peak is present in the output current. Based on the outcome recommendations are given concerning the chip and the measurement setup for improvement. What are important noise sources and how can they be prevented? The research questions concerning the chip performance are: Does a current flow through the resonator? This will indicate if the bonding is done correctly and if graphene is present. In this chapter, first, a test plan is written. What circuit do we use? What are we going to measure? In this section also the design of the printed circuit board (PCB) and vacuum setup are shown. In the modelling section the results of the Matlab model for the resonance frequency and back ground current are presented. Then the results of the measurements are discussed. Issues with the read-out are discussed and solutions are presented. In the conclusions an evaluation of chip performance and electrical read-out performance are given.

7-1 Test plan

In Figure 7-1 the full circuit is shown for the final resonance measurements of graphene. The measurement environment is designed for mechanical resonance detection of a graphene resonator. The resonance frequency of a graphene membrane depends on partial pressure,
electrostatic forces, temperature, mass adsorbates and initial tension. To keep the resonance measurements as simple as possible the partial pressure is zero, no static electrostatic force is applied and temperature is kept constant. So only the initial tension and the mass adsorbates determine the tension and thus the resonance frequency. The chip is embedded in a PCB specifically designed for the chip, which is placed in a vacuum setup. For practical reasons it is chosen to perform the experiments at room temperature. For the quality factor and the electron mobility it would be better to perform low temperature experiments.

**7-1-1 Measurement setup**

The results of the tests with the junction gate field-effect transistor (JFET) have led to adaptations of the PCB design, which are discussed in 6. The PCB version for the chip shown in Figure 7-2. The chip is placed in a vacuum chamber, so all electrical feedthrough is required for the signals. The vacuum chamber is a cross with an electrical feedthrough (KF40 flange) with 4 Bayonet-Neill-Concelman (BNC) connectors. There are four electrical connections: source, drain, gate and ground. The KF flange is single ended, so the vacuum side only has 4 pins. It is chosen to connect the PCB perpendicular to the flange, by soldering two connector plugs onto the PCB which can be plugged onto 2 of the pins. The other two pins are connected via 2 short wires which are fed into screw terminals. The cross of the vacuum chamber is connected to the electrical feedthrough, to the vacuum pump, a gas inlet and a pressure sensor. The vacuum cross is clamped in a holder. The holder is convenient for 2 reasons: clamping of the vacuum cross and reducing the propagation of vibrations of the vacuum pump.
to the chamber. The vacuum pump can reach pressures of $1 \cdot 10^{-3}$ mbar, which is enough to reach the molecular flow regime where gas damping is insignificant [90]. In Figure 7-3(b) it is shown how the chip is connected to the feedthrough flange and is inserted into the vacuum chamber.

## 7-2 Modeling resonator behavior

In this section the resonance frequency of the graphene resonators on chip #1 and #2 are estimated. Also the output signal is predicted and the sensitivity is qualified.

### 7-2-1 Resonance frequency

Via modeling the fundamental resonance frequency of chips #1 and #2 are estimated. For rectangular membrane the fundamental frequency is given by:

$$f_{res} = \frac{1}{2} \sqrt{\frac{T}{\alpha \rho}} \sqrt{(\frac{1}{W})^2 + (\frac{1}{L})^2}, \quad (7-1)$$

where $W$ and $L$ are respectively the width and length of the sides of the drumhead, $T$ the tension per unit length, $\rho$ is mass density per unit area and $\alpha$ is the adsorbed mass coefficient $\frac{\rho_{\text{total}}}{\rho_0}$.

The parameters of the model are:

1. The initial strain $0.002 - 0.2\%$ (from literature)
2. Dimensions chip #1: $W = 3, L = 2$
3. Dimensions chip \#2: \( W = 4, L = 3 \)

4. 2D Youngs modulus: 342 N/m

5. Mass adsorption coefficient: 5 (from literature)

6. 2D mass density: \( 7.4 \times 10^{-7} \text{ kg/m}^2 \)

The resonance frequencies of chips \#1 and \#2 are plotted in Figure 7-4(b). For the chip \#1 de eigen frequency is between 15 MHz and 130 MHz. For chip \#2 the eigenfrequency is between 10 MHz and 90 MHz. Chip \#2 is bigger than \#1 and thus has the lower resonance frequency. These modeling results show very clearly how much the frequency depends on the strain and thus the tension. In Figure ?? the deflection of the membrane of chips \#1 and \#2 are shown as a function of gate voltage, assuming zero initial tension. The deflection increases up to 46 nm (chip \#1) and 70 nm (chip \#2) for a gate voltage of \(-50 \text{ V}\). It is seen that the gate voltage induces more strain in chip \#1 than in chip \#2.

7-2-2 Output current

The following equation describes the output current in graphene:

\[
I_{\text{mix}} = \frac{V_{RF} V_{FM}}{2} \frac{\kappa_{\text{ox}} \kappa_{\text{vac}}}{\kappa_{\text{ox}} (d_{\text{vac}} - \frac{1}{\sqrt{2}} z_{V_{DC}}) + d_{\text{ox}}} \frac{W}{L} \mu \cos(\omega_L t)
\]  

\[ (7-2) \]

where \( \sigma \) is the conductivity, \( W \) and \( L \) are respectively width and length of the membrane, \( \mu \) is the charge carrier mobility, \( C \) is the capacitance, \( A \) is the area, \( V \) are the voltages and \( n \) is the induced charge density estimated with the parallel plate capacitor model [2].

The parameters of the model are:

1. Lock-in reference voltage: \( V_{LI} = 0.3 \text{ V} \)
7-2 Modeling resonator behavior

(a) Resonance frequency chip #1 as function of strain

(b) Resonance frequency chip #2 as function of strain

Figure 7-4: Matlab model results: resonance frequency

(a) Strain as function of gate voltage chip #1

(a) Strain as function of gate voltage #2

Figure 7-5: Matlab model results: strain

(a) Membrane deflection as function of gate voltage chip #1

(b) Membrane deflection as function of gate voltage #2

Figure 7-6: Matlab model results: deflection
The relation between the current and the RF voltage is given for chips #1 and #2 for a mobility value of $3 \text{m}^2\text{s/V}$\cite{l10} in Figure 7-7. The current in chip #1 is larger due to the ratio of width over length $\frac{W}{L}$. For chip #1 $\frac{W}{L} = 1.67$ and for chip # $\frac{W}{L} = 1.33$. The results of the model will be compared to the current measurements.

7-2-3 Sensitivity resonator

The mechanical capacitance change per nanom of the designed resonators is compared to values reported for other graphene resonators with electrical read-out in Table ???. The highest sensitivity reported is 33 times higher than the sensitivity of the resonator under test, chip #1. The low sensitivity translates into a small change in the current, which makes it harder to detect a resonance. The visibility of the resonance depends on the quality factor and the sensitivity of the resonator. The capacitance can be tuned by changing the distance between the capacitor plates or by the surface area. For future resonators it is a good idea to look at the possibilities to increase the resonator area and decrease the gate-graphene distance.
# 7-3 Results

## 7-3-1 Read-out problems

Initially there were problems with the read-out of the chip because even if no chip was inserted on the PCB, a current was measured. First the PCB was cleaned thoroughly in a dish washer and after drying in a vacuum furnace at 80 °C for 45 min the chip was placed on the PCB and inserted into the vacuum system for further measurements. These actions reduced the leakage current, but still the problem was not solved completely. After applying a frequency sweep of the RF voltage, an electrical resonance was visible in the output signal at a frequency of 81 MHz, even without a chip was connecting the wires on the PCB, see Figure 7-8. Such an electrical resonance is created by interplay between inductance and capacitance. Capacitors are added to the PCB, but no inductor is. The inductance can come from cables, and other components in the circuit. Probably the current amplifier is involved in the generation of the electrical resonance. Because when at the drain and gate the cable lengths are changed, the resonance frequency stays constant, but when changing the cable length between current amplifier and vacuum chamber, it shifts. After a lot of troubleshooting (checking cables, connectors, etc) the signals were analyzed with an oscilloscope to determine which frequency components are present at the input of the current amplifier. It was seen that the coax cables pick-up 50 Hz noise and high frequency line noise. But those frequencies should not be present in the output since a low pass filter is located on the PCB to prevent high frequencies from entering the current amplifier. However with the oscilloscope it was seen that a lot of high frequencies are not filtered and thus enter the current amplifier. The current amplifier starts oscillating when high frequencies are supplied. It was decided to add another low pass filter between the chip output and the current amplifier with a cut-off frequency of 1.6 kHz. That cut-off frequency is chosen so that the reference frequency of the lock-in 1 kHz can pass the filter, but the high frequencies are attenuated. After the implementation of the second filter, the electrical resonance was no longer visible and the current amplifier only showed noise in the order of 5 pA, which is expected because there are no hardware connections. Another source of noise that had to be removed was the high frequency noise from the switching behavior of the direct current (DC) power source. By replacing the power source further away from the setup, the noise decreased, but turning it off was the best solution. For future measurements it is recommended to use a battery as a DC power source.
Enhancing graphene mobility

While looking at options to decrease the noise, I also explored possibilities to increase the signal through the chip by annealing. Figure 7-9 shows the dependency of the output current on the electron mobility. It is clear that increasing the mobility leads to higher current, which are easier to detect in the electrical circuit. Annealing the chip increases the electron mobility of graphene. Unfortunately annealing was not possible at Mechanical, Maritime and Materials Engineering (3mE) for practical reasons. I have looked into the possibility of current annealing, since the connections were already available. But current annealing requires a very high vacuum $1 \cdot 10^{-8}$ mbar and such a pump was not available.

7-3-2 Background noise

When nothing is connected to the input of the current amplifier, a signal is detected at the output of 5 pA. This signal originates from thermal noise, noise generated in the current amplifier and lock-in amplifier and coupling with the environment. When the empty PCB is
connected to the setup and supplied with $V_{RF} 200 \text{ mV}$ at $f_{RF} 50 \text{ MHz}$ and $V_{L} 0.3 \text{ V}$, the output is measured. Figure 7-10 shows that when signals are applied a current is measured in the same order as the background noise of 5 pA. This results shows that the leakage current is negligible.

### 7-3-3 Output current verification

The relation between output current and RF voltage obtained with Matlab is compared to actual measurements in Figure ??.

The measured output is used to determine the value for the electron mobility in the model. When $\mu$ is chosen $1 \cdot 10^3 \text{ cm}^2 \text{ s} / \text{ V}$, the model and the result show the same behavior. This result proves that the model is valid and the obtained value for $\mu$ is within expectations. It is a little lower than reported by [??], but his measurements were performed at 5 K, where the scattering is less. Since our result is in the same order and similar values are reported for non-suspended graphene, the obtained $\mu$ is realistic.

### 7-3-4 Resonance measurements

The output current is measured over a very broad frequency range from 32 MHz to 100 MHz. To ensure that the resonance peak is not skipped by sweeping the frequency to fast, the sweep takes 15 min up to 45 min. The output current is measured as a function of time. The data is therefore cut in time frames to spread the output so that it is easier to see a resonance peak. Parameters of first test are:

1. Lock-in reference voltage: $V_{RF} = 0.3 \text{ V}$ locks in at 1 kHz.
2. Gate voltage: $V_{DC} = 0 \text{ V}$
3. RF voltage $V_{RF} = 30 \text{ mV}$
4. Current amplifier gain: $10^9$
5. Sensitivity lock-in: 50 mV

The results show a double resonance sweep divided into 5 steps in Figure 7-12. The frequency sweep gives a positive parabolic output with a maximum at approximately 60 MHz. I assume
(a) Matlab output current $\mu = 1 \text{ m}^2 / \text{V} \text{s}$ (Chip #1)

(b) Measured output current (Chip #1)

Figure 7-11: Comparison relation current to RF voltage for chip #1.
that the total of inductance, resistance and capacitance in series creates a minimum impedance at the center frequencies. The $RLC$ impedance relation is negative parabolic so that would result in a positive parabolic output current. In the signal small oscillations are seen. These oscillation can result from a graphene resonance, but since the oscillations occur at a wide frequency range, it is more likely that they are caused by thermal fluctuations, internal noise, coupling with the environment, etc. At the beginning of every parabola, at frequencies of approximately 35 MHz to 40 MHz the output is negative. Also at the end of the parabola a dip is visible in the output signal. That occured when the input of the lock-in gave an input overload: This occurs for voltage inputs greater than 1.4 V. The maximum output of the current amplifier is 10 V, so it is possible that the current amplifier still works, but the lock-in gives an overload error. This indicates a disturbance, it might be a resonance. More measurements are planned to analyze further what causes the overload error and if it is a mechanical resonance peak.

Figure 7-12: Output as function of frequency sweep (chip #1)
7-4 Conclusions and recommendations

First of all, the output current is very good approximated by the model. From the fit between the model and the measurements a value for the electron mobility of the graphene is obtained \(1 \cdot 10^3 \text{cm}^2 \text{s/V}\). This value is a little lower than reported values for suspended graphene, but the graphene has undergone a lot of process steps after initial transfer and it is exposed to ambient environment, so adsorption of impurities might cause reduced mobility. The mobility is still high enough to see a signal with the electrical setup. An output signal is measured from a graphene resonator. It is seen that the current is frequency dependent. This is probably caused by an \(RCL\) circuit in series. The resistance, capacitance and inductance arise from the components in the circuit. The background noise in the circuit is very low, in the order of \(5 \text{pA}\), and the signal is in the order of tens of \(\text{pA}\) to \(\text{nm}\) so the signal to noise ratio is good. So far no resonance peak is detected. The output shows two irregularities: at a frequency of approximately \(38 \text{MHz}\) and at a frequency of approximately \(95 \text{MHz}\). The absence of a resonance is explained by the low sensitivity of the resonator. Compared to other resonators, chip \#1 has a sensitivity which is one to two orders lower. It is possible to increase the sensitivity by decreasing the gate-membrane distance or increasing the suspended graphene area.

7-4-1 Improvements electrical measurement setup

During the measurements noise was a big issue. Not only noise from the environment, but mainly strange behavior of components as the current amplifier. For such high precision measurements the equipment and the measurement environment are very important. For instance the ground quality, the high frequencies from the power sources, the nominal line voltage, all these effects couple into the setup and make detection of a resonance difficult. Some improvements could be placing the setup in a noiseproof chamber to eliminate 'ambient' signals, and apply a low pass filter on power supplies or use a battery. Another improvement is buying a better current amplifier, because that is a very crucial part. And the current amplifier interferes a lot with system. When all power supplies (except lock-in amplifier) are shut off, still a signal exist which is very spiky. The signal is so spiky due to high frequencies at the current amplifier input. For the best possible measurements, the current amplifier and the vacuum system with cabling should be located inside a noiseproof chamber. Another improvement concerns the data processing. Currently the frequency read-out is manual, only the output voltage is read-in digitally. It is important to have both digitally available. Furthermore the assessment of the data should be improved using for instance Matlab.

7-5 Evaluation chip performance

In this section an evaluation is made of the chip performance in the read-out circuit with respect to the fabrication and design of the chip. Chip \#1 shows an output signal. There is good agreement between the chip response and the model. The response indicates that graphene is present, since the other chip gives no signal at all. It is important to improve the sensitivity of the graphene resonator for capacitance changes. This is realized by decreasing the gate to graphene distance or increasing the surface area. Making a nitride membrane
with a 200 nm thickness in stead of 500 nm oxide and dimensions of 4 µm by 3 µm already improves the resonator sensitivity with a factor 4. Another solution is adding a topgate. Chip #2 doesn’t show any signal in the measurement setup. Therefore the chip was placed in a probestation, and a small DC voltage was applied, but no current is measured. The Raman confirms the presence of graphene, but the graphene was assessed earlier in the fabrication process. However, optically the graphene flake is still visible. The most likely option is the gold bond is disconnected. The Figure 7-13 shows a small crack in the connection. But that is the only clue I have for the nonworking device. It would be good to evaluate the measurement setup with more samples, to distinguish between problems with the setup and problems with the chip.

Figure 7-13: Electrode connecting graphene (chip #2)
Chapter 8

Conclusions, Recommendations and Future Outlook

8-1 Conclusions

In the beginning of the thesis the properties of graphene are assessed. It is seen that graphene has many extraordinary properties, and its impermeability is one of them. Despite of graphene being impermeable it can be a very good alternative for gas separation membranes. Since it is only one atomic layer thick, a very high pore density can be obtained and a very high productivity, because the molecules only have to cross a single barrier. Because graphene is purely 2 Dimensional it has a very high surface to volume ratio. That means that surface effects are dominant. In combination with the negligible bending stiffness, graphene can come in very close contact to a surface and therefore VanderWaals forces are so important for graphene. For instance when graphene is positioned over a trench, theses forces result that the graphene is strained towards the walls. The fabrication technique to fabricate graphene, mechanical exfoliation using scotch-tape, is easy in essence, but it requires some experience to create big, monolayer flakes. In fact you don’t need more than some scotch tape, clean dies, and gloves to create single layer graphene. The transfer of graphene is a lot harder. Especially the positioning of graphene on top of the substrate. But the technique they apply at Applied Physics, the wedge transfer is succesfull. The Raman is very well suited to do single layer graphene measurements. For the Raman it is important the use the correct settings for wavelength and power. But its spectrum gives a very clear distinction between single and few layer graphene. There is looked into two methods to detect a graphene resonance. The electrical read-out is interesting for future permeability measurements and is more easily embedded with a chip. The response of graphene membranes is found to be in the other order of 10 MHz to 100 MHz, that is found in both models and literature. The measured output current of the chip as a function of asRF voltage is accurately predicted by the analytical model. From this relation the value for the electron mbility is extracted, namely around $1 \cdot 10^3 \text{cm}^2 \text{s/V}$. Unfortunately the resonance is not yet detected via the measurement setup. This is attributed to the low sensitivity of the graphene resonator. More
Conclusions, Recommendations and Future Outlook

measurements should be carried out to evaluate what the causes of two disturbances in the frequency dependent output signal are.

8-2 Recommendations

For the resonance measurement setup the quality of the electronics and the amount of shielding is very important. It is seen that noise from the environment, and other components in the setup, couple in the output signal. One could think of improvements as: placing a filter on the power line, using a battery as DC power source, placing the setup inside a soundproof chamber, check the ground quality, and buy another current amplifier which does not interact so much with the signal that is amplified. But the biggest improvement can be achieved by increasing the signal. This can be realized by measuring at low temperature to increase the quality factor, improving the electron mobility by annealing the graphene. Other solutions are changing the resonator design. The easiest method is reusing the same masks for the back gate and make a less deep gate. This requires a stronger membrane which can be made thinner than 500 nm. Nitride is a good membrane material. With nitride it could be possible to decrease the membrane thickness to 200 nm without compromising strength. Another solution is adding a top gate to the design. A top gate can be as close as 300 nm to the undeformed membrane. The design and masks of the top gate are already finished but not included in this thesis. The advantage of the top gate becomes especially clear for permeability measurements when a partial pressure causes the graphene membrane to bulge up. When a partial pressure is applied, the graphene bulges upwards towards the gate and thus the signal increased. However, some problems are foreseen with the vacuum level within the chip, because the flow regime depends on the typical distance in the vacuum chamber. The addition of a top gate would almost seal the graphene and thus gas molecules could stay around which can add damping to the system. The chips with a top gate can be also used for further investigation of the change of conductivity in graphene due to 2 effects: deformation of the membrane due to electrostatic forces and global charge carrier density shift due to ambipolar field effect [77].

8-3 Future outlook

First of all the data should be generated digitally to make data processing easier, faster and more accurate. An idea to improve the setup for permeability measurements would be inserting a feedback loop to track the shift of the graphene resonance automatically. The shift generated pressure over the membrane can be compensated for by a changing gate voltage. The goal is to retain the resonance frequency constant while the partial pressure decreases as a function of time by controlling the gate voltage in a feedback loop. If the shift in gate voltage is read-out, the shift in resonance and thus the pressure decay can be derived. For compensation of the induced strain it is important that the forces generated by the pressure and electrostatics are in the same order. By modeling both electrostatic and pressure induced force on the membrane it is clear that for the current resonator design the electrostatic induced force is 2 orders smaller than the pressure induced force, see Figure 8-1. Therefore the pressure range over the membrane is limited. But if the gate-graphene distance in the new resonators
is smaller, as suggested before, a higher electrostatic force can be exerted. This would leak to
an automated permeability measurement.

8-4 Hermetic sealing

For the permeability measurements it is necessary to hermetically seal the chip while confining
a gas inside. In this section the design of a sealing mechanism is presented. The design is
already fabricated but not yet tested. It is required that the seal is as tight as possible. But depending on the size of the gas molecules, the gas leak rate will vary. A gas with ‘big’ molecules like Argon leaks less than a gas with smaller molecules like Helium. The advantage of using helium would be that the helium leak rate would give us an indication of the leak tightness of the closed chip. Another advantage is that helium is an inert gas and will thus not react with the graphene. On the other hand it is difficult to work with Helium since the sealing must be performed in a helium environment with a known, constant pressure. The preferred sealing mechanism is solder bonding since it relatively easy to carry out and it gives a good seal. This solder bonding must be performed at the melting temperature, which is 240°C for Tin Silver. The three constraints which the closing mechanism must meet are heating the solder to a temperature of 240°C, compatibility with silicon or copper and a single gas environment.

8-4-1 Solder bonding

A chip sealing device has been designed which can confine the gas to a certain region and which can heat the solder to 240°C, see Figure 8-2. The general idea is that the chip closes off a cavity where gas can be confined. Therefore the cavity has a gas in- and outlet. In this cavity a vertical axis is inserted from below which can support a Nickel plate with solder that can be pressed to the back of the chip. The axis with the support will be made from brass which is an good thermal conductor. The axis is partially inside the cavity and partially outside. The outside part is heated with a soldering iron. The heat conducts through the whole axis and will heat the Nickel plate with the solder. When the brass axis reaches the required temperature (240°C), the soldering iron is retracted and by hand the axis is pushed up to apply pressure between Nickel plate and the back of the chip. Next the temperature
is decreased to room temperature again. Then the bond has formed. During operation the temperature is measured with a thermocouple on the brass axis. Protective gloves are necessary for operating the device at 240 °C. The design requirements are:

- possibility to apply linear pressure between chip and Nickel plate from below
- enough space for a hand to operate the device
- possibility to clamp and exchange the chip at the top of the mechanism
- possibility to insert new Nickel plate with Solder
- all components must withstand a temperature of 240 °C
Appendix A

Components read-out setup

A-1 List electronic devices

- **High frequency signal generator** Rohde & Schwarz (SMH 845.4002.52): DEMO (EWI), Giel Hermans
- **Lock-in amplifier** Stanford Research Systems (SR830): PME lab (3mE), Rob Luttjeboer
- **DC power supply** Voltcraft (VSP 2403HE): Meetshop (3mE), Jos van Driel
- **Current amplifier** Keithley (428-Prog): PME lab (3mE), Urs Staufer
- **Digital to Analogue Converter** National Instruments (NI USB-6211): Meetshop (3mE), Jos van Driel
- **Frequency mixer** Mini circuits (ZAD-3+): PME lab (3mE), Rob Luttjeboer
- **Wideband bias tee** Mini circuits (ZFBT-4R2GW): PME lab (3mE), Rob Luttjeboer

A-2 List components vacuum system

- **Vacuum pump** Varian (SD-300): PME lab (3mE), Rob Luttjeboer
- **Pressure sensor - Pirani gauge** Leybold-Heraeus (162 31 B2): Meetshop 3mE, Jos van Driel
- **Controller pirani gauge** Leybold-Heraeus (Thermovac TM220S2): Meethsop (3mE), Jos van Driel
Appendix B

Enhancing permeability of graphene

Porous graphene

Up to now scientists have only simulated the separation of gases through pores of various sizes and shapes, and with different passivation atoms to obtain high selectivities and throughput [?]. The optimal barrier free pore width in the simulated graphene based filters is around 3 Å, which resembles the removal of two hexagons, and mainly nitrogen and hydrogen are used as passivation atoms [92]. These passivating atoms are added in a chemical process. So the pore creation technique can only influence the selectivity of the graphene membrane by manipulating the pore width with respect to the kinetic radius of target molecules. So the most important requirement for a suitable pore creation technique is precise pore width control. Development of a suitable pore-production technology are currently based on electronbeam treatment [19], ion bombardment [21] or bottom-up synthesis [22,94].

Focused electron beam

In 2008 a group of the university of Pennsylvania demonstrated high-resolution modification of suspended multi-layer graphene sheets by controlled exposure to the focused electron beam of a Transmission Electron Microscope (TEM) [19]. Focused electron beam treatment can create nanometer size slits and pores, see ??, at room temperature. This method creates multiple pores of 3.5 nm diameter close to each other. Unfortunately the sizes of the nano pores made with this method are a factor 10 too big to achieve a good selectivity of for instance hydrogen over carbon dioxide. Another disadvantage of this technique is the high voltage of the TEM, 200 keV, which is higher than the knock-on-voltage of carbon atoms in graphene, and thus the graphene around the pores gets damaged.

Decrease pore size

It is shown that it is difficult to create small enough pores with a focused electron beam. But recently a paper was published with a method to decrease the pore size in multilayer graphene [20]. They showed that pores can be shrunk and expanded under the influence of electron beam irradiation at different temperatures. They managed to close smaller pores in the full temperature range, but bigger pores (10 nm range) only closed at
Figure B-1: Different magnifications of pores with scale bars of a) and b) 50 nm, c) 2 nm and d) 10 nm [19]

Figure B-2: Shrinkage of 2.3 nm nanopore in graphene sheet at 400 °C [20]

lower temperatures of 400 °C. The shrinking process can be stopped by blocking the electron beam and so the size of the pores can be tailored. Normally the pores size drilled by focused electron beam is around 2 to 5 nm, but with this technique such a pore can be closed in a timescale of minutes. Unfortunately the refilled area has poor crystallinity and the structure of the edge of the pore is different from freshly drilled pores. This might be a problem for the passivating atoms. The researchers observed that during the shrinkage of a pore a larger terrace-like hole expanded, from this effect it is concluded that carbon atoms knocked out from other multilayers are displaced to the monolayer as ad-atoms for the healing of the graphene. So this method will not work for uniform single layer graphene.

**Ion irradiation** There is an alternative method for making pores in graphene with atomic precision [21]. It consists of inducing defect nucleation centers in graphene with energetic ions, followed by edge-selective electron recoil sputtering, see ?? . Suspended graphene is transferred to a TEM grid where pore nucleation sites are created with an argon ion beam at low temperature of 148 K. Experimentally it is shown that each ion that transits the graphene removes 0.5 carbon atom from the lattice. After this step the graphene was transferred to
a Ultra High vacuum system for further low-energy electron beam irradiation. When a pore reached the desired size, irradiation was stopped. It is seen that the electron recoil sputtering is edge selective. In this process nanopores are created on suspended CVD graphene with radii as small as 3 Å, which corresponds to 10 atoms removed. This is within the size range that pores are highly selective. And compared to the method described before a much lower energy level is required to generate the pores, which reduces the damage to the graphene layer.

**Bottom-up synthesis**  Bottom-up synthesis is another technique to obtain porous graphene [22,94,95]. It is shown that porous graphene networks can be fabricated by surface-assisted coupling of specifically designed molecular building blocks. Covalent bonds are formed between the molecular building blocks to form 2D polyphenylene networks, see ?? . This bonding process occurs only above a annealing temperature of 570 K. A superhoneycomb structure is created with arrays of 0.3 Å diameter pores with an inter-pore distance of 7.4 Å range. The researchers managed to create these networks on a Silver substrate, but unfortunately the membrane didn’t grow homogeneously over the substrate. At the borders of the networks protrusions are shown which are assigned to contamination molecules. Also the exact properties of this assembled material are unknown yet. However in the future this might be a possible graphene fabrication method. An advantage is namely that the porous graphene is fabricated in one step, in contrast with for example pore shooting with electron beams which occurs after the graphene is fabricated. Also the pore size and pore distribution can be designed for a specific gas filter by using different molecular building blocks.
Strain enhanced permeability

The effect of mechanical strain on diffusion of hydrogen atoms through graphene has been studied by first-principles calculations [3]. It is concluded that tensile strain in the armchair direction of the graphene sheet decreases the out-plane diffusion barrier of hydrogen atoms. Without strain applied the out-plane diffusion barrier height through the center of the benzene ring is 2.46 eV. The high barrier blocks diffusion at low temperature. When 10% strain is applied in armchair direction, the diffusion barrier through covalent bond breaking-and-forming process is decreased from 3.85 eV to 0.5 eV. When 15% strain is applied in the same direction, the diffusion through the center of the hexagon, is decreased from 2.46 eV to 0.7 eV. Both barriers are low enough to see out-plane diffusion at low temperature. The potential barrier for increased strain is given in Figure ??.
Figure B-6: Diffusion energy as a function of tensile strain in the zigzag and armchair direction is shown in respectively the top and bottom graph [3].
Appendix C

Fabrication of graphene resonators

C-1 Doubly clamped membranes

The simplest graphene resonators are doubly clamped graphene sheets suspended over predefined trenches. In 2007 nanomechanical graphene resonators were fabricated by mechanically exfoliating single and multilayer graphene onto predefined silicon oxide trenches [75]. Electrical and optical actuation of the resonators is shown in this work and the mechanical properties of a graphene resonator are studied. In 2009 double clamped graphene resonators with lengths up to 20 µm are produced from epitaxially grown graphene on a silicon carbide substrate [23]. The fabrication process is shown schematically in Figure C-1. First graphene is grown on top of a silicon carbide substrate. Second, golden bondpads are deposited on top of the graphene layer. Then with photolithography the bondpads and the graphene are covered with resist in the shape of the double clamped structure. Plasma oxide etching removes the rest of the graphene. Finally a wet underetching technique is applied to release the graphene from the substrate. This process resulted in a yield of 80 – 90%. In 2010 large arrays of suspended single layer graphene membrane resonators are fabricated with CVD graphene [?], see Figure C-2. First CVD graphene is patterned into strips on the copper foil with photolithography and oxygen plasma. Then the patterned graphene is transferred to trenches in a 285 nm silicon oxide substrate. With this method hundreds to hundreds of thousands of devices were produced per fabrication run. The yield was more than 80%.

C-2 Suspended graphene with electrodes

Underetch technique

In 2008, suspended graphene with electrodes is fabricated to measure the ultrahigh electron mobility [?]. The fabrication starts by randomly transferring graphene flakes onto a 300 nm silicon oxide substrate with the scotch-tape technique. With visual inspection potential single layer flakes are identified, and the thickness is confirmed with measurements of half integer
Figure C-1: A schematic of the fabrication steps towards suspended graphene is shown [23]. In a) gold pads are defined by photolithography, in b) photoresist is patterned on top of the graphene, in c) an oxygen plasma etch defines the shape of the graphene flake and in d) photoelectrochemical etching is used for release.

Figure C-2: a) shows two doubly clamped resonators from a b) large array [13]
quantum Hall effect. The graphene is not patterned to avoid introducing additional defects in the bulk and dangling bonds at the edges of the graphene. With electron beam lithography contacts are patterned on the natural flakes. Via a lift-off procedure golden electrodes are deposited onto a chromium adhesion layer. Then the graphene is suspended by an etch in Buffered Oxide Etch, which uniformly removes 150 nm of silicon oxide across the substrate, including the area underneath the graphene flakes. However, the silicon oxide located under the electrodes remains, see figure C-3. Other groups have fabricated suspended membranes with electrodes via this method of underetching as well [33], sometimes patterning the graphene or using CVD graphene [13].

C-2-1 Suspended stamp transfer technique

The drawback of the underetch technique is that it is hard to make small-capitance, localized gates for graphene mechanical resonators. Therefore an electron-beam patterned stamp technique is developed which allows to move individual suspended graphene flakes and assemble them with small localized gates into electrically-controlled mechanical resonators [24]. First, mechanically exfoliated graphene is placed on top of a silicon substrate with a silicon oxide upper layer. After monolayer confirmation by Raman spectroscopy, 50 nm golden electrodes are deposited on the graphene by electron-beam lithography followed by a lift-off procedure. Then polymethyl methacrylate (PMMA) is spun on the chip and with a second electron-beam step, the stamp and hole patterns are defined, see Figure C-4. Next, the whole PMMA membrane with graphene and electrodes is released from the substrate by etching away the silicon oxide layer with hydrogen fluoride (HF). After rinsing the membrane in deionized water, it is scooped out if the water with a ring shaped frame. With an optical microscope the individual stamps are located and taken out of the membrane by breaking the joints between the stamps. Since suspended graphene is invisible under the microscope, the electrodes and holes in the stamp are used for alignment. During transfer the stamp is inverted so that the graphene and electrodes lay on top of the PMMA membrane. By this method a distance between the substrate and the graphene of 0.1 to 0.5 \( \mu \text{m} \) is created, depending on the thickness of the PMMA layer. Finally the hanging electrode is broken and pressed through the hole to make contact with the predefined electrodes on the target substrate. The success rate of the suspended stamp transfer technique depends on the size of the suspended graphene. For samples with a length \(<2 \mu\text{m}\), the yield is \(>50\%\).
C-3 All sides clamped membranes

In 2008 a graphene resonator clamped on all sides is fabricated [25]. These graphene drumheads are fabricated by a combination of standard photolithography and mechanical exfoliation of graphene sheets. First, squares ranging from 1 µm² to 100 µm² are defined by photolithography on a silicon oxide substrate of 285 nm or 440 nm. Second, reactive ion etching is used to etch the squares to a depth of 250 nm to 3 µm leaving a series of wells in the wafer. With the scotch-tape technique graphene drumheads are created, see Figure C-5. Leak rate experiments with these resonators show that graphene is impermeable for all gases. In 2010 [13] also created square membranes clamped on all sides. An unpatterned CVD graphene membrane is transferred onto square holes in a suspended silicon nitride membrane. For small membrane sizes, with sides in the order of 5 µm, the yield is > 90%. However, for membranes with sides longer than 30 µm the yield is lower.


Glossary

List of Acronyms

3mE  Mechanical, Maritime and Materials Engineering
TU Delft  Delft University of Technology
AFM  atomic force microscope
PMMA  polymethylmethacrylate
SEM  scanning electron microscope
NAMECOSH  nanomechanically controlled separation of hydrogen from a carrier stream
HOPG  highly ordered pyrolytic graphite
MEMS  Micro electro Mechanical Systems
FIB  focused ion beam
E-beam  electron beam
FES  Dutch Economic Structure Enhancing Fund
TEM  tunneling electron microscope
JFET  junction gate field-effect transistor
FET  field effect transistor
DRIE  deep reactive-ion etching
DEMO  Electronic and Mechanical Support Division
DIMES  Delft Institute of microsystems and Nanoelectronics
Kavli  Kavli Institute of Nanoscience Delft
PME  Precision & Microsystems Engineering

Master of Science Thesis  CONFIDENTIAL  L. M. Willems
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<thead>
<tr>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>PCB</td>
<td>printed circuit board</td>
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<tr>
<td>EWI</td>
<td>Electrical Engineering, Mathematics and Computer Science</td>
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<tr>
<td>CNT</td>
<td>carbon nanotube</td>
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<tr>
<td>PhD</td>
<td>Doctor of Philosophy</td>
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<tr>
<td>PSD</td>
<td>phase sensitive detector</td>
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<tr>
<td>BNC</td>
<td>Bayonet-Neill-Concelman</td>
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<tr>
<td>RF</td>
<td>radio frequency</td>
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<tr>
<td>DC</td>
<td>direct current</td>
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<tr>
<td>AC</td>
<td>alternating current</td>
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<tr>
<td>DAC</td>
<td>digital to analogue converter</td>
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<td>CNP</td>
<td>charge neutrality point</td>
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<td>Buffered Hydrofluoric acid</td>
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<tr>
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