DISS. ETH NO. 23384

GRAPHENE MEMBRANES

SYNTHESIS AND MASS TRANSPORT ACROSS ATOMIC THICKNESS POROUS MEMBRANES

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

presented by

JAKOB KILIAN BUCHHEIM

MSc. ETH in Mechanical Engineering

ETH Zürich

born on 30.03.1986

citizen of Germany

accepted on the recommendation of

Prof. Dr. Hyung Gyu Park, supervisor

Prof. Dr. Dimos Poulakakos, co-examinor

Prof. Dr. Nicolas Noiray, co-examinor

2016
ACKNOWLEDGMENTS

I want to express my gratitude to Professor Dr. Hyung Gyu Park for supervising this thesis, for the opportunity of working in his lab, to do research at the frontiers of nanotechnology and for sharing his ambition for astonishing scientific questions. The work over the past years would have been fruitless without my lab colleagues Dr. Seulki Youn, Dr. Kemal Celebi, Amir Drouidian, Roman Wyss, Mengmeng Deng, Ning Yang, Dr. Ali Altun, Meng Li, Mahesh Lokesh and Karl-Philipp Schlichting. Thank you very much Seulki for teaching me how to be a good researcher, and the countless discussion about everything. Thank you Amir for becoming my friend, the trust and the great scientific discussions we had all the time in the lab. My gratitude belongs to you Kemal for the experience of a highly collaborative research project and teaching me important aspect about my own weakness. Thank you Roman for you continues teamwork within this project, the multiple graphene samples and astonishing clean transfer recipe. And finally thank you Karl for helping on the last meters to reproduce some of my intial results.

Dr. Ivan Shorubalko gave valuable scientific input in the area of ion beam patterning – and thank you for giving me access to the Helium Ion Microscope. Dr. Wouter Pronk and Jacqueline Traber advised greatly in the area of membrane science. Furthermore, I would like to recognize the
effort of Professor Dr. Dimos Poulidakos and Professor Dr. Nicolas Noiray
serving in my thesis committee.

The membrane fabrication was done in the Binnig Rohrer Nanotechnology Center, a joint research facility between ETH Zürich and IBM Research – Zürich. Many thanks belong to the scientific staff Dr. Roland German, Ute Drechsler, Richard Stutz, Dr. Dave Webb and Dr. Ronald Grundbacher operating this cleanroom, who provided good help and advice with various processes, troubleshooting devices and general support throughout the entire thesis. Special thanks to Steffen Reidt who was always patient enough troubleshooting the focused ion beam system.

The research work was partly funded by Swiss National Science Foundation under the contract 200021–137964.

And last but not least, I want to thank my family and friends. Mom and Dad besides planting all my abilities and supporting my interests you were helping me invaluably by listening to my crude stories from the lab. My friends helped me not to become a lab rat through and through, thank you very much for that reminder: Max, Anna, Fiona, Lucia, Max, Carl und Matthias.

And finally I want to deeply thank Ann my accomplice for life – there is no such support as you were giving to me and I am so happy and curious about our future.

Zürich, June 2016
The discovery of 2D materials like graphene has introduced a paradigm in a variety of research fields. Its outstanding electrical, thermal and mechanical properties enable new advances in science and engineering. Among other fields, membrane technology could greatly benefit from such an ultrathin material. Graphene displays extraordinary mechanical strength and molecular tightness in its pristine state, which render the material a perfect choice as a basis for subsequent pore formation. Due to the atomic thickness such membranes out of porous graphene are expected to impose minimal flow resistance. A successful transformation of graphene into a membrane, therefore, would be a change of paradigm in membrane science, since it would define the ultimate permeation limit.

Here, the laboratory scale synthesis and first macroscopic mass transport characterization of such porous graphene membranes are described. Graphene is synthesized at a centimeter scale by chemical vapor deposition. Two monolayers of graphene are transferred onto a porous support subsequently, which isolates the leak tight, freestanding graphene double layer. The freestanding graphene is then punctured with pores. In order to allow detailed analyses of the transport phenomena across porous graphene, the precise knowledge about created pore sizes and the membrane area is necessary. Therefore, the potential of pattern formation by the
versatile nanopatterning technique of focused ion beam milling is investigated in detail. High energetic focused ion hit the freestanding graphene lattice and can remove a single C atom, a mechanism that can be well described by the binary collision theory of the incident ions with the C lattice atom. Precise control of the exposure dose leads to the formation of pore arrays up to $2 \times 10^6$ in number, having controlled sizes ranging from $\sim 3.7$ nm to 1 μm.

Gas flow measurements through these synthesized graphene membranes exhibit ultimate permeation. For membrane pore sizes smaller than $\sim 50$ nm transport can be described by a free molecular flow at atmospheric pressures, and large pores display viscosity dominated flow following continuum theory for flow through infinitely thin orifices. Small sub-10-nm-pored graphene membranes display gas separation performance based on Graham’s law.

Water flow measurements through graphene with pores between 5.7 nm to 1 μm show that the flow can be described by a continuum theory for flow through infinitely thin orifices which is also an upper limit of permeation through pores of a given size.

The present thesis experimentally confirms the great potential of porous graphene as an ultimately permeable membrane with defining an upper limit for mass transport across membrane materials.

...
ZUSAMMENFASSUNG


In vorliegender Forschungsarbeit wird in einem ersten Schritt die Synthese einer porösen Graphen-Membran auf Labormaßstab beschrieben. Im Folgenden werden erstmalig die makroskopischen Transporteigenschaften dieser Membrane bestimmt. Durch chemische Gasphasenabscheidung wird Graphen großflächig auf Zentimeter-Skala synthetisiert. Anschließend werden zwei Graphen-Monolagen auf ein löchriges Substrat

Die Messung von Gasfluss durch diese hergestellten Membranen weist einen maximalen Durchfluss an der Obergrenze der möglichen Permeation auf. Der Gasfluss durch Membranen, deren Poren kleiner als ~50 nm sind, kann mittels freier Molekularströmung durch Öffnungen bei atmosphärischem Druck beschrieben werden. Für Membranen mit größeren Poren folgt der Durchfluss der klassischen Kontinuumstheorie für Strömung durch unendlich dünne Öffnungen, die von der Viskosität des Gases bestimmt wird. Membranen mit Poren, die kleiner als 10 nm sind,
ermöglichen zusätzlich die Filtration von Gasen auf Basis des Gra- 
ham’schen Gesetzes.

Der Wassertransport durch Graphenporen im Größenbereich zwi-
schen 5.7 nm und 1 μm wird ebenso durch die Kontinuumstheorie für 
Strömung durch unendlich dünne Öffnungen charakterisiert und definiert 
daher eine Obergrenze für den maximal möglichen Durchfluss bei festge-
legter Porengöße.

Damit bestätigt die vorliegende Arbeit experimentell das große Po-
tential von porösen Graphen-Membranen, als maximal permeables 
Membranmaterial.
CONTENT

ACKNOWLEDGMENTS III
ABSTRACT VII
ZUSAMMENFASSUNG XI
CONTENT XV

1 INTRODUCTION 19
1.1 Graphene as a 2D crystal 19
1.2 Graphene as a membrane material 21
1.2.1 Barrier layer properties of graphene and their application 21
1.2.2 Porous graphene membranes 22
1.2.2.1 Graphene membrane synthesis approaches 23
1.2.2.2 Gas transport across porous graphene membranes 24
1.2.2.3 Liquid and ion transport across porous graphene membranes 29
1.3 Scope of this thesis 36

2 GRAPHENE MEMBRANE FORMATION 39
2.1 Preparation of freestanding graphene 40
2.1.1 Graphene growth 40
2.1.2 Graphene transfer 43
2.1.2.1 Destination substrate properties 44
2.1.2.2 Destination substrate preparation 46
2.1.2.3 Graphene transfer process 51
2.1.3 Leakage measurement of freestanding graphene 57
2.2 Patterning of freestanding graphene 59
2.2.1 Ion / freestanding graphene interaction 60
2.2.1.1 Experimental procedure of ion irradiation 61
2.2.1.2 Measurement of ion sputter yield on freestanding graphene 64
2.2.1.3 Theoretical modeling of ion graphene interaction 72
2.2.1.4 Investigation of graphene evolution subject to ion bombardment 80
2.2.2 Graphene puncturing 85
2.2.2.1 Pore formation in freestanding graphene 85
2.2.2.2 Exploring the FIB pattern size limit in freestanding graphene 87
2.2.3 Measurement of pore diameter and total open area in graphene membranes 92
2.3 Overview over fabricated graphene membranes 94
2.4 Graphene pore characterization and modification 100
2.4.1 Graphene pore edge chemistry after patterning 102
2.4.2 Graphene pore shrinkage 104
2.5 Graphene membrane stability 113
2.5.1 Mechanical stability 113
2.5.2 Chemical stability 117
3 MASS TRANSPORT ACROSS GRAPHENE MEMBRANES 121
3.1 Gas transport across graphene membranes 121
3.1.1 Single gas transport 121
3.1.1.1 Experimental Setup 121
3.1.1.2 Results and interpretation of single gas permeation experiments 123
3.1.2 Mixture gas transport 134
3.1.2.1 Experimental setup design 135
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1.2.2</td>
<td>Results and interpretation of mixture gas permeation experiments</td>
<td>137</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Summary of gas transport properties of graphene membranes</td>
<td>141</td>
</tr>
<tr>
<td>3.2</td>
<td>Vapor transport across graphene membranes</td>
<td>143</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Experimental setup design</td>
<td>143</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Results and discussion of graphene membrane vapor permeance</td>
<td>144</td>
</tr>
<tr>
<td>3.3</td>
<td>Liquid water transport across graphene membrane</td>
<td>148</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Design of the experimental setup</td>
<td>148</td>
</tr>
<tr>
<td>3.3.1.1</td>
<td>Measurement setup</td>
<td>148</td>
</tr>
<tr>
<td>3.3.1.2</td>
<td>Reducing membrane clogging</td>
<td>151</td>
</tr>
<tr>
<td>3.3.1.3</td>
<td>Graphene membrane preparation for liquid flow measurement</td>
<td>152</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Onset of water permeation through porous graphene</td>
<td>155</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Modeling the clogging of graphene membranes</td>
<td>158</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Pressure dependency of liquid transport</td>
<td>163</td>
</tr>
<tr>
<td>3.3.5</td>
<td>Pore size dependency of liquid flow through porous graphene membranes</td>
<td>165</td>
</tr>
<tr>
<td>3.3.6</td>
<td>Temperature dependency of liquid transport</td>
<td>169</td>
</tr>
<tr>
<td>4</td>
<td>CONCLUSION AND PROSPECTS</td>
<td>179</td>
</tr>
<tr>
<td>4.1</td>
<td>Graphene Membrane synthesis and observation of ultimate permeance</td>
<td>179</td>
</tr>
<tr>
<td>4.2</td>
<td>Outlook</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>LITERATURE</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>CURRICULUM VITAE</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>PUBLICATIONS</td>
<td>207</td>
</tr>
</tbody>
</table>
1 INTRODUCTION


1.1 Graphene as a 2D crystal

The discovery of an isolated and stable monatomic thickness material made from carbon known as graphene [1] has enabled a leap forward in the quest of novel material science research. Since then an entire new research area of two-dimensional (2D) material has emerged and multiple other 2D crystal were found [2]. The availability of these materials engendered uncountable research opportunities in material science, physics and engineering and the discoverers of this material class were awarded the Nobel Prize in Physics 2010. In particular, graphene remains a widely studied material ever since. The 2D graphene crystal is made of hexagonally arranged, sp²-bonded C atoms (Figure 1-1).
Figure 1-1 Schematic of graphene lattice. Carbon atoms are arranged in a hexagonal manner forming a large honeycomb lattice where they form a planar sp² hybridized structure. The monatomic thickness C-atom crystal has a C atom bond distance $a_b = 1.43$ Å and layer thickness $t_g = 3.35$ Å.

The carbon atoms have a bond length $a_b = 1.42$ Å, and single crystals can span a centimeter scale area [3] with maintaining a thickness $t_g = 3.3$ Å. It exhibits a variety of unmatched properties such as ultrahigh charge carrier mobility [4], thermal conductivity [5], broadband light absorption properties [6], and unique material strength of stiffness and very high breaking strength [7].

The real breakthrough in application of graphene was the discovery of efficient synthesis pathways based on chemical vapor deposition (CVD) [8, 9], which allowed to fabricate graphene at a real large scale [10]. Extraordinary mechanical properties – despite the atomic thickness – and its availability render graphene a widely studied material not only in solid
state physics but also for membrane applications where strong but very thin materials have not been fully explored.

1.2 Graphene as a membrane material

1.2.1 Barrier layer properties of graphene and their application

One of the most important properties of graphene is its strong diffusion barrier characteristic. It has been found that the defect-free, single crystalline graphene lattice is impermeable to all the gas species including the smallest monatomic gas He at room temperature energies [11-13]. Furthermore, density functional theory calculations show a potential of selective atomic passage of B, N, H, O in the overall energy barrier order (~1.3eV < 3.2eV < 4.2eV < 5.5eV), with potentially predicting the boron atom passage via an atomic bond switching process [14]. At room temperature energies, therefore, the 2D carbon crystal does not allow any dissolution of atomic or gas species in the lattice structure, which entitles the single-atom-thick graphene effective barrier for mass transport [15]. For particle energies exceeding room temperature by orders of magnitude and for such miniscule particles as protons, however, molecular dynamics and experimental findings suggest that particles can indeed penetrate the graphene lattice without causing much damage to it [16, 17].
These extraordinary properties of graphene are currently used for corrosion inhibition coatings. Various studies show significant reduction of the substrate corrosion when being covered by graphene layers [18, 19]. For large scale and polycrystalline graphene coatings, however, grain boundaries and lattice defects impose a weak spot, since the imperfect crystal is prone to permeation of water and gases [20, 21]. These localized corrosion damage at graphene grain boundaries [22], however, could be either patched by atomic layer deposition [19] or nullified by multiple layer graphene coating.

### 1.2.2 Porous graphene membranes

As introduced above graphene displays excellent fundamental properties for a strong, impermeable but monatomic thick layer. The presence of pores with controlled size in this crystalline 2D lattice would render the graphene into the thinnest possible porous membrane. Because of the ultimate thinness of such a membrane made from a single layer of atoms the porous graphene can be expected to exhibit unforeseen permeation properties. In all conventional membrane platforms, the mass transfer is limited by the thickness of the selective layer of the membrane. Using the ultimately thin layer represented by graphene, this membrane resistance can be reduced to a minimal extent and therefore enable a leap in membrane technology.
1.2.2.1 Graphene membrane synthesis approaches

The idea of an atom-thick membrane platform that can realize ultrahigh permeation across a 2D orifice has immediately engendered significant research efforts on large-scale pore formation on the otherwise impermeable graphene. Initial methods of pore formation on graphene relied on irradiation of freestanding graphene with high-energy electrons inside transmission electron microscopes (TEM). This method allows the formation of a few pores with diameters ranging from 3 Å to 20 nm [23-25]. Since the number of pores created through this method is limited, this technique was only used for solid-state pore sequencing studies [26, 27]. For membrane technology applications, however, a larger number of pores have to be achieved.

One simple way of obtaining a porous graphene membrane is to use graphene synthesized by chemical vapor deposition (CVD). CVD-grown graphene is intrinsically polycrystalline and therefore has defect sites along the grain boundaries of individual lattice flakes. Furthermore, it was found that at a certain CVD condition graphene could contain nanometer-scale pinholes ranging from 1-15 nm [20] that could be used for mass transport. These pinholes can form if catalyst substrate (e.g., Ni or Cu) has microscale roughness, scratches or surface-contamination during growth. At these sites, graphene is hard to nucleate or easily bears many defects.
Artificially made defects in freestanding graphene with subnanometers in size on larger scale can be realized by ultraviolet-assisted oxidative etching [28] or direct exposure to ozone [29]. Another technique to create subnanometer pores on graphene is to create sparse lattice defects by low-dose (e.g., 8 keV) Ga⁺ ion irradiation followed by a weak oxidative etching, based on KMnO₄ and H₂SO₄, which grows subnanometer pores from the initially created defect sites [30]. The focused ion beam technology (FIB) is used to pattern free standing graphene layers with pores [31], nanoribbons [32] or other geometries [33] and shows the potential as a controlled versatile patterning method. A parallel process promising for large-scale pore formation is the self-assembly-driven nanolithography technique based on block-copolymer, which allows the formation of pores in the range of a few tens of nanometers [34].

1.2.2.2 Gas transport across porous graphene membranes

1.2.2.2.1 MD simulations of gas permeance

The initial finding of pristine graphene being an impermeable diffusion barrier for gaseous species triggered a broad research field investigating the permeation properties of defective or porous graphene. Density functional theory (DFT) calculations were used to calculate the energy barriers associated with the passage of different gases. A graphene pore created by
the removal of 10 C atoms terminated by N exhibits a permeation energy barrier of 0.04 eV for H\textsubscript{2} and 0.51 eV for CH\textsubscript{4} which corresponds to a theoretical H\textsubscript{2}/CH\textsubscript{4} selectivity of 10\textsuperscript{8} [35]. Changing the pore edge to H terminated graphene lattice the pore size reduced from 3.0 Å to 2.5 Å defined by the electron cloud which significantly increased the energy barriers to 0.2 eV and 1.6 eV [35]. Similar studies suggested the application of graphene membranes for H\textsubscript{2} and He separation from other gases [36] by even smaller pores made by 6 carbon vacancy sites. DFT methods were studied in more detail with emphasis on different calculation schemes highlighting the difficulty in predicting an absolute level of permeation by simply calculating the energy barriers associated with the passage [37]. A first attempt to simulate the real passage of gas molecules was done by Schrier [38] confirming the high selectivity of >10\textsuperscript{30} for He over CH\textsubscript{4} in a graphene pore made off 6 vacancy atoms. The flow rate of H\textsubscript{2} was found to be linear in the applied pressure drop until very high pressure of several atmospheres cause a permeation increase [39]. Molecular sieving properties of graphene pores with respect to kinetic diameter of the gas species was shown for 3.2 Å [40], 3.4 Å [41] diameter pores. The potential of isotope separation by thermally-driven diffusion was shown for the separation of He\textsubscript{3} and He\textsubscript{4} [42].

More insight into the real separation performance was given by simulating the real gas mixture passage in a MD simulation. Simulating a H\textsubscript{2}/N\textsubscript{2} gas mixture permeation through graphene pores with 32 down to 11 carbon
atom vacancies revealed that graphene membranes exhibit two separation mechanisms [43]. Sieving mechanism depending on the molecular size is dominant for really small pores the membrane [43]. For intermediate pore sizes however the affinity of the gas molecule towards the graphene and the pore edge causes an enhanced concentration of the adsorbing species in the vicinity of the graphene pore which is augmenting the passage of the corresponding gas. In the case of H\textsubscript{2} and N\textsubscript{2} it is the larger N\textsubscript{2} which is adsorbing on the membrane surface and the selectivity for intermediate pore sizes is reverted towards a N\textsubscript{2} selective membrane [43]. In a theoretically investigation by Drahushuk and coworkers [44] it was confirmed that the adsorptive pathway will have strong implications on the separation performance. Gas species will exhibit competitive adsorption governed by all the gas species partial pressure and the total pressure plus the competing affinities towards the membrane material, which renders the selectivity nonlinear in the pressure [44]. One can conclude that any gas will permeate the graphene pore via two pathways, either by direct permeation of gas phase molecules hitting the pore area or by the passage of adsorbed molecules which remain mobile on the surface [45]. The direct – gas phase – permeation events can be described by an effusion flux describing the probability of hitting the pore area modified by an energy barrier term accounting for sieving effects [45]. The magnitude of the adsorption pathway depends on the total pressure, the competitive adsorption and the surface mobility of the molecules [45]. For example, the strong adsorption of CO\textsubscript{2} and H\textsubscript{2}S compared to N\textsubscript{2} enhances the separation of the two species.
from CH₄ greatly but since CH₄ is better adsorbing than N₂ the sized based separation of N₂/CH₄ is reduced [45, 46]. The effect of adsorbing molecules on the graphene membrane can even cause the blockage of smaller gas species which has been observed for CH₄/C₄H₁₀ where butane is blocking methane from passing but remains its own through pore mobility [47] and CH₄/N₂ where CH₄ inhibits the passage of N₂ [48]. By specifically tuning the affinity of molecules towards the pore mouth researches showed that the selectivity of porous graphene can be altered. Employing charged groups close to the pore edge, the permeation of the polar molecule H₂S versus CH₄ can be enhanced [49]. And exchanging the graphene pore termination atom from Hydrogen to Fluor reverts the N₂ over CO₂ selective membrane into a full N₂ rejecting CO₂ selective membrane [50]. Additional effects of strong adsorption was investigate by the addition of water vapor to the gas mixture [51]. The water molecules will condense into nanoclusters on the graphene membrane surface which are too large to penetrate the sub nanometer pore and allow a pure gas stream to penetrate the membrane [51].

1.2.2.2 Experimental observation of gas transport across graphene

First experimental results of gas molecular transport across graphene was obtained by measuring the deflection of a double layer graphene blister over time by atomic force microscopy (AFM) [28]. The pristine double layer seals a compartment which is containing gas of a certain species. By UV
assisted etching defects in the graphene layer are created and subsequent AFM scanning of the bulged graphene blister surface allows to track the deformation of the blister. Calculating the volume change and the internal pressure the permeance of the graphene membrane could be calculated. It was found that these graphene membranes exhibit molecular sieving properties. Large gas molecules like Ar, N₂ and CH₄ showed similar leak rate as non-etched graphene which is attributed to diffusion through the SiO₂ support [11, 28] but the passage of smaller molecules namely CO₂ and H₂ is enhanced by 2 order of magnitude. Since the number and size of the pores created by UV etching is unknown, the permeation performance of gas molecules through graphene membranes could not be characterized further. A follow up paper using the same experimental design but monolayer graphene instead of double layer exhibit switching permeation states upon very controlled UV exposure [52]. By additional Au particle deposition and laser induced heating the permeation of gas molecules could be altered between two states [52]. Both studies allow the flow characterization through a very small number of pores only and lacks any possibility to observe macro scale flow rates.

A different approach towards large scale graphene membrane synthesis was presented using defective CVD graphene [53]. By transferring multiple graphene layers onto a porous polycarbonate track etched membrane (PCTE) researchers tried to increase the yield of tear free support coverage by graphene. Gas transport occurred through intrinsic graphene
defects pinholes and a larger tears and showed only moderate gas selectivity lower than expected from kinetic gas theory [53] and observed flow could not be rationalized further since the nature of the transport path could not be fully characterized.

1.2.2.3 Liquid and ion transport across porous graphene membranes

1.2.2.3.1 MD simulation of water passage across graphene membranes

Simulations of liquid water flow across porous graphene indicate the high permeation rate of water molecules through such membranes. In molecular dynamics (MD) simulation Suk and Aluru [54] have predicted ultrahigh permeation of water. For pore sizes around 2.7 nm permeance of water molecules through graphene exceeds the mobility inside carbon nanotubes (CNT) or ultrathin silicon membranes. Only collective flow of single-file water molecules inside CNT pores of ~0.7 nm is faster than for comparable pore sizes of graphene. The pressure drop across graphene pore occurs within ~1 nm from the membrane surface, implicating that flow impedance is caused by entrance effects similarly to CNT pores [55, 56].

The effects of pore size and the pore edge termination have been further investigated using MD simulations [55, 57, 58]. For pores smaller than 4 nm the volume flow scaling per pore is roughly $Q_w \propto r^{33}$ [55]. This scaling
indicates that water permeance in this pore size regime can be modeled by the superposition of Sampson theory [59] and Hagen-Poiseuille equation. All available results of MD simulations agree roughly with this scaling, 

\[ Q_w \propto r^x \]

with \( x \) between 3 and 3.3 [54, 55, 57, 58].

For small pores in the subnanometer range the edge termination of the graphene pore can influence the permeance [57]. Cohen-Tanugi et al. have found out that hydrogenated and hydroxylated groups at the pore mouth have a strong effect. In the pore size range below 1 nm, hydrogen-terminated pores have slightly lower per-pore permeance than hydroxyl terminated ones at the same pore area, which allows stronger interaction of the water molecule with the pore edge leading to a larger accessible area inside the hydroxylated pore and therefore a larger effective pore size. In contrast the hydrogen termination renders the pore hydrophobic and therefore suppresses the formation of hydrogen bonds, which induces an artificial ordering of water molecules in the vicinity of the pore [57, 58] to roughen the entropic landscape and reduce the speed of traversing molecules leading to a slower flow compared to hydroxylated pores.

In addition to pure water flux characterization the application of graphene membranes for seawater desalination was investigated [57]. MD simulations of pressurized flow of high salinity aqueous NaCl solution through graphene pore reveal that 100% salt rejection can be achieved for pore size as narrow as 5.5 Å. This high rejection value for pores \( \leq 5.5 \) Å is observed for all pressures from 100 MPa to 225 MPa [57]. For larger pores
of \( \sim 9 \) Å in diameter the ion rejection is reduced to 80% and 40% at pressures of 100 MPa and 225 MPa, respectively. The pressure dependency is attributed a larger effective volume of the hydrated ion which is more sensitive to pressure increase than water molecules [57]. Furthermore, a clear effect of pore edge chemistry is observed. Pores that are terminated by the polar hydroxylated group allow higher salt permeation (lower salt rejection). The OH group on the pore edge interacts similarly with the solvated ion as the surrounding water molecules and therefore the energy barrier for ion passage may be lower [57]. In contrast, hydrogen-terminated pores show greater ion separation performance with up to 80% for \( \sim 8 \) Å pores at 100 MPa.

1.2.2.3.2 *MD simulation of ion permeation across graphene membranes*

MD simulations of ion transport across graphene pores further elucidated the potential of graphene as an ion selective membrane. Simulating a hydroxyl terminated pore with diameter of \( \sim 4 \) Å revealed two rejection mechanisms: (1) electrostatic screening by the charge of the pore edge functional group rejecting oppositely charged ion species for a example hydrogen terminated pore only allows the passage of Br\(^-\) and Cl\(^-\) (33:17) and (2) steric effects, because ions with weakly bound solvation shells have higher permeation rates than those with strongly solvated ions (K\(^+\)>Na\(^+\)>Li\(^+\) for negatively charged pore edges) [60]. Calculating the potential mean
force (PMF) acting on molecules while passing a non-functionalized graphene pore of 7.5 Å in diameter showed that Na$^+$ ions and Cl$^-$ have to overcome the PMF barrier of $\sim$0.61 eV and $\sim$0.43 eV whereas water molecules face a PMF barrier of only $\sim$0.2 eV [61]. For the non-functionalized graphene pores the change of the salinity from 0.025 M to 0.25 M does not change the PMF barrier significantly which is different for modified pore edge chemistries. The attachment of carboxylic groups increases the PMF for Cl$^-$ at low ionic strength to 0.824 eV but at high ionic strength the increased Na$^+$ ion concentration at the pore screens the electrostatic repulsive barrier of Cl$^-$ yielding a relatively lower PMF for the Cl$^-$ ion passage of $\sim$0.47 eV. The attachment of NH$_3$ group causes the same but reverse effect on both ion species, so that the overall passage of ions is not expected to decrease [61]. In contrast, the functionalization of the pore edge with OH groups has beneficial effects on the salt rejection performance, since it allows for high salt rejection even for as saline water as seawater [61].

Equilibrium MD simulations of solvated NaCl and graphene membranes reveal that the concentrations of both ion species in C-terminated graphene pores are reduced compared to bulk, quenching the concentration inside pore smaller than 5 Å to practical 0 [62]. The researchers found that the main factor for the ion partitioning is the high free energy ‘cost’ for dehydration [62] and not the dielectric exclusion as is the case for conventional nanofiltration membranes [63]. In addition, the diffusion constant $D_p$ of ions inside the graphene confinement is reduced when compared with the bulk
diffusion $D_{\text{bulk}}$ and scales with pore radius $r$: 

$\left(1 / D_p - 1 / D_{\text{bulk}}\right) \propto 1 / r$, leading to a remarkable drop of 40% in the ion mobility inside a 5.2 Å pore.

1.2.2.3.3 Experimental observation of water and ion passage

Experimentally, ion diffusion measurements through graphene with subnanometer pores on high flow resistant PCTE supports confirm the potential of ion selectivity and the potential of size exclusion. An initial study displays the feasibility of graphene integration onto a porous PCTE support and ability to measure selective molecular transport across graphene in a diffusion cell setup [20]. In a follow up study artificial pores were created using ion irradiation and wet chemical etching (1.875 mM KMnO$_4$ in 6.25% H$_2$SO$_4$), which allowed for control of pore density as well as pore sizes (e.g. by duration of wet chemistry) [30]. Short etch times lead to the formation of small pores, which exhibit lower ion mobility than the support structure and show some preferential selectivity for positively charged $K^+$ over $Cl^-$, the latter presumably due to membrane charge. For slightly enlarged pores, $K^+$ and $Cl^-$ can pass freely but larger dye molecules such as Allura Red (diameter ~1 nm) cannot. Only after opening up the pores further by extended etching times can the dye molecules translocate the pores of the graphene [30]. These experiments allow the partial graphene transport characterization despite the presence of larger defects an tears since the parasitic pathways are reduced by the high resistance of the support structure [30]. The ion passage through intrinsic and artificial
subnanometer defects was further investigated through ion conductance measurements [29]. Even mild ozone etching was found to create defects in the estimated size range of ~3.8 Å, which allow the electrokinetic passage of Na⁺ and Cl⁻ ions. How the electromotive driving force overcomes the dehydration energy penalty of the ions remains elusive. This report highlights the difficulty in creating nanoporous graphene, as well as correctly characterizing the pore size that has the capability of ion rejection.

Initial attempts to measure water flux across sub nanometer pores in graphene [64] yielded permeances within the expected ultrahigh flow rate predicted by classic Sampson theory and MD simulations of Suk and Aluru [55]. By employing a twofold defect sealing method based on ALD deposition to close intrinsic graphene defects and interfacial polymerization to clog large scale tears, monolayer graphene could be transformed into a membrane allowing to measure osmotic pressure driven water flux through subnanometer pores of 0.48 nm in diameter. Despite the predictions that this pore size is expected to show ion rejection, NaCl (0.76 nm) passed the membrane favorably. Larger sized ions and molecules MgSO₄ (0.86 nm), Allura Red (~1 nm) and Dextran (~3.7 nm) were partly rejected by the graphene membrane. However, the passage of the Dextran molecule and the pumping of NaCl indicate that defect sealing is not perfect and additional large leakage pathways through the monolayer are present, which could not
be found during extensive STEM scanning [64]. These results again highlight the difficulty in fabricating monolayer graphene membranes free of large parasitic defects.

Another method to achieve water permeable graphene monolayer was presented by Surwade and coworkers [65]. Monolayer single crystalline graphene, which is covering a 5 μm hole in a SiNx membrane, is treated by oxygen plasma. The exposure generates Si terminated pores with ~1 nm size at pore densities with $10^{14}$ m$^{-2}$ to $10^{16}$ m$^{-2}$ [65]. Reported results for water permeance are however contradicting. Osmotic pressure driven flow through ~1 nm porous graphene yielded $4.5 \times 10^{-26}$ m$^3$/Pa/s per pore, which is very close to Sampson’s prediction of $6.4 \times 10^{-26}$ m$^3$/Pa/s per pore. In a thermal expansion driven water pervaporation measurement the observed water weight loss through the graphene membrane exceeded by orders of magnitude the predicted water permeability of porous graphene for ~20% of the devices. The mechanism for this high permeation rate remains unclear. As expected in membrane pervaporation the membrane retains the non-volatile ions from the passage through the graphene and therefore shows some potential application of desalination using graphene membranes [65].
1.3 Scope of this thesis

As introduced above the idea of 2D membranes is a unique concept which has gained traction since the discovery of large-scale isolated 2D crystals like graphene. In contrast to various results from MD simulation, there are a very few unsatisfying approaches for the experimental observation of the mass transport across graphene membranes. The difficulty arises from the fabrication of the experimental platform which allows to reproducibly and controllably manufacture graphene membranes which would allow to investigate the mass transport properties. Several key requirements for the synthesis pathway must be met: (i) availability of full coverage large area graphene; (ii) isolation of freestanding graphene on a large porous support substrate; and (iii) creation of controlled pore sizes as well as pore density on the isolated freestanding graphene. Only by mastering these three requirements it would be possible to investigate and rationalize the mass transfer phenomena and to gain some real insight into the new field of 2D membranes.

In this thesis the transport physics of fluids across porous graphene will be experimentally investigated. Here, a reliable lab scale graphene membrane synthesis pathway is developed satisfying the above mentioned criteria. It allows for detailed knowledge about the membrane characteristics such as pore size and total open pore area. Graphene has to be
synthesized in a centimeter scale (section 2.1.1) and is isolated as a freestanding double layer on a holey support by a high-yield transfer process (section 2.1.2). The patterning method of freestanding graphene by focused ion beam (FIB) milling is studied in great detail to enable tailored perforation in the freestanding graphene (section 2.2.2). In single and mixture gas permeation experiments through graphene membranes with various pore sizes, the flow phenomena of gas species across atomically thin graphene membranes are characterized (section 3.1). In addition, the passage of liquid water through pores in the graphene is measured and analyzed (section 3.3), revealing the flow physics of liquid permeation through atomically thin membranes.
2 Graphene membrane formation


The membrane formation relies on three main process steps. First, graphene is synthesized at a large scale via chemical vapor deposition (CVD) on a copper (Cu) substrate (Figure 2-1 I). Second, graphene is transferred from the growth substrate to a porous destination support via sacrificial wet etching, yielding freestanding graphene all over the underlying pores of the support (Figure 2-1 II). Finally, the otherwise leak tight freestanding graphene is perforated using focused ion beam (FIB) technology with pore size and number well under control (Figure 2-1 III). Each individual process is described in greater detail below.
Figure 2-1 Overview over membrane fabrication process. (I) Graphene growth on a Cu foil by CVD yielding full coverage of monolayer graphene. (II) Graphene transfer using sacrificial wet chemical etching onto a porous destination substrate consisting of punctured SiN$_x$ membranes on a Si chip. (III) Graphene perforation of the otherwise impermeable 2D crystal by ion bombardment of FIB, yielding porous graphene membrane.

### 2.1 Preparation of freestanding graphene

#### 2.1.1 Graphene growth

For membrane technology applications graphene has to satisfy two main quality criteria. Specifically, the graphene needs to cover centimeter-scale areas fully without tears, defects, particles or other contaminations. Unlike electronics and thermal application where large grain sizes are often required [3], graphene for membrane technology applications would not need very large grains but would rather require well connected grain boundaries so as to uphold mechanical stability during the perforation process and the mass-transport measurement operation. In particular, recent results of
crack propagation inside monolayer graphene samples have shown that perfect crystalline graphene is prone to catastrophic failure if an artificial defect site causes stress concentration. In contrast, graphene that contains vacancy sites and grain boundaries may suppress the crack propagation and remain more failure resistant than the perfect crystalline counterpart [66].

Our earlier work on graphene CVD on a Cu foil and the growth recipe established therein are described in Celebi et al. [67] In order to optimize the CVD process for meeting the abovementioned criteria, certain key aspects are modified. As for the Cu substrate, foils from two manufacturers, Nippon Mining (sheet type HA35v1) and Alfa Aesar (#13382), yielding similar results are used. To improve the cleanliness of the synthesized graphene the catalyst substrate is cleaned prior to the growth. Physical etching of the Cu foil via Ar\(^+\) ion beam milling for 10 min at 600 V bias, 390 V accelerator (positive bias for ion beam shaping), 70° incident angle and 250 mA current (Ionfab 300, Oxford Instruments) cleans the surface from any other undesirable contaminants by removing the surface layer of the foil which consists of non-uniformly oxidized Cu (Figure 2-2 a i)).
Figure 2-2  a) Schematic of entire graphene growth process. Cu foil is cleaned by Ar\(^+\) ion bombardment (i) yielding a clean top side Cu foil (ii). After annealing growth initiates at multiple nucleation sites (iii) which are expanding to a full coverage graphene coating (iv to v). On the backside of the Cu foil there is as well some formation of graphene during the process (iv). b) Temperature and carbon precursor flow profile over the course of the growth process. c) Scanning electron micrograph of as grown graphene on Cu foil showing clean graphene with some wrinkles and very few secondary nucleation sites (darker spots).

After cleaning it the foil is loaded in a cold-wall reactor CVD chamber (Black Magic\textsuperscript{TM}, Aixtron) on a 300-nm-thick-SiO\(_2\)-coated 4-inch Si wafer. Following the reduction annealing of the foil in a H\(_2\) rich atmosphere (100 sccm H\(_2\), 1500 sccm Ar) at 3.5 mbar and 950°C for 30 min, the growth is initiated (Figure 2-2 a iii)) by adding 25 sccm of carbon feedstock (ethylene) at 950°C for 2 min. The graphene full covering of Cu substrates is
assured through increased supply of ethylene (50 sccm) for 1 min at the end of the growth process (Figure 2-2 b). The high carbon precursor flux in the end of the growth process facilitates the interconnection between different graphene grains (Figure 2-2 a iv) to v). The growth is terminated by turning off the gas supply and heating. The Cu foil is unloaded after cooling to room temperature to avoid oxidation of the Cu substrate. This growth recipe yields clean, fully covering monolayer graphene on the top side of the foil (Figure 2-2 e). Note that the backside of the Cu foil will also catalyze a certain amount of graphene (Figure 2-2 a v)). This back-side grown graphene must be removed in the next graphene transfer step.

2.1.2 Graphene transfer

Reliable, clean and high-yield graphene transfer to a well-defined substrate is one of the key requirements for the graphene membrane synthesis in this study. The transfer process has to result in freestanding stable graphene layers on a large area. It can only be obtained by rational design of the underlying support structure such that the support provides a sufficient number of openings yet moderate in the individual size. The optimal dimension of individual openings is critical to sustaining the graphene membrane stability. Once the individual opening size is determined, the number of openings (or a total membrane area) can be determined to enable macroscale mass transport characterization. Furthermore, a well-controlled
clean transfer procedure is crucial to the sample manufacturing yield. Initial results indicate that double-layer graphene transfer is sufficient to produce stable graphene membranes which can survive the subsequent membrane processing such as perforation and characterization measurements. Therefore, a novel double-layer graphene transfer is developed to show good and reproducible results in the porous membrane fabrication and characterization. In addition, the double layer graphene assembly suppresses strongly a parasitic mass transport pathway through small unavoidable vacancy defect sides at the graphene grain boundaries formed in graphene CVD. [20, 53]

2.1.2.1 Destination substrate properties

Integrating the graphene into a well-defined porous support offers the advantages of process controllability and precise information on the graphene membrane anatomy. A convenient way of substrate preparation with the required accuracy and cleanliness is to use basic microfabrication methodology relying on photolithography and etching steps. A suitable substrate for graphene membrane has to satisfy the following four requirements: i) the substrate has to be porous; ii) the support pore area should be well defined and allow freestanding graphene to span the pore; iii) the substrate should minimize its contribution to mass transport resistance; and iv) graphene pore area should be traceable. Previous findings have shown that
pristine single crystal graphene [11] as well as CVD graphene [68] is able to span 4-μm-wide holes with good stability. The mechanical strength of the graphene spanning an opening with radius \( r_s \) can be calculated by the 2D sheet theory. It is assumes that the material cannot sustain any bending force but only can withstand in-plane stresses. Using well established relationship between in-plane stress and a perpendicular pressure force on a clamped circular membrane eq. (2.1) the maximum differential pressure \( \Delta p \) at the point of fracture can be calculated using the breaking strength \( \sigma_f \) of CVD graphene.

\[
\Delta p = \left( \frac{3(1-\nu)}{E} \right)^{1/2} \frac{4 t_g}{r_s} \sigma_f^{3/2}
\]  

Typical values \((E = 166 \text{ GPa} \ [68], t_g = 0.33 \text{ nm}, \nu = 0.3, \sigma_f \approx 30 \text{ GPa} \ [69])\) yields a breaking pressure of 8.6 MPa for a suspended \( 2r_s = 4 \text{ μm} \) graphene membrane which is in agreement with another report [70]. This breaking pressure is more than 40 times the operational pressure in the lab scale permeation setup available therefore can be expected to be sufficient for the current measurement purpose.

Another critical boundary condition for the destination substrate is the total freestanding graphene area \( A_g \) which is required to measure mass permeation on macro-scale with a conventional mass flow meter \((N_2 \text{ flow rate } V_{N_2} \approx 0.02 \text{ sccm})\). Assuming the validity of 2D gas transport theory defined by effusion \((Q_{\text{effusion}} = (2\pi M_{N_2} R T)^{-1/2})\) in the free molecular range and
a membrane porosity $\kappa$ of 3% the necessary membrane area equals to
\[ A_g = \frac{V_{N_2}}{Q_{\text{effusion}} \kappa \Delta p} \approx 5 \times 10^{-10} \text{ m}^2. \] Therefore, about 40 4-μm-wide openings yield enough freestanding graphene area to enable the measurement.

To nullify the mass transport resistance of the support layer a very thin, freestanding membrane should be used. For pore aspect ratios $2r_s / t < 0.05$ the pressure drop of a porous support in the continuum flow regime ($2r_s = 4 \mu m$) originates from entrance effects, only [71]. The upper bound contribution of flow resistance of the support to the total membrane impedance therefore is maximal equal to the membrane porosity $\kappa$ which is around 3% and therefore can be safely neglected. A low-stress 150 nm thick SiN$_x$ film satisfies this aspect ratio criteria and offers the mechanical stability to span hundreds of μm as a suspended membrane. The SiN$_x$ membrane is incorporated into a Si chip which has large-area trenches across the wafer thickness.

### 2.1.2.2 Destination substrate preparation

The final design comprises a stable 2×2 cm$^2$ 520-μm-thick Si support frame (Figure 2-3 b) which can be mounted in the lab scale mass transport measurement equipment.
Figure 2-3 Overview over support chip design. **a)** Front side of a support chip showing four SiN₅ windows with openings and the number identifier. **b)** Back side of support chip. **c)** Group of four window patterns which have one common identifier, just like the quaternary of **a)** seen from the opposite side of the chip. **d)** An etched-through wafer trench of the quaternary. **e)** Freestanding, 7x7-opening punctured SiN₅ membrane seen from the top side of the support frame. **f)** A through hole (opening) made in the freestanding SiN₅ membrane and covered by graphene.

It has 9 distinct pore arrays grouped into four (Figure 2-3 **c**). A number identifies each group to allow efficient membrane tracing (Figure 2-3 **a**). The punctured area is located on top of an etch-through trench (Figure 2-3 **d**), and each array comprises 7x7 (or 8x8 in later design of the support chip) openings (Figure 2-3 **e**) of 4 (or 6) μm in width (Figure 2-3 **f**) made through a 150-nm-thick freestanding SiN₅ membrane. This punctured SiN₅ membrane acts as a carrier for the graphene layers.
In order to manufacture this structure, both sides of the support structure have to be patterned which increases process complexity. The following processes are used:

**Photolithography (PL)** for pattern generation

1) Spin coat photoresist (PR) AZ 6014 at 4000 rpm for 1 min on SiNₓ wafer
2) Bake at 110°C for 1 min
3) Expose PR with ~140 mJ/cm² to transfer mask pattern using UV light (MA/BA8, Süss MicroTec)
4) Develop PR in AZ 400 1:4 (DI water) for ~20 s
5) Rinse wafer with DI water and blow dry with N₂

**Reactive ion etching (RIE)** of SiNₓ (etch rate: 22 nm/min) with the following process parameters: 50 mTorr, 100 W forward power, 10 sccm O₂ flow, and 50 sccm CHF₃ flow (80 RIE, Oxford Instruments)

**KOH etching** of the Si (etch rate: ~55 μm/h) with 44% KOH solution (Fisher Scientific) at 80°C.

The processing scheme of the Si wafer is visualized in Figure 2-4. Used as a basic substrate is a 4-inch 520-μm-thick Si <100> wafer with one side polished and a 150-nm-thick low-stress SiNₓ coating on both sides. For precise alignment of the front and back side pattern, first a permanent alignment mark has to be patterned into the polished (front) side of the Si wafer (Figure 2-4 a). This patterning is achieved via PL (Figure 2-4 a i and ii) with an alignment mask followed by a 2.5 min RIE etching of the
SiN$_x$ (Figure 2-4 a iii) which results in a permanent 55-nm-deep trench inside the SiN$_x$ which acts as a stable alignment mark (Figure 2-4 a iv).

**Figure 2-4** Overview over the destination substrate preparation. a) Inscription of a front-side alignment mark to 150-nm-thick-SiN$_x$-coated Si wafer. Spin coating PR and patterning an alignment mark on the wafer front side via photolithography: ii). Pattern transfer of alignment pattern into SiN$_x$ by etching 50 nm into the SiN$_x$ thin film: iii). Removal of PR: iv). b) Etch process schematic of back side treatment of Si wafer with alignment marks. PR is spin coated and patterned on the wafer backside. Using photolithography xi) with backside alignment to the marks created before. The hard mask for the KOH etching created by RIE etching: vii). The Si of the wafer is etched in a KOH bath viii) until only 30 μm Si are left. c) Process schematic of wafer front side after KOH etching. After spin coating PR the latter is patterned with the support hole pattern aligned to the marks created before: ix)-xi). RIE is used to etch hole patterns into the SiN$_x$: xi). KOH is used to etch the remaining Si to complete the through wafer etch: xii).
Then, the pattern for the through wafer etch starting from the back side of the Si wafer can be created using a large trench KOH etch mask. In this process the KOH etch mask has to be aligned with the alignment marks created previously (Figure 2-4 b v and vi) and now located on the opposite side. Note that the KOH is an anisotropic etch for the Si and etches preferentially the <100> direction of the crystal but has nearly zero etch rate for the <111> direction of the Si crystal. Therefore, the pattern footprint is getting smaller (Figure 2-4 b viii) throughout the thickness of the wafer. To gain a freestanding 100×100 μm² membrane on the wafer front side, a larger ~850×850¹ μm² has to be patterned on the backside. After the PL process, the RIE etching (Figure 2-4 b vii) of SiNx for 7 min transfers the pattern to the SiNx which acts in the subsequent KOH etching as a hard mask. At an etch rate of 55 μm/h the KOH etching through the wafer (Figure 2-4 b viii) takes more than 9 h. The process should be stopped before the entire Si layer in the bottom of the trench is removed to ensure a reliable pattern formation of the freestanding SiNx membrane on the front side. Straightforward PL (Figure 2-4 c ix) with front side alignment transfers the regular 7×7 or 8×8 hole array pattern with 4-μm-wide holes to the right position on the front side of the wafer. After RIE etching for 7 min (Figure 2-4 c xi) via holes are punctured through the SiNx layer and the remaining 30-μm-thick Si is etched away via additional KOH etching (Figure 2-4 c xii).

¹ 100 μm + 525 μm × 2⁰.⁵
2.1.2.3 Graphene transfer process

The graphene layer is transferred onto the punctured 2×2 cm$^2$ SiN$_x$ substrate via a wet transfer method. The process is adjusted to allow for double layer transfer and further optimized to give exceptionally clean freestanding graphene with high yield on large areas. The general approach towards the transfer is to remove the catalyst substrate by a sacrificial etching step leaving the graphene layer afloat on the etchant solution. Then the graphene is rinsed and scooped by the destination substrate (punctured SiN$_x$ mesh support). The details of this process are described below and depicted in Figure 2-5:

1) Spin coating PMMA photoresist on top of the graphene on Cu foil to float the foil on the etchant solution:
   a) Spread 250 μL PMMA dissolved in Anisol (950 A2) over the 2×2 cm$^2$ graphene-on-Cu foil.
   b) Spin the substrate at 4000 rpm (ramp rate 1000 rpm/s) for 40 s to spread and dry the PMMA film. This step yields a 100–150-nm-thick PMMA layer on top of the graphene.
   c) Bake PMMA on a hotplate for 1 min at 110°C to gain stability of the polymer film.

2) Backside graphene removal
a) Place the PMMA/graphene/Cu foil afloat in a 40-mL beaker containing 10 mL of ammonium persulfate (\((\text{NH}_4)_2\text{S}_2\text{O}_8, 0.5 \text{ M}\)) and etch Cu partly for 20 min. This step releases graphene on the backside from the Cu foil.

b) Take the foil out (with tweezer) and float it in a large beaker of DI water to rinse off contaminants.

c) Take the foil and pull the backside over cleanroom tissue to remove the rest of the backside graphene.

3) Cu foil etching
   a) Place PMMA/graphene/Cu foil afloat in a 40-mL beaker containing 25 mL of ammonium persulfate (0.5 M) and etch away Cu completely for 45 min.
   b) Take the PMMA/graphene foil out by scooping it with an unpolished side of a SiO\(_2\)/Si chip, and release the graphene on top of a beaker filled with 0.5 L of DI water to rinse off the remnant etchant for 30 min.

4) Add additional graphene layers
   a) Scoop the adrift PMMA/graphene film with an additional graphene-on-Cu foil.
   b) Dry the sandwich foil of PMMA/graphene/graphene/Cu for 30 min, to form a double layer of graphene.

5) Repeat the backside graphene removal (step 2)) for the new Cu foil

6) Repeat the Cu foil etching (step 3)) for the new Cu foil
7) Transfer to a destination substrate
   a) After 30-min-long rinsing of the PMMA/graphene/graphene film in DI water, fish it with a destination substrate (punctured 2×2 cm² SiNx).
   b) Dry the film on the destination substrate for 30 min in an ambient condition.
   c) Place the substrate on hotplate at 180°C for 30 min to relax PMMA/graphene/graphene film and promote the adhesion of the graphene double layer to the support.

8) PMMA removal
   a) Pyrolyze away the PMMA via thermal annealing of the sample in a H₂-rich atmosphere (900 sccm H₂ and 100 sccm Ar) at 400°C and atmospheric pressure for 3 h, which removes PMMA clearly. [72, 73]
Figure 2-5 Process flow diagram of the transfer process. 1) Spin coating PMMA on a graphene/Cu foil. 2) Removal of backside graphene by short Cu etching in ammonium persulfate. 3) Etching of the entire catalyst foil. 4) Transfer of the PMMA/graphene film to a fresh graphene-on-Cu foil to form a graphene double layer. 5) Removal of backside graphene from the new Cu foil. 6) Etching of the remnant Cu off the second growth substrate. 7) Transfer to the punctured SiNx destination substrate. 8) PMMA pyrolysis to remove the PMMA carrier layer from the graphene surface.

After the transfer is complete, the quality and cleanliness of the graphene samples is confirmed using scanning electron microscopy (Helios
450, FEI). Each window with freestanding graphene (Figure 2-6 a) is carefully investigated for the presence of tears and pinholes. On each transferred chip at least 4 of the 36 trenches (with each with 8×8 holes) usually had good quality graphene coverage with 100% yield on the individual 4-μm-wide openings. A closeup image of the freestanding double layer graphene confirms the low particle contamination and cleanliness of the transferred graphene (Figure 2-6 b). There are only sparsely distributed ~10-nm-sized particles along presumably grain boundaries and wrinkles. The Raman spectrum obtained from the pristine freestanding graphene (micro Raman CRM200, WiTec) using a 532-nm incident laser beam with 0.4-mW power shows the footprint of high quality double layer CVD graphene (Figure 2-6 a inset). The sharp G peak (1589 cm⁻¹) with a FWHM = 26.1 cm⁻¹ shows the high concentration of sp² hybridized carbon atoms [74].
Figure 2-6 Double layer graphene after transfer. a) Scanning electron micrograph from 8×8 4-µm-wide SiN₆ openings covered with freestanding double layer graphene. The inset Raman spectrum proves high quality of double layer graphene after the transfer. b) Closeup on the pinhole-free, freestanding double layer graphene layer covering the 4-µm-wide opening. Only sparse distribution of ~10 nm particles along wrinkles or grain boundaries are observed.

The D band at ~1340 cm⁻¹, which originates from the first harmonic of the radial breathing of the benzene ring, is only active in the case of asymmetry in the hexagon and therefore is a good measure of various defects like grain boundaries or single vacancy sites [74]. In the present case the D peak intensity is very low yielding a I(D)/I(G) ratio of 0.1, indicating a very low defect concentration. Low defect concentration is also confirmed by the presence of the sharp peak at around ~2679 cm⁻¹ commonly dubbed G' or 2D peak attributable to the second harmonic benzene breathing mode and expected to be about half the G peak intensity for clean multilayer
graphene samples [75]. Therefore, one can conclude that the dark freestanding area (**Figure 2-6 b**) indeed shows excellent quality double layer CVD graphene with very low defect density.

2.1.3 Leakage measurement of freestanding graphene

Having obtained freestanding double layer graphene membranes, the leakage rate of the membranes can be measured. As introduced above the graphene lattice was shown to be impermeable to gases because the diameter of the geometric opening of the honeycomb carbon lattice (0.064 nm) is far smaller than the van der Waals diameter of He atoms (0.28 nm) [11]. Any leakage of gas, therefore, can be considered as a measure of existence of defect-originated pores or other parasitic pathways across the graphene layer or through the membrane fixture. Bunch et al. [11] have measured a He leak rate of 10⁵-10⁶ atom/s having a 4x10⁻⁹ m² freestanding single crystalline graphene (at ~1 bar Δp) attributable to the diffusion inside the supporting SiO₂. Calculating an artificial graphene membrane permeance it corresponds to 4.2x10⁻¹¹ mol/Pa/s/m². In the present case the freestanding graphene area (**Figure 2-6**) is about two to three orders of magnitude larger than that of the reference result [11]. Thus one can expect a maximum leak rate of 10⁸ atom/s through a defect free, freestanding graphene membrane after the transfer process.
Figure 2-7 Schematic of H₂ leakage gas setup. Pressurized H₂ gas with controlled flow rate is fed to the membrane mounted in the membrane holder. Differential pressure is monitored by the pressure gauge and adjusted with the retentate mass flow controller (MFC). Permeate side of the membrane is flushed with Ar, which is adjusted by the MFC to carry any potential leaking H₂ gas towards the mass spectroscope (MS). Total permeate flow is monitored by a mass flow meter after the membrane fixture.

After identifying a defect free double layer graphene membrane with a total area of $3.2 \times 10^{-9}$ m² by careful investigation using SEM, the area is isolated on the membrane support frame and a H₂ leak detection measurement is performed. H₂ gas upstream of the graphene membrane is pressurized up to 800 mbar (Figure 2-7). At the membrane permeate side an Ar (99.995% purity) gas flow with 10 sccm is used as a sweep gas to carry any permeating gas species to the mass spectroscope used. Over the course of the measurement the relative H₂ concentration, $c_{\text{H}_2}$, detected on the permeate side drops from usual ambient values to the noise level of the mass spectroscope (Cirrus 2, MKS Instruments) $c_{\text{H}_2} = 1.5 \times 10^{-7}$. The upper bound for the H₂ leak rate, $Q_{\text{leak}}$, is determined to be
\[ Q_{\text{leak}} = c_{\text{H}_2} Q_{\text{Ar}} \approx 3.3 \times 10^{11} \text{ atom/s} \text{ or } 2.8 \times 10^{-9} \text{ mol/Pa/s/m}^2 \text{ in the permeance unit, which is about two to three order-of-magnitude higher than expected from a prefect crystalline graphene layer} \[11\]. However, this upper bound value of the leakage permeance is still 5-6 order-of-magnitude smaller than the expected \( \text{N}_2 \) transport rates through artificially formed pores (at \( \kappa \approx 3\% \) areal porosity in the range of \( 10^{16} \text{-} 10^{17} \text{ molecule/s} \) depending on membrane samples and \( \Delta p \)). \[2\] Therefore, the mass-transport contribution through double layer graphene by inherent sub-nanometer atomic defects of CVD-grown graphene is negligible.

### 2.2 Patterning of freestanding graphene

In order to allow mass transfer through the leak tight freestanding graphene, artificial pores need to be created into the graphene to serve as controlled transport paths for media. A versatile high precision method for the pore manufacturing is required which allows the controlled creation of a known number of pores with defined size. A few methods for patterning freestanding graphene have been introduced. First reported methods have used transmission electron microscopy where pores \[23\] and vacancies \[24\] can

\[ ^2 \text{Molecule permeation in the effusion limit:} \]
\[
N = \Delta p \times N_A \times (2 \pi M R T)^{1/2} \times A_m \times \kappa \\
= 20000 \times 6.02 \times 10^{23} \times (2 \pi \times 0.028 \times 8.314 \times 298)^{1/2} \\
\times 8.0 \times 10^{-11} \times 0.03 \text{ molecules/s} \\
= 1.3 \times 10^{16} \text{ molecules/s} \\
\text{with membrane area } A_m, \text{ porosity } \kappa, \text{ molecular weight } M, \text{ and pressure } \Delta p. \]
be created with very high precision, though these methods are limited in scale due to the immense irradiation dose required. Large-scale patterning of nanometer-sized features in graphene has been enabled by block-copolymer self-assembly [34] as well as by strain assisted metal intercalcation [76], both being limited to feature sizes of minimal ~20 nm and do not allow to tune pore sizes in a larger size range. For controlled graphene modification and advanced patterning focused ion beam (FIB) technology has been used to pattern support graphene [77-80] as well as freestanding graphene layers with nanoscale pores [31], nanoribbons [32] or other geometries [33]. All of these studies support the applicability of the technology for pore creation into freestanding graphene, but these studies lack understanding of the ion graphene interaction and, therefore, do not exploit the manufacturing capability of FIB technology to the full extend. In the subsequent section a detailed study of ion graphene interaction is presented which enables the fabrication of large scale graphene membranes with pores sizes ranging from 1000 nm down to 5 nm.

2.2.1 Ion / freestanding graphene interaction

The interaction of high energetic ions with a 2D target can be expected to widely differ from sputtering of bulk material where cascading events of the target atom vibration cause the material removal upon ion exposure [81].
Despite a very recent investigation describing the amorphization of graphene by Ga\(^+\) ion bombardment [82], missing is a combined experimental and theoretical investigation about the fate of freestanding graphene layers subject to ion bombardment of different ion species and energies. Currently, most of the insights are obtained by a few theoretical studies using Monte Carlo simulations to elucidate the effect of energetic ions on graphene [17, 83].

2.2.1.1 Experimental procedure of ion irradiation

The freestanding graphene layers (Figure 2-8 a) were irradiated with Ga\(^+\) or He\(^+\) ions at different acceleration voltages via FIB. Ga\(^+\) ion bombardment is performed inside vacuum chamber (\(\sim 7 \times 10^{-5}\) Pa) of a dual beam Helios 450 FIB (FEI) having a state of the art liquid metal ion gun with which the ions are accelerated at 5-30 keV at probe currents \(I_{Ga_p}\) ranging from 1.1 pA to 40 pA. For the He\(^+\) ion irradiation a single beam He\(^+\) ion microscope (Zeiss Orion) is used, which utilizes an ultrasharp tungsten tip trimer consisting of 3 atoms arranged in a triangle to ionize the He gas source. The HIM is equipped with a pattern generator (Raith Elphy MultiBeam) and operated at 10-30 keV using probe currents \(I_{He_p}\) of 5-17.5 pA at a chamber pressure of \(\sim 7 \times 10^{-5}\) Pa.
Figure 2-8 a) Freestanding graphene sample on SiNx frame subject to focused ion bombardment using He⁺ or Ga⁺ ions. b) Atomic level schematic of an ion bombardment process of freestanding monolayer graphene in FIB systems. A red dashed box illustrates a unit cell of graphene.

The probe currents used on the He⁺ FIB are significantly higher than the standard imaging conditions and previously reported patterning currents of 0.5-1 pA [79]. However, the high probe currents were found to be necessary for large-scale graphene patterning because they enable to pattern 10⁶ pores of sub-5 nm in size within 2 hours. For low currents the dose required for the patterning increases substantially (by factor of 10-50). This increase can be attributed to the deposition of amorphous carbon material around the patterned area, which prevents the removal of carbon atoms from the graphene lattice (Figure 2-9 a).
Figure 2-9 He⁺ ion micrograph of etched pores in HIM. a) Probe current of 1.4 pA and dwell times from 100 ms to 4600 ms (top to bottom row in steps of 500 ms). Strong deposition of material is visible around each patterned feature. Only beam-irradiation dwell times higher than 1600 ms show pores clearly visible in the micrograph. b) Probe current of 10.5 pA with a dwell time of 15 ms leads to pore formation with no deposition in the vicinity of it.

Ion beam induced deposition is a widely reported phenomenon [84]. Gas molecules (e.g., volatile carbon species in the vacuum chamber) can adsorb on the target substrate, or the target substrate could already been contaminated by various adsorbates. When incident ions are inelastically scattered and create secondary electrons, these electrons can collide with and dissociate the adsorbates to leave nonvolatile compounds on the surface. This chemical reaction is limited by both the supply of adsorbing molecules as well as the reaction energy provided by the incoming ion flux. At low ion fluxes the contamination molecule mobility is high enough to move to the reaction site and build up material. In this case the reaction is
limited by the energy input. This mechanism can be responsible for the deposition around the defined pattern (Figure 2-9 a) and the very large dose values necessary to etch a hole onto graphene. At high ion fluxes the surface diffusion of the adsorbates to the patterning site is relatively slow, shifting the reaction toward a diffusion-limited regime. Therefore it is crucial to use high current patterning on the HIM to create hole-array patterns at only 2% of the dose hitherto used (Figure 2-9 b).

On both Ga⁺ and He⁺ ion FIB tools the total exposed ion dose is controlled by the exposure dwell time, \( t_d \), of each pixel ranging from 100 ns to 8 ms. This information helps calculate the total number of ions, \( N_{ion} \), directed towards the graphene by \( N_{ion} = \frac{I_{ion \, p}}{e^t \, t_d} \) for each pattern and the total ion dose \( \sigma_{ion} = \frac{N_{ion}}{A_p} \).

2.2.1.2 Measurement of ion sputter yield on freestanding graphene

2.2.1.2.1 Monolayer sputtering
For initial characterization and simplified modeling, the ion sputter yield of monolayer graphene is determined first. Simply skipping abovementioned graphene transfer steps 4) to 6) yields high quality monolayer graphene (Figure 2-10 a). The overall transfer is not as high as for double layer transfer but sufficient enough for the investigation of graphene ion sputter yield. As the double layer graphene the monolayer graphene is very
clean, showing only very few graphene wrinkles and sparse contamination sites. These samples transferred to the FIB chamber were irradiated with energetic ions. When exposed to He\(^+\) irradiation, graphene is known to be resistant to a high dose of ions bombarding the monolayer.

**Figure 2-10** a) SEM micrograph of freestanding clean monolayer CVD graphene after transfer on porous SiN\(_x\) substrate. Brighter lines show graphene wrinkles (double layer) and small bright dots are sparse contaminants of the graphene. b) He\(^+\) ion micrograph of patterned free standing graphene (dark circle was pre-exposed with \(\sim 5.6\times10^{21} \text{ He}^+ \text{ m}^{-2}\)) c) and d) show the same graphene membrane after the additional exposure of \(7.0\times10^{18} \text{ m}^{-2}\) and \(1.4\times10^{19} \text{ m}^{-2}\) He\(^+\) ions over the entire frame, respectively.

One can take images of freestanding monolayer graphene repeatedly at a standard imaging dose (\(\sigma_{\text{He}^+} \approx 10^{18} \text{ m}^{-2}\)) of helium ion microscope (HIM) without significant damage to samples (**Figure 2-10** b to d), in agreement with previous findings [85, 86]. However, in the same experiment on a FIB
system using Ga$^+$ ions, the freestanding graphene quickly deteriorates and is etched away. These findings indicate that the interaction between Ga$^+$ and carbon in the graphene lattice is more destructive than that between He$^+$ and graphene; namely, a Ga$^+$ ion has higher probability to chop off carbon atoms from the 2D lattice than the a He$^+$ ion does. To precisely quantify the difference in C atom removal one can define a sputter yield $\gamma$, which expresses the average removal rate of carbon for graphene pattern formation. The following experiment can be used to determine the sputter yield. Ions are accelerated toward freestanding graphene to form circular pattern arrays with increasing areal doses $\sigma_{\text{ion}}$. On each circular pattern the energetic ions are evenly distributed within the 200 nm diameter (nominal area $A_n = 0.0314$ µm$^2$). After the patterning SEM micrographs of the patterned arrays are acquired and the resulting pattern area $A_p$ is measured using an image analysis program (ImageJ). The lower bound number of removed carbon atoms $N_C = \sigma_C A_p N$ can be easily calculated by using the areal density of carbon in graphene $\sigma_C = 38.1 \times 10^{18}$ m$^{-2}$ and the number of graphene layers, $N$. The sputter yield is defined as $\gamma_{\text{ion}} = N_C / N_{\text{ion}}$, where $N_{\text{ion}} = \sigma_{\text{ion}} A_n$ is the total number of ions irradiating the graphene layer.
Figure 2-11 Energy dependence of graphene sputtering on monolayer. a) and b) Energy dependent, monolayer graphene sputter yields. Red dots are measured sputter yield for Ga$^+$ and He$^+$ ions, with error bars indicating the standard deviation. Each data point is calculated as a mean of more than 20 independent measurements.

The average number of vacancies produced per ion bombardment, or a sputter yield $\gamma$, indeed shows a significantly higher values for Ga$^+$ (Figure 2-11 a). For instance, the sputter yield of freestanding graphene upon 30-keV Ga$^+$ bombardment is about 47% ($\gamma_{Ga^+} \approx 47\%$), which confirms qualitative findings of previous reports for Ga$^+$-based graphene sputtering [33, 87]. This corresponds to a total ion dose necessary to create a pattern in monolayer graphene by 30-keV Ga$^+$ ions of $\sim 8.1 \times 10^{19}$ m$^{-2}$ (Figure 2-12 a) which is very much in line with a recent report of $9.5 \times 10^{19}$ m$^{-2}$ for Ga$^+$ at 35-keV [82]. Furthermore, the sputter yield $\gamma$ of freestanding monolayer graphene showed clear dependency on the energy of the incident particles.
For Ga\textsuperscript{+} the reduction of the accelerating voltage from 30 kV to 5 kV increases the sputter yield from $\gamma_{Ga^+} \approx 47\%$ to 81\% (Figure 2-11 a) in line with predictions of Monte Carlo molecular dynamics simulations [17, 83]. Interestingly, these $\gamma_{Ga^+}$ values of monolayer graphene are significantly smaller than those of its 3D counterpart: reportedly 120-270\% depending on carbon allotropes [87, 88].

For He\textsuperscript{+} FIB the sputtering yield is about two-order-of-magnitude lower ($\gamma_{He^+} \approx 0.7\%$) than for Ga\textsuperscript{+} FIB (Figure 2-11 b). Therefore, pattern generation with 30-keV He\textsuperscript{+} ions requires significantly higher dose of $\sim5.7 \times 10^{21} \text{ m}^{-2}$ (Figure 2-11 b). Reaffirming the mechanism of HIM imaging [85, 86], this finding sheds a renewed light on the possibility that, not only to proton [16, 89], graphene can be nearly transparent to energetic He\textsuperscript{+} ions as shown theoretically [17]. For example, at a kinetic energy of 30 keV approximately $\sim99\%$ of He\textsuperscript{+} ions can penetrate through the monolayer graphene with statistically sputtering no carbon atom from the lattice, reminiscent of the photon and proton transmission. The material transparency of graphene is slightly reduced at lower He\textsuperscript{+} acceleration voltages ($\gamma_{He^+, 10 \text{keV}} \approx 2.4\%$, (Figure 2-11 b)) yet only to $\sim97.6\%$. Both observations of the material transmission of H\textsuperscript{+} and He\textsuperscript{+} through the defect-free graphene lattice offers a new insight on the ability of graphene as the barrier material. In the case of increased particle energy or commensurable particle size, graphene crystals in their freestanding state (let alone crystallographic defects) indeed allow the permeation of small atoms through the lattice.
2.2.1.2.2 Multilayer graphene sputtering

For multilayer graphene sample an increase of the sputter yield is observed (Figure 2-12). As a result, the ion dose necessary to etch a pattern into freestanding multilayer graphene does not linearly increase with the number of layers e.g. a 4-layer graphene sample requires only \(1.2 \times 10^{20}\) m\(^{-2}\) Ga\(^+\) ions at 30 keV which roughly twice the dose required for a monolayer graphene (Figure 2-12 a). For He\(^+\) ions the effect is less pronounced where 3 times the dose of monolayer patterning is required to create a pattern in a 4-layer graphene sample (Figure 2-12 b).

![Figure 2-12 Graphene layer number dependent graphene sputtering. a) and b) Layer number dependent sputter yield and ion dose necessary to pattern graphene using 30 keV Ga\(^+\) and He\(^+\) ions, respectively. Red dots show sputter yield for 1-4 freestanding layers of graphene, and error bars indicate the standard deviation. Black crosses indicate the expected sputter yield assuming the layer number independent probability of the carbon atom removal upon collision. Blue circles show the experimentally measured ion dose for pattern formation.](image-url)
In general results for freestanding multilayer graphene etching are approaching the sputter yield reported for bulk carbon allotropes [87, 88]. In sputtering bulk materials the so-called primary event – the collision of the incident ion with the target atom – does not play a crucial role in target atom removal. Though, the secondary sputtering events – the collisional cascade inside the target material leading to a momentum inversion – contribute mainly to the bulk sputter yield. The events responsible for the target atom removal in the 3D materials are the following: first, cascade of vibration energy into the target material could excite neighboring atoms in the bulk lattice; and second, these neighboring atoms recoil causing a local inversion of the momentum and could escape the bulk if they were close to the surface and ended up gaining sufficient energy. These events could often take place when the bulk material thicknesses are ~20 nm and ~5 nm for Ga\(^+\) and He\(^+\), respectively. However, in the present case even the multilayer graphene samples are comparably thin having maximum quadruple layers. Therefore, one can intuitively surmise that only the probability of ions hitting a carbon atom while passing through the multiple graphene layers should increase with number of layers. This case can be approximated by modeling the collision with each graphene layer as independent stochastic event with constant probability of collision in each layer (assuming that the kinetic energy of a scattered ion remains intact upon collision in a layer). On the other hand, the removal of carbon atoms in one layer would lower the probability that newly incident ions interact with atoms of the same layer since the number of layers at this particular spot is reduced
by one. Therefore, the average expected sputter yield $\gamma_N$ for an $N$-layer-thick sample equals to $\gamma_N = \gamma_{\text{ion}} (N + 1) / 2$. Using this assumption, one can calculate an increase in sputter yields with layer number for both He\(^+\) and Ga\(^+\) FIB processes (Figure 2-12). For freestanding multilayer graphene, the experimentally observed sputter yield for Ga\(^+\) ions increases from $\sim 0.5$ for monolayer graphene to $\sim 1.3$ for quadruple layer samples matching nicely the theoretically prediction(Figure 2-12 a). The consistency between experiment and theoretical prediction shows that interestingly the overall escape of the C atom from the multilayer graphene samples is not inhibited. C atom removal in multilayer graphene could follow the route of a cascading collision of equal collision partners. Once a C atom in the first layers is hit it recoils and collides with a C atom in the lower layers from where the cascade continues until a C atom in the last graphene layer is removed by forward sputtering. Note unlike 3D bulk sputtering the atom removal does not require the inversion of the momentum but the cascade can transmit the momentum directly to the atoms in the layer beneath or even more complicated effects like catalytic etching in the presence of an underlying graphene layer [90] may cause this counterintuitive finding. For He\(^+\) ion the observed increase in sputter yield is less than the model prediction (Figure 2-12 b) possibly attributed to a less efficient vibrational cascade since the average transferred energy to the target atom is significantly lower than in the case of Ga\(^+\) ion sputtering (Figure 2-13 b). Both results show that in contrast to monolayer graphene ion interaction
the presence of additional graphene layers require more extensive modeling attempts.

### 2.2.1.3 Theoretical modeling of ion graphene interaction

The interaction between energetic ions and carbon atoms in the graphene lattice can be elucidated further by considering the classic binary collision theory [81]. This theory assumes an interception of two particle trajectories where the energetic ion at velocity $v_0$ is colliding with a carbon atom at velocity $v_c$ (Figure 2-13 a). Depending on the minimum projected distance between two particle trajectories, $p$, the nuclei start to repel each other to avoid the overlap of the coulombic potential of the nuclei. The scatter angle $\theta(p)$ can be calculated using eq. (2.2):

$$\theta(p) = \pi - 2 \int_{r_{\text{min}}}^{\infty} r^{-2} \left( 1 - \frac{V(r)}{E_C} - \frac{p^2}{r^2} \right)^{-1/2} dr$$

where $E_C = E_0 M_2 / (M_1 + M_2)$ denotes the collision energy with $E_0$ being the acceleration energy of the ion, $r$ the ion-to-atom center-of-mass distance, and $V(r)$ the Ziegler-Biersack-Littmark interatomic potential between ion and atom (Figure 2-13 a). A good approximation for the interatomic potential $V(r) = \frac{Z_1 Z_2 e^2}{r} \Phi(\gamma_r)$ is given by a repulsive coulombic
potential created by the charges carried by the two nuclei which is corrected by a universal fit function $\Phi(r/a) = \sum_{i=0}^{4} C_i e^{k_i r/a}$ accounting for the screening effects of the electron cloud. The fit function depends on the distance of the scattering particles, $r$, the screening length, $a = 0.8854 a_0 \left( Z_1^{0.23} + Z_2^{0.23} \right)^{-1}$, calculated by use of the Bohr radius, $a_0$, the two atomic charges $Z_1$ and $Z_2$ and has 8 parameters $C_1 = 0.1818$, $C_2 = 0.5099$, $C_3 = 0.2802$, $C_4 = 0.02811$ and $k_1 = -3.2$, $k_2 = -0.9423$, $k_3 = -0.4029$, $k_4 = -0.2016$ [81]. It is valid for collisions with kinetic energies higher than a few 100 eV, where interatomic interactions are governed primarily by repulsive nuclei such that the Born-Oppenheimer approximation can be omitted [91]. For each scattering angle, $\theta$, one can now calculate the energy transferred, $T$, from the ion to the atom using eq. (2.3) which yields the transferred energy $T$ depending on the collision parameter $p$ as plotted (Figure 2-13 b).

$$T(E_C, p) = 4 E_C \frac{M_1}{M_1 + M_2} \sin\left( \theta(p) / 2 \right)$$

(2.3)

A carbon atom is removed from the graphene lattice if the transferred energy $T(E_C, p)$ exceeds the lattice displacement energy, $E_L$. Previously reported $E_L$ values for graphene range from experimentally determined 22 eV [90] to density-functional-theory predicted 23 eV [92, 93].
Figure 2-13  a) Binary collision model illustrated in a center-of-mass reference frame moving at a speed of $v_c$, where collision parameters $p$ and $\theta$ are the shortest projected distance and the scattering angle between two colliding particles, respectively (following [81]). b) Calculated transferred energy $T$ from incoming ion with 8 keV (dashed line), 15 keV (dotted line) and 30 keV (solid line) to C atom in graphene lattice. Results for He$^+$ ion are plotted in red for Ga$^+$ ion in blue. c) Schematic of an ion bombardment process of free-standing monolayer graphene in FIB systems. A red dashed box illustrates a unit cell of graphene. d) A contour of superimposed transferred energy $T$ from 15-keV Ga$^+$ to carbon atoms in a graphene unit cell, calculated from the binary collision model. Red shaded area depicts area of double vacancy production.

This energy cut-off is used to calculate a theoretical sputter yield for ion bombardment of graphene. Defining a graphene unit cell with area $A_U$ (Figure 2-13 c) one can superimpose the transferred energy landscape around each carbon atom and calculate the area fraction of $2A_C / A_U$ in which $2A_C$ (yellow area Figure 2-13 d) is the scattering cross section of the both C atoms in the unit cell. Within this area $2A_C$ the transferred energy
$T(E_C, p) \geq E_L$ from the incident ion to the carbon atom exceeds $E_L$ and therefore an ion hitting in this area would remove the C atom from the graphene lattice. Therefore, the area fraction $2A_C / A_U$ can be identified with the single vacancy sputter yield.

$$\gamma_s = \frac{2A_C}{A_U}$$  \hspace{1cm} (2.4)

Moreover, an impact of an ion could produce a double vacancy, if the ion hits the unit cell in the area fraction, $\gamma_d$, where the transferred energy to dual carbon atoms is higher than $E_L$ (red area Figure 2-13 d) The upper bound of the theoretical sputter yield, $\gamma_U$, of a defect-free, relaxed graphene lattice can be calculated by $\gamma_U = \gamma_s + 2\gamma_d$. Therefore, $\gamma_U$ corresponds to the expectation value out of the discrete probability distribution of the following three events: ion passing without sputtering; producing a single vacancy defect; and producing a double vacancy defect. The calculated upper bound corresponds therefore to the chance of C atom removal from a pristine monolayer graphene target and is necessarily higher than the experimental sputter yield which is an average removal rate over the course of graphene etching (Figure 2-14). Continued exposure to ions removes carbon atoms from the lattice, leading to lowered probability of bombarding carbon atoms by the next ion incidence, whose effect is manifested by a decrease in the sputter yield. Therefore, it is reasonable to define a lower bound of the theoretical sputter yield, $\gamma_L$, assuming an average probability
of hitting a carbon atom accounting for already created vacancies through which ions may just pass the graphene lattice with no collision.

![Figure 2-14 Model comparison to experimental measured sputter yield. a) and b) Energy dependent, monolayer graphene sputter yields. Lower and upper bound of theoretical sputter yield for Ga$^+$ and He$^+$ using binary collision model dashed black line and solid black line, respectively. Red dots are measured sputter yield for Ga$^+$ and He$^+$ ions, with error bars indicating the standard deviation.](image)

The lower bound of the sputter yield can be derived by the following consideration. Initially the graphene sheet contains total number of carbon atoms, $n_C$. Each carbon atom has a scattering cross section area of $A_C$ defined by the area in which the transferred energy of the ion hitting carbon atoms exceeds the lattice displacement energy $E_L$ (yellow area Figure 2-13 d). The total scattering-cross-section area occupied by the carbon atoms meeting the sputtering condition equals to $n_C A_C$. Initially the probability of hitting a carbon atom, $p_1$, equals to the ratio of the total scattering-cross-section area to the total defined pattern area, $A_t$ (the 200 nm diameter hole ...)
array), yielding $p_1 = \frac{n_c A_C}{A_t}$. Once sputtering occurs the number of carbon atoms is reduced by one, giving a new probability, $P_2 = \frac{(n_c - 1) A_C}{A_t}$, to the next carbon atom to be removed from the 2D lattice. By continuing this argument all the way to the last of carbon atoms in the lattice one yields $p_{nc} = A_c / A_t$. Therefore, an average sputtering probability can be calculated by (2.5).

$$\bar{p} = \frac{n_c A_C / A_t + (n_c - 1) A_C / A_t + (n_c - 2) A_C / A_t + \ldots}{n_c}$$

$$\ldots + \frac{(n_c - n_c + 1) A_C / A_t}{n_c}$$

(2.5)

$$= \frac{1}{n_c} \sum_{i=1}^{n_c} \frac{A_C}{A_t}$$

Now noticing that $A_C / A_t$ is constant and that $A_t$ can be expressed in number of initial carbon atoms $n_C$ and unit cell area $A_u$ with $A_t = 0.5 n_c A_U$, and using eq. (2.4) one can rewrite the area fraction in terms of the single vacancy sputter yield $\gamma_S$.

$$\frac{A_C}{A_t} = 2 \frac{A_C}{n_c A_U} = \frac{\gamma_S}{n_c}$$

(2.6)

Therefore the mean probability of C atom removal over the course of the sputtering process (eq. (2.5)) can be rewritten using (2.6) which yields
The average sputtering probability can be regarded as the lower bound sputter yield of the graphene target. Simplifying the summation over $i$ and approximating $\gamma_S \approx \gamma_U$ one eventually yields \((2.8)\) for theoretical lower bound of the sputter yield where $n_C$ denotes the total number of C atoms in the pattern area.

\[
\gamma_L = \frac{\gamma_U (n_C + 1)}{2n_C}
\]

\((2.8)\)

In the experimental condition the generated patterns are usually very large ($n_c \gg 1$). For large number of C atoms $n_C$ eq. \((2.8)\) can be simplified to

\[
\gamma_L = \frac{\gamma_U}{2}
\]

\((2.9)\)

These two bounds set for the sputter yield can bracket the presented measured values greatly (Figure 2-14), suggesting that the measured graphene removal sputter yield indeed corresponds to the clean monolayer graphene sputtering. The deviation of the measured yield from the upper bound is attributed to the gradual C atom removal from the target over the course of the ion exposure. In contrast the theoretical calculation of the lower bound does not include secondary C atom removal events such as potential removal of larger amorphous C atom agglomerates in the final
phase of graphene etching. Furthermore, the excellent agreement in the studied energy range substantiates the validity of this collision theory in predicting sputter yields of graphene at various FIB conditions as well as in drawing a mechanistic explanation of the obtained $\gamma$ values.

Since the Ga$^+$ ions carry more charges in the nucleus than He$^+$, $V(r)$ with a carbon atom can be stronger and extend wider in space. From eq. 2.2) and (2.3), this strongly repelling interatomic potential for Ga$^+$ / C atom interaction leads to large scattering angles close to the backscatter condition, $\theta = \pi$, likely transferring a substantial amount of energy to an atom in the target lattice to chop it off as can be seen by the right shift of the transferred energy $T$ compared to He$^+$ (Figure 2-13 b). Besides capturing the different aspects of He$^+$ and Ga$^+$ sputtering, the proposed model provides an accurate description about decreasing sputter yield of monolayer graphene with increasing kinetic energy of incident energetic ions (Figure 2-14), in good agreement with previous predictions [17, 83]. At lower kinetic energies the approaching ions get slower, interaction time prolongs, and the resultant scattering-angle distribution would become wider. Specifically, the interaction cross section extends wider in space, and since the average kinetic energy of the ions is still at least two-order-of-magnitude higher than $E_L$, the bombarded atom in the lattice could possibly be removed upon collision. In addition, the results indicate that the repulsive interaction of the defect-free monolayer graphene becomes very strong when the energy of the colliding particle is comparable to or lower than the
lattice displacement energy, corroborating the barrier property of mono-
layer graphene previously reported [11]. The good model fit, indicates that
indeed the interactions between the ion and the graphene can be modeled
as binary collisions where single C atoms are removed from the lattice when
hit by the incoming ion. Therefore, previous theoretical findings are con-
firmed which show that in the energy range studied the ions create merely
single or double vacancy defects [83]. Only significantly lower energies
<200 eV or >50 keV would lead to other effects like C atom substitution or
ion implantation [94] and graphene amorphization events in the vicinity of
the impact position [83], respectively.

2.2.1.4 Investigation of graphene evolution subject to
ion bombardment

Vacancy generation mechanism in graphene under energetic ion bombardi-
ment can be further elucidated by Raman spectroscopic monitoring of the
evolution of pristine freestanding graphene subject to various ion irradiation
doses. 2D Raman maps are used to acquire a representative Raman
signal from the pristine and irradiated graphene (Figure 2-15 a). Similar to
the excellent Raman spectrum of the double layer graphene shown above
(Figure 2-6 a), the spectrum of pristine monolayer graphene exhibits high
quality monolayer with a sharp G peak of FWHM 23.5 cm\(^{-1}\) at \(~1587\) cm\(^{-1}\)
and a comparably small D peak (Figure 2-15 b). A noticeable difference to
the double layer graphene is the sharp G' peak around $\sim 2679$ cm$^{-1}$ of twice the intensity of the G peak (Figure 2-15 b), which is indicative of defect-free monolayer graphene [75]. Since the Raman spectrum allows precise characterization of the graphene quality, the evolution of graphene subject to ion bombardment can be investigated. In particular, the intensity ratio of the D and G peaks, $I(D)/I(G)$, has been shown to follow a characteristic dependency on the defect density [95]. Using the experimentally determined $\gamma$ and the areal dose, $\sigma$, of applied ions one can calculate the average defect distance, $L_D = (\gamma_{ion} \sigma_{ion})^{-1/2}$. The obtained result for the $I(D)/I(G)$ with respect to $L_D$ for the He$^+$ FIB nicely matches an empirical equation previously reported [95] about low energy Ar$^+$ bombardment (Figure 2-15 c). Indeed, this agreement corroborates the finding that a very high portion (>99% at 30 keV) of He$^+$ is passing through graphene without generating any lattice vacancy and it is only the rare collision events that produce a single vacancy defect on graphene.
Figure 2-15 Raman analysis of He$^+$ ion irradiated graphene. a) 2D Raman map of I(D)/I(G) on freestanding double layer graphene with different exposure dose of He$^+$ ion dose ranging from 0, 2.5, 3.8, 5.0, 6.3, 9.4, 12.5, 31.3 x10$^{18}$ m$^{-2}$. b) Raman spectra of irradiated monolayer graphene with ion doses of 0, 1.25, 2.5, 5, 12.5, 56, 125 x10$^{18}$ He$^+$/m$^2$ (from bottom to top). c) Measured I(D)/I(G) ratio versus average defect distance $L_D$ for monolayer graphene (blue triangle) and double layer graphene (red circle) as compared with calculated empirical function (solid black line) from reference [95]. d) I(D)/I(G) vs I(D$'$)/I(G) for monolayer graphene exposed to low He$^+$ ion doses (1.25-62.5x10$^{18}$ m$^{-2}$), showing linear proportionality (solid black line).
The non-monotonic relation of $I(D)/I(G)$ over the defect distance $L_D$ for freestanding graphene stands in contrast to the reported Tuinstra-Koenig relation reported for graphite [96]. Unlike bulk graphite where ion irradiation renders the surface to sp$^3$-bonded amorphous carbon yielding a monatomic increase of $I(D)/I(G)$, ion irradiation of graphene exhibits three distinct regimes of etching [95]. In the first regime (large $L_D$), single vacancies are produced which lead to increased lattice disorder and a strong D peak. The total number of sp$^2$ bonds remains nearly constant (G peak), yielding an increase of the $I(D)/I(G)$ ratio (Figure 2-15 c, I). In the second regime ($L_D < \sim 4$ nm), the continuous removal of carbon atoms from the graphene layer destroys the hexagonal lattice, and the radial breathing (D peak) of benzene rings decreases in the abundance of intact benzene rings. Still, the layer comprises sp$^2$-hybridized amorphous carbon chains accounting for the G peak. In this regime $I(D)/I(G)$ is getting smaller again (Figure 2-15 c, II). In the third regime ($L_D < \sim 1$ nm), the lose network of sp$^2$-bonded carbon atoms is removed without significant changes in the bonding structure therefore the $I(D)/I(G)$ remains constant around the unity with total peak intensities vanishing slowly until nearly all the atoms are removed (Figure 2-15 c, III).

The creation of individual vacancy defects in the regime I during the He$^+$ FIB of graphene can be supported by spectral decomposition of Raman spectra. The evolution of D ($\sim 1340$ cm$^{-1}$) versus D' peaks ($\sim 1620$ cm$^{-1}$) for low $\sigma_{ion}$ follows a linear proportionality of $I(D)/I(D') \approx 7$ (Figure 2-15 d) in
great agreement with a previous report [97]. This spectral behavior clearly differs from the other defect creation mechanisms such as sp³ bond creation or grain boundaries, which lead to $I(\text{D})/I(\text{D'}) \approx 13$ and $I(\text{D})/I(\text{D'}) \approx 3.5$, respectively [97, 98]. Therefore, albeit the low collision probability, irradiation of a low dose of energetic He⁺ ions onto freestanding graphene could instigate a single ion graphene interaction facilitating single-vacancy-type defect generation in the lattice, preferentially. Furthermore, the resultant $I(\text{D})/I(\text{D'})$ evolution shows clearly that the Raman spectrum does not arise from sp³ amorphous carbon deposit or contamination. Therefore, the precise control of $\sigma_{\text{He}^+}$ at a given He⁺ energy promises to create array patterns of vacancy defects.

The evolution of the $I(\text{D})/I(\text{G})$ ratio of double layer graphene follows the same trend as the monolayer graphene (solid red circles, Figure 2-15 e). When calculating the average distance $L_D$ in which defects are created by considering the area of both graphene layers $L_D = N^{1/2} (\gamma_{\text{ion}} \sigma_{\text{ion}})^{-1/2}$ (with $N = 2$), the results for monolayer and double layer graphene coincide each other, which corresponds to the case where the same amount of ions directed toward the graphene is distributed to twice the amount of lattice atoms. Since the evolution of the $I(\text{D})/I(\text{G})$ ratio is the same as on monolayer, it indicates that the vacancy formation by energetic He⁺ ions on double layer graphene is independent of the presence of a second layer. Therefore, each He⁺ ion hitting the graphene either sputters one of the graphene layers or penetrates without creating a vacancy.
2.2.2 Graphene puncturing

The detailed theoretical and experimental analyses of the impact interaction between energetic ions and graphene allow to establish an efficient graphene patterning process using FIB technology with which to create freestanding graphene membranes. In general the pattern formation will follow the route of gradual vacancy formation at the initial stage ensued by defect agglomeration that ends up amorphizing the graphene in the ion-beam irradiated area as recently proposed by TEM study of irradiated graphene [82]. At the last step of patterning the amorphous yet still sp²-hybridized carbon layer is etched away, and the pattern is formed into the freestanding graphene. For patterning graphene double layers, for instance, total ion doses of $1.0 \times 10^{20}$ m$^{-2}$ (Ga$^+$) and $9.6 \times 10^{21}$ m$^{-2}$ (He$^+$) are irradiated approximately (Figure 2-12).

2.2.2.1 Pore formation in freestanding graphene

Depending on the desired pore size, two different pattern generation schemes are introduced. Larger pores above 40 nm in diameter are created by distributing the ions evenly on the nominal pore area (Figure 2-16 a). Since the sputter yield is significantly (100 times) higher for Ga$^+$ ions, only this FIB system is used to create pore for these pore sizes to save processing time. One way of exposing larger areas is to scan a focused ion beam over
the substrate, thereby irradiating each pixel within the area sequentially. The uniform distribution of ions in the desired area is achieved by defining a spiraling path of the ion exposure point in the discretized domain (Figure 2-16 b).

![Figure 2-16](image)

**Figure 2-16** Large pore pattern formation on freestanding graphene. a) SEM micrograph of 400 nm pore membrane. b) Pattern formation by ion irradiation on graphene. SEM micrograph of closeup onto the 400-nm-wide pore with a sketch of the ion exposure pathway (red overlay).

The pore size is defined by the exposure pathway and is relatively insensitive to the ion dose used, since once the pattern is created the additional ions will just pass through the created graphene pore. Using a probe current of 82 pA of Ga⁺ ions and a pixel spacing of 12 nm, each pixel has an exposure dwell time of 30 μs. Therefore, the dose required to form the
pore equals the above mentioned dose of \( \sim 1.0 \times 10^{20} \text{ Ga}^+ \text{ m}^{-2} \). Using this patterning scheme any pore size down to 40 nm can be easily drilled into the freestanding graphene.

**2.2.2.2 Exploring the FIB pattern size limit in freestanding graphene**

Smaller pores are created by exposing a single pixel per pore on both FIB systems (Figure 2-17). The pore size is strongly depending on the dose applied to the pixel. This effect is caused by the ion beam profile. Even with an excellent focus the spot size of the focused ion beam is not perfectly a point but extends in space. The beam profile can be approximated by a Gaussian curve with a strongly enhanced tail [84]. This in return means that the surrounding area of each pixel will be exposed by ions as well, which eventually leads to graphene etching. As a consequence, the pattern grows when they are overexposed. Due to the ion low but noticeable ion dose in the tail of the focused ion beam, the resulting pore diameter depends on the pore spacing, \( \lambda_p \), the quality of ion beam focus and the achievable probe diameter, which depends on the ion optics of the FIB. In case of the Ga\(^+\) FIB, the smallest probe size of \( \sim 4 \) nm and the best focus is achieved at the smallest possible ion current of 2 pA. In case of the He\(^+\)

\[ \text{Ion dose: } 82 \times 10^{-12} \text{ C/s } \times 30 \times 10^{-6} \text{ s } / (1.6 \times 10^{-19} \text{ C } \times (12 \times 10^{-9} \text{ m})^2 ) = 1 \times 10^{20} \text{ m}^{-2} \]
FIB, the probe size is sub-nanometer even at higher currents up to 20 pA, allowing the creation of much smaller pores in theory.

![Image](image.jpg)

**Figure 2-17** Pattern formation of small pores by ion irradiation on graphene. SEM micrograph of small pore membrane (~16 nm pore) created by single pixel Ga⁺ ion exposure. The gray overlay shows the grid of single pixels (not to scale) and red arrows are exposed highlighting two exposed pixels. To maximize pore density small pores are equally spaced by $\lambda_p$ in each direction (red triangle).

Using this single pixel exposure method at lowest ion doses, the smallest pore-array patterns on graphene perforated by FIB were achieved. The 2D nature of graphene prefers forward sputtering such that each particle removal from the graphene lattice is caused by the particle collision with an incident energetic ion. This idea means that, for a freestanding graphene double layer, one can cut holes with ultimate precision and repeatedly at relatively high rates, enabling an efficient large-scale pattern formation. With $\sim 10^4$ Ga⁺ per pore at 30 keV in a single-pixel exposure experiment, an array of holes smaller than 8 nm (with a mean diameter of 4.8 nm) at the average spacing of $\lambda_p = 50$ nm (**Figure 2-18 a**) could be drilled into double
layer graphene. Reducing the Ga\textsuperscript{+} ion dose to 2500 Ga\textsuperscript{+} per pore and using monolayer graphene there, pore size could be reduced to 3.5 nm (Figure 2-18 e), which is significantly smaller than previously reported results of sub-10-nm pores on graphene [31]. The tight control of the exposed ions does not only allow to pattern at the resolution limit of the Ga FIB system, which is defined by the beam size (~4 nm). The low dose guaranties an exceptional short process time of few μs per pattern, enabling even large scale patterning of graphene for device integration.

Note that these top-down-drilled pore sizes are significantly smaller than sputtering of bulk material could produce. In the 3D sputtering process, an incident ion collides with multiple target atoms to initiate a collision cascade within the target material. Recoiling target atoms can induce a momentum inversion of certain atoms close to the surface, resulting in an escape from the bulk target [81]. These secondary events occur in the vicinity of the incident ion spot, creating a so-called interaction diameter of which reported values are around 20-30 nm [99, 100]. The absence of these effects in purely 2D targets proof to be of great advantage for efficient and small feature size patterning.
Figure 2-18 Pore arrays on graphene perforated via FIB milling. Secondary-electron-detection-mode SEM images of pore arrays having 50-nm-wide a) and 25-nm-wide b) pitch on freestanding double layer graphene perforated by 30-keV Ga\(^+\) at \(~10^4\) per pore a) and by 30-keV He\(^+\) at \(~4.4\times10^5\) per pore b), respectively. Dark contrast indicates pores. The resultant pore-size distributions are 4.8\(\pm\)1.4 nm a) and very narrow 3.3\(\pm\)1.2 nm b). c) Transmission-electron-mode (bright field) SEM image of pores on freestanding monolayer graphene perforated by 30-keV Ga\(^+\) at 2500\(-10^4\) per pore (bottom to top), exhibiting pore sizes from 3.5 to 11.3 nm. d) and e) Transmission-electron-mode (bright field) SEM images of pores on the monolayer graphene perforated by 30-keV He\(^+\) at 3.9-6.2\(\times10^5\) per pore (d), bottom to top) and 2.7\(\times10^5\) He\(^+\) per pore e), showing pore sizes of 4.9-7.1 nm d) and 2.6 and 2.8 nm e), respectively.
For ion exposure of graphene in the HIM one can achieve even smaller feature sizes. Here again the previously reported interaction diameter limit of 5 nm [99] could be overcome, and the exposure of $4.4 \times 10^5$ of 30-keV He$^+$ ions per pixel is sufficient to generate a pore array in free-standing double layer graphene having a mean diameter of 3.4 nm at spacing $\lambda_p = 25$ nm (Figure 2-18 b). Interestingly, smaller pore spacing $\lambda_p$ can be achieved on the He FIB system without disintegrating the membrane during the patterning process. Most likely it is caused by significantly sharper ion distributions in around the focused spot which suppresses the existence of a low dose ions in the vicinity of the exposed pixel and consequently preserves the graphene layer. The effect of total ion dose on the pore size can be observed by exposing a freestanding monolayer graphene with $3.9 \times 10^5$ to $6.2 \times 10^5$ He$^+$ ions (Figure 2-18 d). Despite the single-pixel exposure one can see a pore size increase from 4.9 to 7.1 nm caused by the imperfect spot shape of the irradiating beam. By decreasing the number of He$^+$ hitting the monolayer graphene to $2.7 \times 10^5$ one can produce holes with 2.6-nm-wide diameters (Figure 2-18 e), comparable to pore sizes drilled in graphene using the TEM systems [23, 101]. These results show a significant advancement in graphene patterning via FIB milling in terms of feature size and array dimension, enabled by detailed knowledge of the interaction mechanisms involved and the 2D nature of the target material.
2.2.3 Measurement of pore diameter and total open area in graphene membranes

For a successful analysis of the mass transport properties of the fabricated graphene membranes it is a crucial prerequisite to know the total open membrane area and the membrane pore size. This task is particularly important if the measured volume and mass flow rate across the membrane will be normalized by the membrane area, $A_m$, or the number of pores, $N_p$.

In order to address this issue and reliably measure the membrane pore sizes $d_m$ and the total pore area $A_m$, an image analysis software is used to determine precisely these crucial membrane parameters. A number of SEM micrographs showing the drilled pores are acquired using a secondary electron detector at high resolution. In these gray-value micrographs, the pore area can be identified with the dark regions (Figure 2-19 a) in which no secondary electrons are created upon scanning with the electron beam. Therefore, all pixels in the micrograph with a gray value below a certain threshold (highlighted in red Figure 2-19 b) can be considered as open area.
Figure 2-19 a) SEM micrograph of ~100 nm pore membrane used to determine the pore size distribution. b) Pixel below certain gray values threshold are highlighted in red and used to identify open pores. c) Outline of pores identified by image analysis software (imageJ) which are used to calculated the area \( A_p \) of each pattern.

A particle identification algorithm provided by the image analysis software (imageJ) groups these pixels into larger patterns and the area, \( A_p \), (Figure 2-19 c) of each of the patterns is calculated. The single pattern size, \( d_p \), is approximated by assuming a circular pore shape having the same area as measured \( A_p \) (2.10).

\[
d_p = 2 \sqrt{\frac{A_p}{\pi}}
\]  

(2.10)

Using multiple high resolution SEM micrographs with sufficiently large number of pores one can obtain the pore diameter histogram for each graphene membrane (Figure 2-20). In both cases for large pore membranes
(Figure 2-20 a to e) as well for sub 10 nm (Figure 2-20 h and i) the resulting pore diameter histogram resembles a Gaussian. Therefore, a reliable mean pore diameter, \( d_m \), and a standard deviation, \( \sigma_m \), can be calculated by fitting a normal distribution to the pore diameter.

Since the number of pores patterned, \( N_p \), is precisely defined in the top-down process of FIB pore drilling, a good estimate of the total open area, \( A_m \), of the graphene membrane can easily be calculated (2.11).

\[
A_m = \frac{N_p}{4} \pi d_m^2
\]  

(2.11)

2.3 Overview over fabricated graphene membranes

For the present study, more than 60 graphene membranes were fabricated in total. Their pore sizes are ranging from 1034 nm down to 4.8 nm (Table 2-1). A scanning electron micrograph and a corresponding pore diameter histogram of a graphene membrane in each diameter range is given in Figure 2-20. All these membranes comprise freestanding double layer graphene suspended on 4 \( \mu \)m wide holes in a SiN\(_x\) membrane supported by a 2×2 cm\(^2\) Si chip as described above. The number of pores, \( N_p \), is strongly depending on the membrane pore size, \( d_m \). It was adjusted in order to yield an open membrane area, \( A_m \), larger than 0.7×10\(^{-11}\) m\(^2\) to guarantee that mass transfer rates are detectable with the macroscale transport measurement setups used throughout the study.
Table 2-1 A list of graphene membranes fabricated, giving pore diameter ($d_m$) with standard deviation ($\sigma_m$, in parenthesis), number of pores ($N_p$), and total open membrane area ($A_m$)

<table>
<thead>
<tr>
<th>sample</th>
<th>diameter $d_m$ ($\sigma_m$) [nm]</th>
<th>number of pores $N_p$</th>
<th>area $A_m$ $\times 10^{11}$ [m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NM02</td>
<td>4.7 (1.4)</td>
<td>1484000</td>
<td>2.72</td>
</tr>
<tr>
<td>NM08</td>
<td>5.7 (1.5)</td>
<td>645000</td>
<td>1.67</td>
</tr>
<tr>
<td>NM03</td>
<td>6.2 (1.1)</td>
<td>727000</td>
<td>2.17</td>
</tr>
<tr>
<td>NM12-8</td>
<td>6.2 (1.5)</td>
<td>967000</td>
<td>2.92</td>
</tr>
<tr>
<td>O164</td>
<td>7.3 (1.1)</td>
<td>785000</td>
<td>3.25</td>
</tr>
<tr>
<td>O111</td>
<td>7.4 (1.5)</td>
<td>821000</td>
<td>3.54</td>
</tr>
<tr>
<td>NM05</td>
<td>7.5 (0.9)</td>
<td>773000</td>
<td>3.38</td>
</tr>
<tr>
<td>T60</td>
<td>8.1 (0.8)</td>
<td>633000</td>
<td>3.23</td>
</tr>
<tr>
<td>NM04</td>
<td>8.7 (1.1)</td>
<td>854000</td>
<td>4.96</td>
</tr>
<tr>
<td>A103</td>
<td>9.9 (1.1)</td>
<td>253000</td>
<td>1.94</td>
</tr>
<tr>
<td>NM16</td>
<td>15.6 (1.1)</td>
<td>77000</td>
<td>1.49</td>
</tr>
<tr>
<td>T57</td>
<td>16.0 (3.9)</td>
<td>42900</td>
<td>0.86</td>
</tr>
<tr>
<td>T73</td>
<td>16.3 (3.0)</td>
<td>41100</td>
<td>0.86</td>
</tr>
<tr>
<td>T56</td>
<td>16.6 (3.3)</td>
<td>54500</td>
<td>1.18</td>
</tr>
<tr>
<td>O162</td>
<td>18.6 (1.0)</td>
<td>92300</td>
<td>2.51</td>
</tr>
<tr>
<td>NM11-2</td>
<td>23.3 (1.2)</td>
<td>59100</td>
<td>2.51</td>
</tr>
<tr>
<td>NM12-1</td>
<td>40.2 (1.4)</td>
<td>16300</td>
<td>2.07</td>
</tr>
<tr>
<td>O121</td>
<td>48.0 (1.0)</td>
<td>49600</td>
<td>8.98</td>
</tr>
<tr>
<td>O134</td>
<td>48.6 (0.6)</td>
<td>25600</td>
<td>4.74</td>
</tr>
<tr>
<td>T72</td>
<td>49.0 (2.5)</td>
<td>39600</td>
<td>7.47</td>
</tr>
<tr>
<td>T54</td>
<td>49.4 (2.8)</td>
<td>14900</td>
<td>2.85</td>
</tr>
<tr>
<td>T62</td>
<td>50.4 (1.5)</td>
<td>37900</td>
<td>7.57</td>
</tr>
<tr>
<td>T69</td>
<td>51.3 (0.8)</td>
<td>23300</td>
<td>4.80</td>
</tr>
<tr>
<td>O109</td>
<td>51.5 (1.0)</td>
<td>71600</td>
<td>14.89</td>
</tr>
<tr>
<td>O106</td>
<td>52.1 (1.0)</td>
<td>52600</td>
<td>11.20</td>
</tr>
<tr>
<td>T53</td>
<td>53.0 (2.3)</td>
<td>18600</td>
<td>4.11</td>
</tr>
<tr>
<td>O115</td>
<td>54.2 (1.9)</td>
<td>108000</td>
<td>24.89</td>
</tr>
<tr>
<td>O148</td>
<td>54.4 (1.1)</td>
<td>45200</td>
<td>10.51</td>
</tr>
<tr>
<td>A102</td>
<td>57.3 (2.0)</td>
<td>26500</td>
<td>6.85</td>
</tr>
<tr>
<td>O136</td>
<td>58.2 (1.0)</td>
<td>43300</td>
<td>11.53</td>
</tr>
<tr>
<td>T64</td>
<td>91.5 (3.0)</td>
<td>4900</td>
<td>3.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>sample</th>
<th>diameter $d_m$ ($\sigma_m$) [nm]</th>
<th>number of pores $N_p$</th>
<th>area $A_m$ $\times 10^{11}$ [m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O160</td>
<td>94.6 (1.8)</td>
<td>11600</td>
<td>8.13</td>
</tr>
<tr>
<td>O108</td>
<td>96.1 (3.8)</td>
<td>12100</td>
<td>8.76</td>
</tr>
<tr>
<td>NM07</td>
<td>100.1 (1.8)</td>
<td>9060</td>
<td>7.13</td>
</tr>
<tr>
<td>O120</td>
<td>100.6 (1.4)</td>
<td>13800</td>
<td>10.94</td>
</tr>
<tr>
<td>O114</td>
<td>109.3 (1.8)</td>
<td>20500</td>
<td>19.19</td>
</tr>
<tr>
<td>T55</td>
<td>111.6 (1.8)</td>
<td>4230</td>
<td>4.14</td>
</tr>
<tr>
<td>T50</td>
<td>199.5 (1.9)</td>
<td>768</td>
<td>2.40</td>
</tr>
<tr>
<td>NM13-7</td>
<td>199.5 (5.4)</td>
<td>1600</td>
<td>5.00</td>
</tr>
<tr>
<td>T71</td>
<td>201.9 (2.2)</td>
<td>1519</td>
<td>4.86</td>
</tr>
<tr>
<td>T70</td>
<td>371.5 (4.5)</td>
<td>873</td>
<td>9.46</td>
</tr>
<tr>
<td>O03</td>
<td>378.2 (5.2)</td>
<td>1024</td>
<td>11.50</td>
</tr>
<tr>
<td>T65</td>
<td>382.5 (12.2)</td>
<td>196</td>
<td>2.25</td>
</tr>
<tr>
<td>T52</td>
<td>384.0 n.a.</td>
<td>192</td>
<td>2.22</td>
</tr>
<tr>
<td>O2</td>
<td>388.0 (2.8)</td>
<td>576</td>
<td>6.81</td>
</tr>
<tr>
<td>S1001</td>
<td>388.2 (4.6)</td>
<td>508</td>
<td>6.01</td>
</tr>
<tr>
<td>O161</td>
<td>390.8 (4.3)</td>
<td>1450</td>
<td>17.42</td>
</tr>
<tr>
<td>A100</td>
<td>390.9 (4.8)</td>
<td>567</td>
<td>6.80</td>
</tr>
<tr>
<td>T59</td>
<td>399.2 (4.5)</td>
<td>388</td>
<td>4.86</td>
</tr>
<tr>
<td>O165</td>
<td>404.2 (2.4)</td>
<td>486</td>
<td>6.23</td>
</tr>
<tr>
<td>O155</td>
<td>404.3 (1.9)</td>
<td>1010</td>
<td>12.94</td>
</tr>
<tr>
<td>NM01</td>
<td>408.3 (1.7)</td>
<td>517</td>
<td>6.77</td>
</tr>
<tr>
<td>NM11-9</td>
<td>416.0 (5.0)</td>
<td>256</td>
<td>3.48</td>
</tr>
<tr>
<td>T66</td>
<td>936.8 (12.8)</td>
<td>49</td>
<td>3.38</td>
</tr>
<tr>
<td>T51</td>
<td>947.0 (22.0)</td>
<td>48</td>
<td>3.38</td>
</tr>
<tr>
<td>NM10</td>
<td>955.1 (14.1)</td>
<td>111</td>
<td>7.95</td>
</tr>
<tr>
<td>T48</td>
<td>964.4 (18.3)</td>
<td>49</td>
<td>3.58</td>
</tr>
<tr>
<td>T74</td>
<td>970.2 (7.6)</td>
<td>98</td>
<td>7.24</td>
</tr>
<tr>
<td>O113</td>
<td>970.8 (11.6)</td>
<td>768</td>
<td>56.84</td>
</tr>
<tr>
<td>T63</td>
<td>975.3 (9.5)</td>
<td>49</td>
<td>3.66</td>
</tr>
<tr>
<td>T61</td>
<td>996.4 (15.6)</td>
<td>49</td>
<td>3.82</td>
</tr>
</tbody>
</table>
Figure 2-20 Scanning electron micrographs of various fabricated graphene membranes with pore diameter, $d_m$, of a) 955.1 nm, b) 408.3 nm, c)
199.5 nm, d) 100.1 nm, e) 40.2 nm, f) 23.3 nm, g) 15.6 nm, h) 8.7 nm and i) 4.8 nm. Different sizes of pore diameters are drilled into the double layer graphene using Ga\(^+\) FIB by circular pattern exposure or single pixel exposure. Insets show the pore diameter histogram and fitted normal distribution of the pore diameter which is used to define the mean pore diameter, \(d_m\), of the respective membrane.

The graphene membrane with largest pores has a mean \(d_m\) of 1034 \(\mu\)m. This membrane comprises only one pore in each freestanding graphene spanning a 4-\(\mu\)m-wide SiN\(_x\) hole (Figure 2-20 a). The smallest as-drilled \(d_m\) in a working membrane has a pore diameter of 4.8 nm (Figure 2-20 i). As introduced above (section 2.1.2.1) a total open pore area of \(A_m \approx 2 \times 10^{-11} \text{ m}^2\) is necessary to measure macroscopic gas flux using a conventional mass flow meter assuming that the free-molecular flow theory (i.e., effusion) is valid for the porous graphene membrane. To achieve this sufficient membrane area it is necessary to drill \(\sim 1.5 \times 10^6\) pores\(^4\) into the freestanding graphene. The pore diameter distribution for all fabricated membranes is relatively narrow. For membranes larger than 20 nm the ratio of \(\sigma_m / d_m\) is <5\%. Only the smaller pore diameter membranes have wider pore diameter distribution compared with the mean diameter, since \(\sigma_m\) remains more or less constant at \(\sim 1.5 \text{ nm}\) and \(d_m\) decreases.

For a reliable membrane characterization the calculated pore area has to be most accurate, and there should not be any additional larger tears or

\[ N_p = A_m / A_p = 2 \times 10^{-11} / (2.4 \times 10^{-6})^2 / \pi = 1.1 \times 10^6 \]
defects in the membrane which would contribute to the measured flow. Despite using only clean and defect-free double layer graphene for the patterning process it can happen that the graphene breaks during the bombardment with high energetic ions (Figure 2-21 a). Usually, these tears originate from not well connected grain boundaries in one of the two graphene layers and occur only in about 2-5% of the patterned freestanding graphene membranes. However, their presence would contribute significantly to the open pore area. Therefore, after pore patterning, all of the membrane area are carefully investigated by SEM to check for the presence of larger pores, defects and tears (Figure 2-21 a). Any defect, larger pore or tear is then sealed to block the additional unwanted open area. This patchwork is done inside the Dual Beam FIB system (Helios 450, FEI) via electron beam induced deposition of Pt [84].
Figure 2-21 Sealing of defects and tears in graphene membranes after patterning. a) Scanning electron micrograph of graphene membrane after patterning 6.3 nm pores showing 4 of the 256 4-μm-wide SiNx openings covered with patterned graphene. The opening at the top right corner has large tear, and the bottom right one has slightly increased pore size. b) SEM micrograph after Pt deposition, both defective regions in the graphene membrane are patched via the Pt deposition.

By introducing a gas-phase Pt precursor Pt(PF$_3$)$_4$ via the gas injection system (GIS) into the vacuum chamber of the dual beam system one can locally build up Pt layers by electron beam irradiation (2 keV, 1.9 nA). The precursor adsorbs on the sample surface, and the electrons hitting the surface provide the energy to break the volatile compounds which escape the surface but leave the Pt. Using this deposition technique which is widely used to repair photolithography masks [102], one can deposit material with nanometer-scale precision in the desired area. By continuous deposition it allows to patch the large voids in the torn graphene (Figure 2-21 b). Therefore, the Pt deposition technique can be used to repair the as-perforated
graphene membranes and to allow the fabrication of graphene membranes with uniform pore size distribution at high manufacturing yield, for no membrane has to be discarded because of unwanted defects.

2.4 Graphene pore characterization and modification

In order to understand the morphology of the graphene pore edge, high resolution transmission electron micrographs (Cs-corrected HRTEM, JEM ARM 200F, JEOL) of the perforated graphene were obtained. To ensure perfect similarity to the as-made membranes, TEM samples were prepared after patterning the double layer graphene, by cutting the SiNx support frame and transferring it to a TEM grid in the FIB system. The images obtained at 200 keV reveal a random pore edged (Figure 2-22) of the graphene pore.
The crystalline domains in Figure 2-22 most likely originate from contaminating Pt deposits which originate from the sample manipulation inside the FIB since the lattice constant is too high for graphene. Despite the real high-resolution capability of the TEM it is not possible to resolve the graphene lattice structure. The reason for this problem may be understood considering that both multi-crystalline graphene layers in the double layer arrangement will have random alignment towards each other. Therefore, they do not share a common lattice orientation which makes it difficult to resolve the lattice structure. Furthermore, as described above the process of pattern formation in the graphene lattice by ion irradiation follows the route of first amorphizing the graphene lattice to a loosely sp²-hybridized network of C atoms before etching them completely. Therefore, the lattice
structure of the graphene in the vicinity of every pattern created by ion bombardment will be destroyed and a 2D network of amorphous sp²-hybridized C atoms will define the crystallographic random pore edge.

2.4.1 Graphene pore edge chemistry after patterning

The chemical composition of the pore edge of as fabricated graphene membranes requires more investigation. The patterning process via ion irradiation will leave dangling carbon bonds at the created pore edge. Exposing the samples after patterning in the vacuum chamber to the atmospheric environment one can expect that at these positions water and possibly oxygen would react to saturate these dangling bonds. Passivation by oxygen-containing chemical moieties via strong oxidation has been observed by other researchers, suggesting that the pore edges can be terminated by carbonyl, hydroxyl, or carboxyl groups [30, 103-105]. In order to assess the additional oxygen content of as made graphene membranes, patterned and unpatterned graphene samples were mounted on Au coated Si wafers inside the FIB chamber and later analyzed by X-ray photoelectron spectroscopy (XPS) in courtesy of Dr. J. Patscheider and Dr. L. Bernard at EMPA, Düsseldorf, Switzerland. The utilized probe was a monochromatized Al Kα X-ray beam with a diameter of about 8 µm in a Quantum 2000 imaging XPS spectrometer (Physical Electronics Instruments, Inc.).
The data show that the relative amount of oxygen with respect to carbon (i.e., the sensitivity-corrected intensity ratio O/C) is enhanced in the patterned sample by about 10±5% as compared to the unpatterned sample. Additional time-of-flight secondary ion mass spectrometry (TOFSIMS) data comparing the fragments O+, O-, OH- and CO- from both samples show clearly higher oxygen-containing signals from the patterned sample. These results corroborate the presence of oxygen on porous graphene as a consequence of the FIB patterning and environmental exposure. Therefore, it is likely that the pore edges of the here fabricated graphene membranes also are terminated by oxygen-containing moieties like other graphene edges [30, 103-105]. Another possibility is that trace carbon and hydrogen in the FIB chamber can bind to the edges right after the ion bombardment, providing partial hydrogen termination which could not be resolved by the XPS and TOFSIMS analysis.

Note that the effect of the pore edge chemistry on the mass transport properties is particularly important for very small pores. The theoretical studies showing significant edge effects, such as water permeation enhancement by hydrophilic edge termination (OH) [57], H₂/CH₄ selectivity reduction by N-functionalization [35], anion blockage by F and N functionalization and cation blocking by H-termination [60], as well as ion blockage by carboxyl groups [61, 106]. These studies use sub-nanometer pores, where the electron clouds of the functional group take up a significant portion of the pore area. In the current study, however, the graphene
membranes fabricated have pore sizes larger than 4.8 nm. The size of the different functional groups at the edge which could influence the permeation properties are at least 1 order of magnitude smaller and therefore the effect of the chemical moieties on direct permeation can be presumably neglected.

2.4.2 Graphene pore shrinkage

As described above, the smallest pores in double layer graphene which could be created via Ga+ FIB had an average diameter of 4.8 nm (Figure 2-18 a). Only by using monolayer smaller pores could be achieved in free-standing graphene, which is not feasible though, since the manufacturing yield is too low. Via He+ FIB the smallest pores around 3.5 nm could be constructed in an array format (Figure 2-18 b). However, it was not possible to create a sufficient number of holes with such a narrow pore size distribution, which would allow the mass transport measurements. To approach this small pore size, the double layer graphene has to be ultraclean on the entire patterned area, which is very difficult to obtain on the full support frame.

A different approach to even smaller pore sizes in graphene membranes would be to pattern larger pore sizes and subsequently shrink the graphene pore by an additional coating. The coating should not damage the graphene layer and allow a very high degree of control about the deposited
layer thickness. Both requirements can be met by atomic layer deposition (ALD) a process where in alternating fashion gaseous precursors are exposed to the surface where they undergo a reaction and form atomic thickness layers. There have been numerous studies about ALD deposition on graphene suggesting that the deposition layer would not nucleate on clean defect free graphene but only in regions of vacancy defects, grain boundaries or other contamination the ALD layer would nucleate and grow [107]. Pretreating the graphene to facilitate precursor adsorption could, however, enable the uniform nucleation and film formation on pristine graphene [108].

As described above the graphene pore edge consist of defective graphene which will readily allow the nucleation and film growth of the deposit in the ALD process. Therefore, one can expect a preferential growth of ALD layers in the pore region which should yield a pore size reduction upon coating (Figure 2-23).

Figure 2-23 Schematic of ALD process on porous graphene. Conformal deposition of a TiO₂ layer with thickness $t_c$ leads to reduced pore diameter $d_c$ ($<d_p$).

Preliminary results and literature [109] have shown that chemical stability of nanometers-thick ALD-prepared $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$ in an aqueous environment is limited but TiO₂ yields excellent stability as a coating when
exposed to water. Coating of TiO$_2$ on the graphene membrane could be achieved by the use of the Ti(OC$_3$H$_7$)$_4$ precursor and O$_3$ as non-metal precursor at 110°C (FlexAL, Oxford Instruments) with the following process cycle:

**TiO$_2$ ALD process:**

1) Pump down to 3 mbar
2) Metal precursor dose 1.5 s at 80 mbar in Ar carrier
3) Chamber purge for 8 s with 150 sccm Ar at 15 mbar
4) Non-metal precursor dose 8 s at 230 mbar in Ar carrier
5) Chamber purge for 8 s with 150 sccm Ar at 15 mbar
6) Repeat step 2) to 5) for desired number of cycles.

The resulting thin film growth rate of this process on Si is ~0.55 Å/cycle. As expected the ALD process yields non uniform nucleation on freestanding graphene membranes (Figure 2-24). After a few cycles TiO$_2$ particles begin to appear in the vicinity of the pore patterns or on presumably grain boundaries in unpatterned regions (Figure 2-24 d and e). High-resolution scanning electron micrographs which detect transmitting electrons, or scanning transmission electron micrographs can reveal the ALD nucleation in great detail (Figure 2-24 f). The deposition leads to nucleation of individual particles which will grow with every deposition cycle. Since the patterned region contains more defect sites, nucleation gets dense enough easily to form a continuous film locally even after a few deposition cycles. Away from the pore patterns, on the other hand, graphene remains
uncoated except for arbitrary defect sites, grain boundaries or graphene contaminants which will serve as nucleation seeds for ALD (Figure 2-24 f).

The preferential coating in the pore-patterned region of the graphene membranes causes reduction in the pore sizes. To analyze the small incremental change in the graphene pore diameter, scanning electron micrographs with exactly the same imaging conditions were used. On large pore membranes starting with 54.0 nm pore size the coating of up to 60 cycles of TiO$_2$ yields a total reduction of the pore diameter to 47.8 nm, which corresponds to a diameter shrinkage rate of 0.104 nm/cycle (Figure 2-25 a). Since the diameter reduction is caused by a radial deposition, the growth rate of TiO$_2$ on the pore edge equals to 0.52 Å/cycle that is slightly lower than the thin film growth rate on Si.
Figure 2.24 Scanning electron micrograph of freestanding porous graphene before and after ALD coating. a) and b) ~50 nm graphene membrane before coating showing pore area and hint of contaminants on the double layer graphene. c) Scanning electron micrograph (transmission electrons) of 6.2 nm pore graphene membrane before ALD coating. d) Graphene after 20 cycles of TiO\textsubscript{2} coating showing pronounced contrast (same SEM imaging conditions as in a) and b)) from the grain boundaries and dense particle like nucleation in the vicinity of the pore patterns. e) Close up to graphene pore membrane after 20 cycles of ALD deposition showing clearly a gradient of particle nucleation density towards the pore pattern. f) Scanning electron micrograph (transmission electrons) of 6.2 nm graphene membrane after 18 cycles of TiO\textsubscript{2} deposition showing enhanced scattering of electrons due to additional deposition in pore vicinity and on defect sites.
Figure 2-25 Membrane pore diameter shrinkage by TiO$_2$ ALD. a) Characterization of TiO$_2$ growth rate on graphene pore edge. Blue dots represent average pore diameter, dashed black line shows linear regression of data point giving a diameter reduction rate of 0.104 nm/cycle. b) Pore diameter histogram of graphene membrane before coating (blue bar) having a mean diameter $d_m = 5.7$ nm and after the deposition of 10 cycles (red bars) yielding $d_c = 3.7$ nm.

For small pores of the graphene membrane the TiO$_2$ growth rate deviates from that for the large pores. After 10 cycles of TiO$_2$ ALD on a membrane pore of $d_m = 5.7$ nm, it decreased to $d_c = 3.7$ nm. The deposited film thickness on the pore edge is about $t_c = 1.0$ nm in 10 cycles, twice the deposition rate observed before (Figure 2-25 b). This deviation arises from the initial phase of the TiO$_2$ coating. The deposition thickness is strongly dependent on the nucleation density on the target surface as is widely observed for ALD in general [110]. It is only after a complete coating of the surface that a stable growth rate can be obtained which would be governed
by the reaction site density inherent to TiO$_2$ films. The faster initial deposition of TiO$_2$ to the small pores of the graphene membrane allows to extend the pore size range of the 2D membranes to sub-5 nanometers.

Furthermore, the ALD deposition offers a few more advantages. First the additional coating encapsulates contaminants residing on the membrane surface which could contaminate the membrane (Figure 2-26 a). The conformal coating by ALD would immobilize these particles and dirt on the membrane surface, so that they are not washed towards the active membrane area during liquid transport characterization.

Second, the ALD coating may preserve the integrity of the membranes, since it could patch grain boundaries and pinholes of the graphene layer (Figure 2-26 b). Both defect sites are weak spots of the membrane because they could allow water to penetrate in between the substrate and the graphene layer [22]. The interfacial water layer between the support substrate (SiN$_x$) and the graphene would weaken the van der Waals force that holds the graphene on the support. This loss of adhesion and the membrane disintegration as a result of it [21] could be prevented by an additional coating on the grain boundaries and pinholes (Figure 2-26 b). Also, the ALD coating on the unavoidable defects sites (Figure 2-26 b) will further reduces the leakage rate of the membranes as reported by other researchers [64].
Thirdly, the chemical composition of the graphene pore edge is altered from carbon dangling groups presumably terminated with oxygen and hydrogen to TiO-terminated moieties (Figure 2-26 c).

Figure 2-26 Effect of ALD coating on graphene membranes. a) Encapsulation of dirt particles residing on membrane surface. b) Coating pinholes and grain boundaries reducing membrane damage by strengthening weak spots. c) Changing the pore edge chemistry to that of a TiO$_2$ surface with Ti-O moieties. d) Increasing the thickness of a graphene membrane, $t_g$, to a membrane thickness, $t_m$, caused by the additional coating.

As discussed above (section 2.4.1), in the pore size range of the as-fabricated graphene membranes one cannot yet expect a direct effect of the chemical moieties on the gas transport properties of the membrane. However, there may be secondary effects which could influence the permeation properties of the ALD coated membranes. It has been reported that organic macromolecules have very high affinity towards graphene pores by $\pi$ - $\pi$ interaction and therefore DNA molecules cause severe non reversible pore blocking [27]. The additional coating with TiO$_2$ will suppress this interaction and therefore reduce the odds of the membrane clogging [101].
Furthermore, the TiO$_2$ will greatly change the membrane surface charge, which may in turn have a strong effect on the transport of charged species. And lastly the mechanical strength of the membrane is enhanced because weak spots are patched and the total membrane thickness is increased (Figure 2-26 d).

The increase in thickness, on the other hand, is the main negative aspect of the additional coating with TiO$_2$. After the ALD coating the membrane does not only consist of two graphene layers ($t_g \approx 2 \times 0.33$ nm = 0.66 nm) but will have on the bottom and top sides of the membrane an additional layer with thickness $t_c$. Therefore, the total membrane thickness will be $t_m = t_g + 2 \times t_c$ (Figure 2-26 d). In the case of the membrane sample shown in Figure 2-25 b the expected thickness of the membrane after coating is thus $t_m \approx 4.68$ nm which is comparable to or even thicker than the membrane pore diameter $d_m$. It is obvious that in this situation where $d_m / t_m \approx 1$ the observed mass transport might not follow the properties of an infinitely thin membrane ($d_m / t_m \gg 1$), which will be further discussed in section 3.1.1. Furthermore, one does not expect a significant change of mass transport properties for ALD-coated graphene membranes when the pore sizes are larger than the gas mean free path. These membranes will get strengthened from the additional coating.
2.5 Graphene membrane stability

2.5.1 Mechanical stability

In the permeation experiments the fluid is driven by a differential pressure drop across the graphene membrane. The pressure drop is held only by the porous double layer of graphene, and the two-atom-thick layer of the membrane has to withstand the associated mechanical stress. In the experiments conducted, the graphene membranes, where the individual zones of freestanding graphene span the 4-μm-wide SiNx opening, could withstand a pressure difference $\Delta p$ applied by liquid or gas up to 2 bar (Figure 2-27). Increasing the pressure further leads to sudden failure of the membrane where the freestanding graphene is torn apart. These results were consistent for all samples tested.

![Figure 2-27 Schematic of porous graphene membrane subject to pressure drop, $\Delta p$, across the double layer graphene. Membrane is bulging and has a total displacement, $h$, in the center.](image)

Membranes with larger freestanding graphene area of 6 μm openings were breaking at significantly lower differential pressure $\Delta p$ of 0.8-1 bar.
The total force \( F_p \) which is applied to the graphene during such an experiment can be calculated by a simple force balance eq. (2.12) of the pressure force acting on the freestanding graphene area.

\[
F_p = r_s^2 \pi \Delta p
\]  

(2.12)

Using the pressure at which the graphene membrane is breaking and the respective hole radius, \( r_s \), of the support structure opening one yields \( F_p \approx 2.5 \times 10^{-6} \) N and \( F_p \approx 2.8 \times 10^{-6} \) N for the \( 2r_s = 4 \) \( \mu \)m and \( 6 \) \( \mu \)m membrane, respectively. These results are in agreement with the literature for the fracture force of freestanding double-layer CVD graphene performed by atomic force microscopy indentation which has reported an average indentation force of \( 2.7 \times 10^{-6} \) N when the graphene film started to break [69]. Still, further investigation is needed.

Furthermore, one can calculate the amount of elastic deformation (Figure 2-27) of the double layer graphene membrane by use of the membrane shell theory. The basic assumption is that the membrane structure cannot support any bending moment.
This assumption leads to a very simple situation where the thin membrane is loaded by only in-plane stresses, which are constant over the cross section of the structure. The bulging (deflection $h$ from the flat membrane) caused by a uniform pressure load on the membrane can be calculated by eq. (2.13) (assuming $t_g << r_s$ and $h << r_s$):

$$h = \left( \frac{3\Delta pr_s^4(1-\nu)}{8Et_g} \right)^{\frac{1}{3}},$$

(2.13)

where $\Delta p$ is the applied pressure, $r_s$ the membrane radius, $Et_g$ the two dimensional (2D) elastic modulus with $t_g$ being the membrane thickness, and $\nu$ the Poisson ratio of graphene, respectively [111]. Inserting typical values for the double layer of polycrystalline CVD graphene ($Et_g = 2\times55$ N/m [68], $\nu = 0.3$, $\Delta p = 40$ kPa, $r_s = 2$ $\mu$m) a maximal deflection $h \approx 115$ nm at 4$\times$10$^4$ Pa (the maximum differential pressure at standard permeation measurements), or $h \approx 250$ nm at 2$\times$10$^5$ Pa breaking pressure at the center of the 4 $\mu$m diameter free-standing graphene membrane is obtained. This calculated deflection is slightly higher than the deflection of single-crystalline graphene monolayer flakes measured at low pressures by AFM [28], attributable to the lower Young’s modulus of polycrystalline CVD graphene [68]. Note that the patterned pores can further weaken the elastic response of the graphene membrane. This effect can be easily accounted for by including the notion of membrane porosity, $\kappa$, with which to decrease the 2D elastic modulus: $Et_{g\, porous} = (1 - \kappa) Et_g$. The graphene membranes reported
here have a typical areal porosity of 3-5\%, and therefore the changes of the elastic modulus would be minor. The corresponding in-plane stress, $\sigma_m$, in the freestanding graphene membrane will be homogenous and can be calculated by assuming an undisturbed graphene lattice without any residual tension:

$$\sigma_m = \frac{\Delta p r_s^2}{4h t_g} \quad (2.14)$$

At the point of the membrane failure ($\Delta p \approx 200$ kPa) the graphene double layer experiences the in-plane stress, $\sigma_m = 1.2$ GPa. Following classical fracture mechanics theory, the stress concentration factor, $K$, caused by the presence of the circular pore array with $\kappa \sim 5\%$ porosity can be estimated to yield $K \approx 2.1$ [112]. The stress concentration causes a maximum stress of $\sigma_{\text{max}} = K \sigma_m = 2.5$ GPa inside the double layer graphene which is about a factor 10 lower than the fracture in-plane stress value reported for double layer graphene [69]. Theoretical results from MD simulations of porous graphene state that the breaking strength decreases with pore sizes [113], which is in contrast to the predictions of classical fracture mechanics theory, and point out that interplay between porosity and pore size may cause significant deviation in the fracture strength [70]. Furthermore, although all theoretical results are developed for a perfectly circular pore, the edges of the graphene pores are frayed and reveal sharp notches which may
cause significant stress concentration to the freestanding graphene membrane, leading to an earlier failure even at a mild applied differential pressure.

2.5.2 Chemical stability

Graphene is known to exhibit excellent chemical and temperature stability. Therefore one can expected that membranes made from graphene share similar properties and make the membrane usable in a wide range of applications with aggressive chemicals, or in strongly corrosive environments. To assess the chemical stability of the as fabricated graphene membrane, the samples are exposed to a variety of strong chemicals. Immersion of the membrane into strong caustic solution of 2 M NaOH overnight, as well as strongly acidic solutions as 1 M HCl or 1 M H₂SO₄ (Figure 2-28 a) for more than two hours does not cause any noticeable damage on the membrane surface and average pore diameter of the membrane tested remains the same. Furthermore, the double layer graphene membranes can be immersed in BHF (8% HF) solution for at least couple of minutes without losing its integrity. The exposure to solvents like isopropyl alcohol and acetone (Figure 2-28 b) does neither induce any damage to the membrane surface. Besides the stability in liquid oxidants, the as made graphene membrane survives thermal baking in air at 250°C for more than 4 hours again without compromising the membrane properties (Figure 2-28 c).
Figure 2-28 Scanning electron micrographs of freestanding double layer graphene membrane before and after treatment with various chemicals. a) Graphene membrane before and after exposure to $\text{H}_2\text{SO}_4$. b) Graphene membrane before and after the exposure to acetone. c) Graphene membrane before and after thermal baking in air at $250^\circ\text{C}$ for 4 h. Mass transport across graphene membrane.
3 MASS TRANSPORT ACROSS
GRAPHENE MEMBRANES


3.1 Gas transport across graphene membranes

3.1.1 Single gas transport

3.1.1.1 Experimental Setup

Single gas flow measurements are carried out in a constant-volume / variable-pressure apparatus (Figure 3-1). Gas with purity higher than >99.995% are used as feed gas. Gas pressure is adjusted by a pressure regulator attached to the gas bottle followed by a high precision mass flow controller (MFC) (MF1, MKS Instruments) which can be used to precisely adjust the feed pressure by introducing a controlled amount of gas to the feed of the membrane fixture. The differential membrane pressure is monitored by a handheld manometer (HHP91, Omega) which has the resolution
of 1 mbar. The $2\times2\ \text{cm}^2$ Si support frame that carries the graphene membrane is mounted in a custom made membrane fixture out of polyoxymethylene (POM).

**Figure 3-1** Schematic of gas permeation measurement setup. Gas is provided by high purity gas cylinders. A precision MFC and a differential pressure gauge is used to adjust the membrane differential pressure. Permeate gas flow rate is measured by a high precision MFM before being vented to the atmosphere.

A calibrated high-precision mass flow meter (MFM) (MF1, MKS Instruments) measures the permeate flow rate and the permeating gas is vented to the atmosphere. The gas leak rate of the measurement system is $<0.001\ \text{sccm}$ at a differential pressure of 1 bar. All the measurements were carried out at room temperature ($25^\circ\text{C}$). The mass flow meter has a resolution of $0.001\ \text{sccm}$ and thus allows the detection of gas flow down to $\sim0.005\ \text{sccm}$. To maintain the gas purity, the setup is evacuated and flushed with pure gas repeatedly before each measurement. During the measurement the downstream pressure is kept at atmospheric pressure while the upstream pressure is changed in the range of 0-400 mbar gauge pressure. Basic membrane characterization measurements are conducted
using N\textsubscript{2} but the measurement setup allows the connection of various other gas sources which enables the measurement of H\textsubscript{2}, He, CH\textsubscript{4}, N\textsubscript{2}, CO\textsubscript{2} and SF\textsubscript{6}.

### 3.1.1.2 Results and interpretation of single gas permeation experiments

As designed during the membrane manufacturing process the large number of pores (ca. $10^3$-$10^6$ per membrane) drilled into the graphene allows gas flows detectable by the lab scale permeation setup described above which uses conventional mass flow meters. N\textsubscript{2} flow shows linear pressure dependence (Figure 3-2) for all pore sizes.

![Figure 3-2 Recorded N\textsubscript{2} mass flow across graphene membranes with pore diameter $d_m = 199.5$ nm (light blue cross), 52.1 nm (green asterisk), 23.0 nm (red triangle), 8.7 nm (orange square) and 4.7 nm (blue circle).](image-url)
Normalizing the measured N₂ mass flow rate with the applied differential pressure, Δp, and the pore area, Aₚ, of the corresponding membrane, one obtains a pressure-independent permeance, Qₚ, for each membrane (Figure 3-3). For membrane with pores larger than approximately 50 nm the permeance increases with the pore diameter. However, the N₂ permeance through the graphene membrane is independent of the pore size if \( dₚ < 50 \) nm. This threshold length scale is comparable with the mean free path, \( \lambda \), of the gas molecules:

\[
\lambda = \frac{k_BT}{\sqrt{2\pi dₕ^2 p}},
\]

which depends on the Boltzmann constant \( k_B \), the temperature \( T \), the total pressure \( p \) and the molecular kinetic diameter \( dₕ \) and yields \( \lambda_{N₂} = 66.7 \) nm for N₂ at \( T = 298 \) K and \( p = 1 \) atm. The corresponding Knudsen numbers defined by \( \text{Kn} = \lambda / dₚ \) for graphene membranes (4.7 nm < \( dₚ < 50 \) nm) are between 1 and 15, which lies well within the free molecular flow regime. As a consequence, the probability of intermolecular collisions decreases, and collisions between gas molecule and membrane become dominant. Therefore, the gas molecular flux through the atomically thin graphene pore should be limited primarily by the number of gas molecules that hit the open pore area per unit time, \( \frac{1}{4} n \bar{u} \). Therefore, it depends only on the number density of a gas species, \( n \), and the average thermal speed, \( \bar{u} \). The molecular flux, \( j_E \), across an aperture between the two reservoirs at pressure \( p₁ \) and \( p₂ \), respectively, is quantified by eq. (3.2). This formula is a classic
result of a permeation through a small aperture called effusion and was originally proposed by Knudsen [114].

\[
j_E = \frac{1}{4} \Delta n\bar{u} = \frac{p_2}{\sqrt{2\pi mk_B T}} - \frac{p_1}{\sqrt{2\pi mk_B T}} = \frac{\Delta p}{\sqrt{2\pi mk_B T}}
\]  

(3.2)

Note that eq. (3.2) is indeed independent of the pore diameter, \(d_m\), but linear in the pressure drop, \(\Delta p = p_2 - p_1\), as it is observed here experimentally. Comparing the predicted permeance \(j_E/\Delta p\) with the measured values (Figure 3-3), one finds excellent agreement for small pore membranes below \(~30\) nm. In this way, graphene membranes with small pores allow the observation of an effusive flow, which had been restricted to rarified systems [115], at atmospheric pressures.

**Figure 3-3** N\(_2\) permeance of all graphene membranes fabricated (blue cross) in comparison with predictions of free molecular flow (effusion) theory (horizontal dashed line) and the modified Sampson’s flow model (with 5.5% porosity) for infinitely thin orifices (curved dashed line).
As the pore diameter enlarges, relatively more molecules interact with one another near the aperture, causing a transition from effusion to a more collective, viscous flow. However, well-known collective flow models based on pore-wall interactions (i.e., Hagen-Poiseuille model) are not suitable to explain the flow behavior for atomically thin membranes because of the absence of any pore wall. Nevertheless, there will be dissipation in the flow, since the viscous fluid has to funnel through the aperture with experiencing a velocity gradient nearby the aperture. Such flows can be modelled by Sampson’s formula, a solution of a viscous creeping flow (i.e., Stokes’ flow) through an infinitely thin orifice [59]:

\[
 j_S = \frac{1}{6 \mu} \sum i \frac{d_i^3}{\pi d_i^2} \Delta p
 \]

(3.3)

where \( j_S \) is the orifice flux, \( d_i \) is the diameter of aperture \( i \), \( \mu \) is the dynamic viscosity of the gas species. In the present case of the graphene membrane, not a single but multiple apertures constitute a pore array at the membrane surface. Depending on the porosity of the membrane, \( \kappa \), the flow field in the vicinity of the pore array exhibits smaller velocity gradients, which leads to flow enhancement from the single pore counterpart. Using the average pore diameter, \( d_m \), and the correction term of Sampson’s formula accounting for

\[
 \text{Re} = \frac{ud \rho}{\mu} = \frac{d^2 \Delta p \rho}{6 \pi \mu^2} \quad \text{with} \quad u = \frac{d \Delta p}{6 \pi \mu} = (1 \times 10^{-6} \text{ m})^2 \times 400 \times 10^2 \text{ Pa} \times 1.2 \text{ kg/m}^3 / (6 \pi (1.8 \times 10^{-8} \text{ Pa s})^2)
\]

\[
 = 8
\]

for 1000 nm pore at 400 mbar pressure difference \( \Delta p \)
the porosity which was introduced by Tio and Sadhal [116], one yields eq. (3.4) for the flux, \( j_A \), through a pore array inside an infinitely thin orifice membrane.

\[
j_A = \frac{d_m}{6\pi\mu} \frac{\Delta p}{1 - 0.344\kappa^{3/2} - 0.111\kappa^{5/2} - 0.067\kappa^{7/2} - 0.048\kappa^{9/2}}
\]  

(3.4)

Indeed the permeance asymptotically approaches the \( j_A \) prediction (using an average porosity \( \kappa = 5.5\% \) for all membranes) as the diameter gets larger than the mean free path (Figure 3-3). The diameter dependent gas permeance through graphene membranes, therefore, can be nicely modelled by the two asymptotic flow theories for infinitely thin membranes. This agreement is a striking finding, since both theories represent the ultimate permeation possible through a pore with a given diameter in their respective flow regime. Therefore, porous graphene membranes exhibit maximum possible gas permeation through a porous medium and therefore will define the ultimate limit for permeation in these membranes. Note that any other porous membrane will experience the same flow resistance effects described by both theories in addition to the dissipation occurring inside the membrane pore. In this context both theories are known as entrance effects and described in various theoretical studies [56, 71] but are usually not observed because the flow resistance inside the membranes strongly dominates in both cases of the free molecular flow (described by Knudsen diffusion) and the laminar continuum flow (exemplified by Hagen-Poiseuille model).
A different, comprehensive quantification of gas permeance can be performed with respect to the Knudsen number, Kn. Figure 3-4 shows the gas permeances for various pore sizes and gas species collectively, spanning a Kn range from 0.03 to 15. Here the permeances $j_m / \Delta p$ are normalized by the effusion prediction $j_E / \Delta p$ for the corresponding pore size and gas species. For gas diffusion in a long capillary, for instance, it is known that there exists a so-called Knudsen’s minimum in the flux-Kn diagram at Kn numbers around $O(1)$, stemming from molecular wall interaction and drift-to-diffusion shift [117-119]. However, researchers have observed that such a local minimum attenuates for relatively short capillaries that weakens this molecular wall interaction.

Figure 3-4 Measured permeance, $j_m / \Delta p$, for various gas species and graphene pore diameter normalized by respective effusion prediction, $j_E / \Delta p$, over Knudsen number.

Indeed, the gas permeation data of the extremely thin graphene membranes confirms the omission of Knudsen’s minimum, which underscores
that Knudsen’s minimum is primarily the result of the molecular wall interaction. In the absence of the continuous radial confinement of gas transport, the effusion sets the asymptote in both the transition and molecular flow regimes, thus eliminating any minimum in the permeance.

Since effusion is directly proportional to the average thermal speed, $\bar{u}$, of the molecules (eq. (3.2)), it is expected that the effusive permeance for small pores would be directly proportional with $m^{1/2}$ following Graham’s law of effusion. Moreover, the viscosity, $\mu$, of an ideal gas described by $\mu = Q \bar{u} \lambda$ scales with $m^{1/2}$ as the flow deviates from the effusive to collective transports, leading eventually to the same mass scaling for large pores in graphene membranes. Figure 3-5 confirms these predictions for all pore diameters, showing a permselectivity proportional to $m^{1/2}$. 
Figure 3-5 Gas permselectivity (defined as the permeance of H₂, He, CH₄, N₂, CO₂, or SF₆ normalized by N₂ permeance) for graphene membranes with 8.1 nm (blue circle), 16.0 nm (red square), 49.9 nm (cyan +), 111.6 nm (green cross), 199.5 nm (light blue triangle), 996 nm (orange circle) pore diameter presented with respect to molecular weight. The solid line represents a power law fit of the data, showing an exponent of -0.49, indicating an inverse square root mass dependence.

Gas permeation across porous graphene membranes with a TiO₂ conformal coating displayed similar results for large diameter pores or for very thin coating. Starting from an as-patterned graphene membrane with pore diameter 58 nm subsequent coating of TiO₂ caused a decrease in the pore diameter (Figure 3-6).
Figure 3-6 $N_2$ permeance (blue cross) and pore diameter (orange circle) as a function of number of coated ALD TiO$_2$ cycles on a 54.5 nm graphene membrane. The two solid lines represent the linear interpolation of the data points.

The initial pore diameter shrinks fast from 54.5 nm to 50 nm in merely 5 TiO$_2$ deposition cycles, attributable to a higher-temperature ALD recipe at 250°C which yielded a significantly enhanced nucleation density around the pore edge similarly to the small-pore membranes mentioned above (section 2.4.2). After this initial high deposition rate the pore diameter shrinkage per ALD cycle dropped to the previously characterized rate on graphene surfaces (Figure 3-6). The flow rate measured after each deposition run reduced as well, but upon normalizing it with the decreased membrane area the membrane maintains a constant permeance around the effusion limit (Figure 3-6). After the 50 cycles of ALD coating the membrane pore diameter was reduced by ~9 nm, and therefore the membrane thickness $t_m$ can be estimated to be $t_m = t_g + \Delta d_m \approx 9.7$ nm. One can conclude, that for pore aspect ratios $t_m/d_m \approx 0.2$ the flow regime of the
membrane is not changed. In contrast, two membranes with pore aspect ratios $t_m/d_m$ around 1 strongly deviate from this result.

![Diagram](image)

**Figure 3-7** $N_2$ permeance of TiO$_2$ coated graphene membranes and calculated permeance using effusion, Knudsen diffusion, series resistance flow models and Clausing’s transmission probability, $W_C$. a) 7.7-nm-pored membrane with $t_m/d_m \approx 1.5$ ($W_C = 0.4205$) exhibits significantly lower permeance than effusion prediction and a good agreement with Clausing. b) 3.7 nm pore diameter membrane having a $t_m/d_m \approx 0.83$ ($W_C \approx 0.558$).

Although both membrane diameters $d_m = 3.7$ nm and 7.7 nm lie within the range in which gas permeation across porous graphene is characterized, the measured permeance values are well below the effusion limit (Figure 3-7). The gas permeating the thickened graphene membrane pore, first experienced the flow resistance of pore entrance defined by effusion and then undergoes pore wall collision with inelastic scattering which is described by Knudsen diffusion $j_{Kn}$ (3.5) for rarefied gas flow inside circular tubes with $t_m \gg d_m$ derived by Knudsen [118].
Note that for small thicknesses \( j_{Kn} \) is not valid and the calculated permeance is too high (Figure 3-7). However it can be used to estimate an additional flow resistance \( R \) which can be defined as \( R^{-1} = j / \Delta p \). Combining both resistances of effusion (3.2) and Knudsen diffusion (3.5) one obtains a series resistance model for the expected flux which has been originally described by Dushman [120]

\[
j_{E+Kn} = \frac{1}{R_E + R_{Kn}} \Delta p = \frac{\Delta p}{\sqrt{2\pi mk_B T} + \frac{3t_m}{d_m} \sqrt{\frac{\pi m k_B T}{8} \frac{1}{R_{Kn}}}}
\]

(3.6)

Note that this solution resembles the effusive flux corrected by a factor \( W = (1 + 0.75 \frac{t_m}{d_m})^{-1} \), which depends on the pore aspect ratio \( t_m / d_m \). A comprehensive interpretation of \( W \) as the transmission probability of the molecules which hit the pore area has been given by Clausing [121]. He found that eq. (3.6) is only valid for large \( t_m / d_m \) and derived rigorously a complicate integral differential equation to describe the flow of rarefied gas through a pore for all thicknesses. Tabulated transmission probabilities \( W_C \) for a specific \( t_m / d_m \) are used to calculate the permeation as modification of
the effusive flux \( j_C = W_C \times j_E \). For small \( t_m / d_m \) this factor \( W_C \) is approximately 1, and therefore the additional resistance is negligible. At \( t_m / d_m \approx 1 \), however, the factor is \( W_C \approx 0.5136 \). In the limit of large \( t_m / d_m \), the transmission probability approaches \( W_C = (4/3) \frac{d_m}{t_m} \). For thicker membranes the molecule-to-pore-wall collisions lower the probability for a molecule that hits the pore area and enters the pore, to transmit all the way through the pore. Indeed, the measured \( \text{N}_2 \) permeance of both membranes after ALD deposition fits very well to the prediction of reduced permeation (Figure 3-7). These findings state that gas permeation across porous membranes is governed by the entrance and transmission resistance effects – the impedance associated with flow entrance into the confinement and the impedance that the confinement imposes on molecules transmitting inside the pore. Only atomically thin membranes that have the advantage of very small aspect ratios (\( t_m / d_m \ll 1 \)) pose the ultimate permeation capability.

### 3.1.2 Mixture gas transport

In addition to mass transfer rates, membrane selectivity is a crucial parameter to assess membrane performance. As indicated above, all the graphene membranes investigated here display a permselectivity scaled with the inverse square root of the molar weight (\( m^{-1/2} \)), but it is unlikely that the transport of a real gas mixture in the continuum range (for large pores) would exhibit a great gas separation behavior. Therefore, a true mixture gas
permeation experiment is conducted, and the determination of the separation performance is described in the following section.

3.1.2.1 Experimental setup design

Graphene membranes with different pore diameters ranging from 8.1 to 996 nm are mounted in a custom made cross flow membrane fixture. In order to achieve a considerable selectivity a gas mixture of CO$_2$ (99.995% purity, Pan Gas) and H$_2$ (99.995% purity, Pan Gas) with large difference in molecular weight is chosen as a feed gas for the separation measurements. Two calibrated mass flow controllers (MF1, MKS Instruments) adjust the molar composition $\varphi_{H_2}/\varphi_{CO_2}$ of the feed gas. The total feed flow rate is set to be 100 times higher than the expected permeation rate in order to avoid feed gas composition change due to the permeation of the gas through the membrane (stage cut: Permeate / Feed = 1%). Such a stage cut is known to yield feed flow rate independent separation measurements [122]. During the gas mixture test, the feed pressure is controlled by the retentate MFC (MF1, MKS Instruments) to keep it constant at 350 mbar gauge monitored by handheld manometer (HHP91, Omega), while the downstream pressure is maintained at atmospheric pressure. A controlled flow (MF1, MKS Instruments) of high purity Ar sweep gas on the permeate side of the membrane fixture carries the permeating gases to the mass spectroscope. The low stage cut has the second advantage that the back diffusion rate of the carrier gas
from the permeate side to the feed side through the membrane can be safely assumed to be less than 1% of the retentate flow rate. Hence, the carrier gas effect on the feed side can be neglected safely.

**Figure 3-8** Schematic of mixture gas separation setup. Pressurized CO\(_2\) and H\(_2\) gas with controlled flow rate is feed to the membrane mounted in the membrane holder. The feed gas composition of the mixture is controlled by the individual flow rate of both MFCs. The differential pressure is monitored by the pressure gauge and adjusted with the retentate MFC. The permeate side of the membrane is flushed with MFC adjusted Ar flow to carry the permeating gas mixture towards the mass spectroscope (MS). The total permeate flow is monitored by a mass flow meter after the membrane fixture.

By setting the carrier gas flow rate 100-fold higher than the permeate flow rate, the partial pressure of the permeating gases at the permeate side is greatly reduced. The total permeate side gas mixture of CO\(_2\)/H\(_2\)/Ar is analyzed in a mass spectroscope (Cirrus 2, MKS Instruments) using a Faraday cup detector and the molar composition is determined when the system has reached stable steady state conditions after several hours of permeation. The mass spectroscope measurement is calibrated prior to the
separation measurement using a variety of compositions of calibrating gases similar to composition during the true separation measurement. The separation performance of the membrane can be measured by the separation factor $\alpha$ defined in eq. (3.7) where $\gamma_i$ denotes the mole fraction of species $i$ in the permeate determined by the mass spectroscope and $\varphi_i$ the respective mole fractions in the feed.

$$\alpha_{H_2/CO_2} = \frac{\gamma_{H_2}/\gamma_{CO_2}}{\varphi_{H_2}/\varphi_{CO_2}}$$ (3.7)

Therefore, $\alpha$ is a measure for the real separation capability of a membrane under real conditions.

### 3.1.2.2 Results and interpretation of mixture gas permeation experiments

The results of single gas experiments display a permselectivity of $H_2/CO_2$ matching the limit defined by gas kinetic theory $(M_{CO_2}/M_{H_2})^{1/2} = 4.69$ for all graphene pore sizes characterized here (Figure 3-5). It is shown above that this single gas permselectivity is in agreement with both asymptotic flow theories, which are describing the flow of gas through porous graphene. However, the results of single gas permeance across graphene membranes may not be misinterpreted as true gas separation capability of porous graphene. Intuitively larger pores in graphene should show no or only little selectivity. The mean free path of the molecules dictates that for large pores
the molecules will frequently collide with each other in the vicinity of the pore, since the length scale defined by the pore diameter is too large and the gas mixture will behave as one pseudo species with mixture viscosity. Although the different gas species still keep their individual thermal speed distribution, these intermolecular collisions are too frequent to maintain any different drift speeds, and molecules will therefore move collectively causing a loss of selectivity. Indeed, the measured gas separation factor for 51:49 H₂:CO₂ mixture at low Kn numbers, that is for large pores, is less than 30% of the single gas permselectivity (Figure 3-9).

![Figure 3-9](image_url)  
**Figure 3-9** Normalized H₂/CO₂ gas separation factor (blue circle) vs. membrane Knudsen number, Kn, based on the mean free path of CO₂ for 51:49 mole fraction feed gas. The permeate composition was determined by mass spectroscopy for calculation of the separation factors. Dashed black line represents theoretical separation factor in the kinetic gas theory limit.

Reducing the pore size from 1000 nm to 50 nm so for Kn ≈ 1, the measured separation factor increases to 50% of the single gas selectivity
(Figure 3-9). Even though $Kn > 1$ indicates the rarefied gas flow range, this result shows a significant deviation, in terms of the gas separation factor, from the free molecular flow regime. The discrepancy arises from the shift away from equilibrium situation close to the open aperture in the graphene membrane. At equilibrium the rate of crossing an aperture is purely defined by the mean molecular speed of the gas species. In the experimental condition the transport across porous graphene is not an equilibrium process, but the partial pressure difference of the gas species across the membrane drives it. In other words, a superimposed collective drift speed in addition to the thermal speed of the gas molecules instigates a perturbation of the equilibrium. In a material volume of the non-equilibrium process, frequent intermolecular collision leads to the collective movement. By reducing the linear momentum exchange between different species [123], separation of a gas mixture can be enhanced. This prediction can be observed when pore sizes are further reduced to yield $Kn > 8$. The small pores on graphene decreases the total flow and thus the equilibrium perturbation volume to the range of the molecular mean free path, and the gas separation performance approaches the permselectivity value but reaches merely 80% of the effusion (or Graham’s) limit for $Kn \approx 8$ (Figure 3-9). These findings are very surprising, since it appears that $Kn$ fails to predict the transition to a true free molecular flow across an orifice when it comes to the gas mixture separation. Certainly, it is a topic of further investigation.
3.1.3 Summary of gas transport properties of graphene membranes

The permeation properties determined in this study confirm the validity of gas kinetic theory in describing the pore flow through 2D pores down to ~4 nm. Therefore, the current investigation greatly agrees with results of MD simulations predicting the gas transport through graphene membranes and suggest effusion-like flow across graphene pores as an upper limit for intermediate pore sizes [45]. The effect of sieving and adsorption as suggested by MD simulation [41, 46] could not be observed due to large pores sizes. The measured gas purification performance is limited to separation characterized by thermal speeds of different gas species. However, it is both membrane properties, permeance and selectivity, that provide a figure of merit for membrane performance in practical applications. As shown in Figure 3-10, the gas permeance of the sub-10-nm porous graphene membrane is orders of magnitude superior to other polymeric [124], inorganic [125-127], graphene oxide [128, 129], and composite membranes. It is the atomic thickness of the membrane that, even at relatively low porosities of ~4%, causes this outstanding permeation properties. The data confirms the great potential of graphene membranes for gas separation suggested by MD simulation at least in terms of the permeation capability.
Figure 3-10 Comparison of H$_2$/CO$_2$ gas-selectivity of the porous graphene membranes (8.1 nm pore diameter, with $\kappa = 4.0\%$ porosity) and other membranes: graphene oxide (GO) [128, 129], poly(1-trimethylsilyl-1-propyne) (PMSP) [130], polyetherimide (PEI) [131] carbon molecular sieve (CMS) [132], zeolite [126, 127], silica [125], metal-organic framework (MOF) [133], and SiC [134].

In the currently investigated pore size range down to $\sim$4 nm, the gas separation performance is limited by the nature of the separation mechanism based on thermal speed. Nevertheless, the selectivity is comparable to some conventional polymer or carbon molecular sieve (CMS) membranes [130-132]. For certain applications, permeance becomes more crucial than selectivity, where large amounts of gases with comparable molar ratios are separated (e.g., CO$_2$ removal from natural gas) [135, 136]. In such applications, graphene membranes may prove to offer a great advantage. Effusion-based selectivity is also significant for separation of gases with large mass
differences, such as removal of high carbons from natural gas, flavor selection and organic solvent separation [137], or for separation of gases otherwise impossible.

3.2 Vapor transport across graphene membranes

3.2.1 Experimental setup design

The vapor transport rate of graphene membranes is characterized by the upright cup method [138]. A graphene membrane is mounted in a custom made membrane fixture and seals a close compartment which contains the evaporating liquid. The liquid below the membrane will evaporate to saturate the air in the volume below the membrane. The permeate side of the membrane is left open to the atmospheric condition which is monitored by temperature and humidity sensors. The ambient condition data is used to calculate the ambient partial pressure, \( p_0 \). The difference in partial pressure of the liquid below the membrane and in the atmosphere, \( p_{sat} - p_0 \), will drive the vapor molecules through the membrane. The weight loss, \( \Delta m \), of liquid enclosed below the membrane is recorded for at least 10 hours with a high precision balance (XPE 104, Mettler Toledo) with a resolution of 0.1 mg. Normalizing the measured weight loss rate with the partial pressure difference, \( p_{sat} - p_0 \), and the membrane pore area, one can calculate the vapor permeance of the graphene membrane.
Figure 3-11 Schematic of upright cup evaporation rate measurement setup. The graphene membrane is mounted in fixture which sits on top of a high precision balance. The membrane seals a compartment which is containing the evaporating liquid and is the only pathway for the molecules to escape from the closed volume.

### 3.2.2 Results and discussion of graphene membrane vapor permeance

The graphene membrane is highly permeable to vapors. In particular, water vapor can escape the entrapped volume below a 100.6 nm graphene membrane at high rates of ~0.013 mol/Pa/s/m² (Figure 3-12). The weight loss rate of methanol, ethanol and isopropanol are even higher, but when normalizing the weight loss rate by the significantly higher vapor pressure of the species, one finds a higher permeance for the lighter water molecules (Figure 3-12). These results indicate that vapor phase transport may show molecular weight dependency as pure gas does.
Figure 3-12: Vapor permeance of water, methanol, ethanol and isopropanol through 100.6-nm-pored graphene membrane with respect to the molar weight of the species.

However, it does not resemble the $m^{-1/2}$ scaling of gas permselectivity. In contrast to the single gas permeation, presence of the ambient air renders the vapor phase transport a multicomponent diffusion. Therefore, as in the mixture gas separation, the influence of the second species (air in this case) may not be neglected. Keeping this in mind, water vapor is the only species among those measured in this section that takes higher thermal speed than the surrounding air molecules, which might accentuate the permeance driven by the low partial pressure difference.

Effect of the pore size on the water vapor permeance across the graphene membrane is counterintuitive. The permeance of water vapor with respect to the pore diameter decreases for increasing graphene pore diameter (Figure 3-13). For pore diameter of 970.8 nm the permeance is one-order-of-magnitude lower than that of the sub-10-nm graphene pores. The
fact that smaller pores preferentially allow the water molecule passage may originate from the different flow regimes of gas molecules through the graphene membrane.

Figure 3-13 Water vapor permeance through graphene membranes with different pore diameter ranging from 8.1 to 970.8 nm (blue cross) compared to effusion limit of water molecules (black dashed line).

When the pore diameter is comparable to or smaller than the mean free path of the water vapor molecule in the air (~60-100 nm) the water molecule may escape through the graphene membrane in an effusive manner dominated by the thermal speed of the water molecules. However, the total level of the vapor phase effusion is not met; permeance reaches only 25% of the effusion limit (Figure 3-13). For large pores the membrane is not selective to water molecules but the air molecules are dragged alongside with the water vapor slowing down the total permeation rate of water molecules.
Still, the total amount of vapor permeation driven by the small partial pressure difference is exceptionally high. Since the graphene membrane would not allow liquid water permeation when only one side of the membrane is wet and the other side is dry (see section 3.3.2), the porous graphene membrane might be an efficient waterproof membrane material, while being highly breathable due to ultrahigh vapor permeances observed.

![Figure 3-14 Comparison of water vapor transmission rate for porous graphene membranes (five 400-nm-pore membrane samples, with porosity ranging from 3.6 to 11.5%) and waterproof yet breathable textile membranes (data taken from [139, 140]).](image)

Indeed, the comparison of the water vapor transmission rate of the porous graphene membranes with commercial waterproof membranes [139, 140] confirms up to 4-order-of-magnitude enhancement in breathability (Figure 3-14).
3.3 Liquid water transport across graphene membrane


In contrast to the measurement of gas permeance the characterization of liquid transport properties of a graphene membrane is significantly more difficult. The permeation rate is lower, for the viscosity of water is 3-order-of-magnitude higher than those of gases. There is no low-pressure mass flow meters commercially available for use in measuring the permeation rates of liquids in the expected flow range. Furthermore, water is an excellent solvent, and as such it dissolves most contaminants and washes them towards the membrane surface.

3.3.1 Design of the experimental setup

3.3.1.1 Measurement setup

To minimize the graphene membrane area exposed to the liquid during the transport measurement, a microfluidic chip adapter (NanoPort, IDEX) is employed instead of a membrane fixture (Figure 3-15 a). The adapter with
minimal dead volume is directly glued onto the Si support with epoxy. An embedded O-ring and the epoxy glue seal the interface between the Si chip and the microfluidic port safely against any leakage. The adapter allows the connection of a translucent, 1/16" flexible capillary (PFA tubing, IDEX) with 0.53 mm inner diameter (Figure 3-15 b). The capillary is filled carefully with the DI water (MilliQ Advantage, Merck-Millipore) as membrane feed.

Figure 3-15 a) Schematic of liquid flow experiment. Microfluidic adapter (brown) seals to the Si support chip (dark grey) which carries the freestanding graphene membrane (black punctured structure) on a porous SiN_x support and allows the connection of a feed capillary (light gray) to the membrane chip. Position of liquid meniscus is tracked over taking high-resolution photographs. b) Photograph of the microfluidic setup showing the SiN_x support frame (yellow) and the microfluidic adapter with the translucent tubing. c) Photograph of liquid meniscus in the feed tubing which is used to track the meniscus position (red box) by an edge detection algorithm (b/w inset). Blurred digits above (260) show the readout of the manometer which monitors the applied differential pressure across the graphene membrane.

To the other end of the capillary a pressure controllable N_2 gas line is connected. Using the precision pressure controller (IR 2000, SMC) of the
N₂ gas monitored by a handheld manometer (HHP91, Omega), one can pressurize the feed water in the capillary upstream of the graphene membrane. The permeate side of the graphene membrane is open to ambient air. Unless otherwise noted, water flow measurements are carried out at 25°C and with a feed pressure $\Delta p \approx 250$ mbar. Any liquid permeation through the graphene membrane will result in movement of the meniscus defined by the N₂/water interface inside the translucent capillary. Photographs of the manometer display and the liquid meniscus (Figure 3-15 c) are repeatedly taken to track the motion of the upstream liquid. A custom made image analysis script (Matlab, MathWorks) extracts the position of the meniscus in each individual image by using an edge detection algorithm on a snippet (red box Figure 3-15 c) yielding a clear white line on an otherwise black image (inset Figure 3-15 c). The accuracy of the meniscus position is given by the resolution of the digital image and is usually adjusted to $\lambda_p \sim 75$ pixel/mm. Using the inner cross section area of the capillary ($A_{ca} = 0.217$ mm²) one can estimate the minimal detectable volume change to be 2.9 nL. Therefore, the described setup can be used to reliably measure flow rate in the range of nL/min which should be precise enough to quantify the water permeation through the graphene membranes.

To characterize the effect of temperature variation of the permeating water onto the mass transport properties of the graphene membranes the entire tubing setup containing the liquid water was immersed into a temperature controlled chiller bath (F12-ED, Julabo) with temperature
stability of 0.03°C. In this way the temperature of the permeating water can be varied between 5°C and 45°C. The strong agitation inside the water bath facilitates the heat transfer to the water inside the tubing and to the membrane itself allowing short temperature stabilizing intervals around 20 min. Permeation data is acquired in the same way as above by digital photographs.

### 3.3.1.2 Reducing membrane clogging

Initial water permeation results indicated that the graphene membranes are prone to heavy clogging (Figure 3-16) during the water permeation experiments, lowering the permeance and obscuring the data analysis.

![SEM micrograph of 936.8 nm pore graphene membrane after liquid water flow experiment](image)

**Figure 3-16** SEM micrograph of 936.8 nm pore graphene membrane after liquid water flow experiment. All the graphene pores but one are clogged by unknown contaminant. Inset show a close-up onto a film-like contamination blocking >75% of the pore area.
Extensive testing revealed three main sources for the contamination: (i) the MilliQ DI water used; (ii) the tubing and used connectors; and (iii) the graphene membrane surface itself. The first source of contamination could be avoided by employing an additional DI water distillation step. It was found out that evaporated droplets of the DI water leaves residues at the nanometer scale, similar to the ones found on the graphene membrane (Figure 3-16) despite the MilliQ dispensing system being well maintained and operating within the specifications (TOC count <5 ppm and 18.2 MΩ cm). The water contains neutral nonvolatile compounds which will accumulate in the membrane area when not remove by an additional water distillation step. The use of distilled MilliQ DI water additionally filtered by a 200 nm PEEK membrane finally yields significantly improved permeation results. The second source of contamination can only be addressed by careful rinsing of all tubing, connectors and syringes by acetone followed by isopropanol and finally by distilled and filtered DI water before the experiment.

3.3.1.3 Graphene membrane preparation for liquid flow measurement

The third source of contamination during the water permeation experiment was the graphene membrane itself. To reduce the total amount of contaminants which could be washed off the graphene membrane surface, the
wetted graphene area is greatly reduced by using the microfluidic adapters instead of a membrane fixture (see above).

Another method of reducing the contamination level is to remove the graphene around the active membrane area and cleaning the surrounding region. Otherwise, once the graphene layer on the support structure is exposed to a shear flow of water across the graphene, it can wash off the double layer graphene and destroy the membrane (*Figure 3-17 a*). The membrane lifts of the support structure exposing the bare SiN₅ holes or graphene from the vicinity is washed onto the membrane area covering the drilled pores in the graphene membrane (*Figure 3-17 a*). To suppress the latter, graphene that surrounds the membrane area can be removed by sputtering a high dose of Ga⁺ ions onto the vicinity (orange shading *Figure 3-17 b inset*) of the freestanding graphene, which etches away the double layer graphene as well as other particles in a region of 1 mm outside the membrane active area. In order to ensure the integration between perforated graphene and the holey support, an additional deposition of material (e.g., Pt) around the active membrane area can stitch the graphene onto the support, thereby preventing successfully the membrane disintegration caused by the graphene being washed off the support structure on all samples tested.
Figure 3-17 a) Scanning electron micrograph of a graphene membrane which was damaged during the water flow experiment. Graphene is washed off from the support frame which is breaking the membrane and covering the prepared pores. b) Scanning electron micrograph showing improved graphene membrane preparation before liquid flow experiment. Orange shading indicates area in which support frame is cleaned by high Ga⁺ ion dose to remove the graphene and all unwanted contaminants, green shading indicates area of Pt deposition by electron beam assisted Pt deposition to seal defective graphene holes and stitch the graphene to the support chip (see schematic).

The remaining contaminants residing on the surface of the chip could be encapsulated and immobilized by coating the entire support frame via a few cycles of ALD as described in section 2.4.2. The ALD coating fixates the otherwise dissolvable or washable materials to prevent their agglomeration in the active membrane area. Furthermore, and as mentioned above (section 2.4.2), the ALD coating can render the membrane surface less attractive to organic molecules [101]. Therefore, one may expect that the ALD
coating would be beneficial for the membrane stability and support the water permeation over longer periods. The effect of the additional coating on retaining the water permeation rate needs be carefully investigated, and therefore only a part of the membrane samples will be treated with the ALD coating with TiO$_2$.

### 3.3.2 Onset of water permeation through porous graphene

Initiating the permeation of liquid water through the porous graphene membrane is not found to be easy all the time. After wetting the feed side of a 94.6-nm-pored graphene membrane with DI water (Case I) and applying a pressure drop of 200 mbar across the membrane, the position of the liquid meniscus changes instantaneously when increasing the pressure, but there is no steady movement of the liquid meniscus at stable feed pressure (Case I Figure 3-18). The instantaneous change can be observed for a blank Si chip as well, attributable to compressibility in the measurement system and not to permeation. The stable position of the meniscus indicates that the graphene membrane does not permeate liquid water when it is wetted only on one side. Increasing the feed pressure up to 2 bar or using graphene membranes with different pore diameter up to 1000 nm does neither yield any detectable permeation of liquid water in Case I. The phenomenon can be understood by considering capillarity or the three-phase contact point –
liquid water, solid graphene, and air at the graphene pore edge. The situation resembles a well described problem of a pendant drop at a nozzle exit. The maximum over pressure, $\Delta p_d$, inside the pendant droplet can be estimated by the Young-Laplace equation, $\Delta p_d = 4\gamma / d_p$, using the pore diameter, $d_p$, and the surface tension of the liquid, $\gamma$. Therefore, the feed pressure applied across the graphene membrane for water ($\gamma_{\text{H}_2\text{O}} = 0.072$ N/m at 25°C) at the exit of a 94.6-nm-wide pore has to overcome ~30 bar in order to initiate the permeation. This onset pressure exceeds the value that the present, as-fabricated graphene membrane could sustain, and therefore water permeation cannot be initiated by simple increasing upstream pressure. This finding renders graphene a very interesting membrane material preventing the permeation of water across the wet / dry interface defined by the membrane pore. In this situation, the graphene membrane acts as a perfect waterproof layer yet breathable membrane, since it allows the permeation of water vapor at exceptionally high rates (section 3.2.2). Furthermore, the observation supports the validity of the experimental setup. The upstream liquid tubing system is leak tight, and a liquid meniscus movement due to evaporation of the water from the upstream meniscus could not be observed. The latter can be estimated by $dQ / dt = D_{\text{H}_2\text{O}} / R / T \times M_{\text{H}_2\text{O}} / \rho_{\text{H}_2\text{O}} \times P_{\text{sat}} / L \times A_{\text{ca}}$ which equals to $\sim 2.3 \times 10^{-5}$ μL/min at 25°C using $D_{\text{H}_2\text{O}} = 0.242$ cm²/s, $P_{\text{sat}} = 3.2$ kPa and a capillary length $L = 0.3$ m. The evaporation is far below the detectable range.
Figure 3-18 Onset of water permeation through 94.6 nm pore graphene membrane. Case I (orange triangle): only the membrane feed side is wetted. Pressure increase to 200 mbar leads to immediate compression inside the measurement setup observed as a static volume change (~1 uL / 200 mbar) but no further volume change can be observed over the course of the measurement. Case II (blue x): feed and permeate side of membrane are prewetted. Pressure increase leads to immediate volume change as before. Reaching the pressure set point ~200 mbar the volume change stabilizes at constant rate >4 min showing constant permeation of water across the graphene membrane.

However, to enable the permeation of liquid water, the huge pressure inside a pedant drop has to be overcome. It can only be reduced by lower surface tension of the liquid or even larger pores. Alternatively, it can be eliminated entirely by avoiding the three phase contact point from the beginning. The latter can be achieved by careful prewetting the graphene membrane on the permeate side as well (Case II Figure 3-18) such that water coming from both sides of the graphene membrane touches each other.
and no gaseous phase is present at the pore interface. Indeed, using the same 94.6-nm-pored graphene membrane, which would not permeate water in case I, and carefully wetting both membrane surfaces with water, the position of the N$_2$/water meniscus inside the capillary steadily moves upon applying a pressure drop of 200 mbar across the graphene membrane (Figure 3-18). This steady movement of the liquid inside the capillary at constant pressures upstream and downstream clearly shows that water permeates across the atomically thin membrane. To the best of our knowledge, this observation is the first time measurement of water passage across porous graphene membranes. Neglecting the compressibility effect caused by the onset pressure at the beginning of the experiment, one can calculate the water permeance of the graphene membrane by normalizing the volume change rate, $\Phi_m = dQ_m/dt$, with the applied feed pressure, $\Delta p$, and the membrane area, $A_m$.

3.3.3 Modeling the clogging of graphene membranes

Despite the significant reduction of the contamination level during the water permeation measurement, still the graphene membranes tested exhibit nonlinear flow rate even in the course of a few minutes’ water permeation measurement (Figure 3-19 a). Calculating the initial flow rate $\Phi_i = dQ_i/dt$ during the first minute after applying the feed pressure of 253 mbar of a membrane of 100.1-nm-wide pores (porous graphene membrane coated
with additional 40 ALD cycles of TiO$_2$), one obtains $\Phi_i = 0.269 \, \mu$L/min (determined by the linear regression fit). After 20 minutes of permeation the final flow rate $\Phi_f$ is reduced to 0.018 $\mu$L/min (linear regression fit) which corresponds to only $\Phi_f / \Phi_i \approx 6.7\%$ of permeance left (Figure 3-19 a). After drying, SEM micrographs show that the active membrane surface is partly covered by particles and other contaminants which block the pores of the graphene membrane (Figure 3-19 b). Interestingly the permeance loss is in a perfect agreement with the pore area reduction experienced by the graphene membrane. Comparing the open pore area, $A_{mf}$, after the water permeation experiment (highlighted red area Figure 3-19 b) to the area, $A_{mi}$, before the experiment (highlighted red area Figure 3-19 a inset) one finds a similar reduction of the open pore area: $A_{mf} / A_{mi} \approx 7\%$. This great agreement indicates that the nonlinear permeation behavior of water through the graphene membrane is a result of the loss in the permeable area due to physical clogging of the membrane, which hampers the determination of the intrinsic (or initial) permeation performance of the graphene membrane.
Figure 3-19 Membrane clogging. a) Raw data (blue circle) and modeled membrane flow (black solid line) of water permeation over the course of 20 min across a 100.1-nm-pored graphene membrane at 253 mbar feed pressure. Initial flow rate drops due to membrane clogging. Inset shows a scanning electron micrograph of the free standing graphene membrane area before the water permeation experiment, highlighting the open pore area in red. b) Scanning electron micrograph showing the permeate side of the graphene membrane after the liquid flow experiment. Contaminants on the membrane feed side can be seen through the graphene layer. Open pore area is highlighted in red.

To elucidate the problem of clogging and to improve the data analysis a permeation model accounting for pore clogging is employed. Two basic assumptions lead to a powerful description of membrane permeation loss known as intermediate clogging [141, 142]. These are: first - the feed water contains a constant concentration, $c_c$, of contaminants; and second - the membrane areal reduction is proportional to the total amount of contaminants, $Q_c(t) = c_c Q_w(t)$, washed towards the membrane. Both assumptions
motivate the description of a time dependent membrane area, $A_m(t)$, (equation (3.8)) based on the total permeate volume, $Q_w(t)$, of water at time $t$ and the proportionality constant $k$ describing the areal reduction by the filtered contaminant.

$$A_m(t) = A_0 - k c_c Q_w(t)$$  \hspace{1cm} (3.8)

Inserting into eq. (3.8) the standard flow equation, $Q_w(t) = j_w \Delta p A_m t$, with $j_w$ the membrane permeance and $\Delta p$ the applied pressure drop, one obtains eq. (3.9) which can be solved for $Q_w(t)$ (eq. (3.10)).

$$Q_w(t) = j_w \Delta p A_m(t) t = j_w \Delta p (A_0 - k c_c Q_w(t)) t$$  \hspace{1cm} (3.9)

$$Q_w(t) = \frac{j_w \Delta p A_0 t}{1 + j_w \Delta p k c_c t}$$  \hspace{1cm} (3.10)

Equation (3.10) describes the flow through a continuously clogging graphene membrane over time $t$ depending on measured quantities, $\Delta p$ and $A_0$, and two fit parameters, the unknown membrane permeance $j_w$ and the clogging factor $k c_c$. Note that since $dQ_w/dt|_{t=0} = j_w \Delta p A_0$ represents the unclogged membrane flow rate, $j_w$ denotes the unclogged permeance of the graphene membrane as an intrinsic membrane property that should be determined by the measurement. Fitting the model to the experimentally measured volume change both parameters, $j_w$ and $k c_c$, can be estimated. As Figure 3-19 a shows, the model (black solid line) yields an excellent agreement with the measured volume evolution (blue circles). Similar model
fitting works well for all the water flow measurements carried out in this section. Therefore, the model gives a valid description of the water permeation through continuously clogging graphene membranes, thereby providing estimation of the initial water permeance across unclogged graphene membranes, more reproducibly and reliably than arbitrary linear regression does. All the liquid water permeances, \( j_w \), and the estimated area of clogged membranes, \( A_m \), reported in this section are based on this model fit approach. As mentioned above the flow rate reduction and the post-clogging SEM analysis suggest a total loss of 93% of the active membrane area after 20 min of permeation (Figure 3-19 a). The strong clogging of the membrane area can be qualitatively understood by considering that the size of the total permeation area is \( A_m = 7.1 \times 10^{-11} \text{ m}^2 \) corresponding to an approximate permeance of \( \sim 2.5 \times 10^{-6} \text{ m}^3/\text{m}^2/\text{Pa}/\text{s} \) (open area) which is at least one-order-of-magnitude higher than that of a membrane with cylindrical pores having similar pore sizes and aspect ratio \( \sim 10 \) (using Hagen-Poiseuille equation). This comparison is interpreted that each individual pore permeates \( \sim 10 \) times more liquid and therefore the observed membrane clogging should be that much stronger due to the exceptionally high permeance.
3.3.4 Pressure dependency of liquid transport

The flow rate of liquid water across the graphene membrane is found to be linearly dependent on applied pressure difference. Upon the onset of pressurization at $\Delta p = 250$ mbar water is permeating the prewetted, 199.5-nm-pored graphene membrane at an initial rate of $\sim 0.90$ $\mu$L/min and is reduced to $\sim 0.526$ $\mu$L/min after 4.5 min due to membrane clogging (Figure 3-20 a). Reducing the feed pressure $\Delta p = 153$ mbar, the flow rate drops to 0.314 $\mu$L/min, and further reduction of $\Delta p$ to 49 mbar lowers the flow rate to 0.103 $\mu$L/min. The calculated water permeances, $j_w$, of the membrane at all pressures are constant when accounting for the membrane clogging for the first 4.5 min (Figure 3-20 b). Similar results are obtained for graphene membranes with different pore sizes ranging from 199.5 nm down to 15.6 nm independent of additional TiO$_2$ ALD coating.

Hence, one can conclude that the membrane flow, $Q_w$, scales linearly in the applied feed pressure ($Q_w \propto \Delta p$) as expected for porous membranes and that meaningful membrane properties such as permeance can be calculated by normalizing the initial flow rate observed, $dQ_w/dt \mid_{t=0}$, by the pore area, $A_m$, and the applied feed pressure, $\Delta p$. 
Figure 3-20 Pressure dependency of water transport across graphene membrane. a) Raw data of water permeation experiment at 3 different pressure 250, 153 and 49 mbar using a 199.5 nm pore graphene membrane. Membrane displays low but still noticeable flow rate reduction in the first 4.5 min. To compare flow rates each section is fitted to the clogging model (3.10) separately and the slope is extracted as indicated. b) Per-pore permeance measured at various pressures for 15.6-nm-pored membrane (orange triangle), 44-nm-pored membrane (48 nm pore with 50 cycles TiO₂) (green cross), 100-nm-pored membrane (red rectangle) and 199.5-nm-pored membrane (blue circle).
3.3.5 Pore size dependency of liquid flow through porous graphene membranes

As Figure 3-20 b indicates the water permeance of the graphene membrane strongly depends on the membrane pore diameter, showing smaller permeance for smaller pores. In order to investigate the influence of membrane pore diameter, $d_m$, in greater detail, water permeances are measured for graphene membranes of which pore sizes range from 5.7 nm to 1000 nm (blue circle in Figure 3-21). Plotting $j_w$ in a loglog plot over $d_m$ indicates a linear relation between both. The additional coating of few cycles of TiO$_2$ ALD as described in section 2.4.2 does not cause a noticeable difference in the permeance data (orange cross in Figure 3-21) but exhibits the same total permeance level and pore size dependency. Inserting the viscosity of water, $\mu_{H_2O}$, and calculating the predicted water flux by Sampson’s formula (equation (3.4)), the predicted permeance (black solid line Figure 3-21) agrees very well with the water permeance data. In the measured pore size and viscosity range, Sampson’s formula can, therefore, be used to describe the liquid permeation across the graphene membrane. Unlike the gas permeation in the similar pore size range, there is no observable transition to a different flow regime. The permeation of water through graphene pores with diameters between 5.7 nm and 1000 nm can
be well described by the continuum theory, evidenced not only by the correct scaling with respect to the driving force and the pore diameter but also by the quantitative agreement with the prediction of Sampson’s formula.

Figure 3-21 Measured water permeance (per pore area) at 25°C as a function of pore diameter, \(d_m\). A great agreement is found between measured permeance and Sampson’s formula prediction (black solid line) for water permeation across porous, double-layer graphene membranes with and without ALD coating, orange cross and blue circle, respectively.

It is not surprising that continuum theory holds true for liquid permeation through pore sizes larger than 5 nm. Assuming that a mean free path for liquids is comparable to the molecule’s own sizes, one can take the water molecule size (\(\sim 0.3\) nm) as the mean displacement distance between molecular interactions and compared it with the pore aperture diameters. The equivalent Kn for water lies well below 0.1, placing the transport in the
continuum flow regime. Only further reduction of pore size to the 1 nm range is expected to give results deviating from continuum theory. Figure 3-22 shows all available data on water permeation through graphene membranes. The new experimentally measured data of this thesis is the first observation of water flux across large pores in graphene and representing a full set of data over 3 orders of magnitude of pore diameters. It suggests that water permeation through graphene membranes is described by Sampson’s theory of permeation through infinitely thin membrane. For pore sizes smaller than 3 nm there are only two very recent experimental observations [64, 65] but the majority of data stem from MD simulations [55, 57] and give slightly scattered results. One problem arises from a proper definition of the pore diameter which is controversially reported as distance of edge atoms [54], open area left accounting for the van der Walls radius [55, 57, 64], or number of vacancy sites [58], for small pores in graphene. Regardless, the upper limit for the per-pore permeation through porous graphene membrane is described by Sampson’s theory consistently (Figure 3-22 a). For pore diameters smaller than 2 nm, MD simulations show lower permeation of water through the aperture than Sampsonian prediction, suggesting a hindered passage of the water molecules.
Figure 3-22 a) Overview over all available graphene membrane water permeance data at 25°C through a single graphene pore versus pore diameter (measured as C-to-C distance). Graph shows great agreement between measured graphene permeance and Sampson theory (black solid line) for double layer graphene membranes with large diameter pores. Additional experimental results for subnanometer graphene membranes of [65] and [64] are plotted in blue square and blue circle, respectively. Results of MD simulation are shown as, black triangle [54], black asterisk [55], black diamond [58], black circle [57] and the expected per-pore flow based on the series resistance model is shown as dashed orange line. b) Close up to permeation data in sub-6-nm pore size range.

For pores in the subnanometer range, even monolayer graphene membranes will show a pore aspect ratio of ~1. This notice motivates the consideration of a series resistance model accounting for both the entrance effect and the channel wall resistance insight the membrane similar as described above for the continuum theory [64]. Such a model was proposed in
ref. [71], and it combines Sampson’s theory with the Hagen-Poiseuille equation to

\[ j_D = \frac{d_m}{6\pi \mu} \frac{1}{\frac{8}{3\pi} \frac{l}{d_m} + 1}. \] (3.11)

Using this flow model one can indeed predict a decreased permeation (dashes orange line Figure 3-22), but it is unlikely that the description based on continuum theory will catch all the aspects of permeation through subnanometer-scale pores. The effect of the pore edge chemistry and the affinity of the permeating molecules towards these functional groups will certainly have an effect on the permeation rate [57], and such a series resistance model could only be used to efficiently estimate an order of magnitude permeation through the graphene membrane. However, the precise identification of these relatively small differences by experimental measurements is very challenging, exemplified by the scatter of the experimental data presented here and the huge error range of results reported elsewhere [64].

3.3.6 Temperature dependency of liquid transport

In order to investigate the effect of temperature on the permeation of water through graphene membranes, a series of experiments at different water temperatures is carried out. After prewetting the membrane with water and assembling the membrane into the liquid flow setup, the water temperature
is set by immersing the setup into a chiller bath at a predefined temperature (orange solid line Figure 3-23 b). After temperature stabilization for at least 5 min, a feed pressure $\Delta p \approx 260$ mbar (blue solid line Figure 3-23 b) is applied.

![Figure 3-23](image)

**Figure 3-23** Measurement of temperature dependency of water permeation through graphene membranes. a) Resultant model fit of water permeation data through 40.2 nm pore graphene membrane. Inset shows raw data of permeated volume over time blue circle and the model fit (black solid line). b) Temperature (orange solid line) and pressure set (blue solid line) point for temperature dependent water permeation.

To reduce the effect of membrane clogging the water permeation data is acquired for the initial 2 min upon onset of feed pressure (Figure 3-23)
a). After relieving the pressure a new temperature set point is adjusted, followed by the above measurement procedure. The permeation data at each temperature set point is fitted to the clogging model described above to yield a series of permeances \( j_m(25^\circ C) \), \( j_m(45^\circ C) \), \( j_m(5^\circ C) \), \( j_m(15^\circ C) \), \( j_m(35^\circ C) \), \( j_m(25^\circ C) \). The measurement sequence consists of two measurements at 25°C water temperature, one at the beginning and the other at the end, which helps to estimate the amount of clogging in the course of the measurement. In a particular example (Figure 3-23) the flux decline in the final measurement compared with the first one is 48%. As shown above the reduction of the flow rate can be attributed to the loss of permeable area. The initial membrane area equals \( A_m = 2.07 \times 10^{-11} \text{ m}^2 \) and during the final 6\(^{th}\) measurement only 52% of the entire pores are left open \( A_c = 0.52 A_m \). This areal loss corresponds to a gradual increase in uncertainty in the calculated membrane permeance. The measured flow rate is, thus, normalized by an estimated open area \( A_c = 0.5 (A_m + A_c) \), an arithmetic mean between the initial membrane area and the area extrapolated from the clogging model or measurement. The associated error \( e_A \) in the calculation can be estimated by the difference of both area measures \( A_m \) and \( A_c \) and yields \( e_A = 0.5 \times (A_m - A_c) \). The obtained temperature dependency of water permeance across porous graphene with 40.2-nm-wide pores is visualized in Figure 3-24.
Figure 3-24 Measured per-pore water permeance through 40.2-nm-pored graphene membrane at different feed water temperatures, with a dashed blue line showing linear interpolation. Predicted water permeance by modified Sampson’s formula for the 40.2-nm-wide pore is shown as a solid black line.

The results show that the variation of temperature has a noticeable effect on the water permeance through porous graphene membranes (Figure 3-24). For lower temperatures (≤15°C) the per-pore permeance of water through a 40.2-nm-pored membrane yields ~5×10⁻²² m² Pa s. At temperatures above 35°C the permeance is around 10×10⁻²² m² Pa s (Figure 3-24). The single largest uncertainty arises from the difficulty in the area estimation in the continuously clogging situation. Acknowledging the uncertainty, the general trend obtained from the linear fit of the measurement values supports the Sampsonian transport. The viscosity of water depends strongly on the fluid temperature. It drops from 890 μPa s at 25°C to 570 μPa s at 45°C and is as high as ~1500 μPa s at 5°C. Using these viscosity values in Sampson’s formula (3.4), one would expect a ~3 fold...
increase in permeance with temperature change from 5°C to 45°C (black solid line Figure 3-24). Despite the scattering of the experimental results the general trends of the measured and predicted water permeances are the same. Note that the more membrane clogging, the higher the estimated membrane permeance. As in the example shown in Figure 3-23 temperature was swept from 25°C to 45°C first and then from 5°C to 15°C before returning to 35°C and finally back to 25°C, in order to avoid an artifact caused by convolution of the thermal change of viscosity and the membrane clogging.

The temperature dependency of the water permeance of porous graphene membranes is further elucidated by measuring two additional membranes with 23.2-nm- and 6.3-nm-wide pores. Table 3-1 summarizes the results of the water permeation measurements. The estimated membrane area, $A_e$, decreases over the course of the measurement by up to ~30% and the associated uncertainty, $e_A$, increases with each measurement. The measured membrane permeation coefficient, $q \equiv \frac{dQ/dt}{\Delta p}$, from the clogging model fit reveals clear temperature dependency.

---

6 This is a crucial point to understand which helps to evaluate the effect of temperature change on water permeation. While measuring the permeance with subsequently increasing temperature set point an overestimation of the clogging would artificially enhance the effect of temperature on the permeance, measuring the same set of data in a decreasing temperature sequence the consideration of membrane clogging would decrease apparent permeance change due to temperature.
Table 3-1 A summary of temperature dependent flow measurement results of the estimated membrane area, $A_e$, the error of the area estimation, $e_A$, and the fitted membrane permeation coefficient, $q$.

<table>
<thead>
<tr>
<th>sample</th>
<th>Measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>N12-1-4 40.2 nm</td>
<td>temperature [°C]</td>
<td>25</td>
<td>45</td>
<td>5</td>
<td>15</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>$A_e [10^{-11} \text{ m}^2]$</td>
<td>2.07</td>
<td>1.96</td>
<td>1.85</td>
<td>1.74</td>
<td>1.63</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>$e_A [10^{-11} \text{ m}^2]$</td>
<td>0.00</td>
<td>0.11</td>
<td>0.22</td>
<td>0.33</td>
<td>0.44</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>$q [10^{-9} \mu\text{L/Pa/s}]$</td>
<td>15.01</td>
<td>16.07</td>
<td>7.61</td>
<td>6.32</td>
<td>13.00</td>
<td>7.98</td>
</tr>
<tr>
<td>N11-2-2 23.2 nm</td>
<td>temperature [°C]</td>
<td>25</td>
<td>35</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_e [10^{-11} \text{ m}^2]$</td>
<td>2.49</td>
<td>2.00</td>
<td>1.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$e_A [10^{-11} \text{ m}^2]$</td>
<td>0.00</td>
<td>0.49</td>
<td>0.86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$q [10^{-9} \mu\text{L/Pa/s}]$</td>
<td>7.38</td>
<td>6.55</td>
<td>6.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N12-1-8 6.2 nm</td>
<td>temperature [°C]</td>
<td>8</td>
<td>15</td>
<td>25</td>
<td>35</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_e [10^{-11} \text{ m}^2]$</td>
<td>3.12</td>
<td>2.84</td>
<td>2.56</td>
<td>2.28</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$e_A [10^{-11} \text{ m}^2]$</td>
<td>0.00</td>
<td>0.56</td>
<td>0.84</td>
<td>1.11</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$q [10^{-9} \mu\text{L/Pa/s}]$</td>
<td>13.88</td>
<td>15.91</td>
<td>16.20</td>
<td>21.15</td>
<td>27.65</td>
<td></td>
</tr>
</tbody>
</table>
The Arrhenius plot (Figure 3-25) of the permeances $R \times \ln(q/A)$ summarizes the results of all the water permeation experiments. The slope in the Arrhenius plot can be associated with the activation energy, $E_a$, that governs the permeation process. For a purely viscosity-dependent permeation event the activation energy is expected to be $\sim 4.3$ kcal/mol defined by the viscosity of water (Sampsonian permeance Figure 3-25).

Figure 3-25 Arrhenius plot of water permeance across graphene pores of 40.2 nm (blue circle), 23.3 nm (orange triangle) and 6.3 nm (cyan square). The dashed lines with the same colors represent linear fit, and the black triangles indicate the slope that corresponds to the activation energy, $E_a$. The error bars originate largely from the uncertainty in the open pore area estimation. Solid black line represents model data of Sampsonian permeance of 40.2-nm-wide pores.
The experimentally determined activation energy for water permeation through porous graphene ranges between 3.8 kcal/mol and 5.6 kcal/mol (Figure 3-25). For the two larger pore membranes (40.2 nm and 23.2 nm) the activation energy of water permeation agrees very well with the theoretical value of 4.3 kcal/mol for water viscosity. Therefore, these results confirm the validity of the proposed 2D flow theory which suggests \( Q \propto \mu^1 \). The smallest pore membrane tested (6.3 nm) indicates a slightly increased activation energy for the water permeance of 5.6 kcal/mol (Figure 3-25). It should be noted that the experimental error associated with the pore area uncertainty is increasing as well.\(^7\) In regard of this variation it is likely that the mechanism of water permeation across porous graphene membranes, with pore sizes larger than ~6 nm, follows the water viscosity mediated process.

\(^7\) The lower bound (~3.3 kcal/mol) can be estimated using \((A_e + e_A)\) as a reference area which equals the unclogged membrane area \(A_m\). The upper bound based on the clogged area yields ~8.1 kcal/mol.
4 CONCLUSION AND PROSPECTS

4.1 Graphene Membrane synthesis and observation of ultimate permeance

Since the discovery of graphene as the 2D crystal there has been uncountable reports of extraordinary properties of this material, though their usage and practical visibility remains to be established. In the field of membrane technology, the discovery of such a strong, leak tight 2D material has fueled an entirely new research area. The concept of the thinnest feasible membrane material represents the ideal geometry for membrane applications. Properties of a porous membrane out of atomically thin graphene have been widely studied by means of MD simulation but experimental observations and evidences for the actual mass transport properties of such a 2D membrane have remained very limited.

This thesis presents a comprehensive characterization of graphene membranes and its mass transport properties. A feasible and reliable synthesis pathway for such graphene membranes is developed. For the first time, graphene membranes with controlled pore sizes between 3.7 nm and 1 μm are synthesized with pore numbers up to $2 \times 10^6$, enabling the macroscale observation of gas and liquid transports. The observed flow phenomena of media through pores in 2D media are thoroughly investigated.
and characterized, and the expectation of the ultimate permeation is embodied for the first time.

Graphene is synthesized via our CVD method [67] yielding a fully covering, centimeter-scale monolayer with extraordinary cleanliness. We developed a highly reproducible double-layer transfer process of graphene onto a Si-based holey target substrate. It resulted in a double layer of freestanding hermetically sealing graphene that spans multiple 4–6-μm-wide holes on the inorganic support structure.

To enable efficient perforation of this freestanding graphene layer, the author explored FIB technology and the processes for patterning the 2D material. Characterization of the interaction of energetic Ga⁺ and He⁺ ions with the freestanding graphene revealed that the 2D lattice of graphene is highly transparent to a flux of 30 keV He⁺ ions but can be susceptible to that of similarly energetic Ga⁺ ions with creating multiple defects on it. The sputter yield of graphene is found to be dependent on ion species and bombardment energy, and the experimental observation could be well explained by use of a classic binary collision theory between energetic ions and C atoms in the graphene lattice. Beaming a controlled dose of highly focused He⁺ and Ga⁺ ions onto the freestanding graphene double layer could drill an array of circular pores of 3.3 nm and 4.8 nm in diameter, respectively. On monolayer graphene the FIB patterning could achieve pore sizes as tiny as 2.7 nm. Using this patterning technique the otherwise
impermeable graphene double layer can be perforated with up to $2 \times 10^6$ pores of which sizes range from 4.7 nm to 1 μm.

Single gas permeation through the graphene membranes shows ultimate permeation properties. For membrane pores larger than the molecular mean free path the gas permeation follows the viscous creeping flow through an infinitely thin orifice. For Knudsen numbers larger than 1, or when pore sizes are smaller than the molecular mean free path the intermolecular collisions are rare around the pores, and the gas transport enters the free molecular flow regime governed by a collision frequency of gas molecules with the pore opening. In this size range, permeance is invariant of the pore size. Both flow theories provide upper limit boundaries of possible permeation through a pore with a given size, and therefore the graphene membrane exhibits the ultimate gas permeation feasible.

Having the gas permeation physics understood, the thesis investigates gas separation capability of porous graphene. It is shown that, although large pores in graphene have no separation effect on gas mixtures, pores smaller than the gas mean free path tend to bear the separation capability attributable to deviance in thermal speed of the gas species. Therefore, sub-10-nm pores in graphene can achieve gas separation factor close to Graham’s law of effusion. In comparison to other membrane materials, atomically thin porous graphene exhibits moderate separation performance but far exceeding permeance, rendering a graphene membrane a good candidate for applications requiring large gas throughputs.
Water permeation through porous graphene is characterized thoroughly for the first time in this thesis. The onset of liquid water permeation through an atomically thin graphene membrane was found difficult if only one side of the membrane is wetted. The surface tension of water at the interface of liquid, gas and pore edge counteracts the feed pressure and stops the flow. Removal of the interface by prewetting both membrane sides can finally yield water permeation at exceptionally high rates. At room temperature liquid flow through pores sizes ranging from 5.7 nm to 1 μm in graphene can be described by Sampson’s formula developed for flows through infinitely thin apertures. A liquid volume flow rate according to this formula exhibits linear and cubic scaling in pressure and in pore diameter, respectively. The observed flow rate of water through a graphene membrane is bounded by the Sampsonian ultimate permeation and outperforms that of conventional porous membranes by far.

The high flow resistance to water of the semi wetted graphene membrane renders the porous graphene material a perfect waterproof but highly breathable layer. The measured vapor permeance of the porous double-layer graphene membrane exceeds all conventional waterproof-yet-breathable textile membranes by at least 3 orders of magnitude.

To summarize, the results presented in this thesis are a significant contribution in the field of graphene membrane research. It represents the first full experimental characterization of mass transport through porous
materials of atomic thickness. Furthermore, the observation of ultimate permeation properties under practical conditions can be a breakthrough in science and in particular membrane technology because they set the absolute upper bound limit to the relevant mass transport physics as well as offer a facile way of probing rarefied gas dynamics at ambient conditions.

4.2 Outlook

Graphene membranes are a fantastic platform for future research in the field of membrane science. One key aspect is the development of the large-scale synthesis pathways. To accomplish actual separation applications, the membrane has to be transferred from the current lab scale to large industrial scales. Two main challenges have to be addressed to enable this step. First – a suitable and scalable support structure must be found. Despite its unmatched strength, graphene has to be integrated to a suitable holey support. The support porosity should allow high permeation, and the graphene has to sustain the porosity in the necessary pressure range [70]. Second – a large-scale parallel pore formation process has to be developed. Membrane separation processes demand very narrow pore size distributions. Formation of pores having such a narrow size distribution at large scales is quite a challenge. Several processes like block-co-polymer patterning [34] or strain-assisted metal intercalicination [76] for pore
formation in graphene have been proposed, but their use for the graphene membrane fabrication has not been shown yet, letting alone the pore size limit inherent to each method. These issues leave room for a perforation process via other means that would result in fairly uniform nanometer-scale pores of one’s own choice.

Another direction for future research is a full depth characterization of the separation performance. At this point the proposed membrane can filter gases based on Graham’s law. However, porous graphene membranes certainly have the potential of showing higher gas selectivity than shown. MD simulation give a good guideline on how to achieve this goal. One aspect is to reduce the pore diameter further so that molecule pore edge interaction become more dominant. Another route to higher selectivity is modifying the membrane surface and pore edge chemistry specifically to change the molecules’ affinity towards them. These modification can for example selectively increase the concentration of the desired permeating gas species in the vicinity of the pore [50]. As an example shown in this thesis, an additional coating of the porous graphene by an ALD process can efficiently reduce the pore diameter and change the pore edge chemistry. Ultimately, when the pore sizes can be tuned in the range of the kinetic diameter, the porous graphene could serve as a molecular sieve. Embodiment of this idea might be very difficult to achieve because it will require a nearly perfect uniformity in the pore sizes to avoid any nonselective leakage pathway. In contrast to gas separation the filtration of liquids and the
rejection of dissolved compounds have not been assessed yet. The clogging during the liquid flow experiments shows that graphene membranes could be used as ultimate performance particle filters. There are multiple important applications in the area of water treatment. The holy grail of water purification is certainly desalination which – as MD simulations show – requires uniform pore sizes in the subnanometer range [57]. However, in addition to size exclusion of solvated ions, other rejection mechanisms based on membrane surface charge or edge chemistry could relax the requirements of pore size. Importantly, there are other very important water filtration applications. The presence of pharmaceutical molecules, hormones, pesticides and other man made molecules in natural water supplies are and increasing concern [143, 144]. These molecules are in the size range of 1-2 nm and are very likely to be efficiently filtered by a suitable graphene membrane. Note that it is conceptually very interesting that higher selectivity of porous graphene membranes can only be achieved when the permeating species interact more with the membrane surface. Therefore, any membrane modification will inevitably influence the permeation rate, and there needs be a good tradeoff between selectivity and permeance.

Altogether, the field of porous, atomically thin membranes is at an early stage of research and development. The ideal geometry of the membrane is an excellent research platform to fundamentally understand separation and permeation phenomena in membrane science. Furthermore,
recently results of MD simulations using MoS$_2$ instead of graphene as a base material suggest even higher water permeation rates for subnanometer pores [145]. The herein presented fabrication scheme for membranes can be easily applied to this new material, highlighting the potential of the developed research platform.
LITERATURE


CURRICULUM VITAE

Personal data
Jakob Buchheim
born 30.03.1986 in Munich, Germany (citizenship)

Education
09/2011 - 03/2016 Eidgenössische Technische Hochschule Zürich (ETHZ), Switzerland
Phd student at Institute: Nanoscience for Energy Technology and Sustainability, Department of Mechanical and Process Engineering, supervisor: Professor Hyung Gyu Park

03/2010 - 08/2011 Eidgenössische Technische Hochschule Zürich (ETHZ), Switzerland
Master of Science ETH in Mechanical Engineering. Score: 5.92/6
Masterthesis at Center for Mechanics: “Modeling of Overhead Lines“
Semesterthesis at Center for Mechanics: “Meso-scale Modeling of a Textile Mesh“
supervisor: Professor Edoardo Mazza

09/2006 - 01/2010 Eidgenössische Technische Hochschule Zürich (ETHZ), Switzerland
Bachelor of Science ETH in Mechanical Engineering. Score 5.41/6
Bachelor thesis at Institute of Fluidmechanics: “Fluid-Struktur-Kopplung mit OpenFOAM zur Optimierung eines Fischroboters“

Work Experience
09/2009 - 01/2010 Sensirion AG, Stäfa, Switzerland
Internship R&D for Humidity Sensors: Prototype development of anti-fogging module for cars

09/2008 - 05/2010 Eidgenössische Technische Hochschule Zürich (ETHZ), Switzerland
Teaching assistant for Continuum Mechanics at Center for Mechanics
Teaching assistant for Control Theory 1 at IDSC

06/2006 - 07/2006 Scanditronix Wellhöfer, Schwarzenbruck, Germany
Assistant in R&D team: Prototype development
Awards

2011 **Ernst-Blickle-study-price from SEW Eurodrive**

for outstanding masterthesis on “Modeling of Overhead Lines”

2005 **German Physical Society, Abitur Preis**

Conference Presentations


**PUBLICATIONS**


**Buchheim, J., Youn S. K., Traber J., Pronk W., Park, H. G.,** Micropollutant removal by sub 3 nm carbon nanotube membranes. (in preparation)


