The design, fabrication and analysis of a MEMS-based in-plane tensile device
Optimized for monolayer graphene

Eric Walter Kievit

Report number : MNE 2013.008
Professor : Prof.dr.U.Staufer
Supervisor : H.H.Perez-Garza MSc.
Specialization : Micro and Nano Engineering
Date : March 19, 2013
The design, fabrication and analysis of a MEMS-based in-plane tensile device
Optimized for monolayer graphene

MASTER OF SCIENCE THESIS

For the degree of Master of Science in Micro and Nano Engineering at Delft University of Technology

Eric Walter Kievit

March 19, 2013

Faculty of Mechanical, Maritime and Materials Engineering (3mE) · Delft University of Technology
The work in this thesis was supported by DELMES B.V. and NanoNextNL

Copyright © Precision and Microsystems Engineering (PME)
All rights reserved.
Membrane technology for the separation of gases is likely to play a major role in reducing the environmental impact and costs of global industrial processes. Current ultrathin membranes range from tens of nanometres to several micrometres in thickness. However, these membranes are limited in their overall efficiency and or selectivity. Graphene, which is a single layer of graphite, is the ultimate limit: a chemically stable and electrically conducting membrane with the thickness of a single atom. However, in pristine and relaxed state, graphene was proven to be completely impermeable to all atoms (even as small as Helium).

The core objective of this thesis is the design, fabrication and analysis of a MicroElectroMechanicalSystem (MEMS) based in-plane tensile device. This device can be used as a tool to stress graphene such that high strain percentages (10%) are achieved which alter the intrinsic permeability properties of graphene. This device was fabricated in the DIMES facilities at Delft University of Technology and its performance was thoroughly analysed. Using the developed device, the maximum strain induced on a multi-layer graphene flake was $\geq 10\%$, which is a major step towards implementing graphene as a controllable filtration membrane.
# Contents

<table>
<thead>
<tr>
<th>Acknowledgements</th>
<th>xi</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 Introduction</strong></td>
<td>1</td>
</tr>
<tr>
<td>1-1 Industry scope</td>
<td>1</td>
</tr>
<tr>
<td>1-2 Separation</td>
<td>2</td>
</tr>
<tr>
<td>1-2-1 Membranes</td>
<td>2</td>
</tr>
<tr>
<td>1-3 Thesis objectives</td>
<td>5</td>
</tr>
<tr>
<td>1-3-1 Thesis hypothesis</td>
<td>5</td>
</tr>
<tr>
<td>1-4 Thesis milestones</td>
<td>5</td>
</tr>
<tr>
<td>1-5 Thesis outline</td>
<td>6</td>
</tr>
<tr>
<td><strong>2 Literature review</strong></td>
<td>7</td>
</tr>
<tr>
<td>2-1 The structure of graphene</td>
<td>9</td>
</tr>
<tr>
<td>2-1-1 Hybridization &amp; Anisotropy</td>
<td>10</td>
</tr>
<tr>
<td>2-2 The properties of graphene</td>
<td>11</td>
</tr>
<tr>
<td>2-2-1 Mechanical properties</td>
<td>11</td>
</tr>
<tr>
<td>2-2-2 Thermal properties</td>
<td>15</td>
</tr>
<tr>
<td>2-2-3 Electrical properties</td>
<td>16</td>
</tr>
<tr>
<td>2-3 Synthesis</td>
<td>18</td>
</tr>
<tr>
<td>2-3-1 Adhesion to the substrate</td>
<td>18</td>
</tr>
<tr>
<td>2-4 Characterization</td>
<td>20</td>
</tr>
<tr>
<td>2-4-1 Visible Light Microscope (VLM)</td>
<td>21</td>
</tr>
<tr>
<td>2-4-2 Scanning Probe Microscopy (SPM)</td>
<td>21</td>
</tr>
<tr>
<td>2-4-3 Raman spectroscopy</td>
<td>22</td>
</tr>
<tr>
<td>2-5 Concept for controlled permeability</td>
<td>23</td>
</tr>
<tr>
<td>2-5-1 Strain engineering</td>
<td>25</td>
</tr>
<tr>
<td>2-6 Thesis milestone 1</td>
<td>27</td>
</tr>
</tbody>
</table>
3 Design of a MEMS-based tensile device 29
3-1 Methods to induce strain in graphene ........................................ 30
3-2 Device design ................................................................. 33
  3-2-1 Requirements .............................................................. 33
3-3 Conceptualization .............................................................. 33
  3-3-1 Actuation ................................................................. 34
  3-3-2 Sensing elements ......................................................... 38
  3-3-3 Defining the parameters ................................................. 41
3-4 Final design ................................................................. 44
  3-4-1 Additional designs ....................................................... 45
3-5 Thesis milestone 2 ............................................................. 45

4 Device modelling 47
4-1 Analytical estimations ......................................................... 47
  4-1-1 Model assumptions ....................................................... 47
  4-1-2 System stiffness .......................................................... 48
  4-1-3 System performance ..................................................... 50
4-2 Finite Element Analysis (FEA) ............................................... 52
  4-2-1 Model assumptions ....................................................... 52
  4-2-2 Input parameters ........................................................ 52
  4-2-3 System performance ..................................................... 54
4-3 Analytical estimations vs FEA ............................................... 57
4-4 Thesis milestone 3 ............................................................. 57

5 Fabrication methods & materials 59
5-1 Layer deposition ............................................................... 60
5-2 MEMS Patterning ............................................................. 62
5-3 Graphene Transferring and Structure Release ......................... 63
5-4 Shadow Mask Deposition ................................................... 65
5-5 All designs ................................................................. 66
5-6 Main design with transferred free-standing graphene ............... 72
5-7 Thesis milestone 4 ............................................................. 72

6 Experiments 73
6-1 Phase I: Preliminary experiments ......................................... 73
  6-1-1 Graphene synthesis & characterization ............................. 73
  6-1-2 Strain quantification by Raman spectra using a macro tensile device .... 76
  6-1-3 Experimental clamping concept based on improved dangling bonds .... 79
  6-1-4 Experimental clamping concept based on Focused Ion Beam (FIB) induced deposition of TEOS SiO₂ ........................................ 81
  6-1-5 Experimental clamping concept based on epoxy ........................ 82
### Contents

6-2  Phase II: Device Characterization .................................................. 85  
  6-2-1  Electrical characterization of the polycrystalline Silicon ............... 85  
  6-2-2  Surface roughness analysis .................................................... 91  
  6-2-3  Device linearity after release ............................................... 92  
  6-2-4  Displacement analysis ....................................................... 93  
6-3  Phase III: Tensile experiments ....................................................... 95  
  6-3-1  Micro tensile device with unclamped multi-layer graphene ............... 95  
  6-3-2  Micro tensile device with epoxy clamped multi-layer graphene ........... 96  
6-4  Thesis milestone 5 and 6 ............................................................. 98  

7  Conclusion and recommendations ...................................................... 101  

A  MATLAB listings ......................................................................... 103  
  A-1  Analytical model ................................................................. 103  

Bibliography ................................................................................. 109
List of Figures

1-1 Schematics of separation ....................................................... 2
2-1 Graphene lattice structure ................................................... 8
2-2 Overview of all graphite forms ranging from buckyballs, carbon nanotubes and graphene [1] ......................................................... 9
2-3 Ripples in graphene ............................................................. 9
2-4 Graphene lattice structure ..................................................... 10
2-5 $sp^2$ hybridization of carbon [2] .............................................. 10
2-6 Zig-zag vs. armchair ........................................................... 11
2-7 Zig-zag strain (top) vs. armchair strain (bottom) [3] ......................... 14
2-8 Stress softening in graphene .................................................. 15
2-9 Stiffness reduction in graphene related to loading .......................... 16
2-10 Schematic diagram showing the band structure and resulting ambipolar field effect in graphene [1] ................................................. 17
2-11 Graphene suspended over a cavity [4] ........................................ 20
2-12 STM image of graphene [5] .................................................... 22
2-14 Nitrogen functionalized pores in graphene [7] .............................. 24
2-15 Schematic diagram for out-of-plane diffusion sites of an atom through graphene [8] ................................. 24
2-16 Out-of- and in-plane diffusion [8] ............................................. 26
3-1 SEM image of thermalmechanical manipulation of graphene [9] ............. 31
3-2 Strain coupling between graphene films and a PDMS substrate [9] ......... 31
3-3 Out of plane stress on graphene ............................................... 32
3-4 Schematic representation of in-plane strain .................................. 33
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-5</td>
<td>Actuator design procedure [10]</td>
<td>34</td>
</tr>
<tr>
<td>3-6</td>
<td>Schematic illustration of thermal expansion because of a temperature change $\Delta T$ [11]</td>
<td>35</td>
</tr>
<tr>
<td>3-7</td>
<td>The concept of a Thermal In-plane Micro actuator (TIM) [12]</td>
<td>35</td>
</tr>
<tr>
<td>3-8</td>
<td>The setup for the optical tracking method</td>
<td>39</td>
</tr>
<tr>
<td>3-10</td>
<td>A schematic illustration of capacitance sensing on the shuttle</td>
<td>39</td>
</tr>
<tr>
<td>3-11</td>
<td>A schematic of the read-out scheme [14]</td>
<td>40</td>
</tr>
<tr>
<td>3-12</td>
<td>Four-point measurement of resistance between voltage sensing probes 2 and 3. Current is supplied via probes 1 and 4</td>
<td>40</td>
</tr>
<tr>
<td>3-13</td>
<td>Schematic illustration of MEMS device concept</td>
<td>41</td>
</tr>
<tr>
<td>3-14</td>
<td>Equivalent mechanical representation of a single thermal beam connected to the shuttle</td>
<td>42</td>
</tr>
<tr>
<td>3-15</td>
<td>Device design parameters</td>
<td>43</td>
</tr>
<tr>
<td>3-16</td>
<td>Schematic illustration of final MEMS device design</td>
<td>44</td>
</tr>
<tr>
<td>3-17</td>
<td>Schematic illustration of centre of MEMS device</td>
<td>44</td>
</tr>
<tr>
<td>4-1</td>
<td>Lumped model of MEMS device</td>
<td>48</td>
</tr>
<tr>
<td>4-2</td>
<td>Schematical representation of the geometry and the loads for the thermal beams [15]</td>
<td>48</td>
</tr>
<tr>
<td>4-3</td>
<td>Analytical model of the device</td>
<td>50</td>
</tr>
<tr>
<td>4-4</td>
<td>Device performance</td>
<td>51</td>
</tr>
<tr>
<td>4-5</td>
<td>From Full device to FEA model</td>
<td>53</td>
</tr>
<tr>
<td>4-6</td>
<td>The static temperature profile across the device</td>
<td>54</td>
</tr>
<tr>
<td>4-7</td>
<td>The resulting current density in the thermal beams</td>
<td>54</td>
</tr>
<tr>
<td>4-8</td>
<td>The Von Mises stresses in the device</td>
<td>55</td>
</tr>
<tr>
<td>4-9</td>
<td>Displacement in X-direction (displacements 20x)</td>
<td>55</td>
</tr>
<tr>
<td>4-10</td>
<td>Displacement in Y-direction (displacements 1000x)</td>
<td>56</td>
</tr>
<tr>
<td>4-11</td>
<td>Displacement in Z-direction (displacements 200x)</td>
<td>56</td>
</tr>
<tr>
<td>5-1</td>
<td>L-edit mask design</td>
<td>59</td>
</tr>
<tr>
<td>5-2</td>
<td>Silicon with 1.5 $\mu m$ SiO$_2$</td>
<td>60</td>
</tr>
<tr>
<td>5-3</td>
<td>Deposited Polycrystalline Silicon</td>
<td>61</td>
</tr>
<tr>
<td>5-4</td>
<td>All layers deposited</td>
<td>61</td>
</tr>
<tr>
<td>5-5</td>
<td>Nitride layer patterned</td>
<td>62</td>
</tr>
<tr>
<td>5-6</td>
<td>Polycrystalline Silicon patterned</td>
<td>63</td>
</tr>
<tr>
<td>5-7</td>
<td>Polycrystalline Silicon etched</td>
<td>63</td>
</tr>
<tr>
<td>5-8</td>
<td>Graphene transferred</td>
<td>64</td>
</tr>
<tr>
<td>5-9</td>
<td>Vapor HF release of device</td>
<td>65</td>
</tr>
<tr>
<td>5-10</td>
<td>SEM image Design A (2300x)</td>
<td>66</td>
</tr>
<tr>
<td>5-11</td>
<td>SEM image Design B (2300x)</td>
<td>66</td>
</tr>
</tbody>
</table>
Acknowledgements

The work performed in the thesis lying in front of you is part of the Master of Science program Micro & Nano Engineering at the faculty of Mechanical Engineering (Delft University of Technology).

During this period I was lucky and thankful to have worked together with many inspiring people from various backgrounds. Without these people, this thesis could not have been realized and I sincerely would like to thank everyone who has contributed to the project.

First and foremost I would like to thank my main supervisor Prof. Dr. Urs Staufer for giving me the opportunity to graduate on this topic and for his guidance along the way. Secondly, I would like to give special recognition to Hugo Perez-Garza MSc. who, as my daily supervisor, had a vital role in the successful completion of this project. His contribution was not limited to his role as supervisor, he actively participated in design discussions, fabrication and experiments. I am very grateful to have worked alongside him and learned from him.

In no particular order I would also like to give recognition to: Federico Buja, Dr. Gregory Schneider, Victor Calado, Dr. Murali Ghateskar, Dr. Ir. Hans Goossen, Dr. Merlijn van Spengen, Prof. Dr. Ir. Fred van Keulen, Lotte Willems, Oncu Gunes Atar, Laurens Pluimers, Erik Molenaar, Ir. Jaap Kokorian, Rob Luttjeboer and Marli Guffens.

Last but not least, I would like to thank my girlfriend Stephanie Verhulst for her endless support and motivation, my parents Job & Petronella Kievit and my brothers (Arthur and Rogier) for making it all possible and always being there for me.

Delft, University of Technology
March 19, 2013

Eric Walter Kievit
Chapter 1

Introduction

1-1 Industry scope

Over the last decades the demand for energy has grown exponentially and with it, the cost of energy is rapidly rising. Amongst others this effect is clearly noticeable in the process & energy industry. In the field of energy storage and energy conversion there is an increasing interest in efficient energy utilization by secondary conversion and separation. In this field different methods for converting one energy form into another are studied. Such conversions are important because energy carriers, which are excellent fuels for the end user, are often not equally well suited for transport and handling. A well-known example to illustrate this is hydrogen. During the energy consumption a second conversion takes place at the end user’s site where gases like CO2 are released. For environmental reasons these should be separated, captured and stored.

Project NAMECOSH  The NAMECOSH (NAnaMEchanically Controlled Separation of Hydrogen from a carrier stream) project was initiated by TU Delft and DELMES and is supported by the Dutch Economic Structure Enhancement Fund (FES) in the NanoNextNL program. The project NAMECOSH primarily focuses on separation aspects. It explores how nanoscientific knowledge can be exploited for efficiently separating hydrogen or CO2 out of a carrier stream in a self-controlled process. The aim of the NAMECOSH project is to design and create a nanomechanical element which links two microfluidic flow channels, through which different reactants are transported, and is able to separate hydrogen from the carrier stream (see Figure 1-1). The combination of nanomechanical elements, microfluidics and surface nano-chemistry opens possibilities for implementing bio-inspired, sustainable processes like artificial proton or molecular pumps. For this advancement in the state of the art techniques, high quality membranes, and especially graphene membranes appear to be promising.

Thesis scope  The scope of this thesis is to investigate how one can control the material properties of a certain nanomechanical element (graphene) which can be used to separate hydrogen atoms from a carrier stream.
Introduction

The separation of a material out of a mixture can be achieved via different methods. A classic method is distillation, where the different boiling points of constituents of the mixture are exploited, and the products of this separation undergo at least one, usually two phase changes. Other classic approaches are sieving, where a mixture of solid particles is separated based on the particle size or filtration, where one constituent of the mixture, e.g. the solvent, can pass a porous (usually solid) barrier while ideally all the others are rejected. The interaction between the feed flow and the filter is usually purely physical like with sieving. The thermodynamic conditions on both sides of the filter influence this process and are specifically exploited e.g. in reverse osmosis. This leads to a whole branch of chemical engineering; separation by design. A very wide class of separation techniques are based on the different adsorption coefficients, which components of a mixture have when they get into contact with a surface. Typical examples are chromatography, gas separation by adsorption or pressure swing adsorption. These separation techniques are also suitable for working at the molecular level. The interaction with the surface can be purely physical (“physisorption”) or involve a chemical reaction (“chemisorption”).

The disadvantage of the above mentioned techniques is that they often show a trade-off between selectivity, permeability, energy consumption or lifetime expectancy. For this reason it is worthwhile to seek new techniques that are able to selectively and efficiently separate any atom of choice from a carrier gas stream with a high throughput.

1-2 Separation

As energy costs rise, membrane technology for the separation of gases is likely to play an increasingly important role in reducing the environmental impact and costs of industrial processes.

A membrane is a selective semipermeable barrier that allows different gases, vapors, or liquids to move through it at different rates. Membranes are fundamental components of a wide variety of physical, chemical, and biological systems, used in everything from cellular compartmentalization to mechanical pressure sensing. They divide space into two regions,
each capable of possessing different physical or chemical properties [18]. The membrane restricts the motion of molecules passing across it so that some molecules move more slowly than others or are even excluded. A wide range of mechanisms are available for this restriction; for example, size variability of the molecules, affinity for the membrane material and permeation driving forces (typically concentration or pressure difference). Gas separation membranes offer a number of benefits over other gas separation technologies. Conventional technologies often require a gas-to-liquid phase change in the gas mixture that is to be separated. The phase change adds a significant energy cost to the separation process. Membrane gas separation, on the other hand does not require a phase change. Currently, gas separation membranes are most widely used in the industry for:

- Hydrogen separation
- Separating nitrogen from air
- CO2 and water removal from natural gas
- Organic vapor removal from air or nitrogen streams

At the moment, the most widely used membrane materials for gas separation are polymers. The relatively low cost of manufacturing fibres makes them of interest for large-scale industrial applications. Membrane devices for gas or vapor separation usually operate under continuous steady-state conditions with three streams. The feed stream (a high-pressure gas mixture) passes along one side of the membrane. The molecules that permeate the membrane are swept using a gas on the other side of the membrane in the so-called permeate stream. The non-permeating molecules that remain on the feed-stream side exit the system as the retentate stream. A pressure difference across the membrane drives the permeation process. Each gas component in a feed mixture has a characteristic permeation rate through the membrane. The rate is determined by the ability of the component to dissolve in and diffuse through the membrane material. The key desirable properties for membranes are high flux (permeability), selectivity, processability, stability and cost. The economics of a gas separation membrane process is largely determined by the membrane’s transport properties—that is, its permeability and selectivity for a specific gas in a mixture. Ideally, membranes should exhibit high selectivity and high permeability. For most membranes, however, as selectivity increases, permeability decreases, and vice versa.

Graphene membranes Current ultrathin membranes range from tens of nanometers to several micrometers in thickness. However, although these membranes can already be manufactured on an industrial scale and appear to show reliable operation. These membranes may be limited in their overall efficiency & productivity or are not very well controllable in an on-off fashion. The permeance of a membrane is inversely proportional to the thickness of the membrane [7]. Which means that, the thinner the membrane, the higher the permeability, as the atoms encounter less material during diffusion. Graphene, a single layer of graphite, is the ultimate limit: a chemically stable and electrically conducting membrane one atom in thickness [18]. Gas separation, which is paramount to the chemical industry and subject to huge potential savings of energy, has not yet been explored for graphene membranes. To explore the use
of graphene membranes for gas separation, the permeability of graphene needs to be controlled. Therefore, the aim of this thesis is to explore and implement a method to control the permeability of graphene.
1-3 Thesis objectives

The overall project of creating a graphene based gas separation process is a vast challenge. Because of this, the project was divided into several sub-projects to make it more feasible and increase the chance of success. The first and most prominent challenge is to overcome the proven property of graphene to be impermeable to any atom. So although it is very thin, in its natural state it is useless as a gas filtering material. One of the main objectives of this thesis is to investigate the possibility of utilising graphene in such a way that it becomes a suitable membrane for gas filtration. In this thesis a method to linearly stress graphene is explored. The core subject of this thesis is the design, fabrication and analysis of a MicroElectroMechanicalSystem (MEMS)-based in-plane tensile device (optimized for monolayer graphene) which can be used as a tool to stress graphene such that high strain percentages (≥ 10%) are achieved which alter graphene’s intrinsic properties. These objectives are based on the hypothesis that using the principles of micro & nano engineering it is possible to realize such a device.

1-3-1 Thesis hypothesis

Using MicroElectroMechanicalSystem (MEMS) technology it is possible to fabricate a device which is able to linearly stress a graphene sample to high strain values (≥ 10%) and thereby altering its intrinsic properties.

1-4 Thesis milestones

In order to prove this hypothesis, several milestones were installed to increase the chance of a successful result. In the list below the thesis milestones are shown which should be answered ‘yes’ after each of its corresponding sections in order for the project to proceed on the chosen path.

1. From a theoretical perspective, can the permeability properties of graphene be controlled such that hydrogen atoms can diffuse?
2. Is it possible to design a MEMS device in such a way that it can influence the permeability properties of graphene?
3. Does the MEMS device perform according to the requirements based on analytical modelling and finite element analysis?
4. Is this design realizable with existing fabrication techniques available in the facilities of Delft University of Technology?
5. Does the fabricated device perform according to the requirements?
6. Is this device able to strain graphene ≥ 10% in a real setup?
1-5 Thesis outline

This thesis is structured as follows: In chapter two, the reader is presented with a generic overview of graphene and its intrinsic physical properties. In addition, this chapter introduces the supporting hypothesis of this thesis by explaining the concept of strain engineering graphene and its influence on the permeability. In chapter three, the design of an in-plane tensile MEMS is introduced which is able to stress graphene on the basis of given criteria. In chapter four, this design is modelled via two different approaches, first an analytical model is shown to get a rough estimation of the device performance and secondly, a more detailed Finite Element Analysis is performed. Chapter five describes the fabrication process of the MEMS chip. In chapter six the experiments and relating results are shown and interpreted. Finally, chapter seven gives the overall conclusions and recommendations for future studies.
Chapter 2

Literature review

Chapter goal - milestone 1: from a theoretical perspective, can the permeability properties of graphene be controlled such that hydrogen atoms can diffuse?

In 2004, Andre K. Geim and Kostantin S. Noveselov managed to isolate and identify Single-Layer Graphene (SLG), Double-Layer Graphene (DLG), Few-Layer Graphene (FLG) and Many-Layer Graphene (MLG) using the now well known ‘Scotch-tape method’ [19]. Although not officially documented, SLG is a single graphene layer, DLG are two layers stacked on top of each other, FLG is usually a stack of graphene layers between 3 and 10 layers thick and MLG is used for stacks between 10 and 100 layers. Above 100 layers it is often no longer referred to as graphene but a thin film of graphite. Since graphene’s discovery in 2004, scientists have been able to identify some remarkable properties which resulted in graphene often being referred to as a miracle material. For example, it is the thinnest known material in the universe and yet the strongest ever measured. Its charge carriers exhibit giant intrinsic mobility, exhibit zero-effective mass and can travel for micrometers without scattering at room temperature [20]. Graphene can sustain current densities six orders of magnitude higher than that of copper. It shows record thermal conductivity and stiffness, combines conflicting qualities such as brittleness and ductility and is proven to be impermeable to any gas, even atoms as small as Helium [21].

Because of these properties (which make graphene an excellent candidate for a wide variety of applications for MEMS and NEMS devices) the research on graphene has developed at a truly relentless pace. Several papers appear every day, and, if predictions [22] are to be believed, the amount of research and resulting literature on graphene will rapidly keep increasing over the next few years. For this reason a complete overview of all published literature would fall outside the scope of this thesis. The goal of this chapter is to give the reader a concise yet relevant overview and background knowledge of the concept of strain engineering graphene.

Before introducing graphene it is relevant to first look at the 6th element in the periodic table: carbon. Carbon is often referred to as the the ‘materia prima’ of life as it is the basis of all organic chemistry. Because of its flexibilite capabilities to bond, carbon-based systems
display an unlimited number of different structures with an equally large variety of physical properties. When carbon atoms are arranged in a specific lattice structure and are viewed in a bulk (3D) state they are referred to as graphite, which is basically a stack of graphene layers. Naturally occurring graphite has been known as a mineral for hundreds of years. Even in the Middle Ages, the layered morphology and weak dispersion forces between adjacent sheets of carbon were used to make marking instruments, much in the same way that we use graphite in pencils today. Graphene is the name given to a single 2D crystal plane of carbon atoms (see Figure 2-1). In a single stripe made with a pencil one could find millions of graphene flakes in varying thicknesses. The individual graphene layers that make up graphite are held together by Van der Waals interactions (weak dipole-dipole bonds) between the interstitial layers[23][4]. The interstitial distance between subsequent graphene layers is approximately the diameter of a carbon bond at around .335nm [19][24][25]. These individual graphene layers (also called atomic planes) can be oriented or structured in different ways resulting in the different types of graphitic forms as can be seen in Figure 2-2. The physical properties of the graphitic forms are, in great part, the result of the dimensionality of these structures [26]. This figure shows the difference between a buckyball (spherical fullerene), a carbon nanotube and a sheet of graphene.

Atomic planes are known as the constituent building blocks of bulk crystals. However, one-atom-thick materials made up out of a single element such as graphene, were unknown. For many years, researchers thought graphene could not exist in a 2D state at ambient temperature and pressure conditions. The principle reason behind this, is that nature strictly forbids the growth of low dimensional crystals. The growth of a crystal implies high temperatures, and the resulting thermal fluctuations were seen as detrimental (they segregate into islands or decompose) to the stability of macroscopic one dimensional and two dimensional objects. It is possible to grow flat molecules and nanometer-sized crystallites, but as the lateral size increases, so does the phonon density integrated over the 3D space. The result being that the likelihood of thermal vibrations rapidly grows. This forces 2D crystallites to transition into a variety of more energetically favourable stable 3D structures [20]. This instability typically occurs below a thickness of a few dozen layers [27]. Although theory states that it is impossible to grow two dimensional crystals on their own, it does not deny the possibility of growing a monolayer inside or on top of another crystal and then removing the bulk. The
most stable environment being at low temperature so that thermal fluctuations are unable to break atomic bonds. It is currently thought that a possible explanation for the existence of graphene is that the interaction between bending and stretching long-wavelength phonons stabilizes graphene through its deformation in the third dimension [28]. Fasolino et al [29] performed Monte Carlo simulations on the many-body interatomic potential of carbon and showed that these fluctuations are indeed suppressed by anharmonic coupling between bending and stretching modes. During experiments performed by Meyer et al. [28] it was shown, using nanobeam electron diffraction patterns, that many-layer graphene sheets are in fact not perfectly flat and therefore not actually completely two dimensional (Figure 2-3). These so-called ripples, occur because of thermal fluctuations and have a size distribution between $5nm - 10nm$.

![Figure 2-3: Ripples in graphene](image)

### 2-1 The structure of graphene

The structure of graphene is often represented with a ball and stick model which was previously shown in Figure 2-1. It can be visualized as a triangular lattice with three atoms as a basis, shown by the red and blue dots (Figure 2-4). The two lattice vectors, which describe the inter-atomic distances, can be written as:

$$a_1 = \frac{a}{2}(3, \sqrt{3}), \quad a_2 = \frac{a}{2}(3, -\sqrt{3})$$

(2-1)
where $a_n = 2 \times C_{res} \approx .142 \text{nm}$ is the carbon-carbon distance.

### 2-1-1 Hybridization & Anistropy

The atoms of monolayer graphene are bonded together by $sp^2$ hybridization, forming a tightly packed hexagonal, also known as 'honeycomb' lattice structure [28][1]. The $sp^2$ hybridization between the carbon atoms is of great importance for the properties of graphene. The $sp^2$ hybridization (see Figure 2-5) between one $s$-orbital and two $p$-orbitals leads to a trigonal planar structure with the formation of a $\sigma$ bond between carbon atoms that are separated by $1.42 \text{nm}$. The $s$, $p_x$, and $p_y$ atomic orbitals on each carbon atom hybridize to form strong covalent $sp^2$ bonds, giving rise to $\angle 120^\circ$ Carbon-Carbon-Carbon bond angles (if seen from
2-2 The properties of graphene

a top view perspective) and the familiar chicken-wire-like layers. The $\sigma$ bond is responsible for the robustness of the lattice structure in all allotropes [26][30]. The remaining $p_z$-orbital, which is perpendicular to the planar structure overlaps with its three neighboring carbon atoms to bind covalently, leading to the formation of a band of filled $\pi$ orbitals, known as the valence band, and a band of empty $\pi^*$ orbitals, called the conduction band. While three of the four valence electrons on each carbon form the $s$-(single) bonds, the fourth electron forms one-third of a $\pi$ bond with each of its neighbors producing a carbon-carbon bond order in graphite of one and one-third. With no chemical bonding in the $z$-direction, out-of-plane interactions are extremely weak. This includes the propagation of charge and thermal carriers, which leads to out-of-plane electrical and thermal conductivities that are both more than $10^3$ times lower than those of their in-plane analogues [6]. The atomic structure of graphene results in anisotropic behavior. There are three so-called main chiralities (describing the edge structure): armchair, zig-zag and a third rotated chirality called chiral sheet (see Figure 2-6). The two main chiralities (armchair and zig-zag) exhibit distinguishable properties both from a mechanical and electrical perspective [31], which will be discussed in the next section.

![Zig-zag vs. armchair](image)

Graphene can exist either in a monocrystalline state or a polycrystalline state. Monocrystalline means that it consists of a single crystal without grain boundaries while polycrystalline refers to the existence of multiple crystals with grain boundaries. Theoretically, the monocrystalline state is favorable for its properties since it is defect free and, therefore, exhibits higher electron mobilities and higher strength. However, to produce large area monocrystalline flakes is still a challenge to be solved, more on this in the synthesis section of this thesis.

2-2 The properties of graphene

As mentioned earlier, graphene shows several unique and remarkable properties resulting in tremendous interest around the globe. The properties of graphene will be briefly discussed in the following section, emphasis will be put on the mechanical properties since they are directly related to the thesis’ objective.

2-2-1 Mechanical properties

The mechanical properties of graphene have been studied to great lengths, especially from a theoretical point of view. There are many different ways of analyzing the mechanical
properties of graphene, all giving a slightly varying results. Since the literature on mechanical properties is vast, the main methods used to analyze mechanical properties are listed below. Next to the different methods, several of the highly cited papers are shown:

- Ab-initio calculations [32][33]
- Atomistic modelling [34][35][36][37][38]
- Continuum modelling [34][25][39][35][40][41][42]
- Quantum mechanics [43][44]
- Truss-type models [45][39][25][46][47]
- Experimental results [48][49][50][51][50][52][53]

Based on the research in the above mentioned publications it is possible to distill commonly accepted generic values for graphene. The actual values will always differ due to small defects, intrinsic stresses, contaminations, hybridizations and so on, therefore, the truth will always lie somewhere in the middle depending on circumstances. Graphene’s mechanical properties are usually quantified with the common units of Young’s modulus, Shear modulus, Poisson’s ratio and Bending modulus. For completeness, the relationships can be found below. The Young’s modulus is defined by

$$E^{3D} = \frac{\sigma}{v} = \frac{\sigma_x}{\epsilon_x} = \frac{1}{V_0} \left( \frac{\delta^2 E_S}{\delta \epsilon_x^2} \right)_{E_0}$$

(2-2)

with $E$=Young’s Modulus, $\sigma$ is stress and $v$ the Poisson’s ratio.

Since graphene is a near 2-dimensional material, researchers often also use the two dimensional Young’s modulus instead of the three dimensional bulk formula (Figure 2-2). For graphene it is therefore also common to use:

$$E^{2D} = \frac{1}{A_0} \left( \frac{\delta^2 E_S}{\delta \epsilon_x^2} \right)_{E_0} = E^{3D} c_0$$

(2-3)

with $c_0$ being the thickness of graphene=0.335nm

For an indication of the 3D Young’s modulus of graphene, the mentioned publications show a spread from around 0.5TPa to 1.1TPa [43]. In 2008, the first experimental measurements of graphene’s mechanical properties were reported by Lee et al. [49]. They showed that graphene exhibits an intrinsic strength of $\sigma^{2D}_{int} = 42 \pm 4 N m^{-1}$, which is almost equivalent to the theoretical limit and corresponds to a Young’s modulus of $E^{3D} = 1.0 \pm 0.1TPa$ while the corresponding intrinsic stress is shown to be $\sigma_{int} = 130 \pm 10 GPa$. The commonly accepted value for defect free monocrystalline graphene is 1TPa [43][37]. Lee et al. have also experimentally shown that in most cases, graphene can be considered as an isotropic and continuous medium within an acceptable error. The validity of this assumption depends mainly on the experiment in question.

In theory, pristine graphene can withstand an elastic strain as high as $\approx 25\%$, which is more than any other known crystal [49]. At strains above 10%, the elastic response becomes highly
nonlinear (see Figure 2-8b).

The Poisson’s ratio gives the ratio of expansion divided by the fraction of compression due to stress.

\[ \nu = \frac{-\sigma_y}{-\sigma_x} = \frac{-\sigma_z}{-\sigma_x} = \frac{E}{2G} - 1 \quad (2-4) \]

Where \( \nu \) is the Poisson’s ratio, \( E \) is the Young’s Modulus and \( G \) is the Shear Modulus.

The Poisson ratio of graphene has been reported between .17 and .6 [54][45]. Based on previous research done on carbon nanotubes and bulk graphite, this result was expected. However, the values for graphene are slightly higher, which can most likely be attributed to the fact that graphene obtained with micromechanical cleavage shows virtually no defects. Next to its strength, graphene simultaneously shows high pliability (folds and pleats are commonly observed) and, because of its buckling behaviour, can be considered as a thin plate [55]. This means that it cannot withstand compression or shear forces. When graphene finally does fail at high strains, Booth et. al showed that its fracture behavior is similar to that of glass [56].

The shear modulus of elasticity is given by

\[ G = \frac{\tau}{\gamma} \quad (2-5) \]

The shear modulus has been investigated by many different researchers and was summarized and compared by Scarpa et al [45]. They showed that the shear modulus varies between 0.14TPa and 0.23TPa.

At first glance, it would seem that a graphene sheet would have very little bending rigidity since the atomic carbon–carbon bonds lie very close to the neutral axis during cylindrical bending. This is unlike continuous elastic plates where there is material that is not on the neutral axis, that contributes to inbending that is proportional to the in-plane Young’s modulus. Therefore, the primary atomic bonds, which are the main contribution to the in-plane elastic properties of graphene, should provide little, perhaps negligible, contribution to the bending rigidity of graphene sheets. Wang et al. showed that the bending rigidity of graphene is dependent on the size and shape of the flake. Lu et al.[57] has shown that the non-vanishing bending modulus of the atomically thin graphene monolayers results from multibody atomistic interactions. A new analytical expression is derived for the elastic bending modulus at the ground state, which compares closely with ‘ab initio’ calculations. Slight nonlinearity and anisotropy are noted for tangent bending modulus, obtained from molecular mechanics based atomistic simulations. For a membrane containing an arbitrary number of graphene layers, the bending modulus is approximately given by

\[ D_N = ND_1 + Es^3(N^3 - N)/12 \quad (2-6) \]

Where \( D_1 = 1.16eV \), \( s = 0.34nm \), \( E = 1TPa \), \( N=\)the number of layers and \( D_N \) is given in eV [58]. In real life applications graphene is often considered as a flexible membrane with negligible flexural rigidity because width >> height and length >> height.

### Armchair edge vs. Zig-Zag edge

The two important chiralities to consider are called armchair and zig-zag. As has been reported by many independent research groups ([3][41][59][24][39][60]), the mechanical behaviour of graphene differs in the distinguishable chiralities. It was shown that the armchair
direction shows a slightly higher Young’s modulus (1.03TPa against 1.04TPa), a slightly higher Shear modulus (0.23TPa against 0.21TPa), and a ≈ 10% lower Poisson’s ratio in comparison to the zigzag direction[37]. Due to its atomic structure, zigzag can take higher strains than armchair. This can also be deduced from Figure 2-7, which shows that for a 2nm × 1nm ribbon, the zigzag chirality has four Carbon-Carbon bonds whereas the armchair chirality has three Carbon-Carbon bonds. Pei et al. [60] showed that in pristine condition, zigzag chirality graphene has a failure strain of around 27% and armchair chirality has a failure strain of around 17%.

![Figure 2-7: Zig-zag strain (top) vs. armchair strain (bottom) [3]](image)

**The stiffness of graphene**

Graphene stiffness is related to the dimensions of the flake under examination. Although in most cases, graphene can be considered as an isotropic continuous media, it does not show a linear isotropic elastic response under high values of uniaxial strain (≥ 10%), which was proved by Lee et al. [49]. It was shown that the relation between the Second Piola-Kirchoff stress σ_{PK}, the uniaxial Lagrangian strain ϵ, the sample’s constant Young’s modulus E_s and the third-order elastic modulus D for graphene is given by:

\[
\sigma_{PK} = E\epsilon + D\epsilon^2
\]

(2-7)

where \( E_s = 1TPa, D = -2TPa \) and \( \epsilon \) ranges from 0 to 25% strain.

Combining with

\[
\epsilon = \frac{\sigma_{PK}}{E_{PK}}
\]

(2-8)

where \( E_{PK} \) is the Piola Kirchhoff Young’s modulus. Equation 2-8 can be re-arranged to:

\[
E_{PK} = \frac{\sigma_{PK}}{\epsilon}
\]

(2-9)

Inserting 2-9 into 2-7 and combining it with 2-10

\[
F = \frac{E_{PK}A\delta l}{l_0}
\]

(2-10)

where \( \delta l \) being the sample elongation and \( l_0 \) the original length of the sample, it is possible to calculate the softening effect of graphene caused by increased strain. A graphene flake with dimensions 5μm × 10μm (width × length) and a thickness of 0.335nm is used to illustrate this
The required force on the sample to strain the graphene from 0 to 25% has been calculated for a constant Young’s modulus and decreasing Young’s modulus due to softening. The result can be seen in Figure 2-8b. This graph shows that softening effect results in the fact that $0.34 mN - 0.27 mN = 68 \mu N$ less force is required to strain the sample up to the desired deformation of 10%.

At strain values up to 10%, a constant value of the Young’s modulus (without stress softening) suffices and can be calculated with:

$$K_s = \frac{E_s A_s}{L_s}$$  \hspace{1cm} (2-11)

Using 2-10, combining it with 2-11 and replacing $E_s$ with $E_{PK}$ gives

$$K_s = \frac{F}{\delta L}$$  \hspace{1cm} (2-12)

The relation between stiffness and sample strain can be calculated (see Figure 2-9).

2-2-2 Thermal properties

**Thermal conduction** As electronic devices continue to decrease in size and circuits need to increase dissipation power, the importance of materials that can conduct heat efficiently has grown. Carbon Nano Tubes (CNTs) are known to have an extremely high thermal conductivity with the experimentally determined room temperature value $K \approx 3000 \text{ W/mK}$ for an individual multiwall carbon nanotube (MW-CNT) and $K \approx 3500 \text{ W/mK}$ for an individual single-wall carbon nanotube (SW-CNT). These values exceed those of the best bulk crystalline thermal conductor: diamond, that has a thermal conductivity in the range $K \approx 1000 - 2200 \text{ W/mK}$ [61].

Molecular Dynamics calculations suggest that the thermal conductivity of graphene would be even higher than that of Carbon Nano Tubes. Balandin et al. conducted noncontact measurements of the thermal conductivity of exfoliated graphene by confocal micro-Raman spectroscopy [61]. Room temperature values for the thermal conductivity of single-layer
Figure 2-9: Stiffness reduction in graphene related to loading

Thermal expansion According to work performed by Chen et al. [65], the coefficient of thermal expansion for graphene was found to be \( \alpha_{\text{graphene}} = -7.4 \times 10^{-6} \text{K}^{-1} \), which is in excellent agreement with that reported by Bao [9]. This thermal expansion coefficient of graphene corresponds to that of bulk graphite \( \alpha_{\text{graphite}} = 7.4 \times 10^{-6} \text{K}^{-1} \) except for the sign. Unlike other materials, graphene shrinks with increasing \( T \) (where the magnitude of \( \alpha \) decreases with increasing \( T \) [9]).

2-2-3 Electrical properties

From a general perspective, several features make graphene’s electronic properties unique and different to those of any other known condensed matter system. These extraordinary electronic properties in graphene are really due to the high quality of its 2D crystal lattice. The first and most discussed property is, of course, graphene’s electronic spectrum. Single-layer graphene is a zero-band gap semi-conductor or semimetal in which the Highest Occupied Molecular Orbital (HOMO) touches the Lowest Unoccupied Molecular Orbital (LUMO) at a single Dirac point. For thicker flakes, stacking of multiple layers leads to some overlap of their carrier wave functions and the overall behavior becomes metallic [6]. Electrons propagating
through the honeycomb lattice completely lose their effective mass, which results in quasiparticles that behave like massless Dirac fermions which are described by a Dirac-like equation rather than the Schrödinger equation [26]. The latter—so successful for the understanding of quantum properties of other materials—does not work for graphene’s charge carriers with zero-rest mass. Second, electron waves in graphene propagate within a layer that is only one atom thick, which makes them accessible and amenable to various scanning probes, as well as being sensitive to the proximity of other materials such as high-k dielectrics, superconductors, ferromagnetics, etc.

Third, graphene exhibits the astonishing electronic quality that its electrons can cover submicrometer distances without scattering, even in samples placed on an atomically rough substrate, covered with adsorbates and at room temperature. The high quality of graphene implies an unusually low density of defects, which typically act as the scattering centers that inhibit charge transport. Electrical conductivity has been reported at \( \approx 10^4 \Omega^{-1}cm^{-1} \) [6] and the carrier mobility has been measured to be in excess of \( \approx 200,000 Vcm^{-1}s^{-1} \) for a single layer of free-standing, mechanically exfoliated graphene [66]. At such high carrier mobility, charge transport is essentially ballistic on the micrometer-scale at room temperature. This has major implications for the semiconductor industry because in principle it enables the fabrication of all-ballistic devices, even at today’s integrated circuit (IC) channel lengths. An additional important point about charge transport in graphene is ambipolarity. In the field-effect configuration this implies that carriers can be tuned continuously between holes and electrons by supplying the requisite gate bias. This can be easily visualized given the unique band structure of graphene see Figure 2-10. Under negative-gate bias, the Fermi level drops below the Dirac point, introducing a significant population of holes into the valence band. Under positive-gate bias, the Fermi level rises above the Dirac point, promoting a significant population of electrons into the conduction band [6].

![Figure 2-10: Schematic diagram showing the band structure and resulting ambipolar field effect in graphene [1]](image)

Fourth, as a result of the massless carriers and little scattering, the quantum effects in graphene are robust and can survive even at room temperature [26].
2-3 Synthesis

There are several methods to synthesize graphene, the scotch-tape method (mechanical cleavage of graphite [19]) being the most famous. Besides mechanical cleavage of graphite, other common methods to produce graphene samples are epitaxial growth on an insulator surface, Chemical Vapor Deposition (CVD) on the surfaces of single crystals of metals, arc discharge of graphite under suitable conditions, cleavage by intercalated particles, preparation of appropriate colloidal suspensions in selected solvents, and reduction of graphene oxide sheets [67]. Each of these different methods has its advantages and drawbacks and can often be even further divided into different approaches (for example the cleavage of intercalated particles has well over 20 different variations [68]). Bottom-up techniques have yet to produce large and uniform single layers. Total organic syntheses can only produce limited sized flakes because macromolecules become insoluble and the occurrence of side reactions increases with molecular weight. After nucleating a sheet of graphene, conditions must be carefully controlled to promote crystal growth without seeding additional second layers or forming grain boundaries [6]. The exfoliation of graphite intercalation compounds was thought to be an effective route to produce graphene in a large quantity and at low cost, in comparison to most other routes, but monolayer graphene was only obtained as a mixture with the flakes containing different numbers of layers and a large amount of defects. There has been little success in the preparation of monolayer graphene. The CVD method [69] is a good method to obtain monolayer graphene on metal and metal carbide substrates, and the control in thickness of the resultant films is possible. In order to synthesize large-sized graphene, however, several deposition conditions controls are required [68].

The basic “peeling” method utilizes common scotch-tape (cellophane tape) to successively remove layers from a graphite flake. The tape is then pressed on a substrate to deposit a sample. Although the flakes present on the scotch-tape are much thicker than one layer, van der Waals attraction to the substrate may delaminate a single sheet when the tape is pulled away. The method requires a great deal of patience and practice, as depositions by inexperienced scientists are often a mess of thick slabs in which locating a single layer can be extremely difficult. With practice, the technique results in high-quality crystallites, than can have edge lengths of more than 100\(\mu\text{m}\) in size[6]. The cleavage of graphite crystals is the best method in terms of the structural and electrical quality of the flakes obtained, but a challenge to translate this process to large-scale production. The thickness of the thin flakes is difficult to fine-tune and to obtain monolayer graphene is laborious. The size and shape of the resultant flakes are dependent on the type of graphite used. The process of tearing the graphene from bulk graphite by van der Waals adhesion with the substrate often leads to tapered graphene flakes [70], which could be unfavorable for certain applications. The crystallinity of the flakes can be high if for instance highly crystalline graphite (HOPG) is used. However, even HOPG, which has been frequently used, is not a single crystal and consists of grains with different orientations [68].

2-3-1 Adhesion to the substrate

Interfacial adhesion and friction are important factors in determining the performance and reliability of microelectromechanical systems. At small roughness values, adhesion is mainly
due to van der Waals dispersion forces acting across extensive non-contacting areas is related to \( \frac{1}{D_{\text{avg}}^2} \), where \( D_{\text{avg}} \) is the average surface separation. At large roughness values, van der Waals forces at contacting asperities become the dominating contributor to adhesion. Furthermore to fully understand adhesion, the topographic correlations between the upper and lower surfaces must be considered. London showed that normal van der Waals forces can arise from a temporary dipole moment produced by the instantaneous positions of electrons in a molecule [71]. This temporary dipole polarizes the electron distribution of a nearby molecule, creating an attractive dispersion energy proportional to \( \frac{1}{r^6} \), where \( r \) is the distance between the molecules. This theory, however, assumes that the nearby molecule responds immediately to the temporary dipole and, therefore, only applies for separations less than 10 nm. In reality, information regarding the electron distribution travels at the speed of light with wavelengths corresponding to the emission spectrum of the molecule. Casimir and Polder demonstrated that the interaction energy between molecules becomes proportional to \( \frac{1}{r^7} \) for distances larger than these wavelengths. As a result the Casimir force, or retarded van der Waals force, governs at separations greater than 50 nm. A gradual transition from normal to retarded van der Waals forces occurs between these separations. Assuming that the forces are additive, the normal and retarded van der Waals forces between two smooth parallel surfaces are proportional to \( \frac{1}{r^6} \) and \( \frac{1}{r^7} \) where \( D \) is the surface separation[72]. For graphene, the relevance of retarded forces was considered, but it is more likely that the interaction between graphene and its substrate is mainly due to normal van der Waals forces because of graphene’s dimensions. In order to give an estimation of the adhesion energy between two nearby surfaces due to normal van der Waals forces across extensive non-contacting areas the following is often considered \( \Gamma = \frac{A_0}{12\pi D_{r.m.s}^2} \), where \( \Gamma \) is the adhesion energy per unit area, \( g_c \) is a function based on separation distance that describes the transition from normal to retarded van der Waals energies, \( A \) is the Hamaker constant and \( D_{r.m.s.} \) is the sum of the r.m.s. roughnesses of the surfaces.

Relevant factors influencing the adhesion of graphene on a substrate include, but are not limited to, the distance between graphene and substrate, the substrate roughness (amplitude and wavelength) and the charge density of the substrate.

In 2011, Koenig et al. used a pressurized blister test to measure directly the adhesion energy of graphene sheets on a silicon oxide substrate. They have shown an adhesion energy of 0.45 ± 0.02 J/m² for monolayer graphene and 0.31 ± 0.03 J/m² for samples containing two to five graphene sheets. These values are larger than the adhesion energies measured in typical micromechanical structures, which is attributed to the extreme flexibility of graphene, which allows it to conform to the topography of even the smoothest substrates, thus making its interaction with the substrate more liquid-like than solid-like [73]. Yoon et al. later investigated the adhesion of monolayer graphene on copper and reported adhesion energy up to 0.72 ± 0.07 J/m² which is the highest reported thusfar.

These normal van der Waals forces hold individual graphene sheets together to form bulk graphite. They clamp the membrane to a substrate and lead to internal tensioning which influences its bending rigidity. The nanomechanics of graphene and other ultrathin membranes adhered to substrates have been studied and the results provide fairly simple analytical results to describe equilibrium configurations [4]. In order to explain the process of a graphene flake adhered to a surface and put under stress it is useful to consider the following case where a two dimensional graphene membrane is adhered to a substrate by van der Waals forces and clamped over a cavity (see figure 2-11). The configurations that the graphene membrane will
undergo can be categorized in several states

1. Ground state
2. Peeling
3. Sliding and/or debonding

In the state 1: the ground state the membrane will adhere to the sidewalls of a cavity over some distance (called $L_v$) because of attractive van der Waals forces. The membrane is stretched flat along this sidewall. In experiments performed [49] it was shown that for a suspended graphene sheet of $1\mu m$ in diameter and length $L_w$ between $2 - 10 nm$ was detected, causing a pre-tension in the film in the order of $0.07 - 0.14 N/m$. This ground state is controlled by the balance of surface energy caused by van der Waals force on the side walls and elastic energy associated with membrane stretching. When an upward force is applied to the centre of the free-standing membrane, the membrane is stretched and starts to peel off the sidewalls (state 2: peeling) due to the fact that the elastic energy in the membrane becomes greater than the surface energy. As the load increases the graphene membrane continues to peel until it is completely free of any contact with the sidewalls, which is called debonding (state 3: sliding or debonding). The membrane is now stretched and the elastic energy in the membrane is counterbalanced by the surface energy on the interface between the top of the substrate and the membrane. If the load is again increased, two individual processes or a combination of them can occur: either the membrane slides (state 3a), or debonds (state 3b).

All the research investigating the adhesion of graphene on arbitrary substrates shows that it can adhere strongly to substrates without additional clamping techniques. However, van der Waals adhesion alone will not be sufficient to withstand high-strain applications ($\geq 0.6\%$). For these kind of applications, additional clamping methods will need to be implemented in order to create sufficient force between the graphene and its substrate.

2-4 Characterization

Graphene has been characterized by a variety of microscopic and other physical techniques including atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), Scanning single electron transistor (SSET), Scanning gate microscopy (SGM), X-ray diffraction (XRD), and Raman spectroscopy [67][74]. These different microscopes have with different underlying physics and therefore, different imaging results and corresponding interpretations. For example, a visible light microscope can quickly indicate the potential presence but not the thickness of a graphene flake placed on a silicon wafer.
with a $SiO_2$ top layer. While AFM directly gives the number of layers, STM and TEM images are useful in determining the morphology and structure of graphene. Raman spectroscopy is becoming the standard tool for the characterization of graphene samples since its spectra give a clear identification of several properties such as: thickness, temperature, internal stress, defects and many more [67].

2-4-1 Visible Light Microscope (VLM)

Often, cleaved graphite is transferred onto an oxidized Si wafer and its surface carefully scanned with an optical microscope. Thin flakes are sufficiently transparent to add to an optical path, which changes the interference color of reflected light so that the interference color changes with respect to the one of an empty substrate (phase contrast) [27]. For a certain thickness of $SiO_2$, even a single layer was found to give sufficient albeit feeble contrast to allow the the human brain to spot a few micron-sized graphene crystallites among thicker flakes scattered over a millimeter-sized area. In order to detect graphene with a VLM, the thickness of the $SiO_2$ has to be within a certain range. Blake et al. reported that only flakes thicker than ten layers could be found in white light on top of 200 nm $SiO_2$ [75] resulting in an approximated lower limit, whereas Geim et al. reported that 300nm can be considered as the standard to find single layer graphene. As a note of caution they also gave an indication of the upper limit of the $SiO_2$ thickness since even a 5% difference in $SiO_2$ thickness (315nm instead of the current standard of 300nm) can make single-layer graphene completely invisible [1]. By using Fresnel theory and appropriate filters it is possible to improve the contrast in such a way that graphene becomes visible on any thickness of $SiO_2$ [75].

While optical microscopy (using the interference effect) is a good method to identify thin membranes, it can not provide conclusive evidence that a given flake is single, double or multilayered [6]. This is an important issue because some of the interesting properties of graphene are dependent on crystallite thickness.

2-4-2 Scanning Probe Microscopy (SPM)

Scanning probe microscopy was perhaps the most obvious choice for verification of crystallite thickness. The method is relatively slow, but the 0.34nm step height for each successive layer is well within the detection limits of modern atomic force microscopes (AFMs). Resolving the substrate-graphene height profile proved difficult. This was because of the differences in tip attraction/repulsion between the insulating substrate and semi-metallic graphene. This issue increased under ambient conditions by the preferential adsorption of a thin layer of water on graphene. With such complications, reports of substrate-graphene height profiles by atomic force microscopy have typically ranged from 0.6 to 1.0nm for single layers. Scanning Probe Microscopy has also been used to observe the electronic topography of graphite. Only three carbons of the six-member rings are visible due to the AB stacking of graphite [5]. In this arrangement, electron density is considerably higher for the three R-carbons (those that eclipse carbons in the sheet just below), and hence, they are the only ones visible by STM. This is in contrast with what was expected for single layer graphene, in which the six carbons are completely equivalent and thus should all appear with equal intensity. This was, indeed, confirmed by ultrahigh vacuum STM images taken at Columbia by Stolyarova et al. [5].
Their measurements provided evidence of the high crystal quality in mechanically exfoliated samples, which showed few-to-no defects over tens of nanometers [6].

![STM image of graphene](image.png)

**Figure 2-12:** STM image of graphene [5]

### 2-4-3 Raman spectroscopy

While graphene’s layered structure makes it ideally suited for to study by scanning probe microscopy, sample preparation time and substrate requirements mean that additional methods are necessary to quickly and reliably confirm a specimen’s thickness. Ultimately, it was not a directly topographical technique but instead Raman spectroscopy that emerged as the most useful way to probe the thickness of mechanically exfoliated flakes. This makes good sense because the features of graphite and graphene directly reflect changes in electronic structure from the stacking of successive layers. While Raman spectroscopy is a useful technique for characterizing $sp^2$ and $sp^3$ hybridized carbon atoms, including those in graphite, fullerenes, carbon nanotubes, and graphene. Single, double and multi-layer graphene flakes can also be differentiated by their Raman fingerprints [76]. The major features of the Raman spectra of graphite and graphene are the G band at $\approx 1584\text{cm}^{-1}$ and the 2D band at $\approx 2700\text{cm}^{-1}$. The G band is due to $E_{2g}$ vibrational mode at the $\Gamma$ − point. The G-band arises from the stretching of the Carbon-Carbon bond in graphitic materials, and is common to all $sp^2$ carbon systems. The G-band is highly sensitive to effects of strain in $sp^2$ systems, and thus can be used to probe modification on a flat surface of graphene.

Many different kinds of $sp^2$ carbon materials exhibit a strong peak in the range of $2500 – 2800\text{cm}^{-1}$ in the Raman spectra which is called the 2D-band. The 2D-band is a second-order two-phonon process and exhibits strong frequency dependence on the excitation laser energy [76]. A third feature, the D-band is located at $\approx 1350\text{cm}^{-1}$, is not Raman active for pristine graphene but can be observed where symmetry is broken by edges or in samples with a high density of defects. It is the changes of positions and relative peak heights of the G and 2D bands that serve to indicate the number of layers present for a given flake. The location of the G peak for single layer graphene is $\approx 3 – 5\text{cm}^{-1}$ higher than that for bulk graphite, while its intensity is roughly the same. The 2D peak shows a significant change in both shape and intensity as the number of layers is decreased. In bulk graphite, the 2D band is comprised of two components, the intensities of which are roughly 1/4 and 1/2 that of the G peak for the low and high shifts, respectively. For single layer graphene, the 2D band is a single sharp peak at the lower shift, with intensity roughly 4 times that of the G peak [6].

The Raman spectra evolves with the number of layers. The 2D-band peak changes in shape,
width, and position for an increasing number of layers, reflecting the change in the electron bands via a double resonant Raman process where the G-band peak slightly down-shifts with increasing number of layers [77]. The substrate can also influence the Raman spectrum of the graphene. This is mostly observable for epitaxial graphene. For mechanically exfoliated graphene the effect of the substrate on the atomic/electronic structures of graphene and its correlated Raman spectrum is negligible [78]. Point defects in the graphene can also lead to a difference in the Raman spectra, the comparison of the calculated Raman intensity of the graphitic G-band of perfect graphene and graphene with defects shows that the intensity can be enhanced up to one order of magnitude by the presence of defects [79]. Berciaud et al. showed that the Raman spectra of graphene is also slightly different for suspended or supported graphene. Suspended graphene has a slightly right-shifted G-band, a slightly left shifted 2D-band and an increased intensity in the 2D-band.

The full-width at half-maximum (FWHM) $\Gamma_G$ and $\Gamma_{2D}$ describe the line width for the G-band and 2D-band respectively. For suspended graphene, the values lie around $\Gamma_G \approx 14 cm^{-1}$ and $\Gamma_{2D} \approx 23 cm^{-1}$ [80].

**Figure 2-13:** Raman spectra of Graphite and Graphene [6]

### 2-5 Concept for controlled permeability

In the introduction it was mentioned that graphene in theory could act as an ideal filtration membrane because of its thickness. The perfect graphene sheet, however, is impermeable to gases even as small as Helium as was proven by [21]. This is due to the fact that the electron density of graphene’s aromatic rings is substantial enough to repel atoms and molecules trying to pass through. The property to be completely impermeable (unlike any other material) however, can be turned in to an advantage. Graphene has the potential to become a highly selective filter if controlled permeability can be achieved. From this perspective, various concepts have been proposed to influence graphene’s permeability for atoms. The first is the use of either a Transmission Electron Microscope (TEM) or a Focused Ion Beam (FIB) to shoot so-called nanopores in graphene sheets and thereby creating the possibility for atoms to diffuse [7]. The limitation of this approach is the resolution limit of a TEM/FIB which is currently insufficient (for the required hole sizes). A second possibility is to use chemistry to construct separate molecular building blocks and combining them in a bottom-up approach to construct nanopores (see Figure 2-14)[7].
A third method is enhancing permeability by inducing strain on the graphene membrane.

![Figure 2-14: Nitrogen functionalized pores in graphene [7]](image)

Before going into this method it is useful to first understand the concept of out-of-plane diffusion through the aromatic ring of graphene by considering Figure 2-15. In this figure,

![Figure 2-15: Schematic diagram for out-of-plane diffusion sites of an atom through graphene [8]](image)

two different paths are indicated, \( O_1 \) and \( O_2 \) respectively. \( O_1 \) is based on the possibility of temporarily breaking the carbon-carbon bond whereas \( O_2 \) is based on the possibility of an atom to diffuse through the aromatic ring. To better understand the \( O_2 \) path, it is relevant to consider an atom’s kinetic radius and comparing it to the diameter of the aromatic ring.
of graphene. As was previously discussed in the section graphene structure, the diameter of the aromatic ring of graphine lies in the order of $0.246 \text{nm}$. The actual net diffusion area of graphene’s aromatic ring is in fact even smaller, as the orbitals of the carbon atoms extend to within the aromatic ring, decreasing the actual diffusion area to a diameter of $\approx 0.15 \text{nm}$. As a comparison it is relevant to look at the radius of a hydrogen atom and, for reference sake, a Helium atom as it is the smallest stable element in the periodic table of elements. For completeness, atomic hydrogen is also shown, however because of its highly reactive nature is is unlikely to stay in its unfavorable lonely state and prefers to bond to other atoms.

- The kinetic radius of Helium ($\text{He}$) $\approx 0.26 \text{nm}$
- The kinetic radius of atomic Hydrogen ($\text{H}$) $\approx 0.11 \text{nm}$
- The kinetic radius of Hydrogen($\text{H}_2$) $\approx 0.29 \text{nm}$

This overview suggests that based on the kinetic radius and the diameter of the aromatic ring, only atomic hydrogen would be able to diffuse through the $O_2$ path. Based on modelling performed by Yang et al. it was shown that even atomic hydrogen encounters a substantial potential barrier of $3.85eV$ through path $O_1$ and $2.46eV$ through the $O_2$ path [8]. This potential barrier indicates that the mere size of the atom is not the whole story in explaining the likelihood of diffusion. In the same study, it was shown that during diffusion, atoms also interact with the graphene as they experience a process of bond formations and bond break (a process which increases the potential barrier). In similar studies it was confirmed that the diffusion of atoms is not so much a case of physical displacement (as in a sieve) but is based on tunneling mechanisms through a potential barrier. The Wentzel, Kramers, and Brillouin (WKB) approximation of the tunneling probability is given by

$$p = e^{-\frac{2\pi\sqrt{2m(V-E)}}{\hbar}}$$

(2-13)

where $\hbar$ is Plank’s constant $(6.626068 \times 10^{-34} m^2 kgs^{-1})$ and $p$ is the probability of a particle with mass $m$ and particle energy $E$ to tunnel across a finite potential barrier $V$ and distance of $x$ ($0.335 \text{nm}$ for monolayer graphene).

As an estimation of the tunneling probability of Helium at room temperature its particle energy $\approx 25\text{meV}$ and $V \approx 8.7eV$. This gives a tunneling probability of $p \approx 1 \times 10^{-335}$. In the case of path $O_1$ (with a potential barrier of $V \approx 3.5eV$) the probability can be slightly increased to $p \approx 1 \times 10^{-212}$ which is still too small for any considerable diffusion. In order for graphene to be used as an accepted filter for industrial use, a potential barrier of $0.5eV$ or lower is required for adequate diffusion.

### 2-5-1 Strain engineering

Graphene is structurally malleable, and many of its properties can be modified by strain and deformation. By subjecting graphene to strain it appears to be possible to alter its potential barrier and increase the likelihood of diffusion. Based on atomistic modelling conducted by Yang et al. it was shown that under the influence of strain it is possible to decrease the potential barriers of graphene. They noticed that the chirality plays an important role in the decrease of the potential barrier (see Figure [8]). For graphene put under strain in
zig-zag chirality, out-of-plane diffusion barrier across the $O_1$ path decreased from 3.9 eV to 2.5 eV whereas the $O_2$ path decreased from 2.5 eV to 1.5 eV. For graphene put under strain in armchair chirality, out-of-plane diffusion barrier across the $O_1$ path decreased from 3.9 eV to 0.5 eV whereas the $O_2$ path decreased from 2.5 eV to 0.7 eV. Armchair tensile strain is found to greatly decrease the out-plane diffusion of Hydrogen atoms, making it possible at low temperature. For moderate armchair strain (10%), calculations show that the out-of-plane diffusion is likely to occur along the $O_1$ path, diffusing by temporarily breaking the carbon-carbon. At relatively large strains around 15%, the out-of-plane diffusion is more likely to occur along the $O_2$ path, diffusing through the center of the aromatic ring [8].

![Diagram showing out-of- and in-plane diffusion](image)

**Figure 2-16: Out-of- and in-plane diffusion [8]**

**Additional effects of strain on graphene** It is not just the permeability properties of graphene that are altered by strain. Yang et al. also showed that strain can significantly increase the absorption properties of graphene. This absorption also changes the properties of graphene. When hydrogen atoms absorb to graphene it changes its structure. If 100% of its surface is covered with Hydrogen it is renamed graphane. The mechanical properties of graphane are greatly reduced in comparison to those of graphene as the Young’s modulus reduces by an order of 30% likewise, the tensile strength and fracture strain can be reduced by 65% [60] which is something to take into account when going up to high strains. However, at a strain of 10% this effect is not expected to greatly influence the stability of the graphene. Next to strain induced hydrogen absorption [8], it has also been calculated that compression...
could increase hydrogen desorption [81], which suggests a potential application for hydrogen storage. Next to hydrogen absorption, McKay et al. investigated the influence of strain on the chemisorption of atomic species on graphene and found that the forming of bonds onto the graphene surface is increased by 9% under the influence of tensile strain [82]. The absorption qualities of graphene under strain can also be exploited if the surface is decorated with metal atoms. Zhou et al. showed that by metal-decorating graphene and inducing strain up to 10% it was possible to increase its absorption properties for Li and Ti atoms up to 75% and 71% respectively and increase the gravimetric density of hydrogen storage from 9.5wt% up to 15.4wt% [83].

Next to influences on absorption and diffusion, strain also influences graphene’s electrical properties. It was shown that high strains ≥ 20% can generate a bulk spectral gap along directions that follow the underlying lattice. Pereira et al. further discussed how strain-induced anisotropy and local deformations can be used as a means to create local gauge fields and even alter graphene’s band structure [84]. This band gap opening [85], also discussed by Linnik et al. (who investigated the effective hamiltonian up to 10%) could be used as a convenient tool to investigate strain-related effects such as electron-phonon coupling and pseudo magnetic fields [86][87] induced by uniform strain.

2-6 Thesis milestone 1

*From a theoretical perspective, can the permeability properties of graphene be controlled such that hydrogen atoms can diffuse?*

Based on published literature it seems feasible that graphene will become permeable to hydrogen if strain is induced up to 10% thereby reducing the potential barrier by a factor of ≈ 8.
Chapter 3

Design of a MEMS-based tensile device

Chapter goal - milestone 2: Is it possible to design a MEMS device in such a way that it can influence the permeability properties of graphene?

In the previous chapter it was explained that there are various ways to synthesize graphene. For this research, defect free (and preferably monocrystalline) graphene is needed. Currently, mechanical exfoliation is still the most reliable method to obtain high quality graphene. This chapter investigates the possibility of inducing strain on graphene up to 10%. Strain is defined as

\[ \epsilon = \frac{\Delta L}{L_0} = \frac{\sigma}{E} = \frac{F_N}{EA} \]  

(3-1)

where \( \epsilon \) is strain, \( L_0 \) is the initial length, \( \Delta L \) is the change in length, \( \sigma \) is stress, \( E \) is the Young’s Modulus, \( F_N \) is the normal tensile force and \( A \) is the cross sectional area.

Strain is dimensionless and often expressed as a decimal ratio or percentage. As can be seen from 3-1 the strain is dependent on the dimensions of the graphene flake in question. The downside of the mechanical exfoliation method is that the dimensions of the obtained graphene flakes are limited. On rare occasions one is able to obtain flakes with axis dimensions in the order of 100\( \mu m \), however, one is much more likely to obtain flakes with edge dimensions in the order of 10\( \mu m \) to 20\( \mu m \).

The stiffness of graphene  The force needed to put a sample under strain is defined as the sample’s stiffness times the elongation by:

\[ F_s = K_s \times \Delta U_s \]  

(3-2)

The sample stiffness is related to material properties and sample dimensions and is defined by Hooke’s law (the validity of this assumption was shown by [14] who performed similar
measurements on carbon nanotubes) as:

\[
K_s = \frac{E_s A_s}{L_s}
\]

(3-3)

where \(E_s\) is the sample’s Young’s modulus (1TPa), \(A_s\) is the cross-sectional area in \(m^2\) (0.335nm \(\times\) width) and \(L_s\) is the length of the sample.

In order to proceed with the design of the tensile device, it is first necessary to define a reference flake. Preferably, the sample should not be too stiff in order to prevent high forces (increased power required) and a higher probability that either the device, clamp or sample may fail. Yet, the flake should not be too compliant as the sensing shuttle would then need to be very compliant (for adequate displacement resolution) and, therefore, more fragile. Based on 3-3 it can be seen that only two variables are non-constant, the width and length of the sample respectively. Making the sample narrower or longer reduces the sample stiffness, therefore a rectangular sample shape was chosen as the basis for the design of the MEMS chip.

The final flake dimensions used for calculations is \(10\mu m \times 5\mu m\). The flake being studied will always differ from the reference flake because of the fabrication process. As was indicated in the previous chapter, graphene shows non-linear elastic behavior under large strains \(\geq 10\%\). Since the desired strain for this experiment is on the cross-over point from the linear to the highly non-linear region it was decided to assume a linear behavior (due to stress-softening the needed tensile force only becomes less). However, the non linear behavior at strains \(\geq 10\%\) can be taken into account by designing the system (displacement controlled vs force controlled) such that it can detect the change in stiffness. This will be discussed later in this chapter. Therefore, to simplify the calculations for the analytical model, the Young’s modulus will be assumed constant at 1TPa.

Using 3-3 to calculate the in-plane spring constant results in the following sample stiffness:

<table>
<thead>
<tr>
<th>Sample Formula</th>
<th>(w (\mu m))</th>
<th>(h (\mu m))</th>
<th>(l (\mu m))</th>
<th>(E (GPa))</th>
<th>(K_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene (\frac{E_s A_s}{l_s})</td>
<td>10</td>
<td>0.00034</td>
<td>5</td>
<td>1000</td>
<td>680N/m</td>
</tr>
</tbody>
</table>

From this sample stiffness a rough estimation of the force output of the device needed can be calculated. The initial sample length \(L_0 = 5\mu m\), which needs to be strained by 10% (\(\Delta U_s = 0.5\mu m\)). So the tensile force needed to strain the sample by 10% is \(680N/m \times 0.5\mu m = 300\mu N\).

### 3-1 Methods to induce strain in graphene

There are several methods to put a sample under strain. In the macro world, tensile devices have been used for decades. Over the last years, experiences from the macro world, combined with improved fabrication methods have also lead to increasing applications of tensile devices in micro dimensions.

The dimensions of the graphene flake are the biggest challenge (by comparison, the average diameter of a human hair is \(\approx 100\mu m\), which is many times thicker than our flake). Several straightforward efforts to put graphene under strain have already been investigated. These methods include thermal strain of graphene ribbons \[9\], where the negative Thermal Expansion Coefficient (TEC) was exploited by suspending a graphene flake between two supporting
substrate pillars and heating them up (see Figure 3-1). The increased temperature shrinks the graphene and, since it is clamped by van der Waals adhesion along its edges, a tensile force occurs. This method however is not suited for high strains and secondly, the heat interferes with graphene’s electronic properties which is undesirable. Another method designed by Kim et al. is to transfer graphene onto a flexible substrate and put the substrate under strain [88].

The van der Waals interaction between the substrate and the graphene will then couple a fraction of the tensile stress on the substrate to the tensile stress on the graphene (see Figure 3-2). Although this method is straightforward, again, high strains are not very likely. This is because the van der Waals adhesion between graphene and its substrate is strong, but not strong enough for strains higher than $\approx 0.3\%$.

A third, straightforward method is to strain graphene out of plane by for example a nan indenter (AFM tip) or by a pressure difference (bulg test).

The methods shown in Figure 3-3a and Figure 3-3b seem to be suitable to put strain on graphene and simultaneously offer the possibility to measure permeability directly. Rough analytical models of both methods were performed based on polynomial displacement fields in the graphene. The results of these models show that although it is definitely feasible, the downside is that the outcome cannot give clear insight in the performance of the graphene. In the experiments conducted by Lee et al. the downside of the method was that the graphene had stress concentrations at the contact point with the AFM tip and at the edges because it bulges out-of-plane. In the research performed by Huang, the shape of the membrane has a polynomial curvature which results in a strain gradient across the membrane. Therefore it is difficult to understand the shape of the membrane and the exact strain in the sample as it
is different on every location in the membrane. All studies indicated that clamping is very important to consider as the van der Waals adhesion is not strong enough to adhere at high strains.

For this reason it was decided that an in-plane tensile device had to be designed in order to truly understand the strain process in graphene and to improve the clamping of the sample to the substrate. Since the sample dimensions are very small, the most feasible approach was to use MicroElectroMechanicalSystem (MEMS) technology.
In this section the design of the device will be explained. Before defining any of the parameters, it is necessary to define the performance requirements. In Figure 3-4 a schematic view of the required system is given where the sample (red) is put under strain by two moving shuttles (blue). In order to stress the sample, at least one shuttle needs to be actuated and the other

Figure 3-4: Schematic representation of in-plane strain

can be used as a load sensor.

### 3-2-1 Requirements

There are several requirements that the device must meet. Since graphene shrinks at elevated temperatures, the interface between the actuator and the sample should preferably remain at a constant (ambient) temperature. The device is able to produce enough stress on the sample to achieve the desired strain. The device shows linear in-plane displacement behavior in the desired \( \mu m \) range. Since we are interested in strain and are also interested in stress softening behaviour, the device needs to operate in displacement control. The device has sensing capabilities to characterize displacement and strains. And finally, the device must be able to operate within its own material safety margins to prevent buckling. A brief overview is given of all the requirements:

- Low temperature at the actuator-sample interface \( \approx T = 20^\circ C - 40^\circ C \)
- High force output (\( \geq 300\mu N \))
- Displacement range for the actuator (\( \geq 1\mu m \))
- Linear in-plane actuation
- Device is displacement controlled
- Sensing capabilities to extract sample stress
- Internal forces in device within safety margins to avoid buckling
- The design can be fabricated with approved process steps by the DIMES PAC

### 3-3 Conceptualization

Now that the requirements are defined, the actuation principle used should be defined since this has a major impact on the device’s behavior.
3-3-1 Actuation

Over the last decades, many different types and versions of micro-actuators have been designed. The driving principles of all these actuators are based on principle physics classes and exploit either one or a combination of several. This results in specific characteristics and unique advantages and disadvantages. The majority of micro-actuators can be classified as one of the following types [90]:

- Thermal actuators
- Electrical actuators
- Magnetic actuators
- Chemical actuators
- Optical actuators

In order to choose a design, it is necessary to define the primary quantities of the actuator, which depend on [10]:

- The actuator principle or class
- A set of non-geometrical design variables (e.g. the kind of active material used)
- A set of geometrical variables
- The actuator input quantity
- The external load

In order to extract the specific actuator from the primary quantities, the Springer actuator design procedure was used (see Figure 3-5).

![Figure 3-5: Actuator design procedure [10]](image-url)
3-3 Conceptualization

Thermal actuation

The performance characteristics of each actuator class were compared using different performance indices such as: maximum strain, maximum stress, maximum displacement, maximum volumetric power density, maximum mass power density, efficiency and resolution.\[10]. The actuator type chosen was a thermal actuator since this combines high output forces (up to tens of millinewtons), with high resolution and is scalable to small dimensions. The thermal actuator relies on the principle of thermal expansion which is given by:

\[ \Delta L = \alpha_L L \Delta T \] (3-4)

where \( \Delta T \) is the average temperature difference in the beam, \( L \) is the initial length of the beam and \( \alpha_L \) is the coefficient of thermal expansion of the material. The coefficient of thermal expansion is defined as:

\[ \alpha_L = \frac{1}{L} \frac{dL}{dT} \] (3-5)

The downside of the thermal actuator is its displacement range, which is limited if the desired strain axis is in the same direction as the expansion axis of the heated element (see Figure 3-6). A second disadvantage is the low energy efficiency of thermal actuators, which is considerably lower than most other actuators. The (limited) displacement of the thermal actuator can be amplified (up to tens of micrometers) if a compromise is made with the system output force, by aligning two beams under an angle in a chevron like configuration. In order to improve the efficiency, thermal expansion can be controlled by Joule heating, as it locally heats the relevant elements. An application of this is the Thermal In-plane Microactuator (TIM) (see Figure 3-7).

\[ \begin{align*}
\Delta L &= \alpha_L L \Delta T \\
\alpha_L &= \frac{1}{L} \frac{dL}{dT}
\end{align*} \]
Thermal in-plane Micro actuator physics  In this paragraph, the physics of the TIM device are introduced. As a voltage difference is applied across the contact pads (see Figure 3-7), a current flows through the legs and the shuttle. The high current density in the legs causes ohmic heating and thermal expansion. The legs are connected to the shuttle at a slight angle such that their expansion causes linear motion of the shuttle in y-direction.

Using Joule’s first law:

\[ P = I^2R \]  \hspace{1cm} (3-6)

and if Ohm’s law is applicable:

\[ I = \frac{V}{R} \]  \hspace{1cm} (3-7)

The power relation between current and voltage is given by:

\[ P = VI \]  \hspace{1cm} (3-8)

The power dissipation \( P \) across the heated elements in the (TIM) is directly proportional to the heat generated \( Q \) by

\[ P = VI = I^2R = \frac{V^2}{R} = \frac{Q}{t} \propto T \]  \hspace{1cm} (3-9)

With \( P \) being the power in Watt (J/s), \( I \) the current (A), \( V \) is the potential (V), \( Q \) is the energy (J/s), \( t \) is the duration and \( T \) the temperature (K).

The above mentioned equation 3-9 can be used for a simple qualitative analysis by directly giving an impression of the variables that can be altered to increase the thermal expansion.

- If the device is voltage controlled, the dissipated power can be increased by either increasing the voltage or reducing the resistance.
- If the device is current controlled, the dissipated power can be increased by either increasing the current or increasing the resistance.

In order to understand the physics in more depth and to perform a quantitative analysis of the thermal behavior of the system, additional relevant formulas need to be introduced. The resistance is an object property, whereas the resistivity is a material property which is related by:

\[ R = \frac{\rho l}{A} \]  \hspace{1cm} (3-10)

with \( R \) the electrical resistance, \( \rho \) the electrical resistivity (\( \Omega \)m) and \( L \) is the length of the current conducting beams (m).

The resistivity and conductivity of a material are inversely proportional by:

\[ \sigma = \frac{1}{\rho} \]  \hspace{1cm} (3-11)

where \( \sigma \) is the conductivity (S/m) and \( \rho \) is the resistivity (\( \Omega \)m)
And finally, the current is related to the current density by the cross sectional area of the conducting element by

\[ I = jA \]  

with \( I \) is the current (A), \( J \) is the magnitude of the current density \((A/m^2)\) and \( A \) is the cross sectional area of current carrying beams \((m^2)\).

The power can finally be re-written as:

\[ P = \frac{j^2A^2\rho l}{A} = \rho j^2AL = \rho j^2AL \]  

To limit the possibility of electromigration (a material related effect), the current density needs to be limited to be less than the following criteria:

\[ j \leq j_{\text{limit}} \]  

This limit increases the life expectancy of the device. The power can now be re-written as:

\[ P \leq \rho j_{\text{limit}}^2Al \]  

In order to describe energy dissipation in the current carrying beams accurately, a finite-difference model can be constructed \[91\]. Here, only the relevant parameters will be shown. In the modelling chapter these formulas will be taken into account in a Finite Element Analysis using COMSOL Multiphysics. For completeness, the relations are given below:

\[ q_i + q_{\text{conv}} + q_{\text{rad}} + q_{\text{cond},i-1} + q_{\text{cond},i+1} = q_{\text{st}} \]  

with \( q_i \) being the energy generated in element \( i \) of the beam (ohmic heating), \( q_{\text{conv}} \) is the contribution of free convection, \( q_{\text{rad}} \) is the radiation to the environment, \( q_{\text{cond},i\pm1} \) is the heat conduction to the previous and next element and \( q_{\text{st}} \) is the energy stored in the element.

\[ q_i = J^2\rho_r(T)\Delta V_i \]  

where \( J \) is the current density, \( \rho_r(T) \) = the temperature dependent resistivity and \( \Delta V_i \) the element volume. For metals, the temperature dependent resistivity can easily be quantified since the thermal expansion coefficient \( \beta \) is constant. For semiconductors, such as polycrystalline Silicon, the \( \beta \) is dependent on grain size, doping and internal stresses and can only be calibrated on a real device.

\[ \rho_r(T) = \rho_0[1 + \beta(T - T_s)] \]  

where \( \rho_0 \) is the initial resistivity at ambient temperature, and \( \beta \) the Thermal Coefficient of Resistance (TCR) \((1/K)\). The energy radiation out of an element is given by

\[ q_{\text{rad}} = \epsilon\sigma A_s[T_{\text{surf}}^4 - T_i^4(k)] \]  

where \( A_s \) is the area of the exposed surface, \( \epsilon \) is the emissivity, \( \sigma \) is the Stefan Boltzman constant \((5.6703 \times 10^{-8}(W/m^2K^4))\).

Since the beams are free-standing to allow forward motion, heat can only be conducted to the previous and the next element and this is given by

\[ q_{\text{cond},i\pm1} = \frac{k_pA_x}{\Delta x}[T_{i\pm1}(k) - T_i(k)] \]
where $A_x$ is the cross-sectional area of the beam element, and $k$ is the time increment for a transient analysis. Finally, the energy stored in the beam is given by

$$q_{st} = \frac{\rho c \Delta V_i}{\Delta t} [T_i(k+1) - T_i(k)]$$

(3-21)

where $\rho$ and $c$ are the density and specific heat of Polycrystalline Silicon and $\Delta T$ is the time increment.

### 3-3-2 Sensing elements

In this section, sensing methods will be introduced that are able to detect system displacement and sample strains. As a precaution, the device should not rely on only one sensing concept. To improve the possibility of a successful measurement and to expand the device’s capabilities for future research three different sensing methods will be employed.

In the schematic illustration given in Figure 3-4 it can be seen that if shuttle A (blue) is actuated, the sample (red) put under strain and shuttle B (blue) can be used as a load sensor. If shuttle A is actuated, the displacement of the shuttle will stress the sample, which in turn will stress shuttle B. If the stiffness of shuttle B is known, it is possible to extract the force acting on the sample.

**Displacement sensing**

In order to extract the force on the sample by using the stiffness of the load-sensing shuttle B, it is vital to be able to detect fine displacement of both shuttles. For this reason, two different sensing methods were implemented.

**Displacement detection by curve fitting on VLM images** The first is an optical tracking method developed by Dr. Ir. Merlijn van Spengen at Delft University of Technology. Since the working principle of this method has not been published yet, a detailed description could not be given at the time of writing this thesis. However, a brief description of the working principle can be given. The method is designed for optical detection of sub-nm resolution motion using a visible light microscope. The resolution of an optical microscope is limited by $\frac{1.22 \lambda}{2NA}$ due to diffraction. Where $\lambda$ is the wavelength of the light and $NA$ is the Numerical Aperture. However, by using image processing techniques it is possible to go below this resolution limit. The driving principle of the optical tracking method is based on curve-fitting (fitting a mathematical function to the measured data) a function on the contrast plot, extracted from a VLM image.

**Capacitive sensing** The second sensing method is based on capacitive sensing. The capacitive displacement sensor is a well known and established technique to measure the position and/or change of position of any conductive target [10]. Capacitive sensors use the electrical property of capacitance to perform measurements. Capacitance is a property that exists between any two conductive surfaces within some reasonable proximity. Changes in the distance between the surfaces changes the capacitance. It is this change of capacitance that capacitive sensors use to indicate changes in the position of the target.
The property of capacitance is most commonly illustrated using the example of two parallel conductive plates with a gap between them and a charge applied to them (see Figure 3-9). The capacitance of two parallel fixed plates can be expressed by equation 3-22:

\[ C = \frac{\epsilon_0 K A}{d} \]  

Figure 3-9: A schematic illustration of capacitance [13]

where \( C \) is the capacitance, \( \epsilon_0 \) is the permittivity of free space, \( K \) is the dielectric constant of the material in the gap, \( A \) is the area of the plates and \( d \) is the distance between the plates. However, since this sensor needs to be implemented on a free-standing moving shuttle, the concept of two parallel plates is difficult to realize. Therefore, the actual design should have several beams which are clamped on one end and free-standing on the other (see Figure 3-10). The design of the capacitor used in this device is based on work performed by Zhu et al [92].

Figure 3-10: A schematic illustration of capacitance sensing on the shuttle

The read-out of this setup can be done according to the schematic schedule in Figure 3-11.
The change in capacitance in this setup (Figure 3-10) can be calculated according to

\[ C_\Delta = C_1 - C_2 = N \epsilon A \left( \frac{1}{d_0 - \Delta d} - \frac{1}{d_0 + \Delta d} \right) \approx N K \epsilon_0 A \left( \frac{1}{d_0} \right)^2 \]  

(3-23)

where \( \Delta d \) is the displacement of the sensing shuttle, \( N \) is the number of beams and \( d_0 \) is the initial distance between the beams.

**Four-point-probe resistivity measurement**  
Next to measuring the behaviour (displacements) of the device and indirectly extract the forces on the sample, it is also relevant to measure the behaviour of the graphene directly. As the graphene is put under strain, its electrical properties will also change (as was explained earlier). This change in resistivity can give information about the strain levels on the graphene sample using the gauge factor. Therefore, it is desirable to implement a continuous sheet resistivity measurement of the sample into the device. This can be realized by using a so-called four-point-probe sensor. A four-point-probe measurement is a simple setup to measure the resistivity of conducting sheets (see Figure 3-12). By passing a current through two outer probes and measuring the voltage through two inner probes the resistivity of the sample can be measured [93] while cancelling out the contact resistance of the probes onto the sample. The sheet resistance of the graphene flake can be calculated using the Van der Paauw Method which works if the following requirements are met:

- The contacts are numbered from 1 to 4 in a counter-clockwise order, beginning at the top-left contact.
• The current $I_{12}$ is a positive DC current force into contact 1 and taken out of contact 2, and is measured in amperes (A).

• The induced voltage $V_{34}$ is a DC voltage measured between contacts 3 and 4 with no externally applied magnetic field, measured in volts (V).

• The resistivity $\rho$ is measured in (\(\Omega m\)).

• The thickness of the sample $t$ is measured in metres (m).

• The sheet resistance $R_s$ is measured in ohms (\(\Omega\)).

The sheet resistance $R_s(\Omega)$ can be found by solving the following quadratic function:

$$e^{-\pi R_{12}}_{12} + e^{-\pi R_{23}}_{23} = \frac{V_{34}}{I_{12}} \quad (3-24)$$

where $R_{12} = \frac{V_{34}}{I_{12}}$ and $R_{23} = \frac{V_{41}}{I_{23}}$. If the sheet resistance $R_s$ is multiplied by the thickness of the material, the bulk resistivity $\rho = R_s \times t$ is obtained.

If the sheet resistance is known, the resistivity and also the sample resistance is known. If the sample is put under strain, the sample resistance will change. This change in resistance is related to strain by the gauge factor. The gauge factor is defined as:

$$GF = \frac{\Delta R}{R} = \frac{\Delta \rho}{\rho} + 1 + 2v \quad (3-25)$$

where $R$ is the resistance of the strain gauge in unstrained state, $\Delta R$ is the change in strain gauge resistance, $\rho$ is the resistivity, $v$ is the Poisson’s ratio and $\epsilon$ is the sample strain.

The gauge factor of graphene is $\approx 1.6-1.9$ [94].

### 3-3-3 Defining the parameters

Now that all the building blocks of the device have been introduced, the geometrical parameters have to be chosen and the final design made. The system schematic combining the different building blocks is shown in Figure 3-13. In the next chapter, the analytical model will be given. First the safe operating region of the device was calculated. An intrinsic property
of the TIM is that a compromise must be made between output force, shuttle displacement and internal stresses. These depend on the dimensions chosen and the beam angle (see Figure 3-14). Although various designs for TIM devices have been published, Zhu et al. report the most comprehensive design [95]. The critical force for buckling of a thermally actuated beam at given beam angle $\Theta$ can be written as [95]

$$P_{cr} = \frac{\pi^2 EI_{min}}{l_{tb}} = 3.5\text{mN} \tag{3-26}$$

where $P_{cr}$ is the critical force, $I_{min}$ analyzes the inertia in both X and Y direction and extracts the minimum and $l_{tb}$ describes the length of the beam.

And the axial internal force in the thermal beams is compressive and given by 3-27

$$R_x^{\Delta T} \cos \theta = \alpha \Delta T E A_{tb} \frac{\cos^2 \theta}{\sin^2 \theta \frac{A_{tb}}{12 I_{tb}} + \cos^2 \theta} \tag{3-27}$$

The height and the width of the beams were based on work performed by Espinosa et al. [14] Who reported good mechanical behaviour. The reason of having a rectangular shape (width>height) has to do with the direction of the force vectors acting on the beam. The width gives the beam more stiffness during the expansion such that they will not buckle in-plane. The length of the beam is related to the maximum displacement, as was shown in 3-5 it is directly related to the $\Delta d$ of the shuttle. However, since longer beams are more likely to buckle or undergo stiction during the microfabrication process. Espinosa et al [14] proposed a practical limit for the inclined beam length at 300$\mu$m. Since our design needs to generate relatively high forces, a thermal beam length of 200$\mu$m was chosen, which is within the practical limit, and stronger than that chosen by Espinosa et al. yet long enough to prevent force errors [96].

The following figures give a visual representation of the trade-off between the output force, the maximum displacement and the buckling behaviour of the system.

Based on figures 3-15a, 3-15b & 3-15c, an angle of 7 degrees was chosen. This decision was based on displacement, internal force and a safety margin of two (which means two times the minimum angle at buckling 3-15a). In Figure 3-15d it can be seen that at this 7 degree angle, the internal forces are well below the critical limit (given by the dashed line).
Figure 3-15: Device design parameters

(a) Internal force vs beam angle

(b) Actuator stiffness vs angle

(c) Actuator displacement vs angle

(d) Internal force vs max temperature
3-4 Final design

The electric potential to induce joule heating (the actuator) is applied on the biggest gold bond-pad (Figure 3-16), the biggest grey bond pad is ground. If two needle probes are connected to these bond-pads the circuit for Joule heating is closed. The small gold bond-pads (Figure 3-16 and the small grey bond-pad are used for capacitive read-out. In Figure 3-17 the location of the graphene sample can be seen and the electrical circuit for the four-point-probe sensing is shown, for which the green and purple bond pads are used (Figure 3-17. The reasoning for the location of the bond-pads has to do with minimizing possible electrical interference between the contacts. The difference in resistance because of the asymmetrical shape of the four (green and purple) bond-pads can be cancelled out with the four-probe-measurement.
3-4-1 Additional designs

Next to the main design shown on the previous page, several additional designs were made. All of which have slightly different specifications and characteristics. It was decided to vary the beam angle to investigate the compromise between displacement range (smaller angle is larger displacement range) and maximum force output (larger angle is larger output force). Both thick and thin capacitor beams are used to investigate the compromise between the resolution of the capacitive sensor and the structural stability of the beams used for the capacitive sensing. These final designs include: variations of the angle of the thermal beams, devices with a fixed secondary shuttle (higher forces), compression devices that strain the graphene by stressing the substrate, and finally a two-directional tensile device which is able to stress the graphene in two directions (relevant to investigate flakes in both armchair and zig-zag edge direction).

The actual devices will be shown at the end of the fabrication chapter. Below a concise summary of the eight different designs is given:

- Design A ($7 \Theta$ thermal beams, thick capacitor beams)
- Design B ($7 \Theta$ thermal beams, thin capacitor beams)
- Design C ($30 \Theta$ thermal beams, thick capacitor beams)
- Design D ($7 \Theta$ thermal beams, two directional stress)
- Design E ($7 \Theta$ thermal beams, fixed secondary shuttle)
- Design F ($30 \Theta$ thermal beams, fixed secondary shuttle)
- Design G ($7 \Theta$ thermal beams, cylinder compression)
- Design H ($7 \Theta$ thermal beams, beam compression)

3-5 Thesis milestone 2

Is it possible to design a MEMS device in such a way that it can influence the permeability properties of graphene?

By using the state-of-art MEMS design toolset combined with published literature and personal input, a new MEMS device was designed that implements the necessary functionality to stress a graphene flake and induce strain.
Chapter goal - milestone 3: Does the MEMS device perform according to the requirements based on analytical modelling and finite element analysis?

4-1 Analytical estimations

In order to analyse a thermal actuator, the coupled electric, thermal and mechanical effects need to be investigated. In this section, the mechanical behavior of the device is analytically derived and the performance of the device will be shown, these calculations are build upon work previously conducted on modelling Thermal In-plane Microactuators [14][95][92][97].

4-1-1 Model assumptions

The analytical calculations are intended to give an idea of the general behaviour of the device. The relevant assumptions are listed below:

- 2D linear isotropic model
- Small deflection theory
- Average temperature known
- Shear deformation of the beams is negligible
- Small displacement theory applies
- Only thermal expansion of the actuator (expansion of shuttle and guidance beams neglected)
- All material properties remain constant (e.g. no stress softening)
- Device material is regarded as homogeneous
4-1-2 System stiffness

The lumped model of the device is shown in 4-1. The model shown in Figure 4-1 shows that the device is divided into three different sections; the thermal actuator, the graphene sample and the load sensor. Each of these three sections is made up of different elements. The stiffness of the device will be calculated according to these sections and their corresponding sub-elements.

Thermal actuator

The thermal actuator consists of the following sub-elements: the shuttle, the thermal beams, sink beams and guidance beams. The assumed displacement field of the thermal beams is visualised in Figure 4-2.

The (axial and bending) stiffness of the thermal beam $K_{tb}$ is defined by:

$$K_{tb} = \left(\sin^2\theta + \frac{\cos^2\theta}{\psi}\right)E \frac{A_{tb} I_{tb}^3}{l_{tb}^3} + \sin^2\theta E b_{tb} h_{tb} \frac{l_{tb}}{I_{tb}} + \cos^2\theta E b_{tb}^3 h_{tb} \frac{l_{tb}}{I_{tb}}$$

with $A_{tb} = b_{tb} I_{tb}$, $I_{tb} = \frac{1}{12} b_{tb}^3 h_{tb}$ and $\psi = \frac{A_{tb}^2}{12 I_{tb}}$ (the axial over bending stiffness ratio)
The stiffness of the sink and guidance beams is defined by Euler-Bernoulli beam theory which states:

$$K_{\text{beam}} = \frac{E b_{\text{beam}}^3 h_{\text{beam}}}{4 l_{\text{beam}}^2} \quad (4-2)$$

The results can be summarized as:

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
<th>w (µm)</th>
<th>h (µm)</th>
<th>l (µm)</th>
<th>#</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal – beam($K_{tb}$)</td>
<td>$\sin^2 \theta \frac{E b_{tb}^3 h_{tb}}{l_{tb}} + \cos^2 \theta \frac{E b_{tb}^3 h_{tb}}{l_{tb}}$</td>
<td>8</td>
<td>5</td>
<td>200</td>
<td>$m = 30$</td>
<td>170</td>
</tr>
<tr>
<td>Sink – beam($K_{sb}$)</td>
<td>$\frac{E b_{sb}^3 h_{sb}}{4 l_{sb}^2}$</td>
<td>5</td>
<td>5</td>
<td>50</td>
<td>$n = 28$</td>
<td>170</td>
</tr>
<tr>
<td>Electrode – spring($K_{es}$)</td>
<td>$\frac{E b_{es}^3 h_{es}}{4 l_{es}^2}$</td>
<td>5</td>
<td>5</td>
<td>50</td>
<td>$o = 4$</td>
<td>170</td>
</tr>
</tbody>
</table>

**Sample**

The stiffness of the sample was previously calculated at $K_s = 680 N/m$.

**Load sensor**

The stiffness of the load sensor is more straightforward as all the sub-elements are simple straight beams. The results can be summarized as

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
<th>w (µm)</th>
<th>h (µm)</th>
<th>l (µm)</th>
<th>#</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode – spring($K_{es}$)</td>
<td>$\frac{E w_{es}^3 h_{es}}{4 l_{es}^2}$</td>
<td>5</td>
<td>5</td>
<td>50</td>
<td>$p = 4$</td>
<td>170</td>
</tr>
<tr>
<td>Guidance – spring($K_{gs}$)</td>
<td>$\frac{E w_{gs}^3 h_{gs}}{4 l_{gs}^2}$</td>
<td>5</td>
<td>5</td>
<td>100</td>
<td>$q = 2$</td>
<td>170</td>
</tr>
</tbody>
</table>

$$K_{ls} = K_{es} + K_{gs} \quad (4-3)$$

**Summary**

Taking the three different sections (and their elements) into account the following table shows the overall device stiffness:

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
<th>Stiffness (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actuator($K_o$)</td>
<td>$m \times K_{tb} + n \times K_{sb} + o \times K_{es}$</td>
<td>18892</td>
</tr>
<tr>
<td>Load – sensor($K_{ls}$)</td>
<td>$p \times K_{es} + q \times K_{gs}$</td>
<td>903</td>
</tr>
<tr>
<td>Graphene($K_s$)</td>
<td>$\frac{E s_A s_A}{l_s}$</td>
<td>680</td>
</tr>
</tbody>
</table>
4-1-3 System performance

The schematic shown in Figure 4-1 was further reduced to model the device’s displacement behaviour (see Figure 4-3).

\[ U_{\Delta T} = \alpha \Delta T l_b \frac{\sin \theta}{\sin^2 \theta + \cos^2 \theta \frac{12 l_b}{\psi}} \]  

Where \( U_{\Delta T} \) is the displacement of the actuated shuttle without additional stiffness of the guidance beams, sample and the load sensor. The thermal expansion coefficient \( \alpha \) for polycrystalline silicon (2.6 \( \times \) 10\(^{-6}\)).

\[ U_a = \frac{U_{\Delta T} K_b}{K_a} = \frac{(m\alpha\Delta T E A_b \sin \theta)}{K_a} \]  

\( U_a \) is the displacement of the actuated shuttle without the stiffness of the sample and the load sensor.

\[ \Delta U_s = U_a - U_{ls} \]  

\( \Delta U_s \) is the elongation of the sample and \( U_{ls} \) is the displacement of the load sensor.

\[ F_a = F_s = F_{ls} \]  

\( F_a \) is the force produced by the thermal actuator, \( F_s \) is the force on the sample and \( F_{ls} \) is the force on the load sensor.

\[ F_s = K_s \Delta U_s \]  

\[ F_{ls} = K_{ls} U_{ls} \]  

\[ U_{system} = \frac{(m\alpha\Delta T E A_b \sin \theta)}{K_a + \frac{K_s K_{ls}}{K_s} + K_{ls}} + \frac{(m\alpha\Delta T E A_b \sin \theta)}{K_a + K_s + \frac{K_s K_{ls}}{K_{ls}}} \]  

Where \( U_{system} \) is the displacement of the entire device (system), including the stiffness of all three sections.

\[ F_s = \frac{(m\alpha\Delta T E A_b \sin \theta)}{K_s + 1 + \frac{K_s}{K_{ls}}} \]  

\[ \Delta U_s = \frac{(m\alpha\Delta T E A_b \sin \theta)}{K_a + K_s + \frac{K_s K_{ls}}{K_{ls}}} \]  

\[ U_{ls} = \frac{(m\alpha\Delta T E A_b \sin \theta)}{K_a + \frac{K_s K_{ls}}{K_s} + K_{ls}} \]
Figure 4-4 plots the force generated by the device because of an average induced temperature in the thermal beams (0 to 600°C). Figure 4-4b shows the displacement of the two shuttles at a given temperature where the difference between the two is equivalent to the elongation of the sample $\Delta U_s$. Figure 4-4c shows the elongation of the sample at a given temperature. From figure 4-4c, it can be seen that at $\Delta T = 200^\circ C$ the sample is put under 10% strain. The expected changes in output capacitance $C_\Delta$ due to 100nm displacement of the load sensor (at 10% induced strain in the graphene) is $\approx 12.5 fF$. 
4-2 Finite Element Analysis (FEA)

4-2-1 Model assumptions

In order to get a more accurate approximation of the device’s performance, a Finite Element Analysis (FEA) was made. FEA is a numerical technique to find approximate solutions to partial differential equations (PDE) and their systems. Basically, FEA divides a complicated problem into small elements that can be solved in relation to each other and it can combine their results to give system performance. Although this method is suitable for the analysis of an engineered system, it is important to understand its limitations, since, if not properly interpreted can give misleading results. The model assumptions and parameters are given below. In order to reduce the calculation time only the most relevant areas of interest were modelled (see Figure 4-5b).

Model assumptions:

- 3D linear isotropic
- MicroElectroMechanical coupling
- Analysis class - Joule heating & thermal expansion
- Steady state analysis
- Input parameters remain constant
- Heat dissipation via conduction, radiation & convection
- General physics mesh 2.5µm > element size < 58µm
- The sample is modelled as Silicon with an equivalent stiffness to the reference graphene flake

4-2-2 Input parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus</td>
<td>GPa</td>
<td>170</td>
<td>[98]</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>-</td>
<td>0.22</td>
<td>[98]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W/mK</td>
<td>34</td>
<td>[99]</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>Ωm</td>
<td>1 × 10^{-3}</td>
<td>-</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>2/3s</td>
<td>1 × 10^3</td>
<td>[14]</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>2.6 × 10^{-6}</td>
<td>[99]</td>
<td></td>
</tr>
<tr>
<td>Heat Capacity Poly-Si</td>
<td>J/kgK</td>
<td>678</td>
<td>[100]</td>
</tr>
<tr>
<td>Convective heat transfer coefficient</td>
<td>W/m²K</td>
<td>5</td>
<td>[101]</td>
</tr>
<tr>
<td>Emissivity</td>
<td>-</td>
<td>0.8</td>
<td>[100]</td>
</tr>
<tr>
<td>Material density</td>
<td>kg/m³</td>
<td>2320</td>
<td>[100]</td>
</tr>
<tr>
<td>Reference temperature</td>
<td>K</td>
<td>293.15</td>
<td>-</td>
</tr>
<tr>
<td>Applied potential</td>
<td>V</td>
<td>2.6</td>
<td>-</td>
</tr>
</tbody>
</table>
Because the difference between the dimensions of the graphene sample and the device is so large (several orders of magnitude), the FEA engine is not able to analyze the model. In order to analyze the behaviour of the device with graphene, the sample (long thin element in the middle Figure 4-5b) is made out of Silicon with an equivalent stiffness of 680 N/m.
4-2-3 System performance

Figure 4-6: The static temperature profile across the device

Figure 4-6 shows the static temperature distribution over the device. With the given input parameters, the maximum temperature achieved at an applied potential of $2.6V$ is $398C$ and the temperature of the polycrystalline Silicon at the sample is $<40C$ which is in reasonable limits. Since the sample will also be isolated by a nitride layer, the sample temperature will be even lower, thus meeting the device requirements. The maximum current density in the device obtained from Figure 4-7 is $\approx 1.1 \times 10^7 (A/m^2)$ or $1.1 \times 10^5 (A/cm^2)$. Highly p-doped polycrystalline silicon starts to show electromigration at current densities $> 1. \times 10^6 (A/cm^2)$. So the obtained current density is well within the safety limit. The maximum obtained Von
Mises stress obtained from Figure 4-8 is \( \approx 0.6 \text{GPa} \). There is not a definitive fracture strength of polycrystalline silicon as it depends on several aspects such as grains and doping levels. Common reported values for the fracture strength of polycrystalline silicon lie \( \approx 2 \text{GPa} \). From this it can be concluded that the internal stresses within the device are within the safety limit. From Figure 4-9 the displacements in the x-direction can be extracted.

\[ U_a \approx 0.6 \mu m, \quad U_{ls} \approx 0.1 \mu m \quad \text{and} \quad \Delta U_s \approx 0.5 \mu m. \]

The obtained \( \Delta U_s \) corresponds to a sample strain of 10\% which meets the requirement. From Figure 4-10 the (exaggerated) displacement in y-direction can be obtained, from this figure a maximum displacement in y-direction because of thermal expansion is found at \( \approx 60nm \). Figure 4-11 shows the displacement in z-

**Figure 4-8:** The Von Mises stresses in the device

**Figure 4-9:** Displacement in X-direction (displacements 20x)
direction. This displacement can occur because of thermal expansion or because of the forces generated as the sample is strained. The z-displacement at the sample-actuator interface is the only relevant section as it could influence the in-plane strain measurement. Since the sample is clamped on the top side of the shuttle, a torsional force is expected on the guidance beams. This leads to small deflections in z-direction. From this figure it was concluded that both shuttles deflect downwards to a maximum of $\approx 9\text{nm}$, although they both deflect downward, the slight difference between the two shuttles (because of a difference in stiffness) is $\approx 0.3\text{nm}$ which is negligible for the given requirement.
4-3 Analytical estimations vs FEA

The analytical estimations correspond to the results obtained by FEA. From the FEA model it was concluded that in order to induce a similar strain of 10% on the sample, the average temperature of the thermal beams had to be $\approx 100^\circ C$ higher than that predicted by the analytical model. It was concluded that this was related to the thermal expansion of the shuttle (which was neglected in the analytical model). When the shuttle heats up and expands, this expansion cannibalizes the displacement at the sample’s end. In order to get the same displacement as the analytical model, the temperature (and related displacement) needs to be increased. This hypothesis was checked with the FEA model, the average temperature across the entire shuttle was extracted and then, taking the thermal expansion coefficient of the silicon into account, the expansion corresponded to the difference between the models.

4-4 Thesis milestone 3

Does the MEMS device perform according to the requirements based on analytical modelling and finite element analysis?

Based on both the analytical model and Finite Element Analysis, it was concluded that the device performed according to requirements. However, several aspects need to be taken into account. First of all, these models analyze static behaviour, where in reality the behaviour will be transient (dependent on time). Therefore, the actual temperatures (at a given potential) and corresponding displacement will most likely differ. Secondly, influence by the chosen input parameters is to be expected in comparison to the real device. Especially, the material properties are expected to be non-constant (e.g. conductivity, thermal expansion and Young’s modulus) and actual heat dissipation is expected to change the actual performance. However, this is not viewed as a problem because the resulting difference in performance can be calibrated.
Chapter 5

Fabrication methods & materials

*Chapter goal - milestone 4: Is this design realizable with existing fabrication techniques available in the facilities of Delft University of Technology?*

In this chapter, a general overview of the relevant fabrication steps is given. The fabrication methodology uses a top down approach, where a stack of different layers is etched down in order to sculpt the desired MEMS device. This consists of two micro-shuttles in a chevron-like configuration that are used to stretch a graphene flake in order to study its properties under a given stress. It is important that the graphene flake is transferred onto the system before the underetching the shuttles. This is because the graphene transferring process could damage the free-standing structures.

During the stretching of graphene, a change in resistance is expected. This will be measured by a four-point-probe configuration whose circuitry is patterned on top of the device by means of a metal evaporation step using a shadow mask. The designs of the devices are patterned according to the mask shown in Figure 5-1b.

![L-edit mask design](image)

---

*Figure 5-1: L-edit mask design*
5-1 Layer deposition

The fabrication starts with a double side polished 300\(\mu m\) thick Si wafer which is then thermally oxidized until a 1.5\(\mu m\) thick SiO\(_2\) layer is achieved. This layer will be used as a 'sacrificial' layer, so that shuttles of the chevron-like configuration can eventually be released, forming the free-standing system that is needed to perform our experiments. During this process, the wafer is exposed to a an oxidizing agent which diffuses into the wafer at high temperatures, reaching 1100\(^\circ\)C and reacting with the silicon atoms. The process takes place in a wet environment, so that water vapor is used as the agent to trigger the chemical reaction that gives rise to the final layer. The reaction is given by:

\[
Si + 2H_2O \rightarrow SiO_2 + 2H_2 \tag{5-1}
\]

Figure 5-2: Silicon with 1.5\(\mu m\) SiO\(_2\)

In this model, the water molecule dissociates at high temperatures to form hydroxyl (–OH) groups that can diffuse into the silicon much faster than molecular O\(_2\), which is an other option for an oxidizing agent in a so-called dry environment. Therefore, the wet oxidation process has a significantly higher oxidation rate than the dry oxidation. Since we aim to grow a thick oxide, wet oxidation is the best option. After the oxide is successfully grown, a 5\(\mu m\) thick layer of polycrystalline silicon is deposited on top, which is used as the material from which the system is made. The production of such silicon has been manufactured by chemical vapour deposition in H\(_2\) from the chlorosilanes: SiCl\(_4\), SiHCl\(_3\), SiH\(_2\)Cl\(_2\) and SiH\(_4\) in open tube, vapour transport systems. The reaction conditions were established such that the rate of the added reactants controls the growth rate. This procedure gives a good crystal quality, which is a necessary feature for good device performance. The silicon is normally doped with PH\(_3\), AsH\(_3\) and B\(_2\)H\(_6\). As the dopant solid solubility is approached, extremely high concentrations of dopant are required in the gas stream and the layer can turn into a two-phase polycrystalline deposit if the solid solubility is exceeded. If depositing with chlorosilanes, HCl is created by surface and gas phase reactions. This HCl enhances layer quality by etching the high energy surface atoms during deposition. When HCl is added to SiH\(_4\), the simultaneous etch/deposit process also occurs and the etch reaction can be treated as if it were separate from the SiH\(_4\) deposition process.

Eric Walter Kievit

CONFIDENTIAL

Master of Science Thesis
Finally, a 500nm LPCVD (Low Chemical Vapour Deposition) $Si_3N_4$ layer is deposited on top of the newly grown silicon layer. The layer, used as a passivation film, is deposited inside a furnace in several steps. First a gas is transported to the surface where it becomes adsorbed, enhancing a reaction of surface reactants (without involvement of substrate atoms) and a desorption of by products. This process occurs at 850°C, where the formation of the silicon nitride results from using dichlorosilane (DCS) and ammonia as precursors, in a chemical reaction as follows:

$$3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$$  \hspace{1cm} (5-2)

The reason for using $Si_3N_4$ and not $SiO_2$ as a passivation layer is that during the release of the structures, vapour HF will be used to etch away the sacrificial layer, which is a thick $SiO_2$ layer. Therefore, by using silicon nitride instead, we avoid etching away the passivation during the structure releasing. The final result of the layer deposition process can be seen in Figure 5-4.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5-3.png}
\caption{Deposited Polycrystalline Silicon}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5-4.png}
\caption{All layers deposited}
\end{figure}
5-2 MEMS Patterning

The shape of the device is delineated using a top-down approach based on photolithography and reactive-ion etching (RIE). First of all, the wafer is spin-coated until a standard thickness of 1.4µm of photoresist is reached. An (ASML) wafer stepper is then used to expose a bright-field mask (see Figure 5-1a) to create a photographic negative of the device’s layout using positive resist. During the subsequent developing step, the exposed resist is washed away, leaving the unexposed resist protecting the desired shape. This ensures that during the subsequent dry-etching of the nitride layer, everything will be removed except for the nitride that remains protected by the photoresist. Such etching, done via RIE, uses a plasma generated (under vacuum) by an electromagnetic field. This plasma uses high-energy ions to attack the surface and react with it. Depending on the material to be etched, the mixture of gases to create the corresponding chemically reactive plasma differs. Since the nitride is the upper layer, a mixture of gases including $CF_4$, $SF_6$ and $O_2$. When the process is finished, it is necessary to remove the remaining resist in a plasma etcher, followed by cleaning the wafer in $HNO_3$ 99% at room temperature to remove inorganic residues and cleaning in $HNO_3$ 65% at 110°C to get rid of ionic contamination. Once the wafer is cleaned and the silicon nitride layer is patterned, it is necessary to spin-coat the wafer once again and perform another photolithography step to expose the mask that contains the main profile of the entire MEMS device. Similarly, as before, the exposed bright-field mask leaves the photoresist patterned outline of the intended system, in such way that everything else can be etched down while the layers protected by the resist will remain intact.

RIE is once again used to etch down through the polycrystalline silicon by mixing $CF_4$ and $O_2$. Next, the gas mixture is changed to etch down the thermal oxide, using $CF_4$, $CHF_3$ and $He$. Similarly as before, it is necessary to remove the remaining resist in a plasma etcher, followed by cleaning the wafer in $HNO_3$ 99% at room temperature to remove the inorganic residues and the in $HNO_3$ 65% at 110°C to get rid of ionic contamination.
5-3 Graphene Transferring and Structure Release

At this point, the entire MEMS device is fully patterned and ready to be released. Nevertheless, it is wiser to transfer the graphene flake prior to the release of the structure to prevent misalignments and adhesion problems during the transfer. Furthermore, the transfer method requires dipping the device in water, which can destroy the suspended structures through capillary forces. As a result, the release step is performed at the end. A collaboration was setup between our group and Dr. Gregory Schneider (Faculty of Applied Physics, Delft University of Technology) to perform the transfer procedure.

The transfer method, developed by Schneider et al [17], starts by mechanically exfoliating the graphene from HOPG and identifying a single monolayer. The exfoliation occurs in a hydrophilic SiO$_2$/Si substrate, which is then used to deliver the graphene flake of interest. The graphene-carrying chip is coated with a cellulose acetate butyrate polymer thin film. Dipping the chip into water releases the polymer film (including the graphene flake) from the chip through hydrophobic/hydrophilic interactions. As a result, the polymer film floats on water. Because of the high transparency of the film, an optical microscope and a probe...
needle can be used to align the position of the graphene flake in relation to the target with submicrometer accuracy.

Having positioned the graphene in between the two shuttle structures makes it possible to proceed with the release, using vapour HF. Initial tests on HF vapor etching indicated that several parameters, such as the sample pre-heat time and the sample size, had an influence on the HF vapor etch rate. Therefore, a series of calibration tests were performed in order to set up a reproducible method. As expected, the etching rate decreases with increasing temperature as the amount of condensed water decreases with increasing temperature. This is a disadvantage of working at elevated temperatures, but on the other hand, the chance of stiction (a common problem in microsystems) decreases as the amount of condensed water decreases. In order to ensure the lowest risk for the chip and a controlled etch rate it was decided to etch at 42°C. When using HF vapor etch there are several phases that progress one after the other each starting with a preliminary incubation period before etching really starts. In order to calibrate the etching rate, a dummy chip was used with 1.5μm of thermal SiO₂. Theory states that the incubation period of the vapor HF is around 3 minutes. The before and after thickness of the thermal SiO₂ was measured with a Leitz Elipsometer and showed that during this incubation period the average etching rate was 2nm/min. Secondly the vapor HF reaches its final etch rate between 3 and 15 minutes. During this period it was confirmed that the average etching rate increased to 6nm/min. Theory states that after approximately 15 minutes the etching rate equalizes. So, as a final measurement we put the chip in the vapor HF for a continuous hour and found that the average etch rate equilized at approximately 8nm/min. So, in order to release the devices the exact etching time for 8μm of thermal SiO₂ was determined at 16 hours and 18 minutes at a chip temperature of 42°C. Figure 5-9 shows the same structure before and after the etching process. After release, the devices were checked under the cascade probe station. A needle probe was driven into the smallest anchor to verify its remaining strength and the chip was actuated to verify its release, all confirmed a successful etch process.
5-4 Shadow Mask Deposition

One of the main characterizations needed during experiments, is a four-probe electrical measurement of the graphene membrane while it is being stretched. We expect to see a change in resistance due to the increase in strain (related by the gauge factor). To achieve this, the measurement circuitry will be deposited on top of the insulating Si$_3$N$_4$ layer. A shadow mask has been fabricated in order to evaporate a gold film on top of the insulating layer. Such a mask was made based on a KOH and DRIE etching processes, leaving a thin silicon membrane that protects the chip from gold deposit outside the limits of the device. Both the processed wafer and the shadow mask are aligned and place inside the metal evaporator. Once inside, the gold target is heated until evaporation of the source material starts. This process is done in vacuum to allow vapour gold particles to travel directly to the target object, our MEMS device, where they condense back to a solid state. Because the evaporated gold only attacks the substrate from a single direction, the protruding features of the shadow mask block the evaporated material from unwanted areas. This phenomenon is called shadowing. Prior to the gold deposition, a thin Chromium layer of 5nm is deposited to act as an addition layer.

Because of long-term facility failure at DIMES, fully complete devices could not be fabricated yet. The beta devices shown in the next section lack two processing steps, the deposition of the nitride protective layer and the gold contact pads. The performance of the beta is expected to be the same as the fully complete devices. The only difference between the two is the possibility of electrical read-out and an improved contact interface between the needle probes and the bond-pads.
5-5 All designs

In this section, the fabricated devices are shown by using a JEOL JSM-6010LA Scanning Electron Microscope.

**Figure 5-10:** SEM image Design A (2300x)

**Figure 5-11:** SEM image Design B (2300x)
Figure 5-12: SEM image Design C (2300x)
Figure 5-13: SEM image Design D (2300x)

Figure 5-14: SEM image Design D zoomed (4300x)
Figure 5-15: SEM image Design E (2300x)

Figure 5-16: SEM image Design F (2300x)
Figure 5-17: SEM image Design G (2300x)

Figure 5-18: SEM image Design G zoomed (4300x)
Figure 5-19: SEM image Design H (2300x)

Figure 5-20: SEM image Design H zoomed (4300x)
5-6 Main design with transferred free-standing graphene

(a) Main design (2300x) 45° angle
(b) Main design (4300x) 45° angle
(c) Main design, core (2300x)
(d) Main design, core (4300x)

Figure 5-21: Main design with graphene

5-7 Thesis milestone 4

Is this design realizable with existing fabrication techniques available in the facilities of Delft University of Technology?
The fabrication flowchart was approved by the DIMES PAC committee and the devices were fabricated in the DIMES facilities. The devices (shown in the SEM images) however, are not part of the final chip. Because of long-term facility failure at DIMES, fully complete devices could not be fabricated. The devices shown are purely made out of Silicon and lack the nitride protective layer and the gold contact pads. At the time of writing this thesis, the facilities were still down. The mechanical performance of the fabricated (beta) devices is predicted to be similar to the final devices, the missing fabrication step has to do with the electrical capabilities of the devices. Since the devices shown have a high contact resistance for the needle probe actuation, they are not suitable for four-point-probe sensing on the graphene flake and are unable to perform capacitive read-out. These devices can however, be used to calibrate the device’s mechanical behaviour and by using the optical tracking method the performance (and stress on the graphene sample) can still be measured. Secondly, the device can be used under a Raman spectroscope which is an excellent tool to detect the stress in the sample.
Chapter 6

Experiments

Chapter goal Milestone 5: Does the fabricated MEMS device perform according to the specified requirements? Milestone 6: Is this device able to strain graphene \( \geq 10\% \) in a real setup?

6-1 Phase I: Preliminary experiments

In Phase I, all preliminary experiments were performed which serve as a basis for the final goal of this thesis (stressing graphene). These preliminary experiments are intended to improve the understanding of the fabrication of graphene, how graphene can be characterized and investigate how a graphene flake can be clamped onto the device.

6-1-1 Graphene synthesis & characterization

At the beginning of the project, our department was lacking the expertise to synthesize and characterize graphene. For the project it was necessary to first understand the synthesis process and characterization of graphene. This expertise was found outside the department as Victor Calado (Faculty of Applied Physics, Delft University of Technology) was willing to show the principle of the mechanical exfoliation method and teach the method of localizing graphene.

Methods In order to adequately identify graphene with a visible light microscope it is crucial to select the appropriate substrate material and thickness. The reason for this lies in the fact that graphene itself is almost completely transparant to visible light with an opacity of 2.3\% [6]. It has been shown by various groups that a \( \text{SiO}_2 \) wafer containing an oxide thickness in the range of \( 200\text{nm} < t < 300\text{nm} \) is the most useful to identify graphene. When the graphene is deposited on the \( \text{SiO}_2 \) it changes the diffraction of incident visible light, resulting in a small contrast difference which is visible with a microscope [19]. The difference in contrast gives an indication but not a guarantee of the flakes thickness. For this experiment, a 12inch
SiO$_2$ wafer with a 285nm thick oxide layer was fabricated by IDB technologies in the UK. As a bulk material for the graphene, two different types of graphene were used, one was natural natural KISH graphite, the other was Highly Oriented Pyrolitic Graphite (HOPG). The principle of the mechanical exfoliation is straightforward: stick a piece of bulk graphite on scotch-tape (see figure 6-1) and peel of several layers, repeat this to reduce the amount of layers further and finally stick the scotch-tape with graphene onto a clean SiO$_2$ chip (van der Waals adhesion between the SiO$_2$ chip and the graphene dominate and the graphene sticks on the chip). For a full description of the synthesis procedure, please refer to the appendix.

![Graphene synthesis with scotch tape method](image)

**Figure 6-1:** Graphene synthesis with scotch tape method [16]

**Results**  The result of this procedure is a chip filled with a variety of graphite flakes, multi-layer graphene flakes, double-layer graphene flakes and finally single-layer graphene flakes (see Figure 6-2a). One then has to search for possible matches, one of which is shown in Figure 6-2b, this image was obtained with a Visible Light Microscope at 50x zoom.

![Exfoliated graphene on 285nm SiO$_2$](image)

**Figure 6-2:** Exfoliated graphene on 285nm SiO$_2$

Figure 6-2b shows a flake with varying thickness, this specimen contains multi-layer and mono-layer graphene. Once the graphene was successfully synthesized and a specimen was found that seemed to be graphene, a Raman spectroscope was used to validate either a MLG, FLG or SLG. The device used was (liquid nitrogen cooled) Horiba Labram HR. The specimen was probed with a laser with 488nm and 632nm wavelength, the incident power of the laser was
varied between $0.12\text{mW}$ to $12\text{mW}$. Figure 6-3a shows a graphite flake and its corresponding Raman spectra. Figure 6-3c shows a multi-layer graphene flake with its corresponding spectra and Figure 6-3f shows a monolayer graphene flake and its corresponding Raman spectra. As can be seen from these figures, there is a clear distinction between the ratio of the G-band peak and the 2D-band peak for the different thicknesses of the graphene.

![Graphite flake](image1)

(a) Graphite flake (100x zoom)

![Graphite Raman spectra](image2)

(b) Graphite Raman spectra

![Multilayer graphene](image3)

(c) Multilayer graphene (100x zoom)

![Multilayer graphene spectra](image4)

(d) Multilayer graphene spectra

![Monolayer graphene](image5)

(e) Monolayer graphene (100x zoom)

![Monolayer graphene spectra](image6)

(f) Monolayer graphene spectra

**Figure 6-3:** Graphene characterization using a Labram HR Raman spectroscope showing graphite, multilayer graphene and monolayer graphene respectively

From these experiments it can be concluded that it is possible to synthesize monolayer and multilayer graphene and to locate it using a Visible Light Microscope, the thickness was verified using a Raman spectroscope. During the experiments it was noticed that actual scotch-tape is in fact not suitable for the synthesis. Instead, cleanroom blue tape was used (Blue Low Tack tape, P/N 18733 Shubert Technologies) as the adhesive properties were more suitable and in comparison to ordinary scotch-tape it left no noticeable residues on the
substrate after releasing. Secondly, thorough cleaning of the SiO$_2$ proved to be critical and quick deposition after cleaning (preferably within hours) proved necessary for a successful synthesis procedure.

6-1-2 Strain quantification by Raman spectra using a macro tensile device

In order to validate the possibility of straining graphene and identifying the strain with the Raman specstroscope a simple preliminary experiment was designed.

Methods  A macro scale tensile device was fabricated onto which a flexible substrate could be mounted. Graphene was deposited on this flexible substrate. If the substrate is chosen adequately (on the basis of flexibility, strength and adhesion with graphene) and the substrate is put under stress to induce a strain, the coupling (van der Waals interaction) between the graphene flake and the flexible substrate induces a strain in the graphene flake. The induced strain in the graphene can be analysed by detecting a shift of the 2D-band in the Raman spectra. Based on previous work performed by Kim et al. [88], the substrate can be strained up to around 6% before the graphene starts to slip from the substrate. The strain in a flexible substrate and the strain in the graphene are not directly correlated, this is due to the difference in strength (Young's modulus) and the interstitial clamping. It is believed that graphene can withstand up to 1% strain before it starts to slip from the substrate.

The requirements on the flexible substrate are:

- The flexible substrate must have a sufficient van der Waals interaction with graphene such that graphene strain is detectable (>0.1%)
- The flexible substrate must be able to withstand large strain rates (≥ 10%)
- The Raman spectra of the substrate must not interfere with the Raman spectra of the graphene

As a flexible substrate, PolyDiMethylSiloxane (PDMS) was chosen because of its ability to withstand large strains (ε ≤ 160%), its good van der Waals interaction with graphene [102][103] and the fact that it can fabricated relatively easily in any desired shape or dimension. The Raman spectra of PDMS do not interfere with the peaks of the graphene as the peaks of PDMS lie above 2900cm$^{-1}$. The PDMS substrates are made by mixing the curing agent with the elastomer in a 1:10 ratio and pouring the solution into a mold. For a mold a simple block of aluminum was used out of which, one 0.3mm trench and one 0.5mm trench have been milled (see Figure 6-4). After pouring, the mold was left in a vacuumchamber for 10 minutes to get rid of any airbubbles, after which it was baked at 110 degrees for 45 minutes. After the baking the PDMS strips where cleaned with DI water and dried. The 0.3mm PDMS substrate has a stiffness of ($K \approx 216N/m$) and the 0.5mm PDMS substrate has a stiffness of ($K \approx 360N/m$). The transfer of graphene onto the PDMS substrate was performed by Gregory Schneider (faculty of Applied Sciences at Delft University of Technology). The succesful transfer of the graphene onto the PDMS can be seen in Figure6-5b.

The requirements of the tensile device are:
6-1 Phase I: Preliminary experiments

**Figure 6-4:** Aluminum PDMS mold

(a) Graphene transfer on PDMS (before)  
(b) Graphene transfer on PDMS (after)

**Figure 6-5:** Exfoliated graphene on PDMS by means of ‘wet transferring’[17]

- The height of the setup (available space in the Raman spectroscope) is limited ($height \leq 35\, mm$)
- The edge dimensions of the setup should not exceed $20\, cm \times 20\, cm$ ($width \times length$)
- Minimum force output (force needed to induce a strain in the PDMS $\geq 10\%$) is ($F_{PDMS} = \frac{E \cdot A \cdot \Delta L}{L_0} = \frac{360 \times 3 \times (0.02 + 0.0005) \times 0.001}{0.01} \geq 0.2\, N$)
- The measurement resolution of the induced strain on the substrate is $\leq 1\, mm$

For the setup, a simple device has been constructed to induce strain in the PDMS substrate. In order to stress the PDMS substrate, a PT1/M 25mm manual translation stage from Thorlabs was chosen. The device can produce horizontal forces up to $\approx 400\, N$ and has an engraved graduation of $10\, \mu m$ to measure displacements and a maximum height of $20.3\, mm$. This stage is mounted on a custom fabricated block of aluminum with a milled slot to fit the stage such that the top surfaces are level (see Figure 6-6b). The PDMS with graphene was clamped in the tensile device and the Raman spectra of the graphene flake was measured in order to set a reference position.
Results The following figures show that the strain in the graphene can be read from the shift in the raman spectra. In unstrained condition the 2D peak of the monolayer graphene was at $2692\text{cm}^{-1}$. In the strain condition it can be seen that the 2D-band is downshifted by $\approx 10\text{cm}^{-1}$.

The linear dependence of Raman bands with strain is expected according to the phonon deformation potentials. The frequency shift of the Raman band is related to the uniaxial strain and the shear strain. The shear strain has a much smaller contribution which can be
ignored for simplicity. The shift in Raman frequency is related to the strain by [85]:

$$\frac{\Delta \omega}{\omega_0} = \gamma (\epsilon_{xx} + \epsilon_{yy})$$  \hspace{1cm} (6-1)

where $\gamma = 1.24$ is the Grunesien parameter obtained from experiments on Carbon NanoTubes, $\epsilon_{xx}$ is the uniaxial strain, $\epsilon_{yy} = -0.186 \epsilon_{xx}$ is the relative strain in the perpendicular direction according to the Poisson’s ratio of graphene and $\omega_0$ is the Raman band frequency (the 2D band frequency $\omega_0 = 2680 \text{cm}^{-1}$) and $\Delta \omega$ is the frequency shift due to strain.

Equation 6-1 can be rewritten as a dependence on uniaxial tensile strain as:

$$\frac{\Delta \omega}{\epsilon} = -\omega_0 \gamma (1 - 0.186) = -27.1 \text{cm}^{-1}/\%$$  \hspace{1cm} (6-2)

This formula states that for every 1% strain in the graphene, the 2D-band downshifts 27.1 wavenumbers. If this formula is applied on the results obtained from our strain experiments the induced strain in the graphene is $\epsilon = \frac{\Delta \omega}{27.1 \text{cm}^{-1}/\%} = \frac{2D\text{-band(unstrained)} - 2D\text{-band(strained)}}{27.1 \text{cm}^{-1}/\%} = 0.3\%$

The difference in the peak intensity between the two different Raman spectra had to with the fact that the laser intensity was increased during the second experiment to get a clearer spectra. A downside of this can be seen in Figure 6-7c as it appears that the flake has been burned. Based on additional Raman measurements it was found that actually the graphene was still intact, however, the PDMS below the graphene degraded. After the experiment the same laser intensity was used to irradiate the PDMS directly to check if the laser intensity was too high for the PDMS to remain stable. This experiment verified that the PDMS could in fact withstand the laser intensity without any degradation (irradiation at 12mWatt was performed for 40 minutes).

It appeared that only the combination of graphene together with PDMS (or possibly any arbitrary substrate) could cause a local increase in temperature because of laser irradiation on the graphene.

Although this phenomena falls outside of the scope of this thesis, this effect was further investigated. This research however falls outside the scope of this thesis and has deliberately been left out of this chapter. The results of this additional experiment (Graphene induced heating due to photon absorption by (Raman spectroscope) laser irradiation) show that the effect is related to the property of graphene to absorb photons from all wavelengths which induces small electrical currents inside the flake and heat up the lattice and underlying substrate. To prevent this, laser intensities $\leq 1mWatt$ are recommended (this can be even less, depending on the type of substrate).

### 6-1-3 Experimental clamping concept based on improved dangling bonds

Since the van der Waals adhesion between graphene and its substrate alone is not enough to obtain high strains, three experimental clamping methods were investigated. The first method investigates the possibility of improving the amount of dangling bonds on the clamped end of the graphene flake.
**Methods** In the literature chapter the theory behind the van der Waals adhesion of graphene with arbitrary substrates was explained. Both the $\pi$-bonds and the $\sigma$-bonds contribute to the adhesion of graphene onto a substrate. The hypothesis of the first clamping method is that by increasing the amount of $\sigma$-bonds (dangling bonds on the edge of the flake), the adhesion of graphene onto a surface can be increased. In order to increase the amount of $\sigma$-bonds of a graphene flake (see Figure 6-8a), the circumference of the flake can be patterned such that the total length of the circumference (and total amount of dangling bonds) increases (see Figure 6-8b). This patterning can for example be done using a Focused Ion Beam (FIB) which basically cuts a pre-defined pattern into the graphene. However, a note of caution has to be made when using a FIB for this purpose. The problem with a FIB is that they are often equipt with a Gallium ion source (Gallium ions are known to destroy graphene). The result of using a Gallium ion FIB is that the ions degrade graphene and only amorphous carbon remains. This problem however can be solved by either using a Helium Ion Microscope (HIM) [104] or a Transmission Electron Microscope (TEM) [105]. At the time of writing this thesis we did not have access to either the HIM or the TEM. So in order to show the proof of principle, a graphene flake was deposited on a $\text{SiO}_2$ dice (see Figure 6-9a). The thickness of this flake was verified using the Ramans spectroscope and was confirmed to be mono-layer graphene. An FEI DualBeam Strata 235 (FIB/SEM) was used to pattern the graphene flake. The result of using this machine for the experiment is that the concept can be shown, yet the remaining material is no longer graphene but in fact amorphous carbon.

**Results** In figure 6-9b the result after patterning can be seen. On the bottom edge of the graphene flake, the circumference was increased by patterning simple rectangles into the edge of the flake. In the centre of the flake the abbreviation of the department of Micro & Nano Engineering was patterned. After the experiment was complete, the same flake was analyzed based on its Raman spectra, and it was verified that only amorphous Carbon remained. Based on this experiment it was shown that a FIB can be used to pattern a graphene flake. The concept of improving the dangling bonds can be succesfull, however, in order to do so without damaging the graphene lattice structure, a different ion source is needed. It can be concluded that if the same procedure is performed on the intended device (HIM/TEM) the circumference of the graphene flake can be patterned such that the amount of dangling bonds can be increased, which could increase the adhesive interaction with the substrate. The exact increase on the adhesion has to be further investigated, either by Molecular Dynamics modelling or by an experimental comparison of putting two equally sized graphene flakes (one
unpatterned and one patterned) under strain and measuring its adhesive quality. Within the scope of this thesis, it was concluded that this approach is feasible, however, currently unsufficiently developed to successfully clamp a graphene flake.

6-1-4 Experimental clamping concept based on Focused Ion Beam (FIB) induced deposition of TEOS SiO₂

The second experimental clamping technique is based on the process of FIB induced deposition of an insulator SiO₂ [106] on top of the fixed end of the graphene flake to create a sandwich structure. Similar as the previous clamping method, this experiment is intended to investigate the principle. As we only had access to a FIB with a Gallium ion source the graphene most likely be permanently damaged. However, by using a different ion beam (or electron beam) source this problem can be solved. Therefore, the goal of this experiment is to investigate the principle of creating locally depositing material on top of the graphene edges to create a sandwich structure.

Methods  The principle of the FIB deposition process is based on localized chemical vapour deposition (CVD) by direct writing. The deposition process is illustrated in figure 6-10. A precursor gas is sprayed on the surface by a fine needle (nozzle), the gas molecules get adsorbed on the surface but are not strongly adhered yet. In a second step, the incident ion beam decomposes the adsorbed precursor gases. The volatile reaction products desorb from the surface and are removed through the vacuum system, while the desired reaction products SiO₂ remains fixed on the surface as a thin film. The deposited material is not completely pure, because organic contaminants as well as Gallium ions (from the ion beam) are inevitably included in the deposited film. It should be noted that the adsorption and desorption processes occur continuously during deposition while the decomposition only occurs at the places where the ion beam is present [107].
Results

The result of this deposition process is shown in Figure 6-11b. From this experiment in can be concluded that it is possible to locally and accurately deposit a material on the fixed ends of a free-standing graphene flake. However, the ion source and the precursor gas are vital as they have the potential to permanently damage the graphene. A second note of caution has to be made about using either the SEM or the FIB during the deposition process. High energy incident electrons or ions can cause damage in the graphene (even without the presence of the precursor gas). Therefore, it is recommended to only use SEM or FIB imaging at low acceleration voltages and for short exposure times (maximum several minutes).

6-1-5 Experimental clamping concept based on epoxy

Methods

As a third and final clamping method, the use of an epoxy to clamp graphene is investigated. Once an epoxy is cured it can offer a strong adhesion, high mechanical strength and good chemical resistance. Epoxy resins, which are also known as polyepoxides, are a class of reactive pre-polymers and polymers which contain epoxide groups. Epoxy resins can react (cross-link), either with themselves through catalytic homopolymerisation, or with a wide range of co-reactants including polyfunctional amines, acids (and acid anhydrides), phenols,
alcohols and thiols. These co-reactants are often referred to as hardeners or curatives, and the cross-linking reaction is commonly referred to as curing. Reaction of polyepoxides with themselves or with polyfunctional hardeners forms a thermosetting polymer, often with high mechanical properties, temperature and chemical resistance. For this experiment, the 353ND (EpoTek technology) was used, consisting of bisphenol F and imidazole. Bisphenol F epoxy resin has a lower viscosity than the common Bisphenol A epoxy resin and a higher mean epoxy content per gramme, which (once cured) gives them increased chemical resistance. This epoxy was used in earlier research to bond with graphene and has proven to show very good adhesive results [108]. The second reason why this epoxy was chosen, is that it has a offers an almost hermetic seal (relevant for future research), is electrically insulating, can withstand vapor HF (relevant for the release) and has a high viscosity (with a cps value between 3.000-5,000 which is relevant to make sure that the epoxy doesn’t run over the graphene after deposition). The challenge of implementing this method is to accurately

dispense a small volume of epoxy on the exact desired location. Initial attempts with a setup combining a gold probe needle (with a 15µm tip) connected to a 3-axis manual micrometer screw under a Leitz 40x zoom stereo microscope proved to be inadequate. The final setup consisted of a 4 Degree of Freedom Imina technologies mibot™ which uses piezostages with a maximum resolution of 0.5nm combined with the nanopipette developed at our department (PhD thesis, H.H.Perez-Garza, TU Delft). This project focuses on the capability of locally dispensing minute volumes of different reagents. These manipulations at the nanoscale can be used in different applications such as biology, chemistry and material science. In this thesis, the capabilities of the nanopipette to locally dispense a small volume of epoxy on a desired location are exploited. The nanopipette is a chip with a ≈ 15µm by ≈ 155µm cantilever at is free end. The tip of the cantilever has 8µm × 8µm base and a tip radius of ≈ 20nm. The mibot (with the nanopipette glued on the edge of the actuated arm) shown in Figure 6-12a is positioned inside a probe station which has a two axis manual stage and adequate zoom functionality (2x,10x,20x,50x,100x). This setup can be seen in Figure 6-12b.
Results

In Figure 6-13a the two shuttles of the MEMS device are shown prior to the attempt of epoxy deposition. In Figure 6-13b the result after dispensing is shown.

From this experiment it can be concluded that it is possible to accurately and locally dispense small volumes of epoxy without damaging the graphene flake. Since this epoxy is already known to have a strong adhesion with graphene without damaging, this approach seems to be the most feasible to implement on the final tensile device.
6-2 Phase II: Device Characterization

Before performing the actual tensile experiment, it is necessary to characterize the behaviour of the MEMS device. This characterization has been divided into several subsections. First of all, the electrical behaviour of the polycrystalline Silicon is investigated. Secondly, the relation between the applied potential and the increased temperature (Joule heating) in the Silicon is analyzed. Thirdly, the surface roughness of the shuttle heads were analyzed. And finally, the linearity of the device after releasing is analyzed to confirm that the shuttles are not deformed (e.g. due to internal stresses in the Silicon).

6-2-1 Electrical characterization of the polycrystalline Silicon

In this section the electrical behaviour of the device is measured. It has to be noted that this analysis is performed on the beta devices which have decreased functionality in comparison with the final chip. The beta devices did not have the appropriate gold contact pads. Therefore, the needle probes were directly positioned on the polycrystalline Silicon resulting in a much higher contact resistance (thus high applied potential is needed) and non-linear electrical behaviour is expected (because of local heating).

Two-probe electrical behaviour analysis

**Methods** During operation the device will be actuated using a two-probe electrical setup. Therefore, the electrical behaviour of the polycrystalline Silicon has been analyzed by measuring the relation between applied voltage and resulting current through the circuit. Based on the results obtained, a value for the circuit resistance can be obtained. The electrical circuit used to analyze this the performance of the device is shown in Figure 6-14. A DC current is applied on the circuit which induces a current passing through the elements. The voltage is measured parallel to the circuits resistors. The resistors are connected in series and consist of the contact resistance of the probe-poly Si interface, the resistance of the thermal actuator and again the contact resistance of the probe-poly Si interface. The resistance of the needle probes (gold) themselves are neglected. A voltage sweep from -10V to +10V (digitally controlled stepsize of 200mV) was applied to investigate the conduction linearity and possible Schottky diode behaviour (common in semiconductor-metal interfaces).

**Results** In figure 6-15a the I-V curve of the circuit is shown. As can be seen, the curve is approximately linear and clearly does not exhibit the undesirable Schottky diode behaviour. This is most likely due the the heavy p-doping of the Silicon which reduces this effect and increases the linearity of the conduction. In figure 6-15b the voltage to resistance curve is shown. As expected (in contrast to metals) the resistance decreases because of an increasing voltage (and increasing temperature). The needed applied potential of 10V resulting in a 60mA current is higher than expected from the FEA model. This suggests the currently unknown contact resistance of the probe onto the poly Silicon has a considerable impact on the circuit resistance. In order to analyze the contact resistance, a four-probe measurement is needed to eliminate contact effects. This experiment is performed in the next paragraph.
Figure 6-14: Electrical circuit to measure the I-V curve of the chip

(a) 2-probe PolySi $I - V$ curve
(b) 2-probe PolySi $V - R$ curve
(c) 2-probe PolySi $V - P$ curve

Figure 6-15: 2-probe $I - V$ and $V - R$ $V - P$ curves of PolySi
Four-probe electrical behaviour analysis

Methods  By using a four-probe measurement, it is possible to eliminate contact resistance effects in an electrical circuit. The concept of four-probe-sensing was previously explained (3-24 van der Paauw method). By forcing a current on terminal 1 and measuring the needed voltage from terminal 1 to terminal 2 and simultaneously measuring the induced potential on terminal 3 and 4 (through which no current is allowed to pass) it is possible to measure the material resistance. By substracting the induced potential from the applied potential and dividing by the current, the contact resistance $R_{\text{contact}}$ can be calculated. The four-probe sensing station used was equiped with tungsten probe needles and a current sweep from -8mA to +8mA was forced with a digitally controlled stepsize of 0.8mA.

Results  In figure 6-16a both the applied voltage $V_{12}$ and the induced potential $V_{34}$ are shown related to the enforced current sweep. From this figure it can be seen that the I-V curve exhibits nonlinearity (most likely due to local heating). The plausible reason that the I-V curve in this probe station shows more non-linearity than the the I-V curve obtained in the two-probe setup is because of the fact than in this probe station much thicker tungsten probe needles are used in comparison to the sharp gold plated probes used in the two-probe station. The contact resistance measured during this experiment is given in figure 6-16b. This figure clearly shows a heating effect and thus decreasing resistance. Secondly, it can be seen that the contact resistance in this probe station can be as high as $\approx 950\Omega$. This supports the hypothesis from the previous experiment, that the chosen needle probes and the absence of gold-plated ohmic contacts (probe-poly Si interface) results in a much higher needed applied potential as there currently is a substantial voltage drop over the contact terminals.

Four-probe sheet resistance measurement

Methods  In order to analyze the impact of the contact resistance, it is relevant to calculate the actual material conductivity (because of boron doping of the poly Si). The sheet resistance
is calculated with the van der Paauw method, the method was explained earlier in this thesis 3-24.

Results The obtained value for the sheet resistance was found to be $10.5 \, \Omega_{\text{sq}}$. The bulk resistivity of a material can be calculated by multiplying the sheet resistance by the material thickness ($5\mu m$). The bulk resistivity of the p-doped polycrystalline Silicon was calculated to be $\rho = 10.5 \times 5\mu m = 5.25 \times 10^{-5} \Omega m$. The bulk resistivity can be inserted into 3-10 used to calculate the resistance of a conducting element, which depends on its geometry. The thermal actuator has a total length $l = 430\mu m$ and cross-sectional area $A = (N = 15) \times (8\mu m \times 5\mu m) = 6 \times 10^{-10} m^2$. Therefore, the resistance of the thermal actuator is $R = 37.63 \Omega$. Based on this result and the I-V curves earlier obtained, it can be concluded that the biggest portion of the circuit resistance is due to the contact pads and not because of the resistance of the thermal actuator. This explains why higher than expected applied potentials were needed to induce a required current. The energy dissipated in the contact points results in a voltage drop which leads to decreased effect of Joule heating in the thermal beams. The contact resistance is influenced by the material interface, the radius of the needle probe and the surface roughness. A rough surface decreases the area between the needle probe and the bond-pad. When a certain potential is applied, the small contact area (due to roughness) results in local high current densities and heating effects. This was confirmed by looking at the failure mechanisms when high potentials were applied. The devices failed at the location where the needle probe contacted the bond-pads. The obtained current densities in the MEMS device reached values in the order of $\geq 1 \times 10^4 A/cm^2$. It was concluded that there was no electromigration in the material (which could happen at high current densities $\geq 1 \times 10^6 A/cm^2$). When the devices failed, on some occasions it occurred on the anode(+) and at other occasions the cathode (-). Electromigration in positively doped polycrystalline Silicon only happens at the cathode [109][110] thus further confirming the fact that electromigration is not an issue. Combining the previous three experiments, it can be concluded that it is important to have well-conducting ohmic contact pads and preferably a limited surface roughness (the surface roughness of the device will be analyzed later in this chapter) as this is currently the limiting factor.
Voltage vs shuttle temperature measurement

**Methods** As the device is used as a thermal actuator, it is relevant to understand the relation between an applied potential and the temperature in the thermal beams. Since the devices are fabricated out of polycrystalline silicon it is Raman active (in comparison to single crystalline Silicon). Thus it is possible to extract information about the material temperature based on the Raman spectra of the polycrystalline Silicon. In order to simultaneously apply an electric potential to the circuit and extract the Raman spectra of the polycrystalline Silicon, a needle probe setup was combined with the Horiba Labram HR Raman spectroscope (see Figure 6-17). An analog voltage source was used to apply a voltage sweep from 0V to 20V (increments 500mV ± 100mV). The Raman spectra was taken in the centre of the polycrystalline shuttle. When the temperature of the polycrystalline Silicon increases, a downshift in the Raman

![Figure 6-17: Raman spectroscope combined with probe station](image)

spectra is expected [111]. This shift in the wavenumber is related by:

\[
T = T_{ambient} - \frac{\omega_{ambient} - \omega_{measured}}{C_{Stokes}}
\]

(6-3)

where \(T\) is the material temperature, \(T_{ambient}\) is the reference temperature, \(\omega_{ambient}\) is the reference Stokes peak location (wavenumber), \(\omega_{measured}\) is the measured Stokes peak location at elevated temperature and \(C_{Stokes}\) is the material constant for polycrystalline Silicon (\(C_{Stokes} = -0.0232 \pm 0.0002 cm^{-1}/C\)).

**Results** In figure 6-18a the I-V curve is shown. From this figure it can clearly be seen that the increments of 500mV ± 100mV result in a less continuous curve as was shown earlier. In figure 6-18b the resulting voltage to circuit resistance curve is shown. This curve (and calculated resistance) is comparable to the results obtained in figure 6-15b as the same needle probes were used. Figure 6-19a shows the correlating Raman spectra obtained at each increment. In figure 6-19c the correlating material temperature is calculated using 6-3. After 45 minutes (at an average applied power dissipation of 0.8 Watt) the device fails. The
maximum temperature achieved of 325°C is lower than expected at the applied potential of 19V and induced current of 154mA. After analyzing the device it was found that the device in fact did not fail in the thermal beams but in the needle probe to bond-pad interface. Due to a high contact resistance the bond-pad endured very high current densities and local heating occurred. Because of the voltage drop over the high resistance bond-pads, the effect of Joule-heating in the thermal beams was decreased. Which explained the acceptable, but lower than expected obtained temperatures. This experiment further strengthens the hypothesis that gold ohmic bond-pads are crucial.
6-2-2 Surface roughness analysis

Methods As was explained earlier, the surface roughness has an impact on the contact resistance between the needle probe and the bond-pad. Analyzing the surface roughness of the polycrystalline Silicon is also interesting for a second reason as it is directly related to the adhesion force between the graphene and the substrate. Therefore, a surface roughness analysis was performed using a Nanosurf Nanite B Atomic Force Microscope (AFM) in contact mode.

Results In figure 6-20 the 3-Dimensional surface roughness plot of the shuttle head is shown. The area analyzed was $5 \mu m \times 5 \mu m$ as it corresponds to the expected contact area of the graphene to shuttle interface. The surface roughness values obtained with contact mode AFM

- $S_a = 48.382nm$ (arithmetic average)
- $S_q = 61.314nm$ (root mean squared)
- $S_p = 174.59nm$ (maximum peak height)
Figure 6-20: 3-Dimensional surface roughness plot of the polycrystalline Silicon shuttle head

- $S_v = -174.59\,nm$ (maximum valley depth)

6-2-3 Device linearity after release

Since the device fabrication is based on a top-down approach were several layers are stacked on each other and later patterned down to a desired design, it is possible that residual stresses occur in the material. Most of the materials have a different expansion coefficient, and if during fabrication they are heated to elevated temperatures, the difference in expansion coefficient can lead to internal stresses. If these stresses are high enough, it could even lead to an induced curvature in the wafer. However, even small residual stresses can have a negative impact. Since the MEMS-device fabricated in this thesis consists of free-standing structures which are supposed to be aligned along the same axis, residual stresses could negatively impact the performance of the device. In order to investigate this, the device was examined under a white-light interferometer which is capable of detecting minute height differences (200nm resolution) after releasing the structures.

Methods The whitelight interferometer used for this specific experiment was the Bruker WLI (GTK1-10-096). The devices were first released (according to the process described in the fabrication chapter) and the linearity between the two shuttles (actuator and load sensor) was investigated.

Results Figure 6-21a shows the 3-Dimensional height profile of the unreleased actuator beams and Figure 6-21b shows the 3-Dimensional plot of the released structure. A difference in height is indicated by a color difference. From the data obtained it was concluded that the internal residual stresses were negligible as no significant deformations were identified. Since the graphene is situated between the two shuttles, potential relative displacements between the two could render the device useless. In figure 6-21c a 3-Dimensional image is given of the released structure at 20x zoom. Figure 6-21d shows a close up image (50x zoom) of the 3-Dimensional height profile of the released shuttle heads, from this image (and corresponding data) it was concluded that within the resolution of the white light interferometer there was no distinguishable height difference between the two shuttles.
6-2-4 Displacement analysis

Understanding the displacement resolution and range is important for reliable and reproducible experiments. However, as was concluded in the electronic characterization section, the contact resistance is currently the limiting factor. Every time the needles are connected, a different contact resistance was measured which was many times higher than the resistance of the thermal beams. Therefore, with the beta devices it is not possible to produce reliable performance data for the displacement resolution. As for the displacement range, a rough approximation was made based on pixel analysis from a VLM image.

Methods For this experiment the same probe station was used as in Figure 6-12b. By using a 50x zoom camera and taking still VLM images it is possible to extract displacements based on image pixels. A rough approximation could be given based on calculating the displacement by investigating contrast shift in pixels between 6-22a and 6-22b.

Results Based on this analysis, the maximum displacement that the actuator was able to perform was \( \approx 5\mu m \), which is well beyond the required \( 1\mu m \) for which it was designed.
Figure 6-22: Raman spectra peak shift and corresponding temperature of the PolySi shuttle
6-3 Phase III: Tensile experiments

The final goal of this thesis is to perform a tensile experiment on graphene using the designed and fabricated MEMS device. In order to analyze the displacements, a similar setup as figure 6-17 was used. The devices were contacted by two gold plated tungsten needles which were modified to fit under the raman (see Figure 6-23). The maximum magnification while still contacting the needle probes proved to be 50x. For increased control the analogue voltage source was exchanged with a Hameg HMP2020 digital voltage source.

![Figure 6-23: Connection setup to combine probe station with Raman spectroscopy](image)

6-3-1 Micro tensile device with unclamped multi-layer graphene

Methods In order to set a benchmark of the maximum achievable induced strain in graphene, an unclamped multi-layer graphene flakes was positioned on the device and only adhered because of van der Waals adhesion. The graphene flake under examination (Figure 6-24a) was a multi-layer flake as can be seen in the corresponding Raman spectra 6-24b. The chosen stepsize of the voltage source was 200mV with a current limitation at 100mA.

![Figure 6-24: Unclamped graphene flake in relaxed state and corresponding Raman spectrum](image)
Results  In Figure 6-25a to 6-25c the power output can be found. In Figure 6-25d the dissipated power in the MEMS device is related to the obtained shifts in Raman spectra of the graphene layer.

Just before the graphene membrane slipped from the shuttle, the maximum obtained shift in raman spectra was $-26.52 \, \text{cm}^{-1}$. According to 6-2 this corresponds to a membrane strain of 0.979%. This value was expected based on theory, but with the setup it could be experimentally verified.

6-3-2 Micro tensile device with epoxy clamped multi-layer graphene

Based on the results obtained in the previous experiment it was concluded that the maximum strain obtained for the examined unclamped graphene membrane was 0.979%. Although it shows that graphene indeed has a very good van der Waals adhesion with its substrate, the obtained strain value is still a factor 10 below the required goal. For this reason a second device was fabricated onto which a multi-layer graphene was transferred.

Methods  In order to investigate if it is possible to use the designed MEMS to induce high strain values in graphene, again a multi-layer graphene membrane was glued to the substrate
(see Figure 6-26a). In this experiment, the graphene membrane was glued to the substrate with the same Epotek 353ND epoxy as was investigated during the preliminary experiments. The graphene flake under examination was a multi-layer flake as can be seen in the corresponding Raman spectra (Figure 6-26b). The chosen stepsize of the voltage source was $200mV$ with a current limitation at $130mA$.

![Image](a) Epoxy clamped free-standing multi-layer graphene positioned on MEMS device (50x)
![Image](b) Raman spectra of multi-layer graphene flake

Figure 6-26: Unclamped graphene flake in relaxed state and corresponding Raman spectrum

**Results** In Figure 6-27a to 6-27c the power output can be found. In Figure 6-27d the dissipated power in the MEMS device is related to the obtained shifts in Raman spectra of the graphene layer. The maximum obtained shift observed by analyzing the Raman spectra was $-15.33cm^{-1}$. According to 6-2 this corresponds to a membrane strain of $0.566\%$. Which is is basically a similar result as the previous experiment. However, it was noticed that the flake in fact did not slip, however, the laser went out of focus and we lost signal at higher displacements. It is currently believed that due to the high induced currents ($\approx 142mA$ at $15.6V$) and high contact resistance the needle probes temporarily heated up to very high temperatures and push the chip out of focus. It was confirmed that this effect was reproducible. This can be prevented by using thicker needle probes combined with the gold bond-pads. After switching from the Raman spectra to the visible light microscope it was seen that in fact the strains where many times higher than expected. In Figure 6-28a the multi-layer graphene flake is shown in relaxed state and shows no signs of strain in its Raman spectra. Figure 6-28b shows the highly strained graphene flake at high displacements. Although the strain is not reflected in the Raman spectra, the VLM images are able to give rough approximations of achieved strains. Based on analysis of pixel (contrast) displacement, the induced strain in the graphene flake was calculated to be $\approx 14\%$. The obtained strain is $\approx 14\times$ higher than that obtained with the unclamped chip and is, to the best of our knowledge, the highest achieved so far. Eventually, after increasing the applied potential to the MEMS device to $15.8V$, the graphene started to show effects of damage 6-29a.

After approximate one hour of operation it was finally the MEMS device that failed while the graphene was still intact (see Figure 6-29b). With this experiment it was proven that high strains ($\approx 14\%$) can indeed be induced in free-standing graphene by combining the designed MEMS device with the chosen epoxy.
Experiments

(a) Voltage vs Current MEMS

(b) Voltage vs Resistance MEMS

(c) Applied voltage vs dissipated power in MEMS

(d) Dissipated power in MEMS vs Raman spectra shift graphene

Figure 6-27: Performance data of actuated MEMS with clamped multi-layer graphene

6-4 Thesis milestone 5 and 6

Does the fabricated MEMS device perform according to the specified requirements? Based on the electrical characterization the needed applied potentials are higher than those predicted by the theoretical model. After investigation it was concluded that this was mainly because of the high contact resistance between the needle probe and the polycrystalline silicon bond-pads. The maximum displacements achieved for the thermal actuator was in the region of $\approx 5\mu m$ which is more than the minimum requirement.

Milestone 6 Milestone 6: Is this device able to strain graphene $\geq 10\%$ in a real setup? During the first tensile experiment with a multi-layer graphene flake glued to the substrate with epoxy an approximated strain of $\approx 14\%$ was achieved which is more than the required 10%.
(a) Relaxed multi-layer graphene at 0V applied potential on MEMS

(b) Highly strained graphene at 15.6V applied potential on MEMS

Figure 6-28: VLM image of relaxed and (±14%) strained graphene
Figure 6-29: Graphene flake damaged after high strain and failed thermal actuator
In this thesis, an in-plane MEMS-based tensile device was designed, fabricated and analysed. This device was proven to be able to exert a linear in-plane stress on free-standing graphene flakes and thereby inducing strain. This MEMS device was fabricated in the DIMES facilities at Delft University of Technology and its performance was thoroughly analyzed. Using this MEMS device, the maximum strain induced on a multi-layer graphene flake was \( \approx 14\% \), which is a major step towards implementing graphene as a controllable filtration membrane.

**Literature review** Based on the results obtained in this thesis, a thorough analysis of the underlying physics of graphene is recommended. By knowing exactly what happens within the crystal structure could help the scientific community in exploiting more of the impressive intrinsic properties of graphene.

**Design** The chosen design proved to meet the requirements stated at the beginning of this thesis. However, several improvements could be implemented to increase the functionality. First of all, it is recommended to re-located the optical tracking beams to the heads of the shuttle (a new design has already been made). In order to make this device more widely applicable (also for different samples) a variable stiffness of the load sensor could be beneficial. Therefore, adding a electrostatic comb-drive actuator on the load sensor could in theory be controlled such that the stiffness of the load sensor can be altered depending on the sample under examination.

During the experiments with multi-layer graphene it was noticed that at high strain, the shuttles deform out of plane. The reason for this, most likely is that the multi-layer graphene is stronger than monolayer graphene as its cross-sectional area has increased. Because of this increase in stiffness, the torsional force on the guidance beam also increased (resulting in slight out-of-plane deformation). This effect can be minimized by increasing the out-of-plane stiffness of both shuttles.
Modelling  For the objective of this thesis, the used FEA model suffices. However, for future studies and a more accurate analysis, the FEA model can be improved by incorporating non-constant material properties and switching from a static to a transient analysis. These material properties can be calibrated on fabricated devices and re-inserted into the FEA model.

Fabrication  In order to increase the device’s application scope, it would be an interesting addition to add TEM functionality. This could be done by changing the flowchart such that a hole is created in the substrate (below the sample). This hole allows the electron beam to pass and results in the possibility of in-situ analyzing strain within the graphene flake (or other materials). A second improvement can be made on the type of polycrystalline Silicon. In this thesis, it has been chosen to deposit Silicon, however, a smoother surface can be obtained if a Silicon on Insulator wafer is used as a basis (these however are more expensive).

Experiments  During the experiments it was proven that the MEMS device performed according to the requirements and two different graphene flakes were put under strain up to a maximum of $\approx 14\%$. During the experiments it was proven that improving the contact interface between the needle probes and the device’s bond-pads is important in order to reduce the power dissipation and failure probability and increase the device’s energy efficiency. A second recommendation is to calibrate the Thermal Coefficient of Resistance of the polycrystalline Silicon which can be done on a four-probe-sensing station with an incorporated well-controlled hot plate. Using this method it is possible to accurately relate the reduction in circuit resistance to the increase in temperature in the beams. With an accurate TCR value, it is possible to extract the temperature of the thermal beams by only looking at the power dissipation. A similar experiment can be performed by calibrating the relationship between the temperature of the polycrystalline silicon and its Raman spectra. Although literature already gives a good approximation of this relationship, it could slightly vary because of the fabrication process. The relationship between temperature and a shift in raman spectra for a single batch of devices can be calibrated using a Linkam THMS600 hotplate combined with the Raman spectroscope.

Final conclusions  We did it!
Appendix A

MATLAB listings

A-1 Analytical model

1 clear all
2 close all
3 clc

6 % MEMS DEVICE FOR TENSILE LOADING OF GRAPHENE
7
8 %
9 % Flake parameters
10 t=0.34e-9 % thickness of monolayer graphene
11 Eps=1e12 % Young’s modulus 3-dimensional (N/m^2)
12 v=0.165 % graphene poisson’s ratio
13 lmemb=5e-6 % initial length of freestanding membrane
14 wmemb=10e-6 % width of membrane
15 Acr=wmemb*t % crosssectional area flake
16 Ks=(Eps*Acr)/lmemb % axial stifness graphene flake
17
18 % actuation parameter
19 dT=0.527; % average temperature change in beams
20
22 % Structure properties thickness
23 h=5e-6 % thickness of polysilicon structure
24 Eps=170e9 % Young’s modulus polysilicon structure
25 alpha=2.6e-6 % coefficient of thermal expansion of polysilicon
26
27 %
28 % Mechanical parameters of actuated shuttle
29
30 % V-beam segment (actuator)
angle = 7\%0:.1:30 \% angle in degrees between V-beams and transverse direction to shuttle motion
bvb = 8e-6; \% beam width V-beam
lvb = 200e-6; \% beam length V-beam
Avb = bvb * h; \% beam cross sectional area V-beam
m = 30; \% number of V-shaped beams
Ivby = (1/12) * (bvb^3) * h; \% moment of intertia of one V-beam in plane parallel to substrate (Imin if h>b)
Ivbx = (1/12) * (h^3) * bvb; \% moment of intertia orthogonal to substrate (Imin if b>h)
I = [Ivby Ivbx];
Iminvb = min(I);
psi = (Avb * (lvb^2)) / (12 * Ivby); \% dimensionless parameter, axial over bending stiffness ratio
dirf = (sind(angle) ./ (sind(angle).^2 + (cosd(angle).^2) / psi)); \%directional factor of V-shape
Ktb = ((sind(angle).^2 + (cosd(angle).^2) / psi) * ((Eps * Avb) / lvb)) \% stiffness of V-beam segment
% Connected heatsink beam segment
bsb = 3e-6; \% sink beam width
lsb = 50e-6; \% length of sink beam
Asb = bsb * h; \%sink beam cross sectional area
n = 28; \% number of heat sink beams
Ilsb = (1/12) * (bsb^3) * h; \% moment of inertia of sink beam
Ksb = ((Eps * (bsb^3) * h) / (lsb^3)) \% stiffness of connected heatsink beam segment
% electrode spring
besc = 5e-6; \% width electrode spring current
lesc = 50e-6; \% length electrode spring current
Aes = besc * h; \%electrode springs cross sectional area
Ies = (1/12) * (besc^3) * h; \% inertia of electrode springs actuated shuttle
o = 4; \% number of electrode springs
Kes = ((Eps * (besc^3) * h) / (lesc^3)) \% stiffness of current electrode springs
Kactuatedshuttle = m * Ktb + n * Ksb + o * Kes \% Stiffness of actuated shuttle
% Mechanical parameters of secondary shuttle
% electrode spring
besv2 = 5e-6; \% width electrode spring voltage
lesv2 = 50e-6; \% length electrode spring voltage
Aesv2 = besv2 * h; \%electrode springs cross sectional area
Iesv2 = (1/12) * (besv2^3) * h; \% inertia of electrode springs actuated shuttle
p2 = 4; \% number of electrode springs
Kes2 = ((Eps * (besv2^3) * h) / (lesv2^3)) \% stiffness of voltage electrode springs
% guidance spring
bgs2 = 5e-6; \% width guidance spring
lgs2 = 100e-6; \% length guidance spring
\[ \text{Ags}_2 = b_{gs2} + h; \quad \text{%guidance cross sectional area} \]

\[ I_{gs2} = \frac{1}{12} \left( b_{gs2}^3 \right) h; \quad \text{% inertia of guidance springs actuated shuttle} \]

\[ q = 2; \quad \text{% number of guidance} \]

\[ K_{gs2} = \frac{E_{ps} \left( b_{gs2}^3 \right) h}{l_{gs2}^3}; \quad \text{% stiffness of guidance} \]

\[ K_{\text{secondary shuttle}} = p_2 \cdot K_{es2} + q \cdot K_{gs2} \quad \text{Stiffness of secondary shuttle} \]

\[ \text{Ksystem} = K_{\text{actuated shuttle}} + K_s + K_{\text{secondary shuttle springs}} \text{ are in series not parallel} \]

\[ \text{Uactuatedshuttlenosprings} = \alpha \cdot dT \cdot l_{vb}. \cdot \text{dirf}; \quad \text{Number of guidance springs actuated shuttle} \]

\[ \text{Uactuatedshuttle with springs} = \left( \text{Uactuatedshuttlenosprings} \right) \cdot \left( E_{ps} \cdot l_{vb} \right); \quad \text{Shuttle displacement with sink beams} \]

\[ \% \text{angle determination tool for needed deformations} \]

\[ \% \text{Shuttle displacement vs beam angle} \]

\[ \text{Rx} = \alpha \cdot dT \cdot E_{ps} \cdot l_{vb} \cdot \left( \cos \left( \text{angle} \right) \right) / \left( \sin \left( \text{angle} \right) \right)^2; \quad \% \text{reaction force in X direction} \]

\[ \text{Fy} = m \cdot E_{ps} \cdot l_{vb} \cdot \alpha \cdot dT \cdot \sin \left( \text{angle} \right); \% \text{Generated force by ETA} \]
%figure
%plot(dT,Fy*1000)
%xlabel('Temperature V-beams (Celsius)','FontSize',14)
%ylabel('Force in y-direction (mN)','FontSize',14)
%title('\it{Temperature vs Force}','FontSize',14)
%axis auto

% buckling force of beams
Pcr=(pi^2)*((Eps*Iminvb)/(lvb^2))%buckling force of beams

% figure
%plot(dT,Rxaxial*1000,dT,Pcr*1000)
%xlabel('Temperature V-beams (Celcius)','FontSize',14)
%ylabel('Internal force (mN)','FontSize',14)
%title('\it{Internal force vs beam temperature}','FontSize',14)
%axis([0 527 0 3.8])
%axis auto

%figure
%plot(angle ,Rxaxial*1000,angle ,Pcr*1000)
%xlabel('Angle (Degrees)','FontSize',14)
%ylabel('Internal force (mN)','FontSize',14)
%title('\it{Internal force vs beam angle}','FontSize',14)
%axis auto

%% Overview system calculations
Fs =((m*alpha*dT*Eps*Avb*sind(angle)) ./((Kactuatedshuttle/Ks+1)+Kactuatedshuttle/Ksecondaryshuttle)); % Force in specimen
figure
plot(dT,Fs)
xlabel('Temperature V-beams (Celsius)','FontSize',14)
title('\it{Force on sample (N)}','FontSize',14)
axis auto

Uactuatedshuttlefullsystem =((m*alpha*dT*Eps*Avb*sind(angle)) ./((Kactuatedshuttle+Kactuatedshuttle+Ksecondaryshuttle)/Ksecondaryshuttle)+((m*alpha*dT*Eps*Avb*sind(angle)) ./((Kactuatedshuttle+Kactuatedshuttle+Ksecondaryshuttle)/Ksecondaryshuttle))); % final displacement actuated shuttle including full system stiffness

Usecondaryshuttle =((m*alpha*dT*Eps*Avb*sind(angle)) ./((Kactuatedshuttle+Kactuatedshuttle+Ksecondaryshuttle)/Ksecondaryshuttle)); % displacement of secondary shuttle
figure
plot(dT,Uactuatedshuttlefullsystem*1e6,dT,Usecondaryshuttle*1e6)
legend('Actuated shuttle', 'Secondary shuttle')
xlabel('Temperature V-beams (Celsius)','FontSize',14)
ylabel('Displacement shuttle ( \mu m)','FontSize',14)
title('\it{Shuttle displacement vs temperature}','FontSize',14)
axis auto

DU =((m*alpha*dT*Eps*Avb*sind(angle)) ./((Kactuatedshuttle+Kactuatedshuttle+Kactuatedshuttle+Ksecondaryshuttle)/Ksecondaryshuttle)); % elongation of specimen
figure
plot(dT,DUs)
xlabel('Temperature V-beams (Celsius)','','FontSize',14)
title('\textit{Specimen elongation vs temperature}','FontSize',14)
axis auto

figure
Samplestrain=DUs./lmemb;
plot(dT,Samplestrain)
xlabel('Temperature V-beams (Celsius)','','FontSize',14)
ylabel('Strain','','FontSize',14)
title('\textit{Sample strain vs temperature}','FontSize',14)
axis auto

%% Linear thermal expansion of shuttle
L0=700e-6; % Length of shuttle
dT2=max(dT/2); % average temperature change over shuttle
dLshuttle=L0*alpha*dT2
figure
plot(dLshuttle,dT2)
title('dL1 vs dT1')
Bibliography


E. Toolbox, “Convective heat transfer coefficients.”


Master of Science Thesis CONFIDENTIAL Eric Walter Kievit


