Engineering Electrochemical Setups for Electron Microscopy of Liquid Processes

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Abstract

This work focuses on creating tools for imaging liquid samples at atmospheric pressure and room temperature in two different electron microscopes; the scanning electron microscope (SEM) and the transmission electron microscope (TEM).

The main focus of the project was the fabrication of the two systems; the electrochemical scanning-electron-microscopy cell (EC-SEM cell) and the TEM chip (version 1 and 2), and verifying that they can be used, for liquid phase experiments, in SEM and TEM.

These systems allow imaging of liquids and of objects in the liquid. They also include electrical connection to the liquid allowing measurement of electrical signals or the application of a voltage to the liquid during imaging.

In a SEM, where there is a comparatively large chamber to work with, a polycarbonate holder with micro-fluidic channels was fabricated to contain the liquid. The EC-SEM chip with an electron-transparent window and built-in electrodes was placed above a reservoir, sealing off the liquid from the vacuum, but allowing imaging through the window in the chip.

In-situ electrochemical experiments have been performed with this setup: imaging the electron beam (e-beam) deposition of nickel on the window, electrolysis of $\text{H}_2\text{SO}_4$ and measuring a CV of $\text{K}_3\text{Fe(CN)}_6$.

In a TEM the volume to work with is far smaller and a monolithic micro-fabricated chip was designed and fabricated for this microscope. The chip includes a micro-channel which contains the liquid and runs over an electron-transparent membrane. The channel keeps the liquid in a well defined area and reduces the volume increase from bulging in vacuum. Special windows are defined where the channel wall is thinned down to reduce the mass-thickness in these areas and retain the mechanical stability of the rest of the chip. Electrical connection to the liquid can be achieved with platinum electrodes lithographically defined on the chip.

The TEM chip has been used to image liquids in the TEM and to perform proof-of-concept experiments of holography of liquid.

Furthermore, in SEM, preliminary work has been completed to integrate graphene windows in the EC-SEM cell. In TEM, holography of graphene multi-layer sheets has been performed and the phase change per sheet has been determined as a step towards \textit{in-situ} holography of liquid through graphene.
Resume

Dette arbejde fokuserer på at skabe værktøjer til billeddannelse af væskeprøver ved atmosfærisk tryk og stuetemperatur i to forskellige elektronmikroskoper: skanningselektronmikroskopet (SEM) og transmissionselektronmikroskopet (TEM).

Hovedvægten af projektet var fremstillingen af to systemer, en til skanningselektronmikroskopet (kaldet den elektrokemiske scanning elektronmikroskopi celle eller EC-SEM cellen) og en til transmissions elektronmikroskopet, kaldet TEM chippen (version 1 og 2), og kontrollere, at de kan bruges til væske-fase eksperimenter i SEM og TEM.

Disse systemer tillader billeddannelse af væsker og af objekter i væsken. De indeholder også elektrisk forbindelse til væsken, som tillader måling af elektriske signaler eller tilførelsen af en spænding til væsken under billeddannelse.

I et SEM, hvor der er et forholdsvis stort kammer at arbejde med, blev en polycarbonat holder fremstillet med mikrofluid kanaler til at indeholde væsken. En EC-SEM chip, til cellen, med et elektron-transparant vindue og indbyggede elektroder, blev anbragt over et reservoir, så den afskærer væsken fra vakuum, men muliggør billeddannelse gennem vinduet i chippen.

In-situ elektrokemiske eksperimenter er blevet udført med denne opsætning: observation af aflejring af nikkel på vinduet med elektron-strålen, elektrolyse af H_2SO_4 og optagelsen af et CV af K_3Fe(CN)_6.


TEM-chip er blevet anvendt til at afbilde væsker i TEM og udføre proof-of-concept eksperimenter for holografi af væske.

Endvidere, i SEM, er foreløbig arbejd med at integrere graphen vinduer i EC-SEM cellen, blevet afsluttet. I TEM er holografi af multi-lags graphen plader blevet udført og faseændringen per lag er blevet fastsat som et skridt i retning mod in-situ holografi af væske gennem graphen.
Preface

This thesis is written as a partial fulfilment of the requirements to obtain the Doctorate of Philosophy (Ph.D.) degree at the Technical University of Denmark (DTU). The work has been carried out at the Department of Micro- and Nanotechnology (DTU Nanotech) and Center for Electron Nanoscopy (DTU Cen) in the period from March 2009 to August 2012. The project was financed by a DTU stipend and was a part of the Molecular Windows group at DTU Nanotech.

The main supervisor on the project was associate professor Kristian Mølhave, whom I gratefully acknowledge for his enthusiasm and endless outpouring of ideas. Kristian has an amazing ability to make me come away from a meeting with twice as many questions as I came in with, but also with a sure sense that I can find the answers. I am extremely grateful to have him as a supervisor.

The second supervisor was Dr. Rafal E. Dunin-Borkowski who also was the directed of DTU Cen. Rafal was always enthusiastic about my work and found the time in his busy schedule to hear me out and advise me on the electron microscopy side of the project. He accepted an offer to become the director of another electron microscopy center during my project, but I feel I benefited from his guidance.

After Rafal left Dr. Andrew Burrows stepped up and became the director of CEN as well as my supervisor. Andrew always made me feel welcome at DTU Cen, even though most of my time was spent at DTU Nanotech. Even though he had an entire center to run I was always welcome when I stopped by with questions or request for special considerations on the microscope. I am very grateful for his time and guidance.

I would like to thank all the past and present members of the Molecular Windows group. This group has helped me and motivated me throughout my project and provided a warm and welcoming environment.

A special thanks goes to Palle S. Jensen from DTU Kemi who provided invaluable help with the chemistry in this work at who gave freely of his own experience being a Ph.d student. Also from DTU Kemi are Dr. Jingdong Zhang and Dr. Jens Ulstrup who gave freely of their time and expertise and actively backed the experiments.
There are many people at DTU Nanotech which deserve my thanks, but in particular: Faheem Khan for many great discussions and all the help and collaboration he provided, Carsten Köbler for being a great student in his masters project and a great guy to work with, Thomas Nellemann for his work on the cryo setup and bearing with me when I was away, Tim Booth for teaching me so much about electron microscopy and graphene and for being a linux enthusiast, Filippo Pizzocchero for helping me when my time was short and providing invaluable support, and finally Rafal Wierzbicki for sharing an office with me and giving me lots of laughs.

I would like to thank all the people at DTU Cen. It is a small center and they all took the time to get to know me even though I wasn’t there a lot. Especially Adam Fuller, Filippo Cavalca, Louise H. S. Jensen, Marco Beleggia, Linus D. L. Duchstein, Takeshi Kasmama, Zoltan I. Balogh, Sadegh Yazdi and Berit Wenzel.

The people at DTU Danchip have been completely invaluable to this project. There are so many times were they have bent over backwards to help me with a process or understand why it did or did not work. Without them this project would not be what it is today. Thank you so much.

Finally, I would like to thank my friends and family for their support. My father, Niels Jensen, and mother, Anna M. Jensen, for always being there and encouraging me to work hard. My brother, Jason O. Jensen, and my sisters, Natalie D. Jensen and Juliette Jensen, for all the fun we have and the joy they bring me. Thanks to all my friends, but especially Christian Maden for sticking with me, Nick Hasslet for inspiring me and Emil L. Christensen, Martin Christensen, Henrik Andersen, Tobias Levinsky, Dennis B. Petersen and Helene B. Petersen for giving me someone to play with.

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September 17th 2012.
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1. Introduction

Seeing is believing

The world is full of many things we cannot see with our eyes, yet are vital to our survival and future growth.
In order to understand the things we cannot see we use many tools, one of which is the electron microscope.
Electron microscopy helps us observe smaller and smaller length-scales. Observation of columns of atoms is no longer a novelty, but a regular occurrence with high-end electron microscopes. However, this development was not applicable to all samples. Like any new technology there are new limitations... or challenges. The requirement of vacuum being a primary one in this work. Any sample which is not dry and cannot survive in vacuum cannot be imaged with regular electron microscopy. Today, methods are being developed to accommodate these samples which are considered simple for optical microscopy. Environmental electron microscopes now allow small quantities of gasses and thin layers of liquids to be imaged. New systems are appearing which enclose the sample in a protective casing, separating it from the vacuum, but still allowing imaging through electron-transparent windows (see section 1.1).

With the development of electron microscopy many tools have followed. Focused ion beam milling allows cutting the sample while observing it or deposition of metals or other material on the sample. Peltier stages allow heating or cooling of the sample, and electrical connection to a sample is a simple matter in most cases. Even cryogenically frozen tissue samples can be imaged in special cryo-electron microscopes which are a further development of environmental electron microscopes.

Only recently has it become possible to image an electrochemical process occurring on the nanoscale under conditions which are industrially relevant and with the resolution and contrast necessary to determine what is happening[75, 65, 20, 67]. This work attempts to create better tools for understanding spontaneous and non-spontaneous electrochemical reactions which take place at thermodynamic conditions not normally found in an electron-microscope.
1.1. State of the Art for Electron Microscopy of Liquids

The changes which occur to a given sample when imaging it outside its normal environment can be many and might not be easily accounted for. Observing processes in their natural environment might give more applicable data. New electron-microscope setups and methods allow us to image liquid processes at atmospheric pressure and room temperature or even above [84, 8, 77, 29, 85]. There are special systems for in-situ electron microscopy of liquids in SEM[75, 76], for combined optical microscope and SEM[61], for in-situ TEM of liquids with[40, 51, 86, 65, 88, 20] and without electrochemical electrodes[81, 66, 67], and for in-situ TEM of gasses[16, 17]. With these methods we can start to image and analyse in greater detail the electrochemical processes which are so important to us. However, before these analyses start we must first understand the tool we are going to use and the effects that it has on the sample.

In an optical-microscope setup the microscope will have little or no effect on the electrochemical process\(^1\). The resolution of standard optical microscopes can reach 200 nm, but advanced optical microscopes can reach 50 nm or less\(^3\).

Another method for examining electrochemical processes, especially the solid-liquid interaction is Scanning Tunneling Microscopy (STM)\(^4\). This method has sub-Ångström resolution, but only images the surface of a sample.

X-ray diffraction allows nanometer resolution and sub-second imaging, but generally only works for solid samples\(^5\).

Electron-microscopy allows sub-nanometer resolution and sub-second imaging of both solids and liquids, thus combining the best of both worlds.

In an electron-microscope the system is subject to a high-energy electron beam. This is equivalent to high intensity $\beta$-radiation\(^6\). For electrochemical processes a plethora of different induced effects[27, 87, 35, 74, 79, 78, 14] must be taken into account in order to understand the new electrochemical environment (although some publications claim the effects of the electron beam is negligible\(^8\)).

Many phenomena are based on nanoscale interactions in a liquid environment. Early experiments[1, 22] were proof-of-concept experiments with regards to applying electron microscopy to liquids. More recent experiments\(^7\) have shown

\(^1\)There is a possibility of the photoelectric effect affecting specific processes and a relatively low thermal effect from the intensity of the light. This is dependent on the setup.
quantifiable data from imaging of samples in their natural environment. However, the application of electron microscopy to these samples will affect the sample differently than optical microscopy. These interactions between sample and electron microscope are not well understood and their effect on electrochemical processes needs to be investigated.

The following sections will discuss the current state-of-the-art methods for the scanning electron microscope (SEM) and then the transmission electron microscope (TEM).

1.1.1. Liquids in the Scanning Electron Microscope

There are relatively few systems for electron microscopy of liquids in the SEM. In 2004 Thiberge et. al. published two papers[75, 76] with three different devices for imaging wet samples in SEM (see Figure 1.1 and Figure 1.2). All the devices use a \( \sim 150 \) nm thick polyimide membrane supported by a metal grid.

Using a backscatter detector Thiberge et. al. were able to get a resolution on the first device of about \( \sim 20 \) nm. On the second and third device, using improved methods this was decreased to \( \sim 10 \) nm. The resolution in the SEM is dependent on the atomic number \((Z)\) of the material in question, however a \( \sim 10 \) nm resolution of
Figure 1.2: Second and third device by Thiberge et. al.[76]. The second device is indicated by the "A" and is nearly exactly identical to the first device. The liquid completely fills the cavity below the polyimide membrane. This device is more readily assembled in the SEM. The third device also uses a polyimide membrane under a metal grid, but instead of a completely filled cavity under the membrane there is instead a partially filled reservoir and an open aperture. The aperture allows the pressure inside and outside to equalize over time and is small enough to allow for a very slow rate of evaporation. The reservoir itself wets the inside surfaces keeping whatever is on the membrane hydrated.
low Z materials such as carbon (C) should be considered very good, especially since it is an order of magnitude lower than theoretically predicted[76].

In the first paper[75] they mention the possibility of causing cell-damage due to the high amounts of $\beta$-radiation they are exposing it to. They note that no immediate damage is visible even after repeated scans. After an hour or so signs of damage appear in the form of cell shrinkage.

In the second paper[76] the effects of radiation damage are expanded upon. For biological material damage occurs when the radiation reaches $0.100 \text{ electrons Å}^{-2}$ to 1 electrons Å$^{-2}$ or above. Possible visible effects are listed as: "production of bubbles in fluids, movement and rearrangement of objects in the image, and detachment of parts of the sample from each other and from the membrane"[76]. When considering biological cells in particular less than 20 minutes of exposure did not lead to visible damage, but more could lead to detachment from the membrane and/or the other cells and the loss of the nucleus from the cell.

In both papers emphasis is placed on structural, observable damage. Damage to the DNA structure of the cells which will eventually lead to apoptosis is not considered.

A new electron microscope, called the Atmospheric SEM (ASEM), has recently been made commercially available[61]. The ASEM is a normal optical microscope with an inverted SEM under the sample and with a silicon nitride (SiN$_x$) membrane in the sample holder (see Figure 1.3).

The membranes were 10 nm, 30 nm, 100 nm or 150 nm thick and had the dimensions 0.100 mm by 0.100 mm. Although SiN$_x$ membranes are very electron transparent they are not completely so[33]. Testing on gold (Au) nanoparticles they found that...
the best image was obtained when using the highest electron acceleration of 30 keV since this corresponded to most penetrating electrons. Using these settings with a 30 nm SiNx membrane they obtained a resolution of \( \sim 8 \) nm when imaging Au nanoparticles. The subject of \( \beta \)-radiation induced damage was not discussed.

Finally, another system for in-situ studies of liquids in electron microscopy (EM) is the environmental scanning electron microscope (ESEM)[18]. This microscope was specially developed to allow small amounts of liquid and/or gas in the sample chamber while imaging. The ESEM uses differential pumping to keep any contaminants out of the column where the free electrons are generated and guided. By changing the pressure and temperature, liquid water can be maintained on the sample, however, these conditions are rarely the same as those the sample is subject to in its natural environment. Therefore, the ESEM is an interesting and useful tool, but is ultimately an approximation of the correct conditions for the samples considered in this work. Despite this the ESEM has been used for many interesting experiments[23, 43, 9].

All of these setups lack electrical connection to the liquid for in-situ electrochemical experiments. The setup presented in this work, the EC-SEM cell, contains platinum (Pt) electrodes and a leak-free Ag/AgCl electrochemical reference electrode. The setup is specially designed to create electrical contact to the chip with pogo-pins such that the chip can be easily replaced, or exchanged with a chip with a different electrode design. The chip contains a SiNx membrane which acts as a window to the liquid. Furthermore, the liquid in the EC-SEM cell can be easily flushed and exchanged, making the entire setup reusable.

### 1.1.2. Transmission Electron Microscopy of Liquids

Conventional TEMs do not allow liquids due to the vacuum requirement. An environmental transmission electron microscope (ETEM) contains a special differential pumping system which allows gasses at low pressure and monolayers of liquid[29, 28, 23]. For TEM of liquids there are two main setups used in literature; the sandwich type which uses two chips clamped or glued together (see Figure 1.4) and the electrochemical setup which uses a bottom substrate with electrochemical electrodes and reservoirs built on top (see Figure 1.6 and Figure 1.4c). Commercially, there are several system available. Protochips Inc.\(^2\) sells special TEM holders which allow for imaging liquids in TEM as does Hummingbird Scientific\(^3\).

The sandwich type uses two chips with electron-transparent windows. The simple setup, most widely used, consists of two identical silicon (Si) chips with electron-

\(^2\)http://www.protochips.com/
\(^3\)http://www.hummingbirdscientific.com/
Figure 1.4.: Different types of TEM setups for imaging liquid. 1.4a shows a figure from [65]. This setup shows two identical chips with a thin electron-transparent window enclosing the liquid. Also shown is a spacer which in this case is SU-8. 1.4b is the setup used in [36]. Two specially etched TEM chips are aligned by capillary forces. An Au grid supports one of the windows. Finally, 1.4c shows a sandwich type setup with electrodes from [32].
transparent windows etched out by potassium hydroxide (KOH). The window is made of either SiN$_x$ or silicon oxide (SiO$_2$). More advanced versions include Au electrodes and self-aligning setups with Au grids supporting one of the windows to minimize bulging and improve image quality.

Several different types of samples have been imaged with this system such as NPs, cells, bacteria and bubbles (see Figure 1.5). The electrochemical cells were designed by the group of F. M. Ross. It is a dedicated setup for chemistry in the TEM with an Au working-, an Au counter-, and a Cu reference-electrode. The setup consists of 100 nm thick SiN$_x$ windows and a 0.500 µm to 1 µm thick SiO$_2$ spacer. The electrodes drive the growth of Cu or Pt NPs (see Figure 1.7).

Using a TEM in STEM mode with a High Angle Annular Dark Field (HAADF) detector Peckys et al. imaged 3 nm Au nanoparticles through 7 µm of liquid. Another sandwich setup used a TEM in STEM mode to image 1.40 nm nanoparticles through 0.800 µm water.

The theoretical resolution in TEM through a liquid, assuming the window material is completely transparent and does not affect the resolution, is dependent on how much the beam is spread by the sample. The full width half max beam energy spread, $\Delta E_H$, from going through a sample of thickness $t$ is:

$$\Delta E_H = 4.02 \frac{N_A e^4 Z \rho t}{8 \pi \epsilon^2 A m_e \nu_e^2} \quad (1.1)$$

where $N_A$ is Avogadro’s constant, $e$ is the elementary charge, $Z$ is the atomic number of the liquid, $\rho$ is the density of the liquid, $\epsilon$ is the vacuum permittivity, $A$ is the atomic weight of the liquid, $m_e$ is the rest mass of the electron and $\nu_e$ is the relativistic velocity of the electron (all in SI units).

The resolution, $d_c$, resulting from chromatic aberration and beam energy spreading is:

$$d_c = \frac{1}{2} \alpha_0 C_e \frac{1 + \frac{E}{E_0}}{1 + \frac{E}{2E_0}} \frac{\Delta E_H}{E}$$

$$= \frac{1}{2} \alpha_0 C_e \frac{1 + \frac{eU}{m_e c^2}}{1 + \frac{eU}{2m_e c^2}} \frac{\Delta E_H}{eU} \quad (1.2)$$

The combination of equation (1.1) and equation (1.2), calculated with the parameters used in [20] can be seen in Figure 1.8 (these equations are applicable to TEM in bright-field mode, not in STEM mode). The resolution predicted by this theory is slightly better than the one predicted by de Jonge and Ross [20] which can also be seen in Figure 1.8.
(a) Growth of NPs induced by e-beam. Images from [27].

(b) TEM images of bubble reduction and graph of its progress. Images from [80].

(c) TEM image of bacteria with tellurium particles. Image from [51].

(d) STEM images of cells with Au NPs. Image from [64].

**Figure 1.5.:** Images from sandwich type liquid TEM chips. 1.5a shows six images of areas which were imaged at high magnification to induce growth of NPs and then reimaged at lower magnification. The scale in is the same in I and IV, II and V and in III and VI. The scalebar in IV and V is 500 nm and in VI it is 250 nm. 1.5b shows TEM images of a bubble being reduced in size by the electron beam and a graph of the area of the bubble as a function of time and 1.5c shows an image of a bacteria with tellurium NPs. 1.5d shows an image of Au NPs in cells.
Figure 1.6.: The electrochemical setup. This figure shows the electrochemical TEM cell from [81]. The setup consists of multiple components. The windows are 80 nm SiN$_x$ and the spacer is 200 nm SiO$_2$. There are three electrodes in the system.

(a) TEM of Pt NPs in liquid[88] \hspace{1cm} (b) TEM of the interface between two ferrihydrite (5Fe$_2$O$_3$ · 9H$_2$O) NPs merging[49]

Figure 1.7.: Images from experiments in the electrochemical setup.
The experimentally achieved resolutions seem to match the theoretical predictions seen in Figure 1.8.

A point of note is that in the calculations in [20] it is assumed that the SiN\textsubscript{x} windows are completely transparent and do not affect the images. The SiN\textsubscript{x} windows in the calculations were 30 nm thick and the liquid in excess of 100 nm thick. With an acceleration voltage of 200 kV the SiN\textsubscript{x} is nearly transparent [33] and would cause low scattering of the electron-beam, however, so would a low atomic number liquid. The literature then assumed that for a membrane thickness over liquid thickness ratio of 0.6 or below the membrane contribution can be disregarded. For TEM chip v2, presented in chapter 10, the liquid is designed to be 20 nm thick and the membranes 25 nm thick, each. This gives a membrane/liquid ratio of 2.5. The question then becomes: for a membrane/liquid ratio above 0.6 is it still safe to assume the membrane does not affect the resolution? The answer is unknown and warrants future study.

Figure 1.8.: Graph modified from [20] showing the resolution of different setups. The datapoints are from literature. Reference [19], [44], [49], and [27] use a sandwich setup. Reference [61] uses an Atmospheric SEM (a combined SEM and optical microscope). The three lines, in the legend, show the theoretical resolution in SEM, TEM and TEM in STEM mode from [20]. The red line is the resolution calculated with equation (1.1) and equation (1.2).

A third system for in-situ TEM experiments is a sandwich type setup intended for use with gas, not liquid (see Figure 1.9)[16, 17]. This system uses specially thinned areas as windows, to image through and includes a heater system. Inlets to the system are etched through the Si with KOH and then opened with a needle. This system contains many of the features necessary for advanced in-situ liquid
Figure 1.9.: Sandwich setup for in-situ gas experiments. Figures from [17]. 1.9a shows a schematic of the sandwich type setup used for in-situ gas experiments. 1.9b shows a TEM image of Cu NPs. The black arrow indicates out of focus NPs and the blue arrows highlight formation of NPs.

experiments, but has not been used for such.

All of the aforementioned systems use a window material consisting of SiNₓ or SiO₂ of various thicknesses. Recent work has shown an in-situ experiment with graphene as a window material[85]. This experiment imaged NPs agglomerating in a pocket of liquid between graphene sheets (see Figure 1.10).

The systems presented above expose a comparatively large window to the vacuum of the TEM. This will result in significant bulging which in turn changes volume and mass-thickness imaged in the TEM. The monolithic TEM chip presented in this work contains the liquid in a well defined channel with significantly reduced dimensions compared to literature. The channel is made in 200 nm thick SiNₓ except for the bottom side and special windows on the top where the thickness is only 25 nm. On the same chip both a heater and electrodes are created for electrochemical measurements of the liquid at temperatures up to 1000 K above room temperature. These modifications along with the reduced channel height mentioned above results in a well defined and compact electrochemical setup for in-situ electrochemical measurements in TEM.
1.2. Work in this thesis

This thesis describes the work done in creating two different setups for *in-situ* electron microscopy of liquids and liquid processes. Each setup was designed to be able to function in conventional electron microscopes without any additions such as the differential pumping in ESEM and ETEM. There are many processes which occur on the micro and nanoscale which are important for everyday life and for industry, such as non-spontaneous electrochemical processes driven by electricity, heat, pressure and/or catalysis. Some of these processes are not fully understood or could benefit from high-resolution imaging of the process when it occurs and under the same thermodynamic conditions in which it is used. The two electron microscopy setups in this work are designed to accommodate some of these conditions and further research in these areas.

The first setup designed is for SEM and is called the EC-SEM cell (see Part I). This setup uses a microfabricated chip, which contains Pt electrodes, and a 50 nm thick electron-transparent SiNx membrane, along with a holder to image a liquid as well as measure electrical signals from the liquid (see chapter 3). The electrodes can also be used to apply a current or voltage to the system, through the liquid. The setup includes an electrochemical reference electrode for accurate measurements of electrical signals.

The components of the setup are designed to be easily cleaned and the chip easily replaced. The lid of the setup is made out of aluminium and is grounded during experiments. Two polydimethylsiloxane (PDMS) components (a spacer and a seal) compensate for the stress induced in the window when the chip is clamped in the structure. The deflections in the membrane, caused by clamping-stress, would introduce distortions in the image and are thus avoided.

The fabrication of the setup is described in chapter 4.

Several experiments on the setup in the SEM were performed (see chapter 5). The ultimate goal is to use the system to investigate electrochemical processes, but in order to do so the effect of the SEM on the system must first be understood. The experiments performed and presented in this work are proof-of-concept experiments which show that the setup functions as intended and can be used for these experiments in the future.

The two central experiments are the beam-induced chemical reactions, where nickel is deposited on the SiNx membrane simply by reducing the scanned area size and increasing the beam current, and the electrode-induced chemical reactions, where electrolysis is performed and a CV of K₃Fe(CN)₆ is performed. These two experiments illustrate that the electron-beam can induce chemical reactions without the need of external stimuli, even though these reactions do not spontaneously occur at the specific thermodynamic conditions, and that the electrodes can cause electrochemical reactions in the EC-SEM cell. Other experiments in and for the SEM were also
performed such as observation of living cells and cryo-fixation of cells.

Finally, graphene was recently applied to some of the chips for the EC-SEM cell (see chapter 6). The graphene was placed over openings in the SiN$_x$ membrane made by focused ion beam (FIB) milling and was tested to be resistant to water, acetone and isopropanol. This will allow for even higher resolution imaging of the liquid and components in the liquid when performing electrochemical experiments in the SEM.

The second setup designed is for TEM and is a monolithic microfabricated chip simply called TEM chip (see Part II). Two different versions of this chip were designed and fabricated. The space in the TEM is significantly reduced compared to the space in the SEM. Therefore many features were integrated on to one chip. The chip is fabricated on a Si substrate with a SiN$_x$ membrane etched out by KOH. On the surface of the chip several structures are created. These structures are first patterned in a sacrificial layer of poly-crystalline silicon (poly-Si), then covered in a 200 nm layer of SiN$_x$ and then some of them are etched free by KOH. This creates a channel in semi-electron-transparent SiN$_x$.

The first version of the chip focused on verifying three things: the ability to etch the sacrificial material inside the channel, the usefulness of the protective structures and the function of the thinned windows (see chapter 9). The channel is the central part of the TEM chips. It contains the liquid in a well defined and limited volume. The dimensions of the channel minimize bulging of the channel walls, when subject to vacuum, when compared to literature. The protective structures are structures which are defined in the sacrificial layer, but not etched out. They are designed to remove pressure and stress from the channel when the chip is clamped or when it is handled prior to experiments. The thickness of the SiN$_x$ provides mechanical stability, but reduces the signal in the TEM. To compensate for this select areas of the SiN$_x$ on the channel are thinned down to 50 nm or 25 nm.

Experiments in the system showed that the chips functioned as intended. The fabrication of the chips, however, had a low yield due to the extensive KOH etch time required. To correct this and integrate new features TEM chip v2 was designed and fabricated (see chapter 10).

The second version of the TEM chip included a channel with two different heights, busstop structures to reduce etch time and provide electrical connection to the liquid, inlets placed on the backside, electrodes, and a heater. The channel height of TEM chip v1 was 1 µm. Although excellent resolution can theoretically be achieved through such a mass-thickness it was decided to significantly reduce the thickness to obtain better resolution and make the system more compatible with off-axis electron holography. The channel in TEM chip v2 was therefore fabricated in two different heights. Most of the channel was designed to have a height
of 1 \mu m to reduce the etch time compared to the low part of the channel which was designed to be 20 nm. The achieved thicknesses for the high and low channel were \sim 500 nm and \sim 60 nm, respectively.

In order to reduce KOH etch time, the channel length was reduced and structures, called busstops, were integrated. The busstops were extensions to the channel which did not obstruct the flow in the channel, but provided a room for a small hole to be made. Extra entrances to the sacrificial layer for the etch equals reduced etch time. The holes in the busstops are then subsequently covered with the electrode material which seals the channel from the vacuum and creates electrical connection to the liquid. Unfortunately the sacrificial layer used to define the low channel and the busstops recrystallized into separate islands during fabrication. This ment that the KOH could not etch them out and therefore neither the busstops or the electrodes funcioned as intended.

The inlets to the channel in TEM chip v1 were placed on the front-side. Vacuum tight connection to the channel through these inlets was nearly impossible. Therefore backside inlets were designed for TEM chip v2. With backside inlets the entire Si substrate of the chip can be used as support when creating a seal, instead of only some protective structures and fragile channel wall, as was the case with TEM chip v1.

The sacrificial layer in TEM chip v2 was designed to have a high conductivity. This would allow for structures to be created in it, but not etched out, which could function as an encapsulated heater. Unfortunately the encapsulated heaters were not tested, but in a related project several encapsulated heaters were tested positively.

The successes and failures of the TEM chips were discussed and the features of a new chip are suggested (see section 10.2).

Graphene was recently shown as an excellent window material for high-resolution in-situ electron microscopy of liquids (see Figure 1.10) and therefore preliminary investigation of the material was performed (see chapter 11). Integrating graphene as a window material in the TEM chip in a simple way and on the wafer-scale is currently not possible. However, as was shown with the chip for the EC-SEM cell. It is possible to FIB holes and create windows on a per-chip basis. With the intention of performing holography of liquids in graphene (preliminary experiments of holography of liquid in the TEM chip had already been performed with encouraging results) an investigation of the phase change per layer of graphene was done. This result will help when determining the phase change due to liquid between graphene sheets and is another step towards a more feature rich TEM chip for in-situ electron microscopy of liquids.
Figure 1.10.: Images from Yuk et al.[85]. 1.10a shows the experimental setup of a liquid droplet containing NPs, contained between two graphene sheets. 1.10b shows TEM images of two Pt NPs merging.
Part I.

Scanning Electron Microscopy
2. Introduction to Scanning Electron Microscopy

The SEM was invented in 1935 by Max Knoll\[45\]. A typical SEM allows the imaging of dry conductive samples with a resolution better than 3 nm\[31, 68\]. Basic optical microscopy is limited by the wavelength of visible light, which is from about 750 nm to 390 nm. Modern optical microscopy can push this limit to about 50 nm resolution\[34\]. If the sample in question is on the micrometer scale, SEM is a better choice compared to optical microscopy due to reduced preparation time and the flexibility of the SEM magnification, resolution and depth of field. This, of course, is true only for dry samples. For liquid samples or partially hydrated samples optical microscopy is a simpler method because it does not have the vacuum requirements of electron microscopy. In recent years many advances have allowed electron microscopy to breach into this type of sample.

The superior resolution of electron microscopes has been advanced by the introduction of the environmental electron microscope in the form of the ESEM and ETEM. These systems use differential pumping and slightly different detectors to image partially hydrated samples while maintaining vacuum around the electron source and optics\[7, 13, 18, 23\]. While these systems do not allow for fully hydrated or liquid samples they have none the less pushed the boundaries of what is possible to observe with electron microscopy. With ESEM and ETEM samples with a thin layer of liquid on the surface or samples subject to thin concentrations of gasses have been imaged to observe and quantify processes as they happen\[9, 28, 43\]. The differential pumping technique combined with some ultra-fast freezing techniques have broadened the sample base to include cryo samples, which are snapshots of processes as they occur or simply a different means of obtaining high-resolution images of biological samples\[25, 38\]. Finally, state of the art sample containers are being presented which allow electron microscopy imaging of liquid samples by sealing the sample in a container with one or more electron transparent windows\[17, 20, 65, 51, 67, 76\]. Such systems have several advantages. This opens high-resolution imaging to samples which include atmospheric pressure gas or liquid reactions. Being able to control temperature, electrical potential and flow in the system, as well as measure electrical signals and record high-resolution images of the sample all at the same time opens up these advanced imaging devices to be used in even more state-of-the-art in-situ
experiments. With the exception of two pioneers (one in gas[16], one in liquid[66]), all systems presented lack control over temperature or any type of electrical connection to the sample. The sample can be imaged, even with optical microscopy, in two cases[75, 61], but other than in Francis Ross’ system[67] potential cannot be applied across the sample. In the TEM system from Ross et al. they use the electrodes to measure and control a reaction while imaging it[67, 66]. Niels de Jong has created a system which has flow of liquid from outside the microscope allowing the introduction of new chemical components once imaging is ready or simply allowing nutrients to be flushed in and waste to be flushed out if imaging living specimens[64]. One system intended only for gaseous EM experiments includes advanced heater elements[16]. All these new systems raise the question: how does the e-beam in the SEM affect the sample? The aim of this work is to create a simple system which can help answer that question and then be used for further experimentation with liquid samples in SEM. The system created is called the EC-SEM cell and consists of a holder and a microfabricated chip with electrodes and an electron-transparent window. The design of the EC-SEM cell is detailed in chapter 3. Fabrication of the EC-SEM cell components is detailed in chapter 4. Preliminary experiments performed with the EC-SEM cell setup are detailed and discussed in chapter 5. Finally, the conclusion and outlook on the EC-SEM cell is presented in chapter 6.

2.1. The Scanning Electron Microscope

The SEM scans a beam of focused electrons across a surface and uses the electrons scattered from the sample to generate an image of the surface. Figure 2.1 shows the mechanism of an SEM. The e-beam is generated in the column of the SEM and then focused into a coherent beam by a series of apertures and magnetic lenses called electron optics. The result is a beam of electrons used to image the sample in question. These are called the primary electrons. When the primary electrons impact the surface of the sample many effects occur simultaneously. In this work the two most important effects are the generation of secondary electrons and the backscattered electrons. The secondary electrons are electrons from the sample which have been knocked loose by the primary electrons and have then escaped the sample. The backscattered electrons are the primary electrons which are reflected by the sample.
Figure 2.1.: Mechanism of SEM. The SEM focuses an electron beam at a point on the surface of the sample and then measures electrons escaping from or reflected from the surface with a detector. By doing this in a raster pattern across the surface an image is formed, pixel by pixel. At the top of the image is the column where the electron beam is generated and focused. From the column comes the electron beam, also called the primary electrons, shown here in blue. When the primary electrons impact the surface they generate secondary electrons, backscattered electrons, Auger electrons, X-ray photons and cathodeluminescence.
3. EC-SEM Cell Design

In this chapter the design and features of the EC-SEM cell will be detailed. First the requirements of the system are discussed in section 3.1 and then the final cell components are presented in section 3.2. In section 3.3 some previous designs will be briefly discussed to highlight some of the reasons for certain design considerations.

3.1. Requirements of an Electron Transparent Liquid Container for SEM

The key requirements for a system intended for liquid experiments in the SEM have been summed up in the following list:

- Functional requirements:
  - Be able to contain liquids
  - Fit in the SEM

- Safety requirements:
  - Be vacuum compatible

- Experimental requirements:
  - Have electron-transparent window to liquid
  - Provide simple electrical contact to the liquid
  - Be a multi-use system
  - EC-compatible
  - Optically transparent

The functional requirements are very straight forward. An SEM has a large chamber, but also contain sensitive equipment. The EC-SEM cell must fit in the SEM without touching or obstructing any of the sensitive equipment. The distance from the stage to the poll piece limits the height of the EC-SEM cell and the distance from the stage to the sidewalls limit the lateral dimensions. An entirely microfabricated system could easily fulfill the size requirements, but such a system
is time-consuming and difficult to fabricate. Connection to the system would be an issue, as well as filling and exchanging any liquid in the EC-SEM cell. Furthermore, handling a microscale system also generates unnecessary complications for a system designed for SEM. A system with a size of a few centimetres would be small enough to fit in the system and large enough to work with easily. The EC-SEM cell must be able to contain a liquid, but, furthermore, the liquid must be isolated from the vacuum of the SEM which leads to the safety requirement. Introducing a liquid container to a SEM runs the risk of contaminating the SEM if the system is not vacuum tight. In the best-case scenario the liquid is simply wiped away, but in the worst-case scenario the liquid enters the column and contaminates the magnetic lenses or leaves a residue inside the column which charges in an unpredictable manner, thereby seriously reducing the resolution of the SEM. Before insertion into the SEM the EC-SEM cell must be vacuum-tested to ensure it is leak-free.

The experimental requirements further define the system. A sealed chamber 1 cm by 1 cm by 1 cm of welded steel would essentially fulfill the first three requirements, but would be useless for the experiments. To fulfill the last experimental requirements the EC-SEM cell was designed to be a modular system. The central component would be a microfabricated chip which would contain an electron-transparent window and some electrodes. In the EC-SEM cell it is possible to exchange the chip for a new one if the window breaks or the chip becomes contaminated. The second part is a microfluidic setup where the liquid can be flushed out of the system by conventional means, thus making it a reusable component. Furthermore, the component must be transparent such that bubbles can be seen and flushed out before experiments are done. The modular nature of the EC-SEM cell makes it ideal for multiple uses since the setup can be easily disassembled, cleaned and then reassembled in a short time-frame. Last, and not least, the setup must be compatible with electrochemical processes. The setup must not absorb the chemicals and must not contain electrochemically active components.

3.2. The EC-SEM Cell

An EC-SEM cell was designed based on the requirements discussed in section 3.1. Figure 3.1 shows the assembled EC-SEM cell and Figure 3.2 shows an exploded view of the holder. This design is based on a proposed design by C. Köbler[46]. The seven main components of the EC-SEM cell are: the holder, the lid, the PDMS spacer, the PDMS seal, the circuit board, the tubes and the SEM chip. In Figure 3.1 a special syringe is also shown. This multi-use syringe has a specialized connection which screws directly into the valves at the end of the tubes.

In the following subsections each of the components are described in detail.
Figure 3.1.: The assembled EC-SEM cell setup. The EC-SEM cell with connections for liquid flow to and from the cell (blue fittings) and electrical contact with the liquid in the cell (circuit-board). Also shown is a syringe with a compatible fitting for filling or flushing the EC-SEM cell.
3.2.1. The holder

The holder, as the name implies, is the component into which everything else fits around the central SEM chip. Figure 3.3 shows the holder of the EC-SEM cell setup. The holder is milled out of a block of polycarbonate because this is a cheap and strong material which is easy to mill and which does not have a history of being particularly chemically active. A central channel bisects the device (see B in Figure 3.3). This channel is intersected by an area named the reservoir (shown in turquoise). The reservoir is directly below the chip. The single channel was chosen such that the system could be flushed and such that any liquid under the chip would be sure to be evacuated. Surrounding the reservoir is a single depression to allow for a PDMS seal (shown in magenta). The PDMS seal is designed with a rounded top side and flat bottom side (see Figure 3.5). The rounded top side faces the chip such that when clamping pressure is applied the PDMS can evenly distribute the stress as well as act as a seal for the liquid in the reservoir. The red area is called the chip recession and is a recession in the holder which keeps the SEM chip centred above the reservoir while still allowing for easy chip exchange. Along the edges of the chip recession are 16 holes, eight on each of the long sides of the reservoir. These are holes to allow electrical connection to the chip from beneath the reservoir via spring-loaded metal pogo-pins. Finally, at C in Figure 3.3 a sideview is shown with lid, holder, chip, PDMS spacer and PDMS seal. Below the lid a PDMS spacer (light blue) is seen above the SEM chip (black). Below the chip a PDMS seal creates a seal between the chip and the reservoir. The central inlet and outlet channels in the holder are drawn leading from the reservoir, left and right. The right channel also has a side-channel (indicated by the ring in the channel) leading to the reference electrode.
Figure 3.2.: An exploded 3D view of the EC-SEM cell Holder. The pieces are, from bottom to top: the micromilled, polycarbonate holder, a PDMS seal to avoid clamping stress, the SEM Chip, a PDMS spacer, and the lid. Not shown are the flexible inlet and outlet tubes, the screws to fasten the assembly and the circuit board with pogo-pin connectors.
Figure 3.3.: Schematic representation of the EC-SEM cell. A shows a 3D sketch of the EC-SEM cell. B shows a topview of the holder with dashed lines indicating the location of the channels in the holder. C shows a sideview of the holder, as well as a zoom in around the reservoir and chip recession. The pogo-pin holes are not shown.
3.2.2. The Lid

The lid for the EC-SEM cell is a simple component with an opening through which the e-beam interacts with the sample. Figure 3.4 shows the lid in profile, from the side and from the bottom. The lid is milled out of aluminium, and not e.g. plastic, because it must be conductive to allow grounding of the lid and avoid charging. The extension of the lid on the bottom side is designed to allow the lid to be centred above the chip. When the screws are applied to the EC-SEM cell the lid is presses down on the PDMS spacer, the chip and the PDMS seal creating the vacuum seal.

Figure 3.4: The lid for the EC-SEM cell. 3.4a shows the lid in profile with openings above the chip reservoir and one in each corner for the screws which assemble the system. 3.4b shows a side view of the lid. The extension is located above the chip recession in the holder to center the lid. Finally, 3.4c shows a bottom view of the lid.

3.2.3. The PDMS spacer and seal

In order for the EC-SEM cell to be vacuum tight the SEM chip must be properly clamped on top of the reservoir. Clamping induces stress in the chip and the PDMS spacer and seal (see Figure 3.5 and 3.6) serve to redistribute the stress evenly on the SEM chip and provide a good seal for the liquid in the reservoir. The redistribution
of stress is a key factor and has been an issue which previous designs, of the **EC-SEM cell**, have struggled with.

![3D view](image1)

![Side view](image2)

![Bottom view](image3)

**Figure 3.5.** The PDMS seal for the **EC-SEM cell**. 3.5a shows the PDMS seal in profile. This oval is 1.20 mm tall with a rounded top and flat bottom. 3.5b shows a side view of the PDMS seal. 3.5c shows a bottom view of the PDMS seal.
Figure 3.6.: The PDMS spacer for the EC-SEM cell. 3.6a shows the PDMS spacer in profile. This rectangle is 200\(\mu\)m tall with an ovoid opening accommodating the electron transparent window on the SEM chip. 3.6b shows a side view of the PDMS spacer. 3.6c shows a bottom view of the PDMS spacer.

3.2.4. The Circuit Board

The circuit board for the EC-SEM cell (see Figure 3.7) was designed to facilitate the use of pogo pins. The circuit board is inserted into the holder from below and the pogo pins enter the holder through the openings made specifically for them. The top part of each pogo pin is spring loaded so they can be pressed against the SEM chip for good electrical connection. The pogo pins are welded onto the circuit board. Since the pogo pins are short the circuit board must be placed close to the chip recession (see section 3.2.1 and Figure 3.3). The circuit board is at the same height as the inlet and outlet channel in the holder, and in order to accommodate the tubes for inserting the liquid the circuit board is elongated. The circuit board has a 25-pin connector welded onto it as an interface to other devices (see Figure 3.1).
Figure 3.7.: The circuit board with pogo pins. 3.7a shows the circuit board for the EC-SEM cell which creates the 16 electrical connections to the electrodes on the SEM chip. 3.7b shows a close up of the pogo pins which penetrate the holder. The pogo pins are spring loaded so they can be pressed against the chip for a good electrical connection.

3.2.5. The Tubes

To allow liquid into the EC-SEM cell in a controlled and vacuum safe manner a pair of plastic tubes have been chosen (see Figure 3.8). The tubes were repeatedly vacuum tested by subjecting the assembled EC-SEM cell to a pressure of 10 Pa for periods of 20 minutes, then bringing it to atmospheric pressure and repeating. Furthermore, the tubes were designed to be simple and easily replaceable if necessary. Plastic screws are hollowed out by a drill and the tubes inserted. A latex ring is then applied to secure the vacuum seal when the tube is inserted into the holder and the latex ring depressed by the screw. The opposite end of each tube has a simple valve attached so the syringe shown in Figure 3.1 can be filled with the desired liquid and easily injected into the EC-SEM cell.
Figure 3.8.: The tubes for the EC-SEM cell. One end of the tubes has a latex ring around the tube in front of a hollow plastic screw. When the tubes are screwed into the holder the latex ring is compressed thereby creating a vacuum seal around the tube. The other end of the tubes are attached to valves with a simple lever to open and close the valve.

3.2.6. SEM Chip Design

The final SEM chip design has 3 variants seen in Figure 3.9a, Figure 3.9b and Figure 3.9c. This section discusses material selection and fabrication considerations.

There were many considerations in the design of the SEM chip, but the key requirements are that part of it be electron transparent and that electrodes be integrated allowing electrical connection to the liquid. There are many candidates for the window material and through fabrication considerations they were narrowed down to four: graphene, polyimid, SiN$_x$, and SiO$_2$.

- **Graphene** is one of the strongest materials known today. It consists of a single layer of carbon atoms in a hexagonal arrangement. Most standard grids for TEM have some sort of carbon substrate because of their relatively high strength. The monolayer thickness of graphene and low atomic number of carbon makes it highly electron-transparent\cite{57, 85}. Unfortunately the fabrication methods available today have not reached the point at which graphene can be grown on wafer scale and be manipulated with standard cleanroom (\textit{e.g.}) techniques. There are many methods to integrate graphene into a devices, but each is highly complicated and adds many complications to the cleanroom fabrication.

- **Polyimide** is a cheap polymere available in very low thicknesses around the micrometer scale, which would be required for electron transparency\cite{75, 76}. It is also a polymere used in the semiconductor industry, so fabrication methods are available. However, polyimid has a low Young’s Modulus. When exposed to the 1 atmosphere pressure difference in the SEM it would bulge dramatically causing distortions in the image and possibly changing the state of the matter imaged from a liquid to a liquid and a gas.
• **Silicon Nitride** is material with high Young’s Modulus and is therefore considered a strong material because the deflection, when subject to the vacuum in the SEM, is relatively low. The coefficient of thermal expansion (CTE) of stoichiometric silicon nitride ($\text{Si}_3\text{N}_4$) is significantly different than that of Si. This causes in-plane stress to build up in the $\text{Si}_3\text{N}_4$ layer when grown on Si wafers. For this reason low-stress Si-rich silicon nitride ($\text{SiN}_x$) is considered. $\text{SiN}_x$ contains more Si to match the two coefficients of thermal expansion and reduce in-plane stress. This also degrades the mechanical properties, but is necessary to avoid bulging of the window. $\text{SiN}_x$ is easy to grow on standard Si wafers, is etched at a very slow rate in KOH and is electron transparent on the nanometer scale [33, 27, 44, 64, 65, 72, 80, 32, 36, 66, 67, 81, 86, 88].

• **Silicon Oxide** is also a strong material with fabrication methods available in the local cleanroom. To be electron-transparent sub-micron thicknesses are needed and these can easily be achieved in the cleanroom [51]. However, $\text{SiO}_2$ is etched by KOH at a significant rate requiring deposition of thick layers to act as an etch stop for the KOH etch as well as precise etching time to achieve the nanometer thickness.

The material chosen for the windows was $\text{SiN}_x$ because it is easy to fabricate with nanometer thickness, it has a very high Young’s Modulus, and a very low etch rate in KOH. The ideal material would be graphene and although there is some very promising research being done on this material at DTU, this research is not ready for this type of fabrication. Graphene is investigated further in chapter 6 and chapter 11.

The next consideration was the electrode material. Originally Au was used, but temperature measurements on this material were not stable, so the electrode material was changed to Pt. Pt is an excellent material for chemical reactions, but it is also an expensive material.

Finally, the shape of the chip was considered. The window must be as large as possible to allow a greater viewing area, but must not be so large as to make the chip unnecessarily fragile. Since the chip is contacted by pogopins they dictated some of the dimensions. The membrane was chosen to be 50$\mu$m wide and have a variable length greater than this width. The thickness was chosen to be 50 nm to allow excellent imaging at acceleration voltages above 5 kV while still allowing the wafer to be handled in the cleanroom. The rest of the chip acts as a substrate to stabilize the window and the electrodes.
Figure 3.9: SEM Chip variants. These are a zoom in of the mask file and do not show the entire chip. The blue is the electrode layer and the brown is the KOH layer. Inside the KOH layer is a chequered area which indicates the final size of the window. The chip has the dimension 8.3 × 13.6 mm². Each window is 50 × 1700 µm² for a less fragile chip, ten slim electrode connections (10 µm wide) and three thermistors.
3.3. Path to final chip and holder design

The path to the chip design described in section 3.2.6 was not straight forward. In the following subsections some design considerations along the path are described. Getting to this design required many different setups and variations a few of which will be briefly mentioned here.

3.3.1. The First Chip Variant

The chip design is shown in Figure 3.10[26]. Electrical connection to this SEM chip design was achieved via a zero-insertion-force-socket (zif-socket) widely used in industry. However, the zif-socket was not quite micro-scale and not quite macro-scale making connecting to the zif-socket extremely difficult as specific sockets had to be welded by hand onto circuitboards with each electrode spaced 300 µm apart. Furthermore, the clamping from the zif-socket made loading and unloading the chip in the zif-socket a difficult process with a high chance of breaking the chip. Furthermore, the zif-socket and the leads to it could cause additional stress in the chip when the holder was moved around during pressure testing or mounting in the SEM.

This chip was equipped with two windows, one large and one small. The large window contained a strain-gauge to measure window bulging and the smaller window contained some electrodes for electrical measurements. A thermistor was designed on the chip, but not on the window, to measure the temperature of the chip, and around the edge of the chip a large heater circuit was placed allowing heating of the chip and liquid. Several iterations of this chip were designed to allow different electrode configurations.

3.3.2. The First Holder Variants

The first holder was a small polycarbonate block with a single inlet drilled from the side and a single outlet drilled from the top. This holder was designed to be a quick-and-dirty one-use setup. The chip was glued on top of the outlet and a plastic valve was glued to the inlet. Liquid was filled into the chamber with a syringe. The setup was flipped to make the valve vertical and the syringe inserted through it to the bottom of the L-junction, filling from the bottom and out. This filling method was not ideal. It frequently created bubbles trapped in the channel, valve or under the chip. The main problem with this setup was that it was a one-shot system and it was difficult to create electrical contact to the chip.

Therefore a new setup was designed allowing flow through the system, so the chip could be fixed on top of a reservoir and the liquid exchanged without moving the chip (see Figure 3.11). Electrical connection could be done by zif-socket. The main
Figure 3.10.: The first SEM chip design. This chip was contacted to with a zif-socket and contained strain gauges, a thermistor and a heater.

issue was clamping the chip. Chips were frequently lost due to clamping induced stress in the window.
Figure 3.11: The second holder designs
4. EC-SEM Cell Fabrication

There are two major components of the EC-SEM cell; the chip, and the holder. In the following chapter their fabrication and testing will be discussed.

4.1. SEM Chip Fabrication Procedure

The SEM chip fabrication in the cleanroom at DTU involved the following 5 steps:

1. Grow $\text{SiN}_x$ window layer
2. Pattern $\text{SiN}_x$ Layer
3. KOH
4. Create electrodes
5. Wafer protection and Dicing

The following subsections describe and illustrate how these steps are performed by planar processing in a cleanroom. The fabrication was performed with the best equipment available in the Danchip cleanroom at DTU. Appendix A gives details of a fabrication plan for use in this cleanroom. The entire process is visualized in appendix B.

4.1.1. Step 1: Grow $\text{SiN}_x$ window layer

Fabrication begins with the selection of a <100> double-side polished 350 µm thick 4” Si wafer. The crystal direction is important for the KOH etch step. The wafer must be double-side polished because photolithography will be done on both sides of the wafer. The masks used in this fabrication are designed for a 350 µm wafer. Most wafers come pre-doped, but this fabrication process is not dependent on either p or n type doping.

The electron-transparent window is defined in this step (see Figure 4.1) and it is therefore important that the deposited layer be both strong enough to withstand the pressure difference between atmospheric pressure and 10 Pa, in the SEM and still electron-transparent. $\text{SiN}_x$ was chosen for this because stoichiometric silicon nitride,
Si$_3$N$_4$, has a too high built-in stress because of the difference in CTE between Si$_3$N$_4$ and Si. SiN$_x$ is deposited by low pressure chemical vapour deposition (LPCVD) with a special Si-rich recipe which approximates the CTE of the SiN$_x$ to that of Si.

A thickness of 50 nm was chosen because simulation showed a high electron penetration for acceleration voltages of 5 kV or above while still being feasible for cleanroom fabrication and handling. This thickness is very low and any scratches might break the SiN$_x$ layer and cause the wafer to fail in the KOH etch; hence the wafer must be handled with care.

This step is a furnace process and thus any contaminants must be removed by a RCA clean (RCA) prior to SiN$_x$ growth, but since the wafer is new it is assumed to be clean. The furnace process is a batch process allowing multiple wafers to be processed simultaneously.

![Cross-section](image)

**Figure 4.1.:** SEM fabrication step 1: Growth of a 50 nm SiN$_x$ layer on silicon wafer.

### 4.1.2. Step 2: Pattern SiN$_x$ Layer

This is a backside reverse photolithography step (see Figure 4.2). First, a layer of hexadimethyldisilazane (HMDS) is applied to promote adhesion. Photoresist (AZ5214E) is spun on the backside to a thickness of 1.50 µm. The photoresist is then exposed for 1.70 s in an aligner. There is no alignment in this step other than visual alignment to the wafer flat. To cross-link the exposed photoresist, the wafer is baked for 100 s at 393 K. This is called the reverse bake. The entire wafer is then exposed to UV for 30 s. This is called the flood exposure. Finally, a 60 s development in 295 K warm developer finishes the photolithography. This process will remove the photoresist on the backside where the wafer was not exposed in the first exposure leaving a 1.50 µm protective layer everywhere else.

Using the photoresist as a masking layer, a reactive ion etch (RIE) is used to etch...
through the SiN$_x$ and expose the Si below. After the etch, a plasma asher is used to remove the photoresist.

**Figure 4.2.:** SEM fabrication step 2: Pattern SiN$_x$ Layer.

### 4.1.3. Step 3: KOH

The extremely thin window requires a substantial support in order to withstand handling. This is provided by the 350µm Si substrate. However, the substrate is not electron-transparent. The window must be exposed without the loss of the stability which the substrate provides. This is why the KOH etch was chosen. The anisotropic nature of the etch on <100> Si provides the ideal way to expose the window. The 350µm Si is etched through in approximately 17.4 ks at 353 K (see Figure 4.3). The etch rate of the KOH in SiN$_x$ is about 0.340 µm s$^{-1}$ which etches just under 6 nm in this step. Immediately prior to the KOH etch the wafer is subjected to a buffered hydrofluoric acid (BHF) etch to remove any native oxide on the exposed Si. After the KOH etch the wafer is cleaned in a 7-up bath (7-up).
### 4.1.4. Step 4: Create Electrodes

Unlike the previous photolithography step, this step is on the frontside. Photoresist is spun on the frontside, the wafer is exposed, reverse baked, flood exposed and developed exactly like the previous step, except with a mask to define the electrodes. The electrode mask is aligned to the KOH opening with frontside alignment. The electrodes are deposited as 50 nm of Pt (see Figure 4.4).

A bath of Remover 1165 is used to dissolve the photoresist and thereby remove all the metal except where the photoresist was opened. Normally ultrasound would also be applied to the bath to speed the process, but the SiNx windows are too fragile and would shatter.
4.1.5. Step 5: Wafer protection and Dicing

In order to protect the chips from contamination prior to experimentation, a 10 µm layer of phototresist is spun on to act as a barrier over the frontside of the chip (see Figure 4.5). This barrier can easily be removed in a bath of acetone followed by a bath in isopropanol.

Finally, the wafer is diced into the individual chips using a mechanical automated saw. The wafer is placed on blue-tape prior to sawing and the saw does not saw all the way through the wafer. This means that the chips will still adhere to the blue-tape and can be easily transported.

Figure 4.4.: SEM fabrication step 4: Create Electrodes.

Figure 4.5.: SEM fabrication step 5: Wafer protection and Dicing.
4.2. SEM Holder Fabrication

A schematic of the EC-SEM cell holder can be seen in Figure 3.2. The holder is micromilled out of polycarbonate, after which a regular manual drill is used to widen the inlets. When assembling the setup it is important not to apply irregular stress to the chip. This will weaken the window, which might break in the SEM. To alleviate this two PDMS spacers are used. The bottom spacer is rectangular with rounded ends, 1 mm thick and 1.20 mm tall. The depression it fits into is 1 mm deep, giving 200 µm for clamping. This spacer also seals the liquid in contact with the chip. The second spacer is a thin 200 µm thick rectangle with an opening in the center the shape of a rectangle with rounded ends. Finally, the lid is micromilled in aluminium. An opening to image the chip with the SEM is done with a manual drill. The lid has a rectangular protrusion on the bottom side, which fits into the holder, thus centering it.
5. Experiments with the EC-SEM Cell

Several experiments were performed to verify the performance of the EC-SEM cell. Initially the membrane in the microfabricated chip was tested to ensure it could withstand the vacuum in the SEM. Then the current deposited in the EC-SEM cell was measured since this is relevant for the electrochemical reactions. The two main experiments were the beam induced chemical reactions, where the beam was used to deposit nickel, and the electrode induced chemical reactions, where the electrodes were used to cause electrolysis and perform a CV with a reference electrode. Finally, some experiments with in-situ imaging of cells, both alive and cryo-fixated, are discussed.

5.1. Window Deflection from induced pressure difference

A central component of the EC-SEM cell is the window which separates the liquid from the vacuum in the SEM. The pressure difference across the window causes it to bulge into the low-pressure area. Since the liquid is added to the EC-SEM cell at atmospheric pressure and the pressure in the SEM is 10 Pa the pressure difference is $\sim10^5$ Pa.

To ensure the windows can withstand the pressure difference the fracture pressure for several different thicknesses of SiNx windows were simulated[26] (see table 5.1). The chosen thickness of the window was 50 nm, because it has a high fracture pressure, is electron-transparent and is durable enough to withstand the fabrication process in the cleanroom.

Furthermore, the deflection of the window can potentially cause distortions in the image or change the liquid volume. Because the liquid is completely sealed, if the volume is changed the pressure inside the EC-SEM cell will fall. The extra volume might be filled with a mixture of liquid and liquid vapor. Therefore minimal deflection is ideal for electron microscopy of liquids. In order to estimate the deflection of the window at experimental conditions the Young’s Modulus, $E$, and built-in stress, $s_0$, of the window material are needed. To estimate these the window was subject
Table 5.1.: The fracture pressure for different thicknesses of SiN$_x$ from [26].

<table>
<thead>
<tr>
<th>Thickness [nm]</th>
<th>Pressure [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>$4.40 \times 10^5$</td>
</tr>
<tr>
<td>50</td>
<td>$5.50 \times 10^5$</td>
</tr>
<tr>
<td>75</td>
<td>$8.30 \times 10^5$</td>
</tr>
<tr>
<td>100</td>
<td>$11.2 \times 10^5$</td>
</tr>
</tbody>
</table>

to an over-pressure and the deflection measured. The following theory uses these measurements to estimate the material constants.

The dimensions of the window are $l \times w \times t$, where $t$ is the thickness of the window, $w$ is the width of the window, $l$ is the length of the window and $w < l$ (see Figure 5.1).

![Figure 5.1.: Window dimensions](image)

The theoretical model of the deflection can be seen in Figure 5.2.

The deflection of the window is $d(0)$. The out-of-plane deflection $d(x)$ is described by[82, 83]:

\[
D \frac{d^4}{dx^4} d(x) - ts \frac{d^2}{dx^2} d(x) = P \tag{5.1}
\]

\[
E_{ps} = \frac{E}{1 - \nu^2} \tag{5.2}
\]

\[
D = \frac{E_{ps} t^3}{12} \tag{5.3}
\]
the solution to which, in dimensionless variables, is:

\[ \bar{d}(\bar{s}, \bar{x}) = \bar{P} \times G(\bar{s}, \bar{x}) \]  \hspace{1cm} (5.4)

\[ G(\bar{s}, \bar{x}) = \frac{1}{2\bar{s}} \left( \frac{1}{4} - \bar{x}^2 \right) - \frac{\cosh(\sqrt{3}\bar{s}) - \cosh(2\bar{x}\sqrt{3}\bar{s})}{4\sqrt{3}\bar{s}\sinh(\sqrt{3}\bar{s})} \]  \hspace{1cm} (5.5)

\[ \bar{s} = \frac{s \left( \frac{w}{t} \right)^2}{E_{ps}} \]  \hspace{1cm} (5.6)

\[ \bar{P} = \frac{P \left( \frac{w}{t} \right)^4}{E_{ps}} \]  \hspace{1cm} (5.7)

\[ \bar{d} = \frac{d}{t} \]  \hspace{1cm} (5.8)

\[ \bar{x} = \frac{x}{w} \]  \hspace{1cm} (5.9)

where \( \bar{s} \) is the in-plane stress. The relation between the maximum dimensionless deflection, \( \bar{d}(0) = \bar{d}_0 \), and the built-in zero-deflection stress, \( \bar{s}_0 \) is:

\[ \bar{s} = \bar{s}_0 + \frac{1}{2} \bar{d}_0^2 H(\bar{s}) \]  \hspace{1cm} (5.10)

\[ H(\bar{s}) = \frac{4 \left( (8 + 4\bar{s}) \sinh(\sqrt{3}\bar{s})^2 - 6\bar{s} - 3\sqrt{3}\bar{s} \sinh(2\sqrt{3}\bar{s}) \right)}{\left( \sqrt{3}\bar{s} \sinh(\sqrt{3}\bar{s}) - 4 \sinh(\frac{\sqrt{3}\bar{s}}{2}) \right)^2} \]  \hspace{1cm} (5.11)
Using these equations a numerical script was created in MATLAB (see appendix H) and used to estimate the Young’s Modulus and built-in stress from pressure and deflection measurements which in turn can be used to estimate the window deflection under experimental conditions.

A Vibrometer MSA-500 from Polytec UK was used to measure window deflection as a function of gauge pressure. The vibrometer uses optical images of newton rings to estimate the deflection. The measurements were done at atmospheric pressure outside the holder and a higher applied pressure inside the holder, thus mimicking the pressure difference in a SEM. The associated software to the vibrometer shows a 3D model of the deflection it detects through a microscope. A line is drawn at the center of the window over the 3D model and the profile along the line shows the deflection (see insert in Figure 5.4). COMSOL, a finite-element modelling program, was also used to simulate the deflection at different gauge pressures. The model entailed a 50 nm thick and 50 µm wide membrane of stoichiometric silicon-nitride on a Si substrate. The SiNx in the model had a Young’s Modulus of 132 GPa and a built-in stress of 258 MPa. Using the below method to fit to the COMSOL results, gives a Young’s Modulus of 133 GPa and a built-in stress of 259 MPa indicating that the presented fitting method seems reliable.

Figure 5.4 shows the two measured runs on the Vibrometer (first with increasing gauge pressure, second with decreasing gauge pressure) as well as the two fits based on the theoretical models obtained from [82]. The deflection, \(d_0\), of the window at the center is (\(\bar{x} = 0\)):

\[
d_0(\bar{s}) = \bar{P} \times G(\bar{s}) \tag{5.12}
\]

A numerical fit to the experimental data based on the above equations[82] gave a Young’s Modulus of (53 ± 4) GPa and built in stress of (423 ± 47) MPa. The Young’s Modulus is much lower than the values given in literature[42] for low-stress SiNx of (95 ± 10) GPa. The cleanroom quality-testing gives an average built in stress of 230 MPa for the SiNx layer. Fitting the Young’s modulus with this fixed built in stress gave a higher Young’s Modulus of (81 ± 6) GPa. As can be seen in Figure 5.4, the two different fits are not dissimilar and it is therefore possible that there is some clamping induced stress which is not optically detectable (see Figure 5.3), but which is significant in the measurements giving the high value for \(s_0\). The fitted value of Young’s modulus for a fixed \(s_0\) is therefore assumed to be correct. These measurements indicate that the membrane will be able to withstand the pressure difference in the SEM and that clamping induces some built in stress. The maximum deflection at \(10^5\) Pa pressure difference with the fitted material constants is calculated to be 1.46 µm.
Several chips were tested in a simple burst-test setup where the chip was placed over a enclosure and the pressure increased until the window burst. Despite non-ideal clamping in this setup (no pressure redistributing PDMS rings) the average burst pressure was 440 kPa which is well over the pressure difference of 100 kPa in the SEM. Finally, during the experiments the EC-SEM cell was subject to the vacuum in the SEM of more than 10 hours with no sign of fatigue and no broken windows.
Figure 5.3.: Overview images of a SiN$_x$ window. A SEM image of a window with Pt electrodes on the opposite side can be seen in (5.3a). The window is at the bottom of a KOH etched trench. There are two windows on this chip type, the other window is not shown. Optical Light microscope images of the electron-transparent window with (5.3b) and without visible stress (5.3c). A window which is stressed by non-uniform clamping cannot withstand the pressure difference in the SEM. The optical microscopy images are of a chip type with only one window. This window is longer than the one on a chip with two windows. The scalebar in the images is 100 µm.
Figure 5.4.: Experimental deflection data and fit to experimental data. The first run was done increasing the pressure and the second run was done decreasing the pressure. A fit has been done on the experimental data and another one at fixed built-in stress ($s_0$). As can be seen the two fits do not differ significantly. The inset shows an extract from the Vibrometer software with a profile of the window deflection used in a measurement.
5.2. Electrochemistry in the SEM

The SEM functions by irradiating an area with β-radiation and measuring the result. This radiation affects the sample being imaged and can affect the electrochemical environment. This section briefly describes the theoretical effects of incident radiation on a liquid body.

When electrons are incident on a liquid through an electron transparent window multiple effects occur and I will divide them into three classes; the initial, the secondary and the gradient effects. The initial effects are mostly physical; the knock-on effects which cause multiple ionizations and excitations through inelastic collisions. The elastic collision are assumed only to change the direction of the incident electron. These effects occur in the first $10^{-12}\text{s}$.

The secondary effects are mostly chemical. The ionized and excited species as well as the free and thermalized electrons are created in a non-homogeneous distribution. Therefore conventional bulk chemistry cannot be used to predict the final concentrations. These effects occur in the first $10^{-6}\text{s}$ after which the distribution is assumed to be homogenous[14].

The gradient effects are large-scale effects such as heat-dissipation and convection caused by momentum-transfer.

For water the physical effects cause two reactions:

$$H_2O \rightarrow H_2O^+ + e^- \quad \text{(ionization)}$$ (5.13)

$$H_2O \rightarrow H_2O^* \quad \text{(excitation)}$$ (5.14)

These two reactions generate reactive species in the liquid which react to form new species almost immediately. In the chemical stage the generated species react to create new species which will add to the bulk chemical concentrations. The generation and subsequent reactions of these species is calculated with Monte-Carlo simulation software[35, 78, 79]. Dependent on the chemical reaction being investigated these species may or may not be relevant and others might be generated (such as H-, ·OH, H2 and H2O2[37]). Two species generated by these effects which are relevant are H3O+ and OH− which are electrically charged. These species will change the resistivity of the liquid and possibly affect the chemistry. The G-values (number of generated specimens pr. 100 eV) for these species have been calculated for incident radiation accelerated to 10 keV: 2.60 and 0.600, respectively. This corresponds to $\sim 2 \times 10^{-12}\text{mol s}^{-1}$ and can therefore be neglected (the calculation is based on work found in [35],[78], and [79]).

The gradient effects consists mainly of heating and momentum transfer. Simple calculations [87] indicate that beam-induced heating is not an issue. The momentum transfer to the liquid is not, however, insignificant[87]. Literature suggest that significant convection can be induced by the e-beam[52, 80].
The SEM clearly affects the sample and in order to better understand exactly how, in-situ experiments measuring various effects are necessary.

### 5.3. Current Measurements

One of the crucial initial parameters in understanding the beam effect on the sample is how much current is deposited in the sample because this allows us to better estimate the effects of the beam in future experiments. The current deposited in the EC-SEM cell was therefore measured.

The beam current was first measured using an attached INCA Energy Analyzer setup at high vacuum without the sample in the chamber of the Inspect S SEM from FEI Company. The beam was focused on the stage for these measurements. The chamber was then pumped to low vacuum (10 Pa) and the beam current measurements verified for a beam with zero contrast as non-zero contrast settings in low vacuum mode influences beam current measurements. The sample was then placed in the chamber and the chamber pumped to low-vacuum. Low vacuum mode was used as a precaution in the case of window rupture. Images were recorded using the large field detector (LFD) which gave comparable or even better imaging than the backscatter detector. The beam was focused onto the SiN$_x$ window and all the electrodes were disconnected except one which was grounded through an amperemeter setup. The EC-SEM cell contained 0.100 m H$_2$SO$_4$. The current measured at different spot and acceleration voltages are plotted on the graph in Figure 5.5.

It can be seen on Figure 5.5 that the current measured through the EC-SEM cell is lower than the current measured through the INCA Energy Analyzer setup. This indicates that some of the current is deposited elsewhere in the SEM. The primary concern is whether or not the current difference is deposited in the EC-SEM cell in another manner. The difference can be expressed as:

$$I_{\text{difference}} = \eta I_{\text{INCA}} + I_c + X$$  \hspace{1cm} (5.15)

Where $\eta I_{\text{INCA}}$ is the difference due to backscattering from the SiN$_x$ window, $I_c$ is the current difference due to charging in the EC-SEM cell and finally $X$ is the current difference due to unknown mechanisms. Prior to insertion in the SEM chamber, the EC-SEM cell was covered with a 2 – 4 nm layer of carbon to avoid charging. The aluminium lid, which is present during the carbon coating, is grounded in the entire experiment. Despite this, there might be poor or no conductance from the surface of the chip to the lid due to non-conformal coating. Consequently, charging on the window cannot be neglected. Backscattering cannot account for the entire difference except for high acceleration voltages shown in Figure 5.6.

In Figure 5.6 the current difference between the INCA measurements and the EC-SEM cell measurements have been used to calculate the percentage of the current...
Experiments with the EC-SEM Cell

Chapter 5

Figure 5.5.: Beam current measurements as a function of acceleration voltage at different beam spots (spot 9-5). The (−−−) dashed lines show the current measured using the INCA Energy Analyzer and the (—) solid lines show the current measured using the amperemeter setup through the EC-SEM cell. At nearly all points the current measured with the INCA Energy Analyzer is higher than the current measured using the amperemeter setup.

Deposited in the EC-SEM cell using the following equation[3]:

\[ \eta = 1 - \frac{I_{\text{INCA}} - I_{\text{EC-SEM}}}{I_{\text{INCA}}} \]  

(5.16)

Backscattering coefficients for the EC-SEM cell have been calculated using the Monte-Carlo Simulation software: CASINO. In CASINO a 50 nm stoichiometric Si$_3$N$_4$ window is placed over a substrate of H$_2$O and 1000 electrons were simulated for energies from 1 kV to 30 kV in increments of 1 kV. The total number of backscattered electrons was used to calculate the backscattering coefficient at each acceleration voltage. It is clear that backscattering cannot account for all of the difference. This leaves the unknown factors: \( I_c \) and \( X \). If there is poor connection between the carbon on the chip and PDMS ring to the lid then \( I_c \) will be large and might affect the EC-SEM cell by attracting positively charged particles to the window interface and thereby creating a potential gradient in the EC-SEM cell near the window.
Figure 5.6: The current deposited in the cell. The green solid line shows the mean percentage of beam current measured in the EC-SEM cell. The red stars indicate percentage of beam current after backscattering, based on the coefficients from CASINO simulations. The blue dots is the percentage beam current after backscattering from the experimentally determined backscatter coefficients for water[41].

5.4. Beam-induced Chemical Reactions

In order to analyse electrochemical reactions in the SEM it is necessary to understand how the SEM affects the sample. As a step towards better understanding these effects the e-beam was successfully used to induce a non-spontaneous chemical reaction by using the electron beam. The EC-SEM cell was filled with a solution for electroless plating of nickel (2.50 g nickel (II) sulfate 6-H2O; 2.50 g sodium hypophosphite monohydrate; 100 mL 0.100 M acetic acid). Normally this solution requires the target to be plated with a palladium catalyst and must be heated to 95°C to initiate the nickel plating, however in this experiment nickel was successfully plated at room temperature using only the electron beam to initiate the reaction (see Figure 5.7).

In order to plate nickel (Ni) the minimum beam-current density used was 0.260 A m⁻². The beam was focused into a small rectangular area and allowed to image 4 different areas for 15 s, 30 s, 45 s and 60 s each. The acceleration voltage was then changed in increments of 5 kV from 5 kV to 25 kV at 4 different areas and the 4 depositions undertaken at each area (Figure 5.7a and 5.7b show two of the deposition areas). Deposition was done with spot 5 and was faster with higher current densities. Subsequent imaging of the deposition areas was done at spot 4, 25 kV giving a current density of 7.50 × 10⁻³ A m⁻². At this current density it takes more than 8 min to reach the same dose as with 15 s of spot 5, 5 kV reduced area deposition. See table 5.2 for current densities in the reduced area scans used in this experiment.
Deposition was initially not visible in-situ with an acceleration voltage of 5 kV and beam spot 5, but subsequent drying and imaging of the chip revealed clear deposition. The beam induced deposition did not only occur in the imaged area. Some micrometers adjacent to the imaged area had an evanescent deposition.

Using spot 6 (4.41 A m$^{-2}$) had the opposite effect, that is, no Ni was deposited in the imaged area, but it was deposited around the imaged area (see Figure 5.7c). Spot 6 irradiation could also be used to remove Ni and redeposit it around the imaged area.

The chip was removed from the holder, dried, and images were recorded in conventional SEM mode (see Figure 5.7d). The deposited Ni formed bulbous pillars on the window. With spot 5 at 15 kV the current was 0.350 nA. Assuming each Ni atom requires 2 electrons to release it from NiSO$_4$(H$_2$O)$_6$ the 60 s deposition should have deposited 6.31 pg Ni. Tilting the sample and measuring height and width of a single bulbous column and assuming a solid structure gave 192 pg indicating that deposition is assisted by other processes than the initial primary electrons, as the deposited structure contains of the order of 1000 times more nickel than the primary electrons could deposit. The most likely candidate is therefore the secondary electrons.

**Table 5.2:** Beam current densities at different spots and acceleration voltages in the reduced area scans used in this experiment. Current densities are listed as A m$^{-2}$.

<table>
<thead>
<tr>
<th>Spot</th>
<th>5 kV</th>
<th>10 kV</th>
<th>15 kV</th>
<th>20 kV</th>
<th>25 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0800</td>
<td>0.250</td>
<td>0.240</td>
<td>0.310</td>
<td>0.700</td>
</tr>
<tr>
<td>5</td>
<td>0.260</td>
<td>0.860</td>
<td>0.920</td>
<td>1.22</td>
<td>2.91</td>
</tr>
<tr>
<td>6</td>
<td>0.810</td>
<td>2.90</td>
<td>3.27</td>
<td>4.41</td>
<td>8.84</td>
</tr>
</tbody>
</table>
Figure 5.7.: Ni depositions at different acceleration voltages and current densities. 5.7a and 5.7b are SEM images taken immediately after deposition with liquid still in the chamber. Note the increase in deposition area. Four deposition areas are visible in each of the two images. The lower left is the 15 s deposition, the lower right is the 30 s deposition, upper right is 45 s and upper left is 60 s deposition. 5.7c is a SEM image of the chip with Ni deposition at 25 kV with spot 5 (top square, 1.19 A m$^{-2}$) and spot 6 (bottom square, 3.63 A m$^{-2}$). 5.7d shows a SEM image of the chip where Ni was deposited recorded from the opposite side of the window. The four deposition areas are visible as in Figure 5.7a, but mirrored. The scalebar in each image is 15 µm. 5.7a and 5.7b have the same scale.
5.5. Electrode-induced Chemical Reactions

Electrolysis was successfully induced \textit{in-situ} in the EC-SEM cell. The setup successfully survived the gas-generation and simultaneously recorded the event. In a 0.100 m H$_2$SO$_4$ electrolyte solution a potential difference was applied between two electrodes to induce electrolysis. The current measured between the electrodes as a function of time can be seen in Figure 5.9. Since the goal of the experiment was to induce electrolysis the voltage was quickly increased to levels which would generate the effect. SEM images were taken of the area with the electrodes before (see Figure 5.8a) and after (see Figures 5.8b-5.8e) the electrolysis.

![Figure 5.8: Overview images of an area where electrolysis was performed. The electrodes where the potential difference was applied are visible through the window. The dark voids in the images are the gas generated by the electrolysis. Some of the liquid is still visible under the lower electrode.](image)

A microfabricated chip was half-ways covered with Au to function as an Au electrode. This electrode was then used in the EC-SEM cell along with an electrochemical leak-free Ag/AgCl reference electrode and the Pt-thermister was used as counter
Figure 5.9: Multipotential step plot. The potential between the working and counter electrode was stepped from 0 V to 5.25 V in steps of 0.250 V every 10 s. Electrolysis and bubble generation occurred at 3.75 V. The arrows indicate the potential difference at the specific point.

electrode (chip type B, Figure C.2). Cyclic-voltammograms (CVs) of K₃Fe(CN)₆ were recorded, both in and outside the SEM. Inside the SEM the buffer solution was H₂SO₄, based on [37, 11]. After the measurements the Ag/AgCl electrode was measured vs. a saturated calomel electrode (SCE).

Outside the SEM, a reference experiment was carried out in an electrochemical glass cell using an Au electrode as a working electrode, a saturated calomel electrode (SCE) as reference electrode and a Pt-coiled wire as a counter electrode. The reference experiments was carried out on 10 mM K₃Fe(CN)₆ in 40 mM H₂SO₄ (pH 1) and 40 mM phosphate buffer (pH 7), respectively. Figure 5.10 show the CVs of K₃Fe(CN)₆ inside and outside the SEM, where the CV inside the SEM has been corrected to the potential of a SCE. Figure 5.11 shows the CV of K₃Fe(CN)₆ in the phosphate buffer.

As seen in Figure 5.10 the redox potential of the K₃Fe(CN)₆ at low pH is shifted towards a higher potential compared to Figure 5.11 at neutral pH, which is closer to the values reported in litterature[5].

During one measurement cycle the beam was turned on and off in order to determine if this has any influence. Figure 5.12 shows the cycle where the beam was turned on an off (blue line) and the cycle immediately following it where the beam was turned off (red line). Each time the beam is turned on there is an increase in the measured current. This decreases when the beam is turned off. The cause of this effect is unknown. The Au working electrode was exposed to the beam each time the beam was turned on so a possible explanation is that the beam directly adds
Figure 5.10.: CVs of 10 mM K₃Fe(CN)₆ of Au electrodes in the EC-SEM cell (black line) and reference system outside SEM (red line) in a 40 mM H₂SO₄, pH ca. 1. Scan rate 50 mV s⁻¹. Beam was off.

to the measurement with some proportionality factor from the secondary electrons which are knocked loose and added to the current. It is also possible that charged species are generated which change the electrochemical environment and affect the process being measured. Further investigation is required to determin the cause of the measurements, however, the scans do show that the beam provides a non-trivial difference in the measured current.
The inclusion of a reference electrode in the EC-SEM cell increases its usability for in-situ electrochemical SEM experiments.
Figure 5.11.: CV of 10 mM K₃Fe(CN)₆ of a Au electrode in a 40 mM phosphate buffer, pH 7. Scan rate 20 mVs⁻¹.

Figure 5.12.: CVs of 10 mM K₃Fe(CN)₆ of Au electrodes in the EC-SEM cell (black line) and reference system outside SEM (red line) in a 40 mM H₂SO₄, pH ca. 1. Scan rate 50 mVs⁻¹. The red line shows a scan without the beam and the blue line shows a scan where the beam was turned on and off at the points indicated. The beam used spot 8 at 30 kV.
5.6. In-situ SEM of Living Cells

In order to create more effective medicines it is useful to understand the inner workings of cells or simply observe biological processes with high resolution. There are plenty of methods which can be applied to this achieve this. Electron microscopy offers superior resolution to many of these methods. However, as mentioned earlier, a limiting factor is the vacuum requirement. To circumvent this researchers have covered the cells with a conductive coating\cite{43} stained the biological specimens with various heavy metals and imaged them in ESEM\cite{7} or frozen them (see section 5.7). This kills the cells, so no ongoing processes can be observed and the staining process can cause defect in the cell which do not correspond to the living cell\cite{4, 12}. Recent advances have allowed live, hydrated cells in an ESEM under specific thermodynamic conditions\cite{13}. However, the conditions under which human cells function optimally have not been achieve. The EC-SEM cell could possibly meet the requirements by growing the cells on the EC-SEM chip, filling the EC-SEM cell with a nutrient rich liquid and heating the setup.

In a master project C. Købler investigated the viability of cells in an EC-SEM cell. Initially 3T3 fibroblast cells were stained with osmium tetroxide to verify that stained cells could be image, with liquid, in a setup similar to the EC-SEM cell. Figure 5.13 show SEM images of the result.

Once it had been verified that stained cells in liquid could be imaged in the setup the next step was to estimate the viability of cells imaged by SEM. Yeast cells were grown on chips with a SiN\textsubscript{x} window, subject to radiation in the SEM at a specific dose and then stained with flourescent markers to indicate if the cells were alive or dead. Figure 5.14 shows a graph of the viability of cells as a function of dose.

As can be seen the viability drops off significantly at 0.600 electrons Å\textsuperscript{-2}, which is in good agreement with literature\cite{75, 89}. This means that electron microscopy is not the ideal method for imaging live cells since the dose they can be exposed to before dying is very low.
Figure 5.13.: SEM images of fixated and stained 3T3 fibroblast cells in milliQ water from [46]. 5.13a shows an overview image of the chip with the window in the middle of the image. Through the window 3T3 fibroblast cells stained with osmium tetroxide are visible. The cells adhere to the chip, which is also covering milliQ. 5.13b shows a close up the cells where the nucleoli are visible. The close up is not visible in 5.13a.

Figure 5.14.: Graph of live/dead cells as a function of exposure does from [46]. The dose is in units of electrons Å$^{-2}$. There is a clear decrease in viability around 0.600 electrons Å$^{-2}$. 

(a) Stained cells in milliQ imaged through window

(b) Close up on stained cells
5.7. Cryo-SEM

Another method for imaging samples with liquid components, such as cells and biological processes, is cryo-fixation. By freezing the sample at above $10 \times 10^3 \text{Ks}^{-1}$ the water does not have sufficient time to reorganize into the crystal structure of ice\[^{[25]}\]. Instead it forms an amorphous ice called vitreous ice. This allows snapshots of processes since the entire freezing time is a matter of milliseconds. With thicker samples a faster freezing rate is needed.

In a masters project by T.K. Nellemann the chips shown in Figure 3.10 were used to plunge-freeze cells in a liquid nitrogen slush setup\[^{[58]}\].

The plunge setup was designed to submerge the SEM chip with cells on the window into the liquid nitrogen at velocities around $2 \text{m s}^{-1}$. Plunging the chip into the nitrogen (at a temperature below 77 K) was designed to avoid the Leidenfrost effect where the liquid nitrogen is flash-boiled upon contact with the chip and the resulting gas insulates the chip from further temperature change until it bubbles away. However, it was discovered that plunging still generated a lot of bubbles which insulated the chip. To counteract that, the liquid nitrogen slush setup was designed. The liquid nitrogen is further cooled by reducing the pressure around the deep dewar. This causes ice, or slush, to form in the liquid nitrogen, which is now at around 63 K. When the chip is plunged the thermal energy from the chip must first be used to melt the slush (not causing bubbles) before the liquid nitrogen is boiled. The deep dewar ensures that even when the slush has been melted the resulting gas is swept away by the motion of the chip.

There are other mediums which can be used instead of liquid nitrogen in plunge-freezing setups, such as liquid propane and ethane. Liquid nitrogen slush was chosen for its higher freeze-rate, ease of use and low security requirements\[^{[58]}\].

Using the liquid nitrogen slush plunge-freezing setup, a one-time freezing rate of $1 \times 10^6 \text{Ks}^{-1}$ was achieved. However, repeatable results generated freezing rates around $100 \times 10^3 \text{Ks}^{-1}$ to $500 \times 10^3 \text{Ks}^{-1}$ (see Figure 5.15).

Fibroblast cells were grown on some chips and plunge-frozen. The results can be seen in Figure 5.16. There are two lighter lines in Figure 5.16a which are the gold electrodes used to sense the temperature during freezing. The bumps on the surface are the cells.
Figure 5.15.: Temperature measurements on the window of the chip during liquid nitrogen slush plunge freezing. Graph from [58].

Figure 5.16.: Cryo-fixated cells on a SEM chip. 5.16a is an overview image of the window area with frozen cells under vitreous ice. 5.16b is a zoom in on a cells which has been milled by FIB to reveal some of the internal structures. Both images are from [58].
6. Graphene windows in the EC-SEM cell

The EC-SEM cell is a versatile tool for in-situ electrochemical reactions and it provides a decent resolution through the SiN$_x$ window. However, an improved resolution could be obtained if graphene was used as window material.

6.1. Improving the resolution in the EC-SEM cell

The resolution, $d$, in an SEM is determined by the probe size\cite{31}:

$$d = \sqrt{d_1^2 + d_s^2 + d_d^2}$$  \hspace{1cm} (6.1)

where $d$ is the diameter of the probe size. The other factors are given by:

$$d_1 = d_0 \times \frac{v_1}{u_1}$$  \hspace{1cm} (6.2)

$$d_s = 2 \times C_s \times \alpha^3$$  \hspace{1cm} (6.3)

$$d_d = 1.22 \times \frac{h}{m_e \times c} \times \frac{1}{\sqrt{\left(1 + \frac{e \times U}{m_e \times c^2}\right)^2 - 1}}$$  \hspace{1cm} (6.4)

where $d_0$ is the diameter of the filament, $v_1$ is the distance from the condenser lens to the first focal point, $u_1$ is the distance from the filament to the condenser lense, $C_s$ is the spherical aberration of the microscope, $\alpha$ is the convergence angle of the microscope, $h$ is planck’s constant, $m_e$ is the rest mass of the electron, $c$ is the speed of light, $e$ is the elementary charge and $U$ is the acceleration voltage of the electron. Combining these factors gives the theoretical minimum probe diameter for the microscope in question. Thiberge et. al. mention the Kanaya-Okayama radius\cite{76} which describes the radius of the interaction volume. The radius is described with:

$$R_{KO} = 0.0276 \times \frac{A Z^{0.11} E_0^{1.67}}{\rho}$$  \hspace{1cm} (6.5)

where $A$ is the atomic weight in g mol$^{-1}$, $Z$ is the atomic number, $E_0$ is the electron energy in keV and $\rho$ is the density in g cm$^{-3}$. The backscattered electrons originate
in a diameter proportional to the Kanaya-Okayama radius with Au having $d_{BSE} = 0.4 \times R_{KO}$ and bulk carbon $d_{BSE} = 1.0 \times R_{KO}$[76]. This factor enlarges the probe diameter to:

$$d = \sqrt{d_1^2 + d_2^2 + d_3^2 + d_{BSE}^2}$$

(6.6)

The last factor is especially important. It is determined directly by the interaction between beam and sample. While SiN$_x$ is an excellent material for the electron-transparent membrane graphene would be a better choice since the monolayer thickness reduces the amount of material which interacts with the beam.

Ph.D. student F. Pizzocchero opened small holes in the membrane on some EC-SEM chips by FIB milling. Over these openings he successfully placed graphene flakes which adhered well to the substrate and were resistant to water, acetone and IPA. Figure 6.1 shows three SEM images of a EC-SEM chip with a hole and graphene flakes covering it.

This advance opens up the possibility of high resolution (or at least higher) SEM of liquids.
Graphene windows in the EC-SEM cell

Figure 6.1.: SEM images of a EC-SEM chip with a hole created by FIB milling. The hole has been covered with graphene sheets, creating a new window. The membrane is outlined in white in 6.1a and 6.1b. Images from F. Pizzocchero.
7. Conclusion

A setup for in-situ electrochemical experiments has been successfully designed and tested. The setup is vacuum compatible and easy to maintain. Stress induced in the window, by clamping, has been alleviated with the use of a PDMS spacer and seal. The system survived pressure differences up to $4 \times 10^5$ Pa and multiple uses. Initial experiments have verified the presence of beam-induced chemical reactions, by imaging nickel deposited at current densities above $0.260 \text{ A m}^{-2}$, and shown that there is electrical connection to the Pt electrodes which can perform electrolysis of $\text{H}_2\text{SO}_4$ to produce bubbles and a CV of $\text{K}_3\text{Fe(CN)}_6$. This shows that electrochemical measurements can be performed in-situ in the setup. Measurements on cells showed that the chips used are ideal for cryo-fixation, but that living cells cannot survive for long in the SEM.

The first steps towards including graphene in the EC-SEM cell as a window material have been taken by FIB milling holes in the $\text{SiN}_x$ window and covering it with graphene.

7.1. Outlook

There are still some improvements possible. The electrodes are created in Pt, however, this has proven difficult to properly clean. Experiments with Au electrodes did not have this issue and therefore future experiments should use Au electrodes with the Ag/AgCl reference electrode.

The integration of graphene on the windows shows promise with regards to the potential resolution of the setup.

Future experiments should begin with known reactions to further establish the setup as a viable electrochemical environment, but then move on to experiments were the resolution of the SEM can be useful.
Part II.

Transmission Electron Microscopy
8. Introduction to Liquid Phase Transmission Electron Microscopy

The TEM is a great tool for imaging small samples with high resolution. However, there are some limitations as to which type of samples can be imaged. In this work focus will be on liquid samples. An ETEM can image liquids at specific temperature and pressure (maximum at about 278 K and 1000 Pa), so a different approach is needed in order to image liquids at room temperature or above and at atmospheric pressure and above. The solution is to seal off the liquid from the vacuum of the TEM, but still allow electrons to pass through by making electron-transparent windows in the setup.

There are two different versions of such a TEM chip. A simple setup is to make two identical chips with an electron-transparent membrane in the middle (see Figure 8.1). The liquid and a spacer material is placed on one of the chips and the other chip is placed ontop creating a sandwhiched assembly. The sandwich is then vacuum sealed with epoxy or mechanical clamping. This type of setup is commercially available\(^1\).

![Cross-section and Top view of a sandwich-type chip.](image)

**Figure 8.1.** A typical sandwich-type chip.

However, it does carry some disadvantages. The membranes on the chips are relatively large, to ensure overlap when the chips are manually aligned, and therefore have significant bulging. This makes the mass-thickness vary across the sample; reducing the signal from high resolution electron microscopy. Furthermore, integration of heating or electrical connection to the liquid is not yet part of the commercial setup. To better control the experimental conditions it was decided to focus on a

\(^1\)http://www.norcada.com/
different type of TEM chip; the monolithic TEM chip[39].
The monolithic TEM chip contains all the components on one chip. The liquid is
contained in a well defined and small channel which thereby reduces the bulging
in vacuum. The channel also provides a well-defined flow direction and thermal
insulation. Heating and electrical contact is integrated in the design and since it
is only one chip the size of the setup is halved and no alignment is required post-
fabrication.

Two versions of the chip were created. The first version, TEM chip v1, is discussed in
chapter 9. TEM chip v1 is fabricated using a sacrificial layer to define the structures.
This first design includes an electron-transparent channel over a membrane, an
encapsulated heater and protective structures to avoid damaging the channel during
experiments. Select sections of the channel material were thinned down to create
window areas with reduce mass-thickness. Liquid was filled into these chips and
initial experiments were performed. With this initial proof-of-concept successful,
and since the literature at that point had similar results published, it was decided
to focus on further improving the design to provide a higher fabrication yield and
create a more comprehensive experimental setup for in-situ electrochemistry and
with higher resolution.

The second version of the chip, TEM chip v2, is discussed in chapter 10. This design
streamlines the channel and introduces some new features. Etch time in the KOH
was an issue with TEM chip v1 and therefore the channel was changed from a square
design to a v-shaped design to reduce the length. New features with holes in them,
named Busstops (see section 10.1.2) were included in the channel to further minimize
the etch time and allow electrical connection to the liquid. To further reduce the
mass-thickness imaged in the TEM the channel was fabricated with two different
heights. Most of the channel, all the protective structures and the encapsulated
heater were fabricated in the "high" sacrificial layer and the part of the channel to
be imaged was fabricated in the "low" sacrificial layer. Finally, inlets to the channel
were designed to access the channel from the back of the chip, thus allowing vacuum
seal to use the chip substrate for mechanical support instead of the fragile channel.

The low sacrificial layer was fabricated in amorphous silicon (amorph-Si) and this layer
re-crystalized during the fabrication process. Since it re-crystalized into crystalline
islands it was non-continuous and therefore it was not etched by the KOH. This
means that TEM chip v2 did not function as intended. Suggestions for how to
improve the fabrication process are discussed in section 10.2.
8.1. The Transmission Electron Microscope

The transmission electron microscope functions by sending electrons through a sample and collecting the result with a CCD camera. Free electrons are generated at the source, which is typically at the top of the TEM, they are then accelerated down through the two magnetic condenser lenses C1 and C2 and through the condenser aperture. This is the condenser system which collects and focuses the electrons. The beam current, acceleration voltage and physical dimension of the TEM are generally such that only a single electron, from the source, is present in the sample at any given time. The wave nature of the electron is modulated by the sample and this modulation is the source of the image in bright-field TEM. After passing through the sample the electrons are collected and focused by the objective lense and passed through the objective aperture. The objective lense is directly below the sample and can partially encompass the sample. Finally, the electrons are passed through a series of lenses and apertures collectively known as the projector system. The electrons are then viewed on a phosphor screen or imaged by the CCD camera.

Two of the main factors which reduce resolution in the TEM are spherical aberration, $C_s$, and chromatic aberration, $C_c$. Spherical aberration is due to a non-planar electron wave. In the ideal case the electron is generated from a point-source at infinite distance from the sample resulting in a completely planar wave incident on the sample. To compensate for a non-point source at finite distance from the sample a special lense system called a $C_s$-corrector can be used.

Chromatic aberration is due to energy spread in the beam and can come from the source and from passing through the sample. Spreading the beam and utilizing apertures can compensate for some of this effect.

An image of the general TEM setup can be seen in Figure 8.2.

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2 Some microscopes use photographic film
Figure 8.2.: The general TEM system. At the top of the TEM is the source of the free electrons. Directly below the source is the condenser system. The condenser system focuses the electrons onto the sample. Below the sample is the objective lens and aperture which collect and convey the electrons to the projector system. The projector system (drawn here as a large lens) usually consists of 2-3 lenses and 1-3 apertures. The imaging surface shown here could be a phosphor screen or the entrance to a CCD camera imaging system.
9. TEM Chip version 1

The first version of the monolithic TEM chip is a prototype to verify the fabrication method. Earlier work fabricating hollow cantilevers by Ph.D student M. F. Khan (see Figure 9.1) and in literature from the group of K. F. Jensen ([2]) fabricated hollow channels in SiN$_x$. These projects verified the method of channel formation with a sacrificial layer etched out by KOH.

![SEM images of hollow cantilevers. 9.1a shows a SEM image of a SiN$_x$ channel on a cantilever. There are two measurements in the image, one showing the height of the cantilever (2.12µm) and the other the thickness of the SiN$_x$ (487 nm). 9.1b shows a SEM image of cantilever fractured to reveal the hollow channel. This channel is approximately 4 µm wide and 4 µm high.](image)

**Figure 9.1:** SEM images of hollow cantilevers. 9.1a shows a SEM image of a SiN$_x$ channel on a cantilever. There are two measurements in the image, one showing the height of the cantilever (2.12µm) and the other the thickness of the SiN$_x$ (487 nm). 9.1b shows a SEM image of cantilever fractured to reveal the hollow channel. This channel is approximately 4 µm wide and 4 µm high.

The dimensions on the chip fabricated by M. F. Khan were very large compared to the typical samples in the TEM. Additionally the channel in the chips was on a free-standing cantilever designed for mass detection. Therefore a new chip was designed, specifically for the TEM, to include a smaller channel with a supporting membrane for mechanical stability and thermal isolation. The new chip, called TEM chip v1, was similar to half of the sandwich type TEM chips; a single chip with with a SiN$_x$ membrane. Figure 9.2 shows one of the first versions TEM chip. The labelled features are discussed in the sections below.
Figure 9.2.: An optical image of a TEM chip v1. The large blue area is thinned SiN_{x}. The mask used to open the backside for KOH also contained the structures to created the thinned windows. The mask was rotated 180° and then used on the frontside.

On the membrane a channel is constructed with a sacrificial layer. The channel height is designed to be 1\,\mu\text{m} and the thickness of the SiN_{x} to be imaged through was designed to be 100\,\text{nm}. Additional structures were included on the chip to provide support for tubes filling the channel, protect the channel from damage and heat the liquid in the channel. In this first version there were 13 different variants in order to explore different types of channels, inlets and membranes.

Three main features were the focused of TEM chip v1. With a channel which is decreased in height and width, compared with M. F. Khan’s chips, it is assumed that the etch rate decreases because the cross-sectional area exposed to the KOH etch is decreased. In TEM chip v1 it was important to verify that these smaller channels could be etch out.

While the channel is designed in SiN_{x} due to, among other things, the high Young’s modulus of this material, it is still vulnerable to point forces from fx clamping in a TEM holder. In TEM chip v1 the protective structures were included in an attempt to avoid damaging the chip.

Finally the third focus of the fabrication was the ability to selectively thin areas of the SiN_{x} to form thinned windows for imaging in the TEM.
This chapter describes the fabrication method (section 9.1) and features of the TEM chip v1 (section 9.1.1 - 9.1.3). A liquid containing Au NPs (see appendix D) was introduced to an inlet on one of the channels. These chips were then imaged in the TEM as discussed in section 9.2.

### 9.1. Fabrication

The fabrication procedure for TEM chip v1 consists of 11 steps (see table 9.1). Five of these steps are photolithography where a layer of photoresists is spun on the wafer, patterned by UV-light through a mask and then developed. This transfers the mask pattern to the wafer which can then be used as a protective layer to selectively etch the wafer or in a lift-off procedure to remove unwanted material after deposition. The yield of the first fabrication was approximately 97.1%.

The first step is to grow the bottom SiN$_x$ layer of the channel. The thickness of this layer is designed to be 50 nm thick so that it is both mechanically stable and electron-transparent.

The second step grows the sacrificial layer in which the channel, protective structures and heater will be defined. The protective structures are discussed in section 9.1.1 and the heater is discussed in section 10.1.1.

There are two different materials ideal for this layer: SiO$_2$ and poly-Si. Both layers are routinely deposited in the 1 µm thickness the layer needs and both can be etched by a wet etch which does not significantly etch the membrane material, SiN$_x$. However, patterning SiO$_2$ is mainly a physical etch which means it has a low selectivity and the processes available in the local cleanroom did not have the necessary wafer-scale uniformity. The bottom SiN$_x$ layer under the sacrificial layer would be etched away at the central part of the wafer before the sacrificial layer at the edge was etched down to the underlying layer. Therefore poly-Si is selected since it can be patterned with advanced silicon etch (ASE) which has a high selectivity to SiN$_x$ (see Figure 9.3).

After patterning the sacrificial layer in Step 3 the sacrificial layer on the backside is removed in Step 4. The top layer of the channel is deposited in Step 5. The thickness deposited is 200 nm. This provides high mechanical stability and resistance to scratches. Furthermore, a thick layer of SiN$_x$ provides protection from the extended KOH etch needed to etch the channel.

The SiN$_x$ is opened on the backside, in Step 6, to allow the KOH to etch the membrane clear in Step 7. Before etching the channel the SiN$_x$ is thinned down over the channel in Step 8 (see section 9.1.3) and the inlets are opened in Step 9. Finally, the channel is etched out in Step 10 (see section 9.1.2).

The SiN$_x$ covering the contacts to the heater is etched away in Step 11.
Figure 9.3.: SEM images of a cleaved wafer. 9.3a shows a zoom in on the interface between the bottom Si, the SiN$_x$ of the membrane and the poly-Si of the sacrificial layer. The thickness of the SiN$_x$ layer was within tolerance. 9.3b shows the edge of one of the structures. The sacrificial layer has clearly been underetched, however this was not visible in subsequent steps (probably due to the many plasma ashings). The two white lines indicate the edges of the SiN$_x$ layer which continues past the etched poly-Si layer indicating the etched stopped on the SiN$_x$ layer. The thickness of the sacrificial layer is also shown and it is within tolerance. These images are of TEM Chip v2 which uses the same etch.
### Table 9.1: TEM chip v1 Fabrication Steps 1-11

<table>
<thead>
<tr>
<th>Fabrication Step</th>
<th>Schematic</th>
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</thead>
<tbody>
<tr>
<td>1 Grow $\text{SiN}_x$ Membrane Layer</td>
<td>![Schematic of step 1]</td>
</tr>
<tr>
<td>2 Grow Sacrificial Layer</td>
<td>![Schematic of step 2]</td>
</tr>
<tr>
<td>3 Pattern Sacrificial Layer</td>
<td>![Schematic of step 3]</td>
</tr>
<tr>
<td>4 Remove Backside Sacrificial Layer</td>
<td>![Schematic of step 4]</td>
</tr>
<tr>
<td>5 Grow Top $\text{SiN}_x$</td>
<td>![Schematic of step 5]</td>
</tr>
<tr>
<td>6 Open backside $\text{SiN}_x$</td>
<td>![Schematic of step 6]</td>
</tr>
<tr>
<td>7 KOH etch</td>
<td>![Schematic of step 7]</td>
</tr>
<tr>
<td>8 Thin $\text{SiN}_x$</td>
<td>![Schematic of step 8]</td>
</tr>
<tr>
<td>9 Open inlets</td>
<td>![Schematic of step 9]</td>
</tr>
<tr>
<td>10 KOH etch</td>
<td>![Schematic of step 10]</td>
</tr>
<tr>
<td>11 Open heaters</td>
<td>![Schematic of step 11]</td>
</tr>
</tbody>
</table>
9.1.1. Protective Structures

The monolithic chip is fabricated with a SiN$_x$ channel and although this channel is designed to withstand the pressure difference in the TEM it is susceptible to failure if subject to directed point force such as that from tweezers or clamping in the TEM holder. To avoid damaging the channel when handling the chip, protective structures are included in the sacrificial layer (see Figure 9.4). These structures are not opened in the photolithography steps which means they should remain intact after the KOH etch.

The protective structures also act as support if the chip is clamped on the frontside and as support for the membrane. If a membrane is fractured the fracture does not typically progress past the protective structures.

The growth of the SiN$_x$ layer in Step 5 includes small defects called pin-holes. These are openings in the SiN$_x$ layer which allow the KOH etch to by-pass it and etch the underlying Si or poly-Si. To avoid a single pin-hole destroying all the protective structures the edge of the chip is lined with 10µm by 10µm protective islands (see Figure 9.4b). Pin-holes and their effect are discussed further in section 9.1.2.

The protective structures around the inlets and channels are designed to be continuous (see Figure 9.4a). The reason for this is twofold. The open annulus around the inlet is designed to support a tube to create a seal around the inlet and provide liquid flow or simply fill the channel. Furthermore if the liquid is dropped on the chip it can flow over the channel and contaminate the image. To avoid this there are two lines running parallel to the channel and connected to the open annulus which liquid would encounter before contaminating the channel. It is also possible for the reverse to happen with a liquid being contained between the two protective structures. However, this only occurred once in experiments.

The seal, however, did not function (see Figure 9.5). It required a very good alignment between tube and inlet. Because of this a liquid sealant was used in the experiments.

In experiments it is clear that the protective structures have worked well. They prevent the flow of liquid if it is dropped on the chip and protect the channel from accidental tweezers (although careful handling minimized such events). The TEM chip v1 chips also survived being clamped in a TEM holder. The structures around the inlet to support a tube did not function as intended and another method to access the channel is designed in section 10.1.6.
Figure 9.4.: Protective structures on TEM chips. 9.4a is an image of the mask design in program L-Edit by Tanner EDA. The black circles are the inlets to the channel and the thin purple v-shaped line connects them. The green area is the opening on the backside for KOH with the checkered area showing the area of the membrane on the frontside. The open annulus around the inlets are the protective structures with lines running parallel to the channel to prevent the flow of spilled liquid contaminating the channel. 9.4b shows the protective islands and a cutting line. The protective islands are approximately 10 µm by 10 µm. The cutting line, also made in the sacrificial layer, are there to align the saw-blade when releasing the chip from the wafer.
Figure 9.5.: Sealing inlets. The figures show a cross-section of an inlet on TEM chip v1, called a front-side inlet. The walls of the inlet are thin lines (marked by "inlet") surrounded by the protective structures (marked by "support"). Above the inlet a tube is placed (marked by "tube"). Obtaining a good seal without destroying the channel requires a very good alignment of tube and inlet. Frequently this was not achieved due to the walls of the inlet breaking or the tube having an surface which was not perfectly flat.
9.1.2. Sacrificial Etch

In order to shape the channels a sacrificial layer is deposited by LPCVD and then patterned by photolithography and ASE into the shape of the channel and inlets. They are then covered by SiNx. The inlets are then opened with another photolithography step and a RIE. The entire chip is then submerged in a KOH etch which removes the sacrificial layer in the channel.

![Figure 9.6:](image)

**Figure 9.6.:** Length of channel etched as a function of time. The data shown here is from a single chip-type with a cross-sectional channel area of 800 µm² and a channel height of 4 µm. As can be seen the etch progresses linearly with time. The data is from M. F. Khan.

The etch rate of 80°C KOH in bulk Si is $1.3 \times 10^{-6}$ m s⁻¹. Because the channel has small dimensions, the etch rate is approximately 50 times lower than this. Figure 9.6 shows the length of the channel which has been etched as a function of time for a single type of chip from M. F. Khan. The progression is linear with time and therefore a linear fit to the data has been done.

Etch data from M. F. Khan, TEM chip v1 and TEM chip v2 has been compiled and a linear fit to estimate the etch rate has been performed (see Figure 9.7).

The fit to the data gives an etch rate of $2.15 \times 10^{-8}$ m s⁻¹. The channel in TEM chip v1 was 1 µm high and 3710 µm long requiring 23.9 h to etch out and it was etched out in just under 22 h giving an etch rate of $2.36 \times 10^{-8}$ m s⁻¹. The channel in TEM chip v1 was 500 nm high and 2060 µm long requiring 13.3 h to etch out, however it was etched out in 23.6 h giving an etch rate of $1.22 \times 10^{-8}$ m s⁻¹. This indicates that the cross-sectional area of the channel affects the etch rate.
Figure 9.7.: Etch rate of the sacrificial layer in the channel. The datapoints show the length of the sacrificial layer in the channel, which has been etched. The green line is a fit to the data with a slope of $2.85 \times 10^{-8}$ m s$^{-1}$. The data measured from images of etched TEM chip v1 (blue squares), TEM chip v2 (green squares) and from images provided by M. F. Khan (red squares).

Figure 9.8 shows a graph of the etch rate data as a function of the cross-sectional area of the channel. The data is measured from optical images of the TEM chip v1 chips, TEM chip v2 chips and images of KOH etch test structures provided by M. F. Khan. Each point is generated by dividing the length etched by the time it took to etch. There is a clear difference between the tall and wide channels from M. F. Khan (>100 µm$^2$) which have an RMS etch rate of $(27.7 \pm 2.35)$ nm s$^{-1}$ and the low and narrow channels in TEM chip v1 (<10 µm$^2$) which have an RMS etch rate of $(22.2 \pm 3.46)$ nm s$^{-1}$ and TEM chip v2 (<2 µm$^2$) which have an RMS etch rate of $(14.9 \pm 3.10)$ nm s$^{-1}$. This indicates that the etch rate is dependent on the cross-sectional area of the channel which agrees with the initial assumption.

Figure 9.9 shows an image of the result of pin-holes. KOH is an anisotropic etch in Si. It etches different crystal directions at different speeds. This results in the square structures seen in the image. The SiNx in the area imaged had been damaged by tweezers during handling. However, the longer the area is etched the larger the pin-holes will grow and eventually merge. This will cause non-rectangular membranes which are more susceptible to failure. If there is a pin-hole in one of the protective structures the longer it is etched the weaker it becomes. Pin-holes can also cause channels to be leaky.
Furthermore, the etch rate of SiN\textsubscript{x} by KOH was measured in order to estimate how much is lost when etching the sacrificial layer. The thickness of the SiN\textsubscript{x} on two test wafers was measured by ellipsometer before and after a KOH etch. The etch rate was measured to be $3.43 \times 10^{-13}$ m s\textsuperscript{-1} which translates to approximately 27 nm in 22 h. This means that the designed final thickness of the SiN\textsubscript{x} must be at least 27 nm thicker than the desired thickness. Additionally if defects are buried in the SiN\textsubscript{x} a long KOH time might free more pin-holes. Therefore it is necessary to ensure as small an KOH etch time as possible. This issue was addressed in the design of TEM chip v2 by reducing the channel length and including extra holes in the channel called busstops (see section 10.1.2).

Figure 9.8.: Etch rate as a function of the cross-sectional area of the channel (9.8a).
9.1.3. Thinning Windows

One of the limiting factors on TEM samples is the mass-thickness. A high mass-thickness reduces the intensity of the signal. Therefore the vertical dimension of the channel as well as the thickness of the top and bottom walls in the channel need to be as small and as thin as possible. In TEM this means that the entire imaged area, should be 200 nm or less in the vertical direction. In TEM chip v1 the vertical dimension of the channel is fixed at 1 µm.

Reducing the thickness of the SiNₓ channel walls will make the channel very fragile. To compromise between the mechanical stability of a thick SiNₓ layer and the image quality of a thin SiNₓ layer the SiNₓ was selectively thinned over the channel. The top layer was designed to be 200 nm thick and the thinned windows there reduced to 50 nm.

Figure 9.10 shows schematic representations of the concept of thinned windows. The bottom layer of the channel has a fixed an continuous thickness. The top layer is deposited with a high thickness and then masked with photolithography. The openings in the photolithography are then etched with RIE and reduced in thickness. As can be seen in Figure 9.10a the area thinned is wider than the channel to make alignment in the photolithography step easier.

Figure 9.11 shows two SEM images of a TEM chip v1. One is taken at 10 kV (see...
Figure 9.10: Thinned window in a TEM chip. 9.10a shows a 3D diagram of a channel with a thinned window on the middle. A small portion of the channel has been cut out to show the differences in thickness of the un-thinned section and the thinned window. The light-blue cut through the structure indicates where the cross-section in 9.10b is taken.

Figure 9.11a) and the thinned windows are clearly visible on the membrane as dark areas. They are dark because the SEM gets little or no signal from these areas. When the acceleration voltage is increased to 20kV (see Figure 9.11b) the entire membrane becomes darker indicating that the contrast change is due to a thickness difference and not a material difference.
Figure 9.11: SEM images of a membrane on TEM Chip v1. The channel running perpendicular the membrane has not been etched out. 9.11a is an image taken at 10 kV. The top left and bottom right areas are the Si. Running diagonally across the image is the membrane with the unetched channel snaking perpendicular to it. In the membrane are dark rectangles with dark squares at either end. These are the thinned windows which are 50 nm thick. The rest of the membrane is 200 nm thick. 9.11b shows the same area taken at 20 kV. In this image the entire membrane is transparent.

9.2. Results and conclusion

After the TEM chip v1 chips were fabricated some were filled with a Au NP containing liquid and sealed with an acrylic polymer (nail varnish). The hydrophillic channel draws the liquid in. Figure 9.12 shows image of the chip before and after the channel is filled.

The filling was initially continuous as can be seen in Figure 9.12. The method of sealing the inlets caused some of the liquid to be evacuated from the channel as part of the drying. Figure 9.12c shows an image of a chip after it is filled and sealed and vacuum tested. It is important to note that the liquid visible in the image was inspected before and after the vacuum test and did not change.

The sealing method also caused bubbles in the liquid. This was then imaged in the TEM (see Figure 9.13). The NPs move around in the very large volume and are therefore difficult to focus on and since the TEM used did not have the capability of taking a video the NPs are not visible in the TEM images. There is no electrical connection to the liquid so no electrochemical measurements can be done on the...
liquid.

Figure 9.14 shows a close up of part of the channel in Figure 9.13. The entire image is taken through the SiN\textsubscript{x} of the channel. Since the NPs have 1 µm vertical distance to move around in they move in and out of focus and while they were visible to the TEM operator they are not visible in the image.

Finally, Figure 9.15 shows an image of a TEM Chip v1 imaged in the Analytical TEM. Visible in the image are the walls of the channel in the top right and bottom left corners. In the center of the image and on the top left are dark areas of Au NP containing liquid. Around these areas are circles. These circles are not present on the surface of the membrane and come from the poly-Si. The surface of the poly-Si is transferred to the SiN\textsubscript{x} when the top layer is deposited. They can potentially distort the image and need to be considered in the next version.

TEM chip v1 successfully proved the fabrication method could work. The KOH etch removed the sacrificial layer in channels with significantly lower dimensions than previous work. The protective structures functioned almost as intended with the exception of the open annulus around the inlets. The thinned windows worked as intended, allowing imaging of the liquid while maintaining the structural integrity of the rest of the monolithic TEM chip.

With these features realized the next, more advanced and complex, version of the chip was designed and fabricated.
Figure 9.12: Filling a TEM chip v1. 9.12a is an image of the membrane on a TEM chip v1 with an empty channel. 9.12b shows the channel filled. 9.12c shows another TEM Chip v1 filled with the same liquid by the same method. This chip has been sealed with nail varnish which has sucked some of the liquid out of the channel in the drying process. The chip was viewed before and after subjecting it to a vacuum of 100 Pa for 20 min. There was no change from 9.12c.
Figure 9.13.: A composit of multiple TEM images of a TEM chip v1 channel with NP liquid in. The thinned windows are visible as are multiple bubbles in the liquid.

Figure 9.14.: A zoom in of the interface between the liquid and the gas in the imaged TEM Chip. The liquid is imaged through the SiNx and no NPs are visible because they are not in focus. The part labeled "Air" is vapor in the channel.
Figure 9.15.: A TEM image of liquid in a channel. Visible around the drop are several circles in the channel. These are protrusions from the surface of the channel created when the SiNx was deposited on the poly-Si.
10. TEM Chip version 2

In order to create a chip for *in-situ* TEM experiments on liquid with better resolution than what was possible with the 1 µm tall channel in TEM chip v1[20] and include electrodes and a working heater, TEM chip v2 was designed (see Figure 10.1).

(a) A profile sketch of a TEM chip v2

(b) A zoom in on the channel low channel

Figure 10.1.: A profile model of a TEM chip v2. Visible on the chip are the open inlets to the channel with the protective structures around them. The edge of the chip is lined with protective islands. The gray is the Si of the substrate and the green-brown is the SiNx. The blue structures are the electrodes which contact to the liquid in the channel through the busstops. A heater is also visible with contact pads aligned to the electrode contact pads. A zoom in around the center of the chip is visible in 10.1b. The chip is not to scale and thinned windows are not visible.

The fabrication of TEM chip v1 also had a very low yield, even for an exploratory fabrication process, due to extensive KOH etch time. TEM chip v2 was designed to have significantly lower etch time by redesigning the channel to be shorter, but maintaining the position and size of the inlets, and including a feature called busstops. The busstop feature was an extension from the channel which would contain an opening to allow extra entrances for the KOH. These openings would then be sealed with electrode material, simultaneously creating a seal and electrical contact to the liquid. The inlets were maintained in position and size to allow for easier interaction with the makro-scale of pincets and syringe tips. To improve resolution, but not
significantly increase etch time in KOH a channel with multiple heights was designed. The majority of the channel would have a height of 1 µm, but the main part would only be 20 nm.

There were 21 different variants of TEM chip v2. These variants experimented with different heater design, electrode design and inlets design. There were two different sizes. One type of chip (type A-O) were designed for a preexisting holder with four electrical connections and the remaining types (type P-U) were designed for a new holder with ten electrical connections.

TEM chip v2 required a significantly more involved fabrication process as described in section 10.1. It includes many new features described in section 10.1.2-10.1.6. Unfortunately there were some issues with fabrication as described in section 10.1.3. Based on the successes and challenges of TEM chip v2 a new chip is presented in section 10.2.

10.1. Fabrication

To include new features such as a lower channel to reduce the imaged liquid volume, electrical connection to measure chemical reactions or apply voltages or currents to the liquid and decrease the etch time a new chip was designed. The fabrication process can be seen in table 10.1 and table 10.2. Appendix E lists the fabrication steps in more detail, appendix F provides a detailed fabrication plan for use in the Danchip cleanroom and appendix G shows a more detailed visualization of the fabrication process.

The first step grows the bottom SiN$_x$ layer of the channel. This layer must be as thin as possible, but still withstand the KOH etch. The bottom SiN$_x$ layer in TEM chip v1 was 50 nm because previous work had shown that this thickness is feasible to work with and electron-transparent[26]. Due to the extensive KOH etch time the thickness was reduced to 25 nm. Since the TEM chip v1 functioned, without any issues, with this thickness the designed thickness of TEM chip v2 was 25 nm. The bottom layer of TEM chip v2 is not exposed to KOH for as long as TEM chip v1 since it is first released at the same time the channels are being etched. It is, however, exposed and the etch time required must be taken into account since KOH etches SiN$_x$ as mentioned previously. Estimating the etch time for the channels at 13.3 h the SiN$_x$ etched is approximately 10.3 nm (the bottom layer is first exposed after 5 hours of etch time). The full designed thickness of the bottom SiN$_x$ layer is the 35 nm and the achieved thickness was (34.7 ± 0.31) nm which was within tolerance since layers this thin are deposited very quickly and the dynamics of the process used to grow the layer was not characterized at these thicknesses.

The next step deposits the conductive poly-Si sacrificial layer. The designed thickness was 1 µm and achieved thickness was (996 ± 1.27) nm. The conductivity of this layer
was measured by four-point probe to be \((0.725 \pm 0.476) \, \Omega \cdot \text{cm}\).

Steps 3, 5, 10, 11, 12, 16 and 17 all include photolithography and separate masks. Step 3 uses photolithography and ASE to etch the sacrificial layer. The recipe used had a high selectivity to SiN\(_x\) allowing the etch through 1000 nm poly-Si to stop on the 35 nm SiN\(_x\) layer.

The sacrificial layer for the low channel, amorph-Si, is grown in Step 4. The wafer was then etched in Step 5 with another photolithography and ASE process. This reduced the high sacrificial layer to about 500 nm thickness. The thickness of the amorph-Si layer was determined to be 60 nm from detak measurements of the structures. Step 6 reduced the surface roughness of the channel and is described in section 10.1.5). Step 7 removes the sacrificial layer on the backside in preparation for Step 8 and 9. In an attempt to minimize pin-holes the top SiN\(_x\) layer is deposited in two steps.

The growth of the top SiN\(_x\) layer is done in two steps in an attempt to minimize pin-holes. The source of pin-holes is poorly understood. Some are fractures caused by damage to the layer during handling, others are created during deposition of the SiN\(_x\) layer. By growing the top SiN\(_x\) layer in two steps the pin-holes from the first grown layer might be covered by the second grown layer. Conversely the pin-holes in the second layer would be blocked by the first layer. Although the number or pin-holes present in TEM chip v1 and TEM chip v2 have not been quantified optical inspection of the wafers during production indicated that there was significantly fewer pin-holes when depositing the SiN\(_x\) in two layers.

![Figure 10.2: Images of TEM Chip v1 and TEM Chip v2. In TEM Chip v1 (10.2a) the protective structures and the heater have been etched out due to the presence of pin-holes. On TEM Chip v2 (10.2b) this was not as common an occurrence due to the double SiN\(_x\) deposition.](image)

To reduce the KOH etch time all areas which need to be etched by KOH are
opened prior (Step 10-12) to the KOH etch in Step 13. One feature, the backside inlets (see section 10.1.6), require a KOH etch before they can be opened which is why there are two KOH etch steps despite the focus on reducing the duration of this step.

Finally the heaters are opened in Step 16 and the electrodes are deposited in a lift-off process in Step 17. Step 18 spins on a thick, protective layer of photoresist to avoid dust contaminating the surface of the chips while they are stored prior to experiments.
<table>
<thead>
<tr>
<th>Fabrication Step</th>
<th>Schematic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Grow SiN_x Membrane Layer</td>
<td><img src="image1" alt="Schematic 1" /></td>
</tr>
<tr>
<td>2 Grow High Sacrificial Layer</td>
<td><img src="image2" alt="Schematic 2" /></td>
</tr>
<tr>
<td>3 Pattern High Sacrificial Layer</td>
<td><img src="image3" alt="Schematic 3" /></td>
</tr>
<tr>
<td>4 Grow Low Sacrificial Layer</td>
<td><img src="image4" alt="Schematic 4" /></td>
</tr>
<tr>
<td>5 Pattern Low Sacrificial Layer</td>
<td><img src="image5" alt="Schematic 5" /></td>
</tr>
<tr>
<td>6 Reduce Surface Roughness</td>
<td><img src="image6" alt="Schematic 6" /></td>
</tr>
<tr>
<td>7 Remove Backside Si</td>
<td><img src="image7" alt="Schematic 7" /></td>
</tr>
<tr>
<td>8 Grow First Top SiN_x Layer</td>
<td><img src="image8" alt="Schematic 8" /></td>
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### Table 10.2: TEM Fabrication Steps 9-18

<table>
<thead>
<tr>
<th>Fabrication Step</th>
<th>Schematic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grow Second Top SiNₓ Layer</td>
<td><img src="image1" alt="Schematic" /></td>
</tr>
<tr>
<td>Open Backside SiNₓ for KOH</td>
<td><img src="image2" alt="Schematic" /></td>
</tr>
<tr>
<td>Open Frontside SiNₓ for KOH</td>
<td><img src="image3" alt="Schematic" /></td>
</tr>
<tr>
<td>Thin SiNₓ Around Imaging Area</td>
<td><img src="image4" alt="Schematic" /></td>
</tr>
<tr>
<td>KOH Etch</td>
<td><img src="image5" alt="Schematic" /></td>
</tr>
<tr>
<td>Open Backside Inlets</td>
<td><img src="image6" alt="Schematic" /></td>
</tr>
<tr>
<td>KOH Etch</td>
<td><img src="image7" alt="Schematic" /></td>
</tr>
<tr>
<td>Open Heaters</td>
<td><img src="image8" alt="Schematic" /></td>
</tr>
<tr>
<td>Create Electrodes and Fill Busstops</td>
<td><img src="image9" alt="Schematic" /></td>
</tr>
<tr>
<td>Prepare Wafers for Outside</td>
<td><img src="image10" alt="Schematic" /></td>
</tr>
</tbody>
</table>
10.1.1. Encapsulated Heater

Including a heater in the design allows for experiments to be conducted on a range of temperatures. There are two main possibilities for including a heater in the TEM chip. A simple metal layer can be used to heat the structure. Platinum has a melting point at 2040 K [70] and is therefore an ideal candidate. However, TEM chip v1 does not include a metal deposition step and therefore the sacrificial layer is used. The poly-Si layer is grown with boron-doping making it conductive. Current is then run through the structures made from it. The melting point of poly-Si is 1690 K and the melting point of SiNx is around 2170 K [6]. This means that if the poly-Si melts the encapsulating SiNx should contain it and prevent recrystallization into islands. Furthermore an exposed heater would oxidize in an atmosphere and the encapsulation prevents this. This method has the added benefit of not requiring an additional fabrication step except for the step which opens the encapsulating SiNx.

There are four variables to consider when designing the encapsulated heater: joule heating, conductive heat loss, radiative heat loss and convective cooling [59]. The latter, convective cooling, is the cooling due to the presence of a thermally conductive gas such as a regular atmosphere. Since the experiments will be conducted in a vacuum this can be neglected.

According to Stefan-Boltzmann’s law [10] the total irradiated power, \( I_{\text{irr}} \), by an object is:

\[
I_{\text{irr}} = \alpha \sigma_{\text{SB}} T^4
\]

where \( \alpha \) is the absorptivity of the object, \( \sigma_{\text{SB}} \) is Stefan-Boltzmann’s constant and \( T \) is the temperature. The difference between the power irradiated by and object, at temperature \( T \), and its surroundings, i.e. the emitted power is described by:

\[
P_{\text{radiative}} = A_{\text{surface}} \alpha \sigma_{\text{SB}} \left( T^4 - T_0^4 \right)
\]

where \( A_{\text{surface}} \) is the surface area of the object and \( T_0 \) is the temperature of the surroundings. Since melting point of SiNx is 2170 K the heater must be operated below this. Even if the heater reached 1500 K and the surrounding was cooled to 77 K by liquid nitrogen the radiative heat lost would be on the order of \( 10^{-4} \) W and it can therefore be neglected.

The final two variables, joule-heating and conductive heat loss, cannot be neglected. The effect, \( P_{\text{joule}} \), of a object heated by joule heating is:

\[
P_{\text{joule}} = R_{\text{electrical}} I^2 = \rho \frac{L}{A} I^2
\]

where \( \rho \) is the resistivity of the object, \( L \) is the length of the object, \( A \) is the cross-sectional area and \( I \) is the applied current. The heater in TEM chip v2 has a thin
segment designed to heat up and two thick segments leading to it from the contacts. The resistance of these segments is such that the majority of the effect is deposited in the thin segment which is close to the low channel. The thin segment is 200 µm long, 2 µm wide and 500 nm high. The final variable, conductive heat loss, assumes the end of the chip (where the contacts are located) is at thermal equilibrium with the surroundings. The thermal resistance between the heater and the end of the chip affects the heating process by leading thermal energy away from the heater.

The heater is placed 50 µm from the channel. Figure 10.3 show a sketch of the heater position on a TEM chip. The part of the chip which is at thermal equilibrium with the surroundings is the end of the chip where the contact pads for the heater are located. In a direct line from the thin segment of the heater to the thermal equilibrium there is 249 µm of free-standing SiNx membrane (shown as ”a” on Figure 10.3) and 1530 µm Si (covered by SiNx and shown as ”b” in Figure 10.3). The thermal resistance of an object is described by[59]:

$$R_{\text{thermal}} = \frac{L}{A\kappa}$$  \hspace{1cm} (10.4)

where $\kappa$ is the thermal conductivity of the object.

**Figure 10.3.** Sketch of heater position on the TEM chip. The distance from the heater to the point of thermal equilibrium with the surroundings, at the far end of the chip (where the heater contacts are located) is a+b. The first part, a, is the distance over the membrane, the second is the distance over the substrate of the chip.
The total temperature increase from an encapsulated heater is given by:

\[ \Delta T_{\text{max}} = R_{\text{thermal}} \times R_{\text{electrical}} \times I^2 \]  

(10.5)

Inputting the variables (\(\kappa_{\text{Si}} = 148 \text{ W m}^{-1} \text{K}^{-1}\) and \(\kappa_{\text{SiN}_x} = 30 \text{ W m}^{-1} \text{K}^{-1}\)):

\[ \Delta T_{\text{max}} = \left( \frac{L_{\text{membrane}}}{A_{\text{membrane}} \kappa_{\text{SiN}_x}} + \frac{L_{\text{chip}}}{A_{\text{chip}} \kappa_{\text{Si}}} \right) \times \frac{L_{\text{heater}}}{A_{\text{heater}}} I^2 \]

\[ = \left( \frac{200 \mu m}{200 \text{ nm} \times 249 \mu m \times 30 \text{ W m}^{-1} \text{K}^{-1}} + \frac{200 \mu m}{350 \mu m \times 1530 \mu m \times 148 \text{ W m}^{-1} \text{K}^{-1}} \right) \times \frac{500 \text{ nm} \times 2 \mu m}{200 \mu m} \times \rho I^2 \]

\[ = 6.78 \times 10^{13} \text{ K s}^2 \text{ kg}^{-1} \text{ m}^{-3} \times \rho I^2 \]  

(10.6)

The resistivity of the poly-Si in the heater is measured to be \((0.725 \pm 0.476) \Omega \text{ cm}\) by 4-point probe. In order to achieve a temperature increase of 1000 K a voltage of 65.4 V is required. The fabricated encapsulated heaters were not tested so this has not been verified.

In a bachelor project, by A. A. Nilausen\[59\], conductive poly-Si with a resistivity of \(2.77 \times 10^{-3} \Omega \text{ cm}\) was encapsulated in SiN\(_x\) for \textit{in situ} TEM\[59\]. Electrical connection to the heater was achieved and Figure 10.4 shows images of the chip were the heater is glowing due to a temperature of about 1500 K (this heater has different dimensions than the TEM chip v2 heaters).

This project was a proof-of-concept for the encapsulated heater. If the poly-Si layer in TEM chip v2 had a resistivity of \(2.77 \times 10^{-3} \Omega \text{ cm}\) it would require a voltage of 4.04 V to achieve a theoretical temperature difference of 1000 K. The poly-Si in the bachelor project was deposited in a new oven which has a high degree of control over the resistivity. Future TEM chips should use this oven.
Figure 10.4: Optical microscope image of an encapsulated heater from [59]. There are four heaters visible, three with two connections and one with four. The dark area in the center of the image is a SiN\textsubscript{x} membrane with a lot of perforations for TEM. A red line in the center of the membrane is an encapsulated heater of conductive poly-Si with 33 mA running through it. It is approximately 1500 K. The microscope light is on in the image. The inset in the top right corner (marked with ”A”) shows the heater with the microscope light turned off.
10.1.2. Busstops

One major factor which reduced the yield of TEM chip v1 was the extensive channel etch time about 22 h. The SiNx deposition contains defects called pin-holes. These defects allow the KOH etch to bypass the protective SiNx and etch the underlying Si or poly-Si. The longer a wafer is etched the more these pin-holes reduce the yield. In TEM chip v2 the channel was designed to be shorter, but to further reduce the etch time structures, called busstops, were introduced. They were called busstops because their initial design looked a lot like the small bulges from the road where busstops enter to pick up passengers. These bulges as designed not to inhibit the flow of traffic as is the intention for busstops in this work.

A busstop is an opening in the channel which initially allows the KOH to etch the sacrificial layer in the channel and is subsequently closed to seal the channel. Figure 10.5 shows the fabrication process of the busstop. The first image shows the design of the busstop (see Figure 10.5a). The busstop extends away from the main flow of the channel such that when it is sealed the seal will not obstruct the flow in the channel. The second image shows the opening of the SiNx over the busstop (see Figure 10.5b). The third step etches out the sacrificial layer in the channel (see Figure 10.5c). Sealing the busstop is done in one of two different ways. The simple way, which is also the one used in this work, is to cover the opening with a metal layer thick enough to seal the opening and extend through the channel (see Figure 10.5d). This also has the added benefit of providing an electrical connection to the liquid in the channel.

The second method, which was not tested, is to grow a layer of poly-Si on the chip and then use a ASE to remove it. The grown poly-Si extends beyond and around the opening in the channel. This means that SiNx of the channel protects this part of the poly-Si when the directional ASE removes the rest of the poly-Si (see Figure 10.5e), thereby removing the poly-Si ontop of the channel.

TEM chip v2 uses the metal from the electrode layer to stop the busstops and simultaneously create electrical connection to the liquid in the channel. Since the main part of the channel is 1 µm tall and the top SiNx layer is 200 nm thick, the metal layer must be more than 1200 nm thick which is difficult with standard cleanroom processing. Therefore the busstops are designed in the amorph-Si layer used to define the low-channel. This requires a metal layer on the scale of 270 nm which is easy to deposit. Since the amorph-Si was re-crystalized and not etched out the busstops did not work.
Figure 10.5.: The fabrication process for busstops. Steps 1-4 is used for electrodes, Step 1-5 if poly-Si is used to seal the channel. The dashed line in the top view shows where the side view was taken.
Figure 10.6.: Optical image of busstops on the channel. In the top right corner of the image is the inlet with the protective structure around it. The channel runs diagonally from the inlet to the bottom left corner. Part of the channel has been etched out and the rest has not. The busstops are spaced evenly along the channel.
10.1.3. Multi-height Channels

To reduced the mass-thickness imaged in the TEM the channel can be reduced in height. However, decreasing the height of the channel will increase the necessary etch time because it will reduce the access to the sacrificial layer for the KOH. To avoid this the main part of the channel is still 1 µm tall and the central part which will be imaged is designed with a lower height of about 20 nm creating a multi-height structure as seen in Figure 10.7. The achieved height of the tall channel was, as mentioned previously, ∼500 nm and the height of the low channel ∼60 nm.

Figure 10.7.: The channel with multiple heights

To decrease the etch time the layer is designed in amorph-Si which should be faster to etch with KOH and have a smoother surface. The low channel will have a high-flow resistance making flushing and refilling difficult due to the limited pressure which can be applied. To compensate for this the high-channel also has part which by-passes the low channel (see Figure 10.8).

Unfortunately, the amorphous and continuous layer was subject to heat, in Step 8, which re-crystalized the layer into a non-continuous layer[47, 62]. Figure 10.9a shows an TEM image of the low-channel in a thinned window. The low channel is non-continuous. Figure 10.9b shows a diffraction image of the area with the
Figure 10.8.: Optical image of the multi-height channel. The low channel also has thinned windows evenly spaced along it. "A" points to the interface between the etched an unetched parts of the high channel. There is a clear color difference between the etched and unetched high channel, but the busstops on both the high and low channel have the same color. This indicates that neither of them have been etched or that they both have. Since the low channel is connected to a part of the high channel which is unetched, the former must be true.

clear points indicating crystalline structures. Since the SiN$_x$ is amorphous the only source of the crystalline structures is the previously amorphous Si. Since the layer is relatively thin it is conceivable that this happened in Step 8, but further investigation is required to verify this. Since the layer was no longer continuous the KOH did not etch it out.

Figure 10.10 shows a SEM close up of the overlap between the high channel, the low channel, a thinned window and an electrode. It also shows a dark TEM image of the overlap between the high channel, the low channel and the thinned windows, sans the electrodes. The image is dark because the signal through the thinned windows is significantly higher than through the non-thinned areas.

As mentioned previously the amorph-Si layer recrystallized during fabrication, probably during the 40 min LPCVD growth of the first top SiN$_x$ layer in Step 8. This process occurs at $\sim$923 K and at this temperature the recrystallization rate of
Figure 10.9: The unetched low channel. 10.9a shows an image of the unetched low channel. The reason the channel was unetched is clear; it was non-continuous. A selected area diffraction image of the low channel in the thinned window shown in 10.9b has the distinct points from crystalline structures.

amorph-Si is $\sim1\text{ nm s}^{-1}[47, 62]$. This rendered the busstops and electrodes useless. The bypas channel included in the design and seen in Figure 10.10c allowed the channel to be filled, but since there are no thinned windows over the high-channel it cannot be used.

This fabrication has highlighted many areas which need to be improved.
Figure 10.10: Images of TEM chip v2. 10.10a shows an SEM image. The surface roughness of the poly-Si high channel and the amorph-Si are clearly visible. 10.10b shows a sketch of the areas in 10.10a. The low channel is sketched in blue, the electrode in cyan, the thinned window in black and the high channel in magenta. 10.10c shows a TEM image of a TEM chip v2 without electrodes. The thickness difference causes the thinned windows to be bright and the rest of the image to be dark. This image has been modified. The original is seen in an inset in the upper left corner.
10.1.4. Electrodes

Although there are many experiments which can be conducted with TEM chip v1, the range of available experiments is greatly increased with the inclusion of electrical contact to the liquid.

In order to establish electrical connection, to the liquid, metal electrodes are used. The busstoppers designed in TEM chip v2 allow access to the liquid in the channel without disrupting the flow. The metal selected for this was Pt with an adhesion layer of 10 nm titanium (Ti). Platinum was selected as the metal for the electrode because it is a noble metal with a high Young’s Modulus, a melting point of 2040 K[70] and high electrical conductivity. The melting point is important when heating the chip. Since the melting point of the electrode is higher than the melting point of the heater the electrode should survive any heating experiments.

The top SiNx is 200 nm thick and the channel is 60 nm high which therefore requires a metal layer of at least 260 nm. To ensure full coverage of the openings in the busstoppers and a good electrical connection the deposited Pt layer was 270 nm thick. This was in addition to the 10 nm Ti layer.

Figure 10.11 shows a SEM image of the electrodes on TEM chip v2 and a sketch describing the different areas.

There are two different types of electrodes in the system. Shown in yellow in Figure 10.11 are the grounding and thermistor circuit. The busstoppers along the high channel must be closed to ensure vacuum compatibility. This is done by depositing the metal layer. In addition to sealing the busstoppers the metal layer along the high channel is also designed to create electrical connection to the liquid for the purpose of removing charging or other effects which might disrupt the image or the electrical measurements. Sharing the same outlet connection as the grounding circuit are the thermistors. This meandering structure is designed to measure the temperature on the chip during experiments[26, 58].

The second type of electrode in the system are shown in cyan in Figure 10.11. These are simple and direct connections to the liquid, each with its own outlet. Two of the connections are placed on the high channel close to the low channel and two are placed directly on the low channel.

Figure 10.12 shows a SEM image with electrodes and an accompanying sketch of the components in the image. Each of the two electrodes in the image have circular vacancies. These are the openings in the busstoppers where the metal filling has fallen out. This means that even though the busstoppers were not etched out some of the electrical connections failed. There are three possible explanations for this. The first is that the bottom membrane layer failed in the KOH due to pin-holes and the metal layer simply fell through. The second is that the phororesist used to mask the chip prior to metal deposition was not fully removed and therefore the covering metal was removed in the lift-off. The third possibility is that the metal layer was not thick
Figure 10.11: SEM images of TEM chip v2. 10.11a shows an overview of the membrane area. The green bar is 200 µm wide. 10.11b shows a color-coded map of the different components visible in 10.11a. Visible in the image is the membrane (green), the encapsulated heater (red), the protective structures (purple), the channel (magenta), the thinned windows on the low channel (black, low channel shown in blue) and the busstops (gray). The two different types of electrodes are also visible. The yellow area shows the electrodes which run along the high channel and can be used to ground the liquid in the channel. This electrode also includes a thermistor which can allow temperature measurement on the chip during experiments. Finally, the cyan area indicated the four separate electrodes which can contact the liquid next to and in the low channel.

enough to fill the opening and connect to the rest of the metal layer. More time in the developer and thicker metal layer might alleviate this in future devices.
10.1.5. Surface Roughness

In order to have a high quality image of the liquid the top and bottom layer of the channel must be free of obstruction. Additionally any obstructions on the surface could possibly be focus points of stress. As seen in Figure 9.15 there previous fabrication method did not account for this.

The SiNx of the channel conforms to the surface it is deposited on. Because of this the surface roughness of the layer it grown on is partially transferred to the SiNx. The bottom layer is deposited on a polished Si surface and should therefore already have a low surface roughness. The top layer is deposited on the sacrificial layer and therefore the surface roughness of the sacrificial layer is important.

Figure 10.13 shows a SEM image of a channel in a TEM chip v1. In the image protrusions on the surface of the channel have been circled in green. To minimize the surface roughness standard cleanroom technique is used\[60]. A SiO$_2$ layer is grown and then etched away by HF acid. When an oxide layer is grown it partially consumes the Si layer it is grown on. Any protrusions would be significantly reduced by this. Figure 10.14 shows the surface roughness, measured by
Figure 10.13.: A SEM image of the channel with thinned windows on either side of the image. The channel is on the top part of the image and the bottom part shows the membrane. The green circles mark protrusions from the flat surface. The SiN$_x$ was grown on the top of the poly-Si of the channel and therefore the surface roughness of the poly-Si has been partially transferred to the SiN$_x$. The contrast and brightness in this image have been slightly modified to ensure the protrusions are visible.

AFM, for the surface of the poly-Si, SiN$_x$ and amorph-Si in the different fabrication steps (see Figure 10.15 and Figure 10.16). The surface roughness is increased with the deposition and patterning of the amorph-Si layer, but then reduced again by the growth and etch of the SiO$_2$.

While it is clear that this method reduces the surface roughness the reduction is not significant and therefore this step is not necessary in future fabrications.
Figure 10.14.: Plot of RMS surface roughness of the different materials measured by AFM. The deposition and patterning of the amorph-Si, in Step 4 and 5, increases the surface roughness, but this is again reduced by the growth and removal of the SiO$_2$ in Step 6.

Figure 10.15.: AFM scan of the patterned sacrificial layer. 10.15a is the AFM scan of part of the channel. 10.15b is a drawing explaining the composition of the AFM scan. The scan is taken after the high sacrificial layer has been grown and patterned in Step 3.
Figure 10.16.: AFM scan of the patterned sacrificial layer. 10.16a is the AFM scan of part of the channel. 10.16b is a drawing explaining the composition of the AFM scan. As can be seen the amorph-Si overlaps the poly-Si. The scan is taken after the low sacrificial layer has been grown and patterned in Step 5.
10.1.6. Backside Inlets

Experiments in the TEM can include the manipulation of several factors. Temperature and electrical potential are two variables which the TEM chip v2 is designed to be able to manipulate. Exchanging the liquid or simply providing flow of liquid in the channel is what the backside inlets are designed to achieve. The inlets on the frontside were too fragile to withstand the mechanical stress of a vacuum seal from a tube. When a TEM chip v1 was filled, vacuum seal was achieved with a liquid sealant. The sealing method for backside inlets included in some of the TEM chip v2 designs is seen in Figure 10.17.

![Figure 10.17: A backside inlet. An opening is made in the back of the chip and etched out with KOH. The SiNx at the bottom of the inlet is then etched by RIE with a shadow mask. The substrate of the chip is then used as a stable surface to achieve a vacuum seal.](image)

The backside inlets were initially opened on the backside in Step 10 and etched out in Step 13. In order to remove the SiNx on the bottom of the backside inlets and expose the poly-Si in the channel, a shadow mask is used. This mask is a physical mask with openings corresponding to the position of the backside inlets in the channel. Without this mask, the RIE used to remove the SiNx would also remove the SiNx on the bottom of the channel. The shadow mask is fabricated by growing a SiNx layer on a Si wafer, patterning it with photolithography and RIE, etching it with KOH and finally removing the SiNx. This leaves a Si wafer with square openings of specific dimensions and positions. The openings on the shadow mask are designed to be larger than the backside inlets because the shadow mask is aligned manually. The SiNx at the bottom of the inlet is only 35 nm thick, but the SiNx on the backside is 235 nm thick. This means that the SiNx exposed by the shadow mask can tolerate a significant amount of additional etch time with RIE and still survive the subsequent KOH etch in Step 15.

---

\(^1\)the fabrication process is identical to steps 1-3 of the EC-SEM chip fabrication with different masks
Figure 10.18: An optical image of the backside inlet. There is a square KOH opening in the inlet. This opening is etched from the backside. Part of the channel has also been etched which indicates the backside inlet has functioned as intended.

Figure 10.18 shows an optical image of a backside inlet. The square opening in the circular inlet is clear indication of a KOH etch. Part of the channel has been etched out and since this is a clear progression from the inlet it indicates that the backside inlet has been opened as intended and KOH has entered through the backside and etched the channel. Since the frontside inlets were also included on the design of TEM chip v2 and they were opened in Step 13 they were etched for more time than the backside inlets. The extended etch time it would have required to completely etch out the backside inlet channels was deemed not to be worth the risk.

10.2. Next TEM Chip Version

The central features of TEM chip v2, such as a low-channel and busstops, are still of interest. These features simply need to be redesigned. In the next version of the monolithic TEM chip for in-situ liquid TEM the following features should be considered:

- **Different material for the low sacrificial layer**: Selecting another material for the low-channel such as SiO$_2$ should remove the possibility of recrystallization. A wet-etch is used to pattern it and the same wet etch is then used to remove it, inside the channel, prior to the KOH etch. It is possible
that this etch will create curved walls, but since such curved walls were visible in Step 3, but were not visible in the final device it is possible any overhang is removed by the repeated photolithography steps (each of which ends with a plasma ashing to remove the photoresists). Using a wet etch to pattern the sacrificial layer changes this step to a batch step which results in faster and cheaper processing.

- **Conductive sacrificial layer**: The sacrificial layer in TEM chip v2 was not conductive enough to be used as an encapsulated heater. This was caused by a poorly controlled doping during the deposition. A new oven has become available and heaters manufactured in this oven[59] worked as intended. The next version of the TEM chip should use this oven.

- **Busstops**: The busstops did not function as intended since they were all placed on the low sacrificial layer in order to be closed by the electrodes. Including busstops on the high sacrificial layer would probably reduce etch time, but it presents the problem of closing them. In section 10.1.2 two methods for closing the busstops were discussed. The method of using a poly-Si layer to close them would be more suited if including them on the high sacrificial layer. If the low sacrificial layer is etched after this step a number of busstops could be included on the low sacrificial layer and be closed by the electrodes. This would require a metal layer which can be removed by conventionally photolithographical lift-off.

- **Backside inlets**: The inlets placed on the back of the TEM chips worked as intended. They were opened from the backside with a controlled etch and the channel was etch by KOH entering through these opening. The backside inlets provide better support for flow and do not run the risk of contaminating the front-side if a drop is spilled.

- **Height of the sacrificial layer**: The high sacrificial layers were not protected when the low sacrificial layer was patterened. This was not thought necessary because the height of the low sacrificial layer was not significant when compared to the high sacrificial layer. The etch, however, removed almost half of the height of the high sacrificial layer. This resulted in lower etch rates of the channel and therefore the high sacrificial layer should be protected when the low sacrificial layer is patterned.

- **No surface roughness reduction step**: The surface roughness was not significantly reduced by this step and any uncessesary processing should be avoided.
• **Use a thicker metal layer:** The metal layer deposited failed in some of the busstops. To counteract this a thicker metal layer should be deposited to ensure sufficient mechanical contact between the part *in* the busstop and the part *on* the busstop.

• **Membranes:** There were two different types of membranes, one large, quadratic membrane and one small, rectangular membrane. None of the large, quadratic membranes survived the extensive KOH etch. By reducing the etch time it is possible they could survive the entire process. However, this is not necessary since the liquid is confined to the channel and it is only necessary to image this area. The large membranes did, however, offered better thermal insulation and therefore could possibly be included on a limited number of chips in the next design.

• **Supporting cross-bars:** The deflection of a 25 nm thick and 4 µm wide channel subject to a pressure difference of $10^5$ Pa is, according to theory in section 5.1, $\sim 102$ nm. This greatly increase the channel dimensions for a 60 nm tall channel. However, the presence of thinned windows leaves thick bars of SiNx along the channel which act to support the window, reducing the deflection. This might be further reduced by the inclusion of actual bars made of poly-Si (see Figure 10.19) and should be considered in the next version.
**Figure 10.19.** COMSOL simulation of the deflection of a SiN$_x$ channel with poly-Si braces to reduce deflection. The top and bottom layer of the channel is 25 nm thick and the sides are 200 nm thick. The braces are 500 nm thick. The channel is 4 µm by 4 µm due to simulation difficulties at lower dimensions. The maximum deflection between the braces is approximately 12 nm.
11. Towards Holography in Liquids in TEM

Off-axis electron holography is a TEM technique for measuring the phase of the electron wavefunction after it passes through a sample\[56\]. This technique can be used to image electro-magnetic fields in the sample\[24\] or measure the mean inner potential of a homogenous sample. The mean inner potential is the effective potential from the atoms and electrons of the sample and is unique to every material. This chapter introduces the theory of electron-holography and initial experiments with holography of graphene. SiN\(_x\), which is used as a window material in TEM chip v1 and v2, will most likely charge when imaged in the TEM.

11.1. Introduction to Off-axis Electron Holography

Holography is a method of imaging the phase change of the electrons after they have passed through objects. Figure 11.1 shows a possible holographic setup. Part of the electron beam passes through the sample and the other part continues uninhibited. The uninhibited part is called the reference wave. A biprism, which is simply a thin biased wire, creates an electric field which bends and overlaps these two beams and causes an interference pattern also known as a hologram. The hologram contains information about the phase of the electrons. This is called off-axis electron-holography.

As described in \[56\] the intensity distribution of the electron wave visible in the hologram (see Figure 11.2a) can be described as:

\[
I(r) = 1 + A(r)^2 + I_{\text{inel}}(r) + 2\mu A(r) \cos (2\pi q \cdot r + \phi(r))
\]  

(11.1)

where the reference wave, passing through vacuum, is assumed to have unit intensity, \(\mu\) is the contrast of the fringes in the hologram, \(A(r)\) and \(\phi(r)\) are the amplitude and phase of the hologram, \(q\) is the carrier frequency and \(r\) is the real space position vector. The amplitude and phase modulate the interference pattern of the hologram. \(I_{\text{inel}}\) is the inelastically scattered part of the wave. The fourier transform, \(\text{FT}\{\}\), of
Figure 11.1.: Off-axis Electron holography setup

the hologram is:

\[
\text{FT}\{I(r)\} = \text{FT}\left\{1 + A(r)^2 + I_{\text{inel}}(r)\right\} + \mu \text{FT}\left\{A(r)e^{i\phi(r)}\right\} \otimes \delta(q + q_C) + \mu \text{FT}\left\{A(r)e^{i\phi(r)}\right\} \otimes \delta(q - q_C) \tag{11.2}
\]

The first part is the center-band and the two other parts are the sidebands (see Figure 11.2b). The amplitude and phase of the hologram is extracted by using a mask around one of the sidebands (they carry the same information because they are complex conjugates of each other so which one is irrelevant)(see Figure 11.2c). The mask has a tapered edge in order not to create distortions. The shape and size of the mask determines the amount of information returned. Multiple different masks are usually tried before an optimal ratio of information and noise is found. A reference image is also taken to subtract the imperfections in the source and background. The selection is then transformed back to real space with an inverse FFT. The amplitude
and phase images are then created from the resulting complex image:

Amplitude image = $\sqrt{\Re^2 + \Im^2}$ \hspace{1cm} (11.3)

Phase image = $\tan^{-1}\left(\frac{\Im}{\Re}\right)$ \hspace{1cm} (11.4)

where $\Re$ and $\Im$ are the real and imaginary parts of the complex image resulting from the inverse FFT. From the amplitude image it is possible to determine the thickness, $t$, relative to the electron-mean-free-path, $\lambda$:[53]:

$$\frac{t}{\lambda} = -2 \ln \left(\frac{A_0}{A_r}\right)$$ \hspace{1cm} (11.5)

where $A_0$ is the energy-filtered zero-loss amplitude and $A_r^2$ is the total energy-filtered incident intensity obtained from the amplitude image of the reference hologram. The mean inner potential, $V_0$, of a material can be determined from the phase change, $\Delta \phi$, by[48]:

$$\Delta \phi = C_E V_0 t$$ \hspace{1cm} (11.6)

where $C_E$ is a constant of proportionality, weakly depending on the acceleration voltage[48].

![Figure 11.2: Reconstructing a hologram.](image)

(a) Hologram  \hspace{1cm} (b) FFT of Hologram \hspace{1cm} (c) Mask of side-band

The phase image then needs to be unwrapped since the phase may oscillate more than $\pi$. Special algorithms are used to do this[30]. This creates a phase image...
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showing the relative phase change through the sample. Finally a reference hologram, taken at the same conditions, but in vacuum, can be used to remove any artifacts from the microscope, leaving only the phase change from the sample. The hologram may still contain charging artefacts from local fields in the sample.

11.1.1. Results

A hologram was taken at the area indicated in Figure 11.3b in order to try and determine if an interference pattern can be observed as a first step towards measuring the mean inner potential of the liquid. A TEM chip v1 was filled with Au NP liquid (see appendix D) and imaged in the ATEM. The chip vacuum tested twice after it was sealed. Optical inspection with an optical microscope, after the channel was sealed and after the two vacuum test, showed no change in the liquid distribution. Figure 11.3 shows bright-field images of the channel with thinning sections. The windows in the thinning sections are 50 nm thick SiNx and the rest is 200 nm thick. The channel is 1 µm thick. The operator of the ATEM when these images and holograms were taken was Dr. T. Kasama.

The unwrapped phase image can be seen in Figure 11.4.

A line profile along the arrow in Figure 11.4a and averaged between the two dashed red lines can be seen in Figure 11.4b. Interpreting the phase image is difficult because the quality of the hologram is low due to the large mass-thickness of the channel. The channel extends 1 µm in the vertical direction and the height of the channel filled by the liquid is unknown. In the line profile the phase decreases for the first part of the image which corresponds to the part of the hologram where the liquid is present and is decreasing in thickness (t/λ)[53]. Then the phase increases again without the t/λ-ratio increasing. This could be due to charging in the SiNx. The charging is not present in the area containing the liquid because the salts in the liquid remove it. Although this sample was covered with a thin layer of carbon to alleviate charging, the backside was not and neither was the inside of the channel which means that while the top layer of carbon could possibly reduce the effect of charging it could not remove it. These interpretations cannot be verified because there are unknown factors such as the shape of the liquid drop, the presence of NPs, the lack of a vacuum reference, the presence of vapor and the thickness imaged in the hologram. To alleviate these factors the height of the liquid must be reduced and a vacuum reference must be integrated by making a hole in the chip.
**Towards Holography in Liquids in TEM**

**Chapter 11**

(a) Overview

(b) Selection

**Figure 11.3.** TEM images of TEMChipv1 with liquid inside. The liquid is not continuous in the channel. 11.3a shows an overview image of the channel and thinning areas on a TEMChipv1. The channel runs diagonally across the image from top left to bottom right. The top left part of the channel is filled with liquid. The bottom right part of the channel only has one drop. A red box shows the area selected for holography. 11.3b shows the selected area for holography. The area around the drop is used as vacuum reference for the hologram even though it contains both the SiNx of the channel and liquid vapor. The box indicates where the hologram was taken.
Figure 11.4.: Unwrapped phase image of from the hologram. There is a clear gradient in the phase image (11.4a) indicated by the black arrow. The green triangles mark areas outside the biprism used to create the hologram. These areas are not part of the phase image. 11.4b shows the phase across the arrow in 11.4a averaged between the two dashed red lines. Also shown on the graph is the thickness over mean-free-path (of the electron), $t/\lambda$, variation over the same line.
11.2. Holography of Graphene

An alternative window material to SiN is graphene. The low atomic number of carbon combined with the monolayer thickness, high Young’s Modulus and conductivity of graphene makes it an ideal window material for liquid phase electron microscopy. Experiments with liquid enclosed in graphene have already been performed\[85\]. The fabrication methods to include graphene in the monolithic TEM chip are still in their early stage (see section 6.1). Therefore preliminary experiments to determine the phase change per graphene layer were performed as a first step towards holography of liquids through graphene windows.

The phase change of graphene (or few-graphene-crystal as it is called in \[63\]) was determined with holography by Ortolani et al.\[63\]. However, the method they used for layer determination was FFT of the bright-field image, not a TEM image in diffraction mode. In order to improve on these measurements more accurate methods were used. Lin et al.\[50\] have also measured the phase change of graphene on a few carbon nanotubes. Their method for thickness determination was more accurate since they simply counted the number of walls in the carbon nanotube.

Off-axis electron holography can be used to determine different properties such as the mean-inner-potential of the liquid imaged. This method is sensitive to the material containing the liquid and therefore holography of graphene is performed as a step towards holography of liquid in graphene and to determine if charging is an issue in such a setup.

Graphene samples were prepared, by Dr. T. Booth, according to the second method in \[54\]. Images and holography of the multi-layer graphene in these samples were taken with the ATEM and the operator was Dr. T. Kasama. Each image is named with the following convention: A1-H1-01. The ’A1’ denotes which experimental area the image was taken in. The ’H1’ indicates which hologram it was ie. ’H1’ is the first hologram, ’H2’ is the second etc. Finally the ’01’ is the numerical sequence of the images ie. ’13’ was taken before ’15’. MATLAB scripts were developed to facilitate analysis of the images. These scripts are included in appendix H.2.

11.2.1. Image processing

The goal of this work was to estimate the phase change per graphene layer. In order to do this the phase of smooth and clean patches of graphene of a known number of layers is needed.

Each hologram contains noise from two different sources: random noise and interference fringes. The random noise can be reduced by truncating the data to within three standard deviations (this should contain about 99.2% of the data) and the noise from the fringes can be reduced by blurring the data. This smooths the areas needed
for determining the phase change. The blurring does not significantly affect the data since the spatial resolution in a hologram is three times the fringe spacing[15]. The holograms were reconstructed with a reference hologram taken at the same conditions in vacuum. The unwrapped phase images were processed in the following steps:

1. Truncation and blurring
2. Correction for x-direction charging
3. Correction for y-direction charging
4. Adjustment of phase-change relative to vacuum

These adjustments were done on a per-image basis. The image shown in the example figures is A3-H1-10.

11.2.2. Truncation and blurring

The phase data from each phase image was first blurred with a gaussian filter in an attempt to homogenise the data and remove artifacts from the interference fringes. Then the phase data was truncated to within $3\sigma$ of its rms value to remove random noise.
Figure 11.5.: Truncating and blurring the data. The images on the left (11.5a,11.5c) are the phase image in a heatmap scaled to the values in the image. The graphs on the right (11.5b,11.5d) are histograms of the values in the images.
11.2.3. Correction for x-direction charging

Figure 11.6b show a column mean of a truncated and blurred phase image. There are two plateaus, the large one on the right is from the graphene and the small one on the left is from the vacuum. Since there is no matter present in the vacuum to induce a phase change, yet there is a definite slope on this plateau, the phase change must be due to an electric field. Furthermore there seems to be a similar slope in the graphene. As a first approximation it is assumed that the field in both the vacuum and in the graphene are the same and the slope of this field is then subtracted to remove its contribution.

To assess the charging in the x-direction, in the phase image, the slope of the phase in the vacuum area was used. To do this a column-mean of the image was taken. The edge of the graphene layer is not perfectly aligned to the columns in the image. To find the vacuum area the differential of the column-mean was calculated and the section 5 pixels from the edge of the image and 20 pixels from the maximum in the differential was selected. Both the 5 pixels and the 20 pixels are arbitrary values which worked sufficiently well in this analysis. A line was then fitted to this section and this line was then subtracted row-by-row from the image.

Any charging in the vacuum would be from a field in the graphene. Consequently the charge in the vacuum is not the same as the one in the graphene. The linear systematic correction is used as a first-approximation.
Figure 11.6.: Correcting for charging in the x-direction. 11.6a and 11.6c are unwrapped phase images and 11.6b and 11.6d are histograms of the data in the phase images.
11.2.4. Correction for y-direction charging

This was done in the same manner as with the x-direction charging. The slope in the vacuum level was used to find the systematic correction and this was then substracted column-by-column from the image. The correction in the vacuum level are clear in most cases, but the correction in the graphene is not always as clear.

![Figure 11.7: Correcting for charging in the y-direction.](image)

11.2.5. Adjustment of phase-change relative to vacuum

The mean value of the vacuum area used to correct for charging was subtracted from the entire phase change image to set the vacuum level to zero. The area used was from the blurred, truncated and charge-corrected images.

11.2.6. Measuring the number of graphene layers

There are 3 different areas used in the investigation (see Figure 11.8).

The number of layers present in each image was determined by two different methods. For Area 3 and Area 4 the edge of the sample (shown in Figure 11.8b) was used. Each of these areas shown folded graphene sheets. At the edges of these sheets the graphene is perpendicular to the beam and therefore the number of layers can be counted. However, there are fresnell fringes present in the image and therefore there is an uncertainty on the number of layers. In area 5 a diffraction image was taken. The points in the diffraction image doubled in intensity from the inner circle to the next. This occurs when there are two graphene layers present.
Figure 11.8.: The different areas of interest. The first area (11.8a) has vacuum on the left side. It is a fold of a 6 layer graphene sheet giving 12 layers. This is judged from the 6 white lines near the edge (see 11.8b). The second area (11.8c) is from the same folded graphene sheet, but in an area with an additional fold. The extra fold gives 24 layers. Finally the third area (11.8d) is of a single graphene layer folded over itself giving 2 layers. The third area has vacuum on the right.
11.2.7. Phase change of Graphene

Areas in each phase image were selected and the mean phase of that area was selected as the mean phase for the specific number of layers of graphene. Table 11.1 shows the name of the phase images, the number of layers in the selected area and the mean phase change of the area. Each area was chosen to be free of contaminants. The six bottom entries have an extra descriptor (high, medium, low). These are from the area of graphene with a quadruple fold. The "high" entries are from the quadruple fold, the "low" entries are from the double fold, and the "medium" entries are from the area directly adjacent to the quadruple fold, but with a lower phase change.

Table 11.1.: Phase Change in Phase images

<table>
<thead>
<tr>
<th>Image name</th>
<th>Layers</th>
<th>Layer Error</th>
<th>Phase</th>
<th>Phase Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3-H2-13</td>
<td>14</td>
<td>2</td>
<td>0.448</td>
<td>0.0383</td>
</tr>
<tr>
<td>A3-H3-14</td>
<td>14</td>
<td>2</td>
<td>0.508</td>
<td>0.0123</td>
</tr>
<tr>
<td>A3-H4-17</td>
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<td>2</td>
<td>0.557</td>
<td>0.0331</td>
</tr>
<tr>
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<td>14</td>
<td>2</td>
<td>0.540</td>
<td>0.0360</td>
</tr>
<tr>
<td>A3-H5-22</td>
<td>14</td>
<td>2</td>
<td>0.523</td>
<td>0.00608</td>
</tr>
<tr>
<td>A3-H6-25</td>
<td>14</td>
<td>2</td>
<td>0.516</td>
<td>0.00542</td>
</tr>
<tr>
<td>A3-H8-38</td>
<td>14</td>
<td>2</td>
<td>0.463</td>
<td>0.00308</td>
</tr>
<tr>
<td>A3-H8-39</td>
<td>14</td>
<td>2</td>
<td>0.436</td>
<td>0.00437</td>
</tr>
<tr>
<td>A4-H1-41-high</td>
<td>28</td>
<td>4</td>
<td>1.06</td>
<td>0.0121</td>
</tr>
<tr>
<td>A4-H1-41-medium</td>
<td>7+7</td>
<td>2</td>
<td>0.471</td>
<td>0.0136</td>
</tr>
<tr>
<td>A4-H1-41-low</td>
<td>14</td>
<td>2</td>
<td>0.407</td>
<td>0.0173</td>
</tr>
<tr>
<td>A4-H2-43-high</td>
<td>28</td>
<td>4</td>
<td>1.26</td>
<td>0.0654</td>
</tr>
<tr>
<td>A4-H2-43-medium</td>
<td>7+7</td>
<td>2</td>
<td>0.633</td>
<td>0.0675</td>
</tr>
<tr>
<td>A4-H2-43-low</td>
<td>14</td>
<td>2</td>
<td>0.571</td>
<td>0.0866</td>
</tr>
<tr>
<td>A5-H1-59</td>
<td>2</td>
<td>0</td>
<td>0.216</td>
<td>0.0140</td>
</tr>
<tr>
<td>A5-H3-63</td>
<td>2</td>
<td>0</td>
<td>0.0700</td>
<td>0.0529</td>
</tr>
</tbody>
</table>

In order to find the phase change per layer linear regression was done (see Figure 11.9). The phase change per layer was found to be 0.0284 radians with an intercept of 0.135. This value is below the theoretical value for graphene of 0.04 mentioned in Ortolani et al. [63], and different from the value of 0.06 they found for the so-called few-graphene crystal membranes. The determined value also differs from the 0.05 radians per layer mentioned in Lin et al. [50]. The intercept does differ considerably from 0, indicating that there is some additional effect.
**Figure 11.9.** Change in phase as a function of number of graphene layers. The phase change measured on the different phase images as a function of the number of graphene layers is seen here as black boxes with error bars. The blue line is a linear fit to the values and has a slope of 0.0284.
12. Conclusion

Two versions of the monolithic TEM chip for \textit{in-situ} electrochemical experiments were designed and fabricated. The first version verified the ability to etch out small channels (smallest cross-sectional area $2 \mu m^2$) of poly-Si in SiN$_x$ with KOH. Protective structure designed to protect the channel and provide support for the inlet were tested and it was found that they provided protection for the channel when the chip was clamped in the TEM holder, but that the inlets could not be successfully contacted with a tube to fill the channel in this manner. Additionally it was verified that a broken membrane can be maintained if the protective structures intersect the damage. Finally the first version also verified the ability to selectively thin the SiN$_x$ down over the channel to create windows with lower mass-thickness for better imaging in the TEM.

In the second version of the chip it was attempted to reduced the etch time with KOH, by shortening the channel and introducing busstops. This did not work as intended since the amorph-Si deposited as the low sacrificial layer, and in which the busstops were created, recrystalized at some point during the fabrication process, becoming non-continuous. This resulted in the busstops not being etched out. Furthermore, in an effort to reduce the total mass-thickness of the sample the channel was designed with two heights, one at about 1 $\mu$m and one at about 20 nm. The high channel was designed to have this height in order to achieve a high etch rate, but the fabrication resulted in a channel thickness of $\sim$500 nm, reducing the etch rate compared to TEM chip v1. The low channel was created in the low sacrificial layer which was fabricated to be 60 nm and which was not etched out and therefore did not work as intended. The extensive KOH etch in TEM chip v1 resulted in channel walls which where $\sim$25 nm thick. Because experiments were successfully performed in these devices, the top and bottom walls of the channel in TEM chip v2 were designed to result in this thickness. This required a thinner bottom SiN$_x$ layer, which was achieved, and the inclusion of thinned windows with a slightly longer etch time.

TEM chip v2 also included inlets on the backside and these were successfully fabricated and opened in a controlled process. The heaters included in TEM chip v2 was not tested since the conductivity did not meet requirements. However, a heater with identical design was tested successfully. Based on the experience gained from the fabrication of TEM chip v1 and v2, features for a third design have been presented.

In preparation for inclusion of graphene as a window material, and holography
through it, the phase change per graphene layer was measured.

12.1. Outlook

The two TEM chips have both been successful in furthering our knowledge of the fabrication of such setups and the requirements for future setups. Assuming all the features in the next version of the TEM chip are successful, initial experiments should focus on recreating *ex-situ* electrochemical measurements to verify the setup functions as intended. Once this has been achieved focus should be shifted to experiments where the superior resolution of the TEM in this chip can be utilized. The electrochemical measurements of any experiment should be verified *ex-situ* to ensure results are not due to effects from the microscope, whenever possible. Specific experiments need to be designed to measure effects such as current contributed to the liquid, charging in the system, and induced flow in the system.
Part III.

Appendicies
A. SEM Chip Fabrication Plan

The following is a fabrication plan for creating SEM chips. At the top of each table is the date of fabrication, the name of the batch and the contact information for the person responsible. Each step has a full width cell with the number and name of the step. The columns are as follows:

1. The time to complete the specific sub-step. If it is a batch step it is for the entire batch. If it is a serial step it is for a single wafer.

2. Batch step (B) or a serial step (S).

3. Front-side step (FS) or a back-side step (BS).

4. The name of the machine to be used and which mask to use.

5. The specifics of the step.

The entire process is visualized in appendix B.

The complete list of fabrication steps and sub-steps is:

1 Grow SiN$_x$ window layer
   1.1 New DSP Si Wafer
   1.2 Grow SiN$_x$

2 Pattern SiN$_x$
   2.1 HMDS bake wafer
   2.2 Spin on photoresist
   2.3 Expose photoresist
   2.4 Reverse bake photoresist
   2.5 Flood expose photoresist
   2.6 Develope photoresist
   2.7 Etch SiN$_x$
   2.8 Remove photoresist
3 KOH
  3.1 BHF Etch wafer
  3.2 KOH Etch wafer
  3.3 7-up bath

4 Create electrodes
  4.1 HMDS bake wafer
  4.2 Spin on photoresist
  4.3 Expose photoresist
  4.4 Reverse bake photoresist
  4.5 Flood expose photoresist
  4.6 Develope photoresist
  4.7 Deposit Pt
  4.8 Lift-off

5 Wafer protection and dicing
  5.1 Spin on photoresist
  5.2 Apply blue-tape
  5.3 Saw
### Friday d. 8/6-2012

**Batch: MoWinSEMChip**

**Eric Jensen** (s031815)
Mobile: 31123059, email: eric.jensen@nanotech.dtu.dk

**Molecular Windows**

<table>
<thead>
<tr>
<th>Step 1: Grow SiN$_x$ Window Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:05</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>06:00</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>00:20</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
**Friday d. 8/6-2012**  
Batch: MoWinSEMChip  
Eric Jensen (s031815)  
mobile: 31123059, email: eric.jensen@nanotech.dtu.dk  
Molecular Windows

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B</td>
<td>(HMDS oven)</td>
</tr>
<tr>
<td>00:07</td>
<td>S BS</td>
<td>(SSE Spinner)</td>
</tr>
<tr>
<td>00:20</td>
<td>S BS</td>
<td>(Aligner 6-inch)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[KOH Mask]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Hotplate, cleanroom 3)</td>
</tr>
<tr>
<td>00:45</td>
<td>B</td>
<td>(Plasma Asher II)</td>
</tr>
</tbody>
</table>

### Step 2: Pattern SiN<sub>x</sub> Layer

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B</td>
<td>HMDS</td>
</tr>
<tr>
<td>00:07</td>
<td>S BS</td>
<td>Spin on 1.5 µm AZ5214E photoresist</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Recipe &quot;1.5 4inch&quot;</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bake for 100 s at 90 °C.</td>
</tr>
<tr>
<td>00:20</td>
<td>S BS</td>
<td>Reverse photoresist procedure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expose for 1.7 s.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bake for 100 s at 120 °C.</td>
</tr>
<tr>
<td>00:20</td>
<td>B</td>
<td>Development</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Developer: 800 mL AZ351B (NaOH) and 4000 mL H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Time: 60 seconds</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature: 22 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rinse for 2 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dry 3 min in spindryer</td>
</tr>
<tr>
<td>00:20</td>
<td>S BS</td>
<td>Log: Check Photoresist in microscope</td>
</tr>
<tr>
<td>00:16</td>
<td>S BS</td>
<td>Etch SiN&lt;sub&gt;x&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Use recipe TMHNITR2 for 3.5 min.</em></td>
</tr>
<tr>
<td>00:45</td>
<td>B</td>
<td>Remove photoresist with Plasma Asher II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O&lt;sub&gt;2&lt;/sub&gt;: 210 ml/min, N&lt;sub&gt;2&lt;/sub&gt;: 70 ml/min,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Watt: 1000</td>
</tr>
</tbody>
</table>
**Friday d. 8/6-2012**  
Batch: MoWinSEMChip

Eric Jensen (s031815)  
mobile: 31123059, email: eric.jensen@nanotech.dtu.dk  
Molecular Windows

<table>
<thead>
<tr>
<th>Time</th>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>05:30</td>
<td>B (KOH 3)</td>
<td>KOH etch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 sec BHF etch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rinse for 2 min.</td>
</tr>
<tr>
<td>01:00</td>
<td>B (7UP 4&quot;)</td>
<td>7UP cleaning</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rinse for 5 min.</td>
</tr>
</tbody>
</table>
**Friday d. 8/6-2012**  
**Batch: MoWinSEMChip**  
**Eric Jensen (s031815)**  
**mobile: 31123059, email: eric.jensen@nanotech.dtu.dk**  
**Molecular Windows**

### Step 4: Create Electrodes

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Equipment/Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B</td>
<td>(HMDS oven)</td>
</tr>
<tr>
<td>00:07</td>
<td>S</td>
<td>(SSE Spinner)</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>(Aligner 6-inch)</td>
</tr>
<tr>
<td></td>
<td>FS</td>
<td>[Electrodes Mask]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Hotplate, cleanroom 3)</td>
</tr>
<tr>
<td>00:20</td>
<td>B</td>
<td>HMDS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spin on 1.5 µm AZ5214E photoresist</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Recipe &quot;1.5 4inch&quot;</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bake for 100 s at 90 °C.</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>Reverse photoresist procedure</td>
</tr>
<tr>
<td></td>
<td>FS</td>
<td>Expose for 1.7 s.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bake for 100 s at 120 °C.</td>
</tr>
<tr>
<td>00:20</td>
<td>B</td>
<td>Wait for 10 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Flood expose for 30 s.</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>Development</td>
</tr>
<tr>
<td></td>
<td>FS</td>
<td>Developer: 800 mL AZ351B (NaOH) and 4000 mL H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Time: 60 seconds</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature: 22 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rinse for 2 min.</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>Log: Check Photoresist in microscope</td>
</tr>
<tr>
<td>00:30</td>
<td>S</td>
<td>Deposit Pt</td>
</tr>
<tr>
<td>01:00</td>
<td>B</td>
<td>Lift-off</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Remover 1165 for 45 min. NO ultrasound!</td>
</tr>
</tbody>
</table>
**Friday d. 8/6-2012**  
Batch: MoWinSEMChip  
Eric Jensen (s031815)  
mobile: 31123059, email: eric.jensen@nanotech.dtu.dk  
Molecular Windows

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Equipment</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:10</td>
<td>S</td>
<td>FS</td>
<td>(KS Spinner) Spin on 10 µm photoresist Bake for 120 s at 90 °C.</td>
</tr>
<tr>
<td>00:10</td>
<td>S</td>
<td>BS</td>
<td>Put on blue-tape</td>
</tr>
<tr>
<td>01:00</td>
<td>S</td>
<td>(Saw)</td>
<td>Saw wafers Approx 25 min./wafer</td>
</tr>
</tbody>
</table>
B. SEM Chip Process Flow Visualization

The following images visualize selected steps from the fabrication procedure of the SEM chips.

**Step 1.1: [Grow SiN\(_x\) window layer] New Si Wafer**

<table>
<thead>
<tr>
<th>Cross-section</th>
<th>Front side</th>
<th>Back side</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Cross-section Diagram" /></td>
<td><img src="image2.png" alt="Front side Diagram" /></td>
<td><img src="image3.png" alt="Back side Diagram" /></td>
</tr>
</tbody>
</table>

**Step 1.2: [Grow SiN\(_x\) window layer] Grow SiN\(_x\)**

<table>
<thead>
<tr>
<th>Cross-section</th>
<th>Front side</th>
<th>Back side</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4.png" alt="Cross-section Diagram" /></td>
<td><img src="image5.png" alt="Front side Diagram" /></td>
<td><img src="image6.png" alt="Back side Diagram" /></td>
</tr>
</tbody>
</table>

*Figure B.1.: SEM fabrication step 1.1 and 1.2: New Si wafer and growth of SiN\(_x\)*
Step 2.2: [Pattern SiN<sub>x</sub> layer] Spin on photoresist

Step 2.3: [Pattern SiN<sub>x</sub> layer] Expose photoresist

Figure B.2.: SEM fabrication step 2.2 and 2.3: Spin on and expose photoresist
**Step 2.4: [Pattern SiN\textsubscript{x} layer] Reverse bake photoresist**

**Step 2.5: [Pattern SiN\textsubscript{x} layer] Flood expose photoresist**

*Figure B.3.*: SEM fabrication step 2.4 and 2.5: Reverse bake and flood expose
Step 2.6: [Pattern SiN\textsubscript{x} layer] Develop photoresist

Cross-section

Front side

Back side

Silicon

Silicon Nitride

Exposed Photoresist

Step 2.7: [Pattern SiN\textsubscript{x} layer] Etch SiN\textsubscript{x}

Cross-section

Front side

Back side

Silicon

Silicon Nitride

Reverse baked Photoresist

Exposed Photoresist

Figure B.4.: SEM fabrication step 2.6 and 2.7: Develop photoresist and etch SiN\textsubscript{x}
**Step 2.8: [Pattern SiN$_x$ layer] Remove photoresist**

**Step 3.2: [KOH] KOH Etch**

*Figure B.5.: SEM fabrication step 2.8 and 3.2: Remove photoresist and KOH etch*
**Step 4.2: [Create electrodes] Spin on photoresist**

Cross-section

<table>
<thead>
<tr>
<th>Front side</th>
<th>Back side</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Cross-section" /></td>
<td><img src="image2" alt="Cross-section" /></td>
</tr>
</tbody>
</table>

**Step 4.3: [Create electrodes] Expose photoresist**

Cross-section

<table>
<thead>
<tr>
<th>Front side</th>
<th>Back side</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image3" alt="Cross-section" /></td>
<td><img src="image4" alt="Cross-section" /></td>
</tr>
</tbody>
</table>

- Silicon
- Silicon Nitride
- Thin Silicon Nitride
- Photoresist
- Exposed photoresist

**Figure B.6.:** SEM fabrication step 4.2 and 4.3: Spin on photoresist and expose
Step 4.4: [Create electrodes] Reverse bake photoresist

Step 4.5: [Create electrodes] Flood expose photoresist

Figure B.7.: SEM fabrication step 4.4 and 4.5: Reverse-bake and flood expose
Step 4.6: [Create electrodes] Develop photoresist

Cross-section | Front side | Back side

Step 4.7: [Create electrodes] Deposit Pt

Cross-section | Front side | Back side

- Silicon
- Silicon Nitride
- Thin Silicon Nitride
- Exposed photoresist
- Pt

Figure B.8.: SEM fabrication step 4.6 and 4.7: Develop photoresist and deposit Pt
Step 4.8: [Create electrodes] Lift-off

Step 5.1: [Wafer protection and dicing] Spin on

Figure B.9.: SEM fabrication step 4.8 and 5.1: Lift-off and spin on photoresist
Step 5.3: [Wafer protection and dicing] Blue-tape

Figure B.10.: SEM fabrication step 5.2: Blue-tape
C. SEM Chips

These are some large images of the entire SEM chips.
Figure C.1.: SEM Chip variant A. The blue is the electrode layer and the brown is the KOH layer. Inside the KOH layer is a chequered area which indicates the final size of the window. The chip has the dimension $8.3 \times 13.6$ mm$^2$. This chip has two windows (each $50 \times 1700$ µm$^2$) for a less fragile chip, ten slim electrode connections (10 µm wide) and three thermistors. Each window has a long, thin thermistor with few turns, but located wholly on the window and between the windows is a larger thermistor.
Figure C.2.: SEM Chip variant B. The blue is the electrode layer and the brown is the KOH layer. Inside the KOH layer is a chequered area which indicates the final size of the window. The chip has the dimension 8.3 × 13.6 mm². This chip only has one long window (50 × 4610 \(\mu\)m²) to allow for a larger continuous viewing area, twelve slim electrode connections (10 \(\mu\)m wide) and two thermistors. There is a thermistor at each end of the window. One end has a long, thin thermistor with few turns, but located wholly on the window and the other end has a larger thermistor bordering it.
Figure C.3.: SEM Chip variant C. The blue is the electrode layer and the brown is the KOH layer. Inside the KOH layer is a chequered area which indicates the final size of the window. The chip has the dimension $8.3 \times 13.6 \text{ mm}^2$. This has two windows (each $50 \times 1700 \mu\text{m}^2$) for a less fragile chip, twelve wide electrode connections ($40 \mu\text{m}$ wide) and two thermistors. There is a thermistor at each end of the window. One end has a long, thin thermistor with few turns, but located wholly on the window and the other end has a larger thermistor bordering it.
D. Positively Charged Gold Nanoparticles

Au nanoparticles were prepared based on [71]. 80 µL Chlorauric Acid (HAuCl₄, 1.24 wt%) was mixed with 10 mL MilliQ. The mixture is then stirred for one minute. The solution is then mixed with 20 µL Polyethyleneimine (PEI, 18.3 wt%) and stirred for one minute. Sodium borohydride (NaBH₄) is then added, drop by drop, while stirring, until the solution turns red. Finally the solution is stirred for five minutes.

Table D.1.: Positive Gold Nanoparticle Ingredients. Au particle concentration is adjusted according to the step in the recipe.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS</th>
<th>Weight %</th>
<th>Quantity</th>
<th>#ₐu/µL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroauric Acid</td>
<td>(HAuCl₄)</td>
<td>1.24</td>
<td>80 µL</td>
<td>1.46 × 10^{18}</td>
</tr>
<tr>
<td>MilliQ</td>
<td>(H₂O)</td>
<td>100</td>
<td>10 mL</td>
<td>1.17 × 10^{16}</td>
</tr>
<tr>
<td>Polyethyleneimine</td>
<td>(PEI)</td>
<td>18.3</td>
<td>20 µL</td>
<td>1.17 × 10^{16}</td>
</tr>
<tr>
<td>Sodium Borohydride</td>
<td>(NaBH₄)</td>
<td>?</td>
<td>drop</td>
<td>?</td>
</tr>
</tbody>
</table>
E. TEM Chip Fabrication Plan

The following is a fabrication plan for creating TEM chips. At the top of each table is the date of fabrication, the name of the batch and the contact information for the person responsible. Each step has a full width cell with the number and name of the step. The columns are as follows:

1. The time to complete the specific sub-step. If it is a batch step it is for the entire batch. If it is a serial step it is for a single wafer.

2. Batch step (B) or a serial step (S).

3. Front-side step (FS) or a back-side step (BS).

4. The name of the machine to be used and which mask to use.

5. The specifics of the step.

The entire process is visualized in appendix G.

The complete list of fabrication steps (18) and sub-steps (98) is:

1 Grow SiN\textsubscript{x} Window Layer
   1.1 New DSP Si Wafer
   1.2 Grow SiN\textsubscript{x}
   1.3 Log: Measure SiN\textsubscript{x} thickness

2 Grow High Sacrificial Layer
   2.1 RCA clean
   2.2 Grow boron-doped poly-Si
   2.3 Log: Measure poly-Si thickness

3 Pattern High Sacrificial Layer
   3.1 HMDS
   3.2 Spin on photoresist
   3.3 Expose photoresist
3.4 Develop photoresist
3.5 Log: Check photoresist in microscope
3.6 Etch poly-Si
3.7 Remove photoresist in plasma asher
3.8 Log: Measure profile on detak
3.9 Log: Measure surface roughness on AFM

4 Grow Low Sacrificial Layer
4.1 RCA clean
4.2 Grow amorphous-Si
4.3 Log: Measure amorphous-Si thickness

5 Pattern Low Sacrificial Layer
5.1 HMDS
5.2 Spin on photoresist
5.3 Expose photoresist
5.4 Develop photoresist
5.5 Log: Check photoresist in microscope
5.6 Etch amorphous-Si
5.7 Remove photoresist
5.8 Log: Measure profile on detak
5.9 Log: Measure surface roughness on AFM

6 Reduce Surface Roughness
6.1 RCA clean
6.2 Grow SiO₂
6.3 Log: Measure SiO₂ thickness
6.4 Etch SiO₂
6.5 Log: Measure profile on detak
6.6 Log: Measure surface roughness on AFM

7 Remove Backside Si
7.1 Etch Si
8 Grow First Top SiNx Layer
   8.1 RCA clean
   8.2 Grow SiNx
   8.3 Log: Measure SiNx thickness

9 Grow Second Top SiNx Layer
   9.1 RCA clean
   9.2 Grow SiNx
   9.3 Log: Measure SiNx thickness

10 Open Backside SiNx for KOH
    10.1 HMDS
    10.2 Spin on photoresist
    10.3 Expose photoresist
    10.4 Reverse bake photoresist
    10.5 Flood expose photoresist
    10.6 Develop photoresist
    10.7 Log: Check photoresist in microscope
    10.8 Etch SiNx
    10.9 Remove photoresist in plasma asher

11 Open Frontside SiNx for KOH
    11.1 HMDS
    11.2 Spin on photoresist
    11.3 Expose photoresist
    11.4 Reverse bake photoresist
    11.5 Flood expose photoresist
    11.6 Develop photoresist
    11.7 Log: Check photoresist in microscope
    11.8 Etch SiNx
    11.9 Remove photoresist in plasma asher

12 Thin SiNx Around Imaging Area
12.1 HMDS
12.2 Spin on photoresist
12.3 Expose photoresist
12.4 Reverse bake photoresist
12.5 Flood expose photoresist
12.6 Develop photoresist
12.7 Log: Check photoresist in microscope
12.8 Thin $\text{SiN}_x$
12.9 Remove photoresist in plasma asher

13 **KOH** Etch
   13.1 **KOH** Etch
   13.2 7UP cleaning
   13.3 Critical Point Drying

14 Open Backside Inlets
   14.1 Etch $\text{SiN}_x$ through shadow mask

15 **KOH** Etch
   15.1 **KOH** Etch
   15.2 7UP cleaning
   15.3 Critical Point Drying

16 Open Heaters
   16.1 HMDS
   16.2 Spin on photoresist
   16.3 Expose photoresist
   16.4 Reverse bake photoresist
   16.5 Flood expose photoresist
   16.6 Develop photoresist
   16.7 Critical Point Drying
   16.8 Log: Check photoresist in microscope
   16.9 Etch $\text{SiN}_x$
16.10 Remove photoresist in plasma asher

17 Create Electrodes and Fill Busstops
   17.1 HMDS
   17.2 Spin on photoresist
   17.3 Expose photoresist
   17.4 Reverse bake photoresist
   17.5 Flood expose photoresist
   17.6 Develop photoresist
   17.7 Critical Point Drying
   17.8 Log: Check photoresist in microscope
   17.9 Deposit electrodes
   17.10 Lift-off
   17.11 Critical Point Drying

18 Prepare Wafers for Outside
   18.1 Spin on photoresist
   18.2 Put on bluetape
   18.3 Saw wafers
F. Fabrication plan for TEM Chip v2

Notes on the fabrication

The following are some notes on the fabrication of TEM chip v2 which are fabrication specific.

The alignment of the different layers is important. In one case the thinning window overlapped with an open busstop. This caused the chip to fail since the thinning window was etched 160 nm and the thickness of the low channel and the bottom SiNx layer is 95 nm.

In Step 5, when etching the amorph-Si, the high channel is not protected in the photolithography. The etch used has a quite high etch rate per cycle compared to what is necessary. In order to alleviate this a liquid etch such as a poly-Si etch, should be used. Additionally an ultra-short or ultra-slow ASE process could be optimized to remove the overhanging channel part if an isotropic etch is used.

The microscope image with the KS aligner is superior to that of Aligner 6-inch and therefore this machine should be used in the future.
Additional Information:

**Total batch size**: 12 + wafers. 12 for tests and the additional are for devices. 5 of the test wafers are present at the beginning.

- B = Batch
- S = Serial
- FS = Front Side
- BS = Back Side
**Friday d. 8/6-2012**

**Batch:** MoWinRRTEMChip

**Eric Jensen (s031815)**

**mobile:** 31123059, **email:** eric.jensen@nanotech.dtu.dk

**Molecular Windows**

### Step 1: SiN<sub>x</sub> Grow Window Layer

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:05</td>
<td></td>
<td>New Si wafers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n-type</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Orientation: &lt;100&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polished on both sides</td>
</tr>
<tr>
<td>06:00</td>
<td>B (Furnace: LPCVD Ni-</td>
<td>Grow 25 nm SiN&lt;sub&gt;x&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>trid)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low-stress Si-rich recipe for 6 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max 10 device wafers pr. run</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Test wafers: 1, 4, 6, 10, 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[tolerance: 30 nm − 20 nm]</td>
</tr>
<tr>
<td>00:20</td>
<td>S (Ellipsometer M-2000V)</td>
<td>Log: Measure SiN&lt;sub&gt;x&lt;/sub&gt;-thickness on ellipsometer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Approximately 20 min/wafer, test wafer 1, 10, 12</td>
</tr>
</tbody>
</table>

### Step 2: Grow High Sacrificial Layer

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>02:00</td>
<td>B (RCA Bench)</td>
<td>RCA clean</td>
</tr>
<tr>
<td>05:00</td>
<td>B (Furnace: LPCVD Poly-Si)</td>
<td>Grow 1 µm boron doped poly-Si</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Recipe &quot;POLY620PX′′ for 87 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max 10 device wafers pr. run</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Test wafers: 2, 3, 4, 6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[tolerance: 1.1 µm − 0.9 µm]</td>
</tr>
<tr>
<td>00:20</td>
<td>S (Filmtek)</td>
<td>Log: Measure poly-Si-thickness on filmtek</td>
</tr>
<tr>
<td></td>
<td></td>
<td>test wafer 2</td>
</tr>
</tbody>
</table>
**Friday d. 8/6-2012**  
Batch: MoWinRRTEMChip

**Eric Jensen (s031815)**  
**mobile:** 31123059, **email:** eric.jensen@nanotech.dtu.dk

**Molecular Windows**

### Step 3: Pattern High Sacrificial Layer

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B</td>
<td>HMDS</td>
</tr>
<tr>
<td>00:07</td>
<td>S FS (SSE Spinner)</td>
<td>Spin on 2.2 µm AZ5214E photoresist</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Recipe &quot;2.2 4 inch&quot;</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*Test wafers: 4,6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*Bake for 100 s at 90 ºC.</td>
</tr>
<tr>
<td>00:20</td>
<td>S FS (Aligner 6-inch)</td>
<td>Positive photoresist procedure</td>
</tr>
<tr>
<td></td>
<td>[SAC high Mask]</td>
<td>*Expose for 4 s.</td>
</tr>
<tr>
<td>00:20</td>
<td>B</td>
<td>Development</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Developer: 800 mL AZ351B (NaOH) and 4000 mL H₂O</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*Time: 60 seconds</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*Temperature: 22 ºC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*Rinse for 2 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*Dry 3 min in spindryer</td>
</tr>
<tr>
<td>00:20</td>
<td>S FS</td>
<td>Log: Check Photoresist in microscope</td>
</tr>
<tr>
<td>00:16</td>
<td>S FS (ASE)</td>
<td>Etch poly-Si</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Use recipe &quot;mshallol’’ for 3 cycles (34 s)</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*test wafer 3</td>
</tr>
<tr>
<td>00:45</td>
<td>B (Plasma Asher II)</td>
<td>Remove photoresist with Plasma Asher II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*O₂: 210 ml/min, N₂: 70 ml/min, Watt: 1000</td>
</tr>
<tr>
<td>00:20</td>
<td>S FS (Detak)</td>
<td>Log: Measure profile on detak (test wafer 4)</td>
</tr>
<tr>
<td>00:20</td>
<td>S FS (Nanoman AFM)</td>
<td>Log: Measure surface roughness on AFM (test wafer 4)</td>
</tr>
</tbody>
</table>
### Friday d. 8/6-2012

**Batch:** MoWinRRTEMChip

**Eric Jensen (s031815)**  
**Mobile:** 31123059, **Email:** eric.jensen@nanotech.dtu.dk

**Molecular Windows**

<table>
<thead>
<tr>
<th>Time</th>
<th>Task</th>
<th>Location/Details</th>
</tr>
</thead>
</table>
| 02:00 | RCA clean | Grow 30 nm doped amorph-Si  
*Recipe "AMORPH560′′ for 15 min.  
Run recipe from computer  
Max 10 device wafers pr. run  
Test wafers: 4,5,6  
[tolerance: 35 nm – 20 nm]* |
| 05:00 | (RCA Bench) LPCVD Poly-Si |  
Run recipe from computer  
Max 10 device wafers pr. run  
Test wafers: 4,5,6  
[tolerance: 35 nm – 20 nm]* |
| 00:20 | FS (Ellipsometer M-2000V) | Log: Measure poly-Si-thickness on ellipsometer  
*test wafer 5* |
**Friday d. 8/6-2012**  
Batch: MoWinRRTEMChip

Eric Jensen (s031815)  
mobile: 31123059, email: eric.jensen@nanotech.dtu.dk

### Molecular Windows

#### Step 5: Pattern Low Sacrificial Layer

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B</td>
<td>(HMDS oven)</td>
</tr>
<tr>
<td>00:07</td>
<td>S FS</td>
<td>(SSE Spinner)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>00:20</td>
<td>S FS</td>
<td>(Aligner 6-inch)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[SAC low Mask]</td>
</tr>
<tr>
<td>00:20</td>
<td>B</td>
<td>Development</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>00:20</td>
<td>S FS</td>
<td>Log: Check Photoresist in microscope</td>
</tr>
<tr>
<td>00:16</td>
<td>S FS</td>
<td>(ASE)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>00:45</td>
<td>B</td>
<td>(Plasma Asher II)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>00:20</td>
<td>S FS</td>
<td>(Detak)</td>
</tr>
<tr>
<td>00:20</td>
<td>S FS</td>
<td>(AFM)</td>
</tr>
</tbody>
</table>
**Friday d. 8/6-2012**  
Batch: MoWinRRTEMChip  
Eric Jensen (s031815)  
Mobile: 31123059, email: eric.jensen@nanotech.dtu.dk  
Molecular Windows

## Step 6: Reduce Surface Roughness

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Equipment</th>
<th>Notes</th>
</tr>
</thead>
</table>
| 02:00 | B      | RCA Bench | RCA clean  
|       |        | (Furnace: Anneal Oxide [C1]) | Grow 20 nm SiO$_2$  
|       |        |           | Recipe "dry1000” for 26 min.  
|       |        |           | Max 10 device wafers pr. run  
|       |        |           | Test wafers: 4, 6, 7  
|       |        |           | [tolerance: 25 nm – 15 nm] |
| 06:00 | B      | Ellipsometer M-2000V | Log: Measure SiO$_2$-thickness on ellipsometer test wafer 7  
| 06:20 | S      | Detak | Log: Measure profile on detak (test wafer 4, 6)  
| 06:20 | S      | Nanoman AFM | Log: Measure surface roughness on AFM (test wafer 4, 6) |

## Step 7: Remove backside Si

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Equipment</th>
<th>Notes</th>
</tr>
</thead>
</table>
| 00:16 | S      | ASE | Etch poly-Si  
|       |        |           | Use recipe "mshallol” for 3 cycles (34 s) |
### Molecular Windows

**Step 8: Grow First Top $\text{SiN}_x$ Layer**

<table>
<thead>
<tr>
<th>02:00</th>
<th>B</th>
<th>(RCA Bench)</th>
<th>RCA clean</th>
</tr>
</thead>
<tbody>
<tr>
<td>06:00</td>
<td>B</td>
<td>(Furnace: LPCVD Nitrid)</td>
<td>Grow 100 nm $\text{SiN}_x$</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>FS</td>
<td>Low-stress Si-rich recipe for 24 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ellipsometer M-2000V)</td>
<td>Max 10 device wafers pr. run</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Test wafers: 1,8,10,12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[tolerance: 110 nm – 90 nm]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Log: Measure $\text{SiN}_x$-thickness on ellipsometer</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Approximately 20 min/wafer, test wafer 8</td>
<td></td>
</tr>
</tbody>
</table>

**Step 9: Grow Second Top $\text{SiN}_x$ Layer**

<table>
<thead>
<tr>
<th>02:00</th>
<th>B</th>
<th>(RCA Bench)</th>
<th>RCA clean</th>
</tr>
</thead>
<tbody>
<tr>
<td>06:00</td>
<td>B</td>
<td>(Furnace: LPCVD Nitrid)</td>
<td>Grow 100 nm $\text{SiN}_x$</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>FS</td>
<td>Max 10 device wafers pr. run</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ellipsometer M-2000V)</td>
<td>Test wafers: 1,9,10,12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Low-stress Si-rich recipe for 24 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[tolerance: 110 nm – 90 nm]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Log: Measure $\text{SiN}_x$-thickness on ellipsometer</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Approximately 20 min/wafer, test wafer 1,9,10,12</td>
<td></td>
</tr>
</tbody>
</table>
**Friday d. 8/6-2012**  
**Batch: MoWinRRTEMChip**

**Eric Jensen (s031815)**  
**mobile: 31123059, email: eric.jensen@nanotech.dtu.dk**

**Molecular Windows**

### Step 10: Open backside SiN<sub>x</sub> for KOH

<table>
<thead>
<tr>
<th>Time</th>
<th>Step</th>
<th>Equipment</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B</td>
<td>HMDS oven</td>
<td>HMDS</td>
</tr>
</tbody>
</table>
| 00:07 | S    | SSE Spinner | Spin on 2.2 µm AZ5214E photoresist  
**Recipe “2.2 4 inch”**  
**Test wafers: 1**
**Bake for 100 s at 90 °C.**  
| 00:20 | S    | Aligner 6-inch | Reverse photoresist procedure  
[KOH Mask]
[Hotplate, cleanroom 3]  
**Expose for 2 s.**
**Bake for 100 s at 120 °C.**
| 00:20 | B    | Plasma Asher II | Remove photoresist with Plasma Asher II  
**O<sub>2</sub>: 210 ml/min, N<sub>2</sub>: 70 ml/min, Watt: 1000**

**Ph.D Thesis 183 DTU Nanotech**
**Friday d. 8/6-2012**

**Eric Jensen (s031815)**  
mobile: 31123059, email: eric.jensen@nanotech.dtu.dk  
**Batch: MoWinRRTEMChip**  
**Molecular Windows**

### Step 11: Open frontside SiN<sub>x</sub> for KOH

<table>
<thead>
<tr>
<th>Time</th>
<th>Process Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B (HMDS oven)</td>
</tr>
<tr>
<td>00:07</td>
<td>S (SSE Spinner)</td>
</tr>
<tr>
<td></td>
<td>Spinning 2.2 µm AZ5214E photoresist</td>
</tr>
<tr>
<td></td>
<td><em>Recipe &quot;2.2 4 inch&quot;</em></td>
</tr>
<tr>
<td></td>
<td><em>Test wafers: 8</em></td>
</tr>
<tr>
<td></td>
<td><em>Bake for 100 s at 90 °C.</em></td>
</tr>
<tr>
<td>00:20</td>
<td>S (Aligner 6-inch)</td>
</tr>
<tr>
<td></td>
<td>[Opening Mask]</td>
</tr>
<tr>
<td></td>
<td>(Hotplate, cleanroom 3)</td>
</tr>
<tr>
<td></td>
<td>Reverse photoresist procedure</td>
</tr>
<tr>
<td></td>
<td><em>Expose for 2 s.</em></td>
</tr>
<tr>
<td></td>
<td><em>Bake for 100 s at 120 °C.</em></td>
</tr>
<tr>
<td></td>
<td>Wait for 10 min.</td>
</tr>
<tr>
<td></td>
<td><em>Flood expose for 30 s.</em></td>
</tr>
<tr>
<td>00:20</td>
<td>B (Aligner 6-inch)</td>
</tr>
<tr>
<td></td>
<td>Development</td>
</tr>
<tr>
<td></td>
<td><em>Developer: 800 mL AZ351B (NaOH) and 4000 mL H&lt;sub&gt;2&lt;/sub&gt;O</em></td>
</tr>
<tr>
<td></td>
<td><em>Time: 60 seconds</em></td>
</tr>
<tr>
<td></td>
<td><em>Temperature: 22 °C</em></td>
</tr>
<tr>
<td></td>
<td><em>Rinse for 2 min.</em></td>
</tr>
<tr>
<td></td>
<td><em>Dry 3 min in spindryer</em></td>
</tr>
<tr>
<td>00:20</td>
<td>S (Aligner 6-inch)</td>
</tr>
<tr>
<td></td>
<td>Log: Check Photoresist in microscope</td>
</tr>
<tr>
<td>00:16</td>
<td>S (RIE I)</td>
</tr>
<tr>
<td></td>
<td>Etch SiN&lt;sub&gt;x&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td><em>Use recipe TMHNITR2 for 5 min. 45 s</em></td>
</tr>
<tr>
<td></td>
<td><em>[Etch depth tolerance: 200 nm – 210 nm]</em></td>
</tr>
<tr>
<td></td>
<td><em>test wafer 8</em></td>
</tr>
<tr>
<td>00:45</td>
<td>B (Plasma Asher II)</td>
</tr>
<tr>
<td></td>
<td>Remove photoresist with Plasma Asher II</td>
</tr>
<tr>
<td></td>
<td>O&lt;sub&gt;2&lt;/sub&gt;: 210 ml/min, N&lt;sub&gt;2&lt;/sub&gt;: 70 ml/min, Watt: 1000</td>
</tr>
</tbody>
</table>
## Step 12: Thin SiN<sub>x</sub> around imaging area

<table>
<thead>
<tr>
<th>Time</th>
<th>Step</th>
<th>Equipment</th>
<th>Action/Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B</td>
<td>(HMDS oven)</td>
<td>HMDS</td>
</tr>
<tr>
<td>00:07</td>
<td>S</td>
<td>(SSE Spinner)</td>
<td>Spin on 2.2 μm AZ5214E photoresist</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><em>Recipe &quot;2.2 4 inch&quot;</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Test wafers: 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bake for 100 s at 90 °C.</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>(Aligner 6-inch)</td>
<td>Reverse photoresist procedure</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Expose for 2 s.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Thinning Mask]</td>
<td>Bake for 100 s at 120 °C.</td>
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<td></td>
<td></td>
<td>(Hotplate, cleanroom 3)</td>
<td>Wait for 10 min.</td>
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<td></td>
<td></td>
<td>Flood expose for 30 s.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Development</td>
</tr>
<tr>
<td>00:20</td>
<td>B</td>
<td></td>
<td>Developer: 800 mL AZ351B (NaOH)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>and 4000 mL H&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td></td>
<td>Time: 60 seconds</td>
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<td></td>
<td>Temperature: 22 °C</td>
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<td></td>
<td>Rinse for 2 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dry 3 min in spindryer</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>FS</td>
<td>Log: Check Photoresist in microscope</td>
</tr>
<tr>
<td>00:16</td>
<td>S</td>
<td>(RIE I)</td>
<td>Thin SiN&lt;sub&gt;x&lt;/sub&gt; down to 37 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><em>Use recipe TMHNITR2 for 5 min.</em></td>
</tr>
<tr>
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<td></td>
<td><em>Etch depth tolerance: 150 nm – 165 nm</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><em>test wafer 10</em></td>
</tr>
<tr>
<td>00:45</td>
<td>B</td>
<td>(Plasma Asher II)</td>
<td>Remove photoresist with Plasma Asher II</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O&lt;sub&gt;2&lt;/sub&gt;: 210 ml/min, N&lt;sub&gt;2&lt;/sub&gt;: 70 ml/min, Watt: 1000</td>
</tr>
</tbody>
</table>
**Friday d. 8/6-2012**  
Batch: MoWinRRTEMChip

Eric Jensen (s031815)  
mobile: 31123059, email: eric.jensen@nanotech.dtu.dk  
Molecular Windows  

**Step 13: KOH etch**

<table>
<thead>
<tr>
<th>Time</th>
<th>Condition</th>
<th>Step</th>
<th>Details</th>
</tr>
</thead>
</table>
| 05:30 | B         | KOH etch | 30 sec BHF etch. Rinse for 2 min.  
Etch time 5 hours [etch rate: 1.2 µm/min.]  
Test wafers: 3,11 |
| 01:00 | B         | (7UP 4”) | 7UP cleaning  
Rinse for 5 min. |
| 01:00 | S         | (Critical Point Dryer) | Dry carefully |

**Step 14: Open Backside Inlets**

<table>
<thead>
<tr>
<th>Time</th>
<th>Condition</th>
<th>Step</th>
<th>Details</th>
</tr>
</thead>
</table>
| 00:16 | S  BS     | Etch SiNₓ | Use recipe TMHNITR2 for 4 min.  
Use carrier to protect frontside  
Use capton tape to secure masking wafer  
test wafer 12 |

**Step 15: KOH etch**

<table>
<thead>
<tr>
<th>Time</th>
<th>Condition</th>
<th>Step</th>
<th>Details</th>
</tr>
</thead>
</table>
| 05:30 | B         | KOH etch | 30 sec BHF etch. Rinse for 2 min.  
Etch time 5 hours [etch rate: 1.2 µm/min.]  
Rinse for 5 min. |
| 01:00 | B         | (7UP 4”) | 7UP cleaning |
| 01:00 | S         | (Critical Point Dryer) | Dry carefully |
## Step 16: Open Heaters

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B (HMDS oven)</td>
<td>HMDS</td>
</tr>
<tr>
<td>00:07</td>
<td>S (KS Spinner)</td>
<td>Spin on 2.2 μm AZ5214E photoresist</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Use no vacuum chuck</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Bake for 100 s at 90 °C.</em></td>
</tr>
<tr>
<td>00:20</td>
<td>S (KS Aligner)</td>
<td>Reverse photoresist procedure</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>(global mode)</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Use global chuck.</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Expose for 2 s.</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Bake for 100 s at 120 °C.</em></td>
</tr>
<tr>
<td>00:20</td>
<td>B Development</td>
<td>Development</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>[Heater Mask]</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>(Hotplate, cleanroom 3)</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Wait for 10 min.</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Flood expose for 30 s.</em></td>
</tr>
<tr>
<td>01:00</td>
<td>S (Critical Point Dryer)</td>
<td>Dry carefully</td>
</tr>
<tr>
<td>00:20</td>
<td>S FS (Critical Point Dryer)</td>
<td>Log: Check Photoresist in microscope</td>
</tr>
<tr>
<td>00:16</td>
<td>S FS (RIE I)</td>
<td>Etch SiNₓ</td>
</tr>
<tr>
<td>00:45</td>
<td>B (Plasma Asher II)</td>
<td>Remove photoresist with Plasma Asher II</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Use recipe TMHNITR2 for 7 min.</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>O₂: 210 ml/min, N₂: 70 ml/min, Watt: 1000</em></td>
</tr>
</tbody>
</table>
### Step 17: Create Electrodes and Fill Busstops

<table>
<thead>
<tr>
<th>Time</th>
<th>Action</th>
<th>Chamber</th>
<th>Device</th>
<th>Step Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:45</td>
<td>B</td>
<td>FS</td>
<td>(HMDS oven)</td>
<td>HMDS</td>
</tr>
<tr>
<td>00:07</td>
<td>S</td>
<td>FS</td>
<td>(KS Spinner)</td>
<td>Spin on 2.2 μm AZ5214E photoresist. Use no vacuum chuck. Bake for 100 s at 90 °C.</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>FS</td>
<td>(KS Aligner)</td>
<td>Reverse photoresist procedure (global mode). Use global chuck. Expose for 2.2 s. Bake for 100 s at 120 °C.</td>
</tr>
<tr>
<td>00:20</td>
<td>B</td>
<td>FS</td>
<td></td>
<td>Development. Developer: 800 mL AZ351B (NaOH) and 4000 mL H₂O. Time: 70 seconds. Temperature: 22 °C. Rinse for 2 min.</td>
</tr>
<tr>
<td>01:00</td>
<td>S</td>
<td>FS</td>
<td>(Critical Point Dryer)</td>
<td>Dry carefully. Log: Check Photoresist in microscope.</td>
</tr>
<tr>
<td>00:20</td>
<td>S</td>
<td>FS</td>
<td>(Alcatel)</td>
<td>Deposit Electrodes. Deposit 2 ± 1 nm Ti. Deposit 270 ± 5 nm Pt.</td>
</tr>
<tr>
<td>02:00</td>
<td>B</td>
<td>FS</td>
<td>(Lift-off bath)</td>
<td>Lift-off. Remover 1165. Heat to 65 °C in waterbath in fume hood. No ultrasound!</td>
</tr>
<tr>
<td>01:00</td>
<td>S</td>
<td>FS</td>
<td>(Critical Point Dryer)</td>
<td>Dry carefully.</td>
</tr>
</tbody>
</table>
### Friday d. 8/6-2012

Batch: MoWinRRTEMChip

**Eric Jensen (s031815)**

**mobile: 31123059, email: eric.jensen@nanotech.dtu.dk**

**Molecular Windows**

---

**Step 18: Prepare Wafer For Outside**

<table>
<thead>
<tr>
<th>Time</th>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>00:07</td>
<td>S</td>
<td>Spin on 10 µm AZ4562E photoresist. Bake for 120 s at 90 °C.</td>
</tr>
<tr>
<td>00:10</td>
<td>S</td>
<td>Put on Blue-tape</td>
</tr>
<tr>
<td>01:00</td>
<td>S</td>
<td>Saw wafers</td>
</tr>
</tbody>
</table>

---

**Test Wafer | Steps | Description**

<p>| 1 | 1, 8, 9, 10 | Window Layer SiN(_x) thickness, second top layer SiN(_x) thickness, RIE1 SiN(_x) etch rate |
| 2 | 2 | High poly-Si thickness |
| 3 | 2, 5 | poly-Si etch rate |
| 4 | 1-6 | High poly-Si profile and surface roughness, poly-Si profile and surface roughness after Step 6 |
| 5 | 4 | Low poly-Si thickness |
| 6 | 1-6 | Low poly-Si profile and surface roughness, poly-Si profile and surface roughness after Step 6 |
| 7 | 6 | SiO(_2) thickness |
| 8 | 8, 11 | First top SiN(_x) thickness, RIE1 SiN(_x) etch rate |
| 9 | 9, 12 | Second top SiN(_x) thickness, RIE1 SiN(_x) etch rate |
| 10 | 1, 8, 9, 13 | KOH 3 SiN(_x) etch rate |
| 11 | 14 | poly-Si thickness |
| 12 | 1, 6, 9, 16 | RIE1 SiN(_x) etch rate and shadow mask |</p>
<table>
<thead>
<tr>
<th>Step</th>
<th>Test Wafer 1</th>
<th>Test Wafer 2</th>
<th>Test Wafer 3</th>
<th>Test Wafer 4</th>
<th>Test Wafer 5</th>
<th>Test Wafer 6</th>
<th>Test Wafer 7</th>
<th>Test Wafer 8</th>
<th>Test Wafer 9</th>
<th>Test Wafer 10</th>
<th>Test Wafer 11</th>
<th>Test Wafer 12</th>
</tr>
</thead>
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</tbody>
</table>
G. TEM Chip Process Flow Visualization

The following images visualize selected steps from the fabrication procedure of the TEM chips.

<table>
<thead>
<tr>
<th>Term</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoresist</td>
<td>PR</td>
</tr>
<tr>
<td>Sacrificial Layer</td>
<td>SL</td>
</tr>
</tbody>
</table>
Step 1.1: [Grow SiN Window layer] New DSP Si Wafer

Step 1.2: [Grow SiN Window layer] Grow SiN_x

Figure G.1.: TEM fabrication step 1.1 and 1.2: New Si wafer and growth of SiN_x
**Step 2.2: [Grow High SL] Grow poly-Si**

![Cross-section](image1)

**Step 3.2: [Pattern High SL] Spin on photoresist**

![Cross-section](image2)

**Figure G.2.:** TEM fabrication step 2.2 and 3.2: Grow poly-Si and Spin on photoresist
Step 3.3: [Pattern High SL] Expose PR

Figure G.3.: TEM fabrication step 3.3 and 3.4: Photoresist exposure and development

Step 3.4: [Pattern High SL] Develop PR
Step 3.6: [Pattern High SL] Etch poly-Si

Step 3.7: [Pattern High SL] Plasma ash PR

Figure G.4.: TEM fabrication step 3.6 and 3.7: Etch of poly-Si and plasma ashing
Step 4.2: [Grow Low SL] Grow amorph-Si

Step 5.2: [Pattern Low SL] Spin on PR

Figure G.5.: TEM fabrication step 4.2 and 5.2: Grow amorph-Si and spin on photoresist
Step 5.3: [Pattern Low SL] Expose PR

Cross-section
Front
Back

Step 5.4: [Pattern Low SL] Develop PR

Cross-section
Front
Back

Figure G.6.: TEM fabrication step 5.3 and 5.4: Photoresist exposure and development
Figure G.7.: TEM fabrication step 5.6 and 5.7: Etch amorph-Si and plasma ash photoresist
Step 6.2: [Reduce Surface Roughness] Grow SiO$_2$

![Cross-section diagram]

Step 6.4: [Reduce Surface Roughness] HF etch SiO$_2$

![Cross-section diagram]

Figure G.8.: TEM fabrication step 6.2 and 6.4: Grow SiO$_2$ and etch SiO$_2$
Step 7.1: [Remove Backside Si] Etch backside Si

Step 8.2: [Grow Top SiN_x] Grow SiN_x

Figure G.9.: TEM fabrication step 7.1 and 8.2: Etch backside amorph-Si and poly-Si and grow first top SiN_x layer
**Step 9.2**: [Grow Top SiN$_x$] Grow SiN$_x$

**Step 10.2**: [Open Backside SiN$_x$] Spin on PR

*Figure G.10.*: TEM fabrication step 9.2 and 10.2: Grow second top SiN$_x$ layer and spin on photoresist
Step 10.3: [Open Backside SiN₃] Expose PR

Step 10.6: [Open Backside SiN₃] Develop PR

Figure G.11.: TEM fabrication step 10.3 and 10.6: Photoresist exposure and development
Step 10.8: \([\text{Open Backside SiN}_x]\) Etch SiN$_x$

Figure G.12.: TEM fabrication step 10.8 and 10.9: Etch SiN$_x$ and plasma ash photoresist
Step 11.2: [Open Frontside SiN₆] Spin on PR

Cross-section

Front

Back

Step 11.3: [Open Frontside SiN₆] Expose PR

Cross-section

Front

Back

Figure G.13.: TEM fabrication step 11.2 and 11.3: Photoresist spin on and exposure
Figure G.14: TEM fabrication step 11.6 and 11.8: Photoresist development and SiN$_x$ etch
Figure G.15.: TEM fabrication step 11.9 and 12.2: Plasma ash photoresist and photoresist spin on
Step 12.3: [Thin SiN$_x$] Expose PR

Step 12.6: [Thin SiN$_x$] Develop PR

Figure G.16.: TEM fabrication step 12.3 and 12.6: Photoresist exposure and development
Step 12.8: [Thin SiN$_x$] Thin SiN$_x$

Cross-section

Front

Back

Step 12.9: [Thin SiN$_x$] Plasma ash PR

Cross-section

Front

Back

Figure G.17.: TEM fabrication step 12.8 and 12.9: Thin SiN$_x$ and plasma ash photoresist
Step 13.1: [KOH] KOH etch

Cross-section

Front

Back

Step 14.1: [Open Backside Inlets] Etch SiN_x

Cross-section

Front

Back

Figure G.18.: TEM fabrication step 13.1 and 14.1: KOH etch and open backside inlets with shadow mask
Step 15.1: [KOH] KOH Etch

Step 16.2: [Open Heaters] Spin-on PR

Figure G.19.: TEM fabrication step 15.1 and 16.2: KOH etch and photoresist spin on
Figure G.20: TEM fabrication step 16.3 and 16.6: Photoresist exposure and development
**Step 16.9: [Open Heaters] Etch SiN$_x$**

**Step 16.10: [Open Heaters] Plasma ash PR**

*Figure G.21.*: TEM fabrication step 16.9 and 16.10: Etch SiN$_x$ and plasma ash photoresist
Figure G.22.: TEM fabrication step 17.2 and 17.3: Photoresist spin on and exposure
Step 17.6: [Create Electrodes] Develop PR

Step 17.9: [Create Electrodes] Deposit Electrodes

Figure G.23.: TEM fabrication step 17.6 and 17.9: Photoresist photoresist development and metal deposition
Step 17.10: [Create Electrodes] Lift-off

Figure G.24.: TEM fabrication step 17.10: Lift-off
H. MATLAB Scripts

H.1. Window Deflection

These scripts were used to calculate the deflection of a SiNx window.

H.1.1. membraneDeflectionFit2

function membraneDeflectionFit2
% This function fits experimental data to obtain the Young’s modulus and in plane stress. The inputs are P, the pressure in pascal and s, the maximum deflection in meters.

%% Initial setup and parameters
disp('Initializing...');
clear
clf %clear current figure
close all

format compact

% Initial guesses for the Young’s module and the built-in stress these % values are from the work of C.F. Elkjær and J.L. Rasmussen
% guesses = [s,E]
guesses = [100e6,255e9];

% poisson’s ratio for the SiNx membrane
nu = 0.23;

% the length of the shortest side of the membrane
shortwidth = 50e-6;

% the thickness of the membrane
Matlab Scripts

27  thickness = 50e-9;
28
29  \%
30  Data
31  disp('Preparing data...');
32  P_COMSOL=[0.1,0.3,0.5,0.7,1.5,3.0,4.0];
33  w0_COMSOL=[0.2277,0.5882,0.8389,1.027,1.522,2.063,2.319];
34  Ptemp = [0,53003.4465926378,91355.5339645465,95664.757264761,
35         163319.563078128,197793.349479844,222355.922291066,
36         282685.048494068,301214.708684991,332241.116446535,
37         390846.55329451,401619.611579988,525725.242626164];
38  w0New = [0,0.6479,1.055,1.122,1.688,2.088,1.965,2.346,2.634,
39         2.781,2.793,2.693,2.968];
40  PNew1 = [0,95664.757264761,197793.349479844,301214.708684991,
41         390846.55329451,525725.242626164];
42  w0New1 = [0,1.122,2.088,2.634,2.793,2.968];
43  PNew2 = [0,53003.4465926378,91355.5339645465,163319.563078128,
44         222355.922291066,282685.048494068,332241.116446535,
45         401619.611579988];
46  w0New2 = [0,0.6479,1.055,1.688,1.965,2.346,2.781,2.693];
47  VNew = [0.53,0.652,0.741,0.752,0.908,0.989,1.045,1.185,1.229,
48         1.3,1.437,1.461,1.75];
49  VNew1 = [0.53,0.752,0.989,1.229,1.437,1.75];
50  VNew2 = [0.529,0.652,0.741,0.908,1.045,1.185,1.3,1.461];
51
52  \%
53  converting units to Pa and m
54  P_COMSOL = P_COMSOL*1e5;
55  w0_COMSOL = w0_COMSOL*1e-6;
56  PNew = Ptemp;
57  w0New = w0New*1e-6;
58  PNew1 = PNew1;
59  w0New1 = w0New1*1e-6;
60  PNew2 = PNew2;
61  w0New2 = w0New2*1e-6;
62  Pmix = [ P_new PNew];
63  w0mix = [w0_new w0New];
% conversion factors from voltage to Pa
mVpsi = 16; % mV/psi
Vpsi = mVpsi * 1e-3; % V/psi
VPa = Vpsi * 0.000145037738; % V/Pa

for i = 1:length(VNew)
    PNew(i) = (VNew(i) - VNew(1))./VPa;
end

for i = 1:length(VNew1)
    PNew1(i) = (VNew1(i) - VNew1(1))./VPa;
end

for i = 1:length(VNew2)
    PNew2(i) = (VNew2(i) - VNew2(1))./VPa;
end

% Uncertainties
DefUncert = 0.0035; % uncertainty of 0.35%
VUncert = 0.02; % uncertainty of 0.02 V

for i = 1:length(VNew)
    if (VNew(i) - VUncert - VNew(1)) < 0
        PNewLower(i) = 0;
    else
        PNewLower(i) = (VNew(i) - VUncert - VNew(1))./VPa;
    end
    PNewUpper(i) = (VNew(i) + VUncert - VNew(1))./VPa;
    w0NewLower(i) = w0New(i) - w0New(i)*DefUncert;
    w0NewUpper(i) = w0New(i) + w0New(i)*DefUncert;
end

for i = 1:length(VNew1)
    if (VNew1(i) - VUncert - VNew1(1)) < 0
        PNew1Lower(i) = 0;
    else
        PNew1Lower(i) = (VNew1(i) - VUncert - VNew1(1))./VPa;
    end
    PNew1Upper(i) = (VNew1(i) + VUncert - VNew1(1))./VPa;
    w0New1Lower(i) = w0New1(i) - w0New1(i)*DefUncert;
    w0New1Upper(i) = w0New1(i) + w0New1(i)*DefUncert;
end

for i = 1:length(VNew2)
    if (VNew2(i) - VUncert - VNew2(1)) < 0
        PNew2Lower(i) = 0;
    else
        PNew2Lower(i) = (VNew2(i) - VUncert - VNew2(1))./VPa;
    end
    PNew2Upper(i) = (VNew2(i) + VUncert - VNew2(1))./VPa;
    w0New2Lower(i) = w0New2(i) - w0New2(i)*DefUncert;
    w0New2Upper(i) = w0New2(i) + w0New2(i)*DefUncert;
end
PNew2Lower(i) = 0;

else
    PNew2Upper(i) = (VNew2(i) - VUncert - VNew2(1))./VPa;
end

w0New2Lower(i) = w0New2(i) - w0New2(i)*DefUncert;

w0New2Upper(i) = w0New2(i) + w0New2(i)*DefUncert;

% Fitting for E and s

disp('Fitting for E and s0...')

oldopts = optimset('fminsearch');
optionsF = optimset(oldopts,'Display','off');

[fittedValues, error] = fminsearch(@(x) fitfunction(x,...
    PNew,w0New,thickness,shortwidth),guesses,optionsF);

[fittedValues_comsol, error_comsol] = fminsearch(@(x)
    membraneFitError2(...
    x,P_COMSOL,w0_COMSOL,nu,thickness,shortwidth),guesses,
    optionsF);

[fittedValues_New, error_New] = fminsearch(@(x)
    membraneFitError2(x,...
    PNew,w0New,nu,thickness,shortwidth),guesses,optionsF);

[fittedValues_New1, error_New1] = fminsearch(@(x)
    membraneFitError2(x,...
    PNew1,w0New1,nu,thickness,shortwidth),guesses,optionsF);

[fittedValues_New2, error_New2] = fminsearch(@(x)
    membraneFitError2(x,...
    PNew2,w0New2,nu,thickness,shortwidth),guesses,optionsF);

[fittedValues_NewConsts0, error_NewConsts0] = ...
    fminsearch(@(x) membraneFitError3(x,PNew,w0New,nu,
    thickness,...
    shortwidth),[255e9],optionsF);

Eps_comsol = fittedValues_comsol(2)/(1-0.23^2);
s0bar_comsol = fittedValues_comsol(1)*(shortwidth/thickness)^2/Eps_comsol;

Eps_New = fittedValues_New(2)/(1-0.23^2);
s0bar_New = fittedValues_New(1)*(shortwidth/thickness)^2/Eps_New;

Eps_New1 = fittedValues_New1(2)/(1-0.23^2);
\[ s_{0\text{bar}}_{\text{New1}} = \frac{\text{fittedValues}_{\text{New1}}(1) \times (\text{shortwidth}/\text{thickness})^2}{E_{\text{New1}}} \]

\[ E_{\text{New2}} = \frac{\text{fittedValues}_{\text{New2}}(2)}{1 - 0.23^2} \]

\[ s_{0\text{bar}}_{\text{New2}} = \frac{\text{fittedValues}_{\text{New2}}(1) \times (\text{shortwidth}/\text{thickness})^2}{E_{\text{New2}}} \]

\[ E_{\text{NewConsts0}} = \frac{\text{fittedValues}_{\text{NewConsts0}}(1)}{1 - 0.23^2} \]

\[ s_{0\text{bar}}_{\text{NewConsts0}} = \frac{230e6 \times (\text{shortwidth}/\text{thickness})^2}{E_{\text{NewConsts0}}} \]

%% Fitting for the curve based on the fitted E and s

```
disp('Fitting for the curve...')
Pfit_comsol = linspace(0, max(P_COMSOL), 100);
Pfit_New = linspace(0, max(PNew), 100);
Pfit_New1 = linspace(0, max(PNew1), 100);
Pfit_New2 = linspace(0, max(PNew2), 100);
Pfit_NewConsts0 = linspace(0, max(PNew), 100);

fitpoints = length(Pfit_comsol);
oldopts = optimset('fsolve');
optionsF = optimset(oldopts, 'Display', 'off');
for i = 1:fitpoints
    Pbar_comsol = (Pfit_comsol(i) \times (\text{shortwidth}/\text{thickness})^4) / Eps_comsol;
    sbar_solved_comsol = fsolve(@(x) membraneFitStrain(x,... s0bar_comsol, Pbar_comsol), 1000, optionsF);
    w0fit_comsol(i) = Pbar_comsol \times G(sbar_solved_comsol) \times thickness;

    Pbar_New = (Pfit_New(i) \times (\text{shortwidth}/\text{thickness})^4) / Eps_New;
    sbar_solved_New = fsolve(@(x) membraneFitStrain(x,... s0bar_New, Pbar_New), 1000, optionsF);
    w0fit_New(i) = Pbar_New \times G(sbar_solved_New) \times thickness;

    Pbar_New1 = (Pfit_New1(i) \times (\text{shortwidth}/\text{thickness})^4) / Eps_New1;
    sbar_solved_New1 = fsolve(@(x) membraneFitStrain(x,... s0bar_New1, Pbar_New1), 1000, optionsF);
    w0fit_New1(i) = Pbar_New1 \times G(sbar_solved_New1) \times thickness;
```
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Pbar_New2 = ((Pfit_New2(i)*(shortwidth/thickness)^4) / Eps_New2;

sbar_solved_New2 = fsolve(@(x) membraneFitStrain(x, ... 
    s0bar_New2,Pbar_New2),1000,optionsF);

w0fit_New2(i) = Pbar_New2*G(sbar_solved_New2)*thickness;

Pbar_NewConsts0 = ((Pfit_NewConsts0(i)*(shortwidth/thickness)^4) ... 
    / Eps_NewConsts0;

sbar_solved_NewConsts0 = fsolve(@(x) membraneFitStrain(x, ... 
    s0bar_NewConsts0,Pbar_NewConsts0),1000,optionsF);

w0fit_NewConsts0(i) = Pbar_NewConsts0*G(sbar_solved_NewConsts0 ... 
    )*thickness;

end

%% Plot data

disp('Plotting...');

fig1 = figure(1);
hold on
plot(Pfit_comsol,w0fit_comsol,'m-');
plot(P_COMSOL,w0_COMSOL,'m+');
plot(Pfit_New,w0fit_New,'c-');
plot(Pfit_New1,w0fit_New1,'g-');
plot(PNew1,w0New1,'go');
plot(Pfit_New2,w0fit_New2,'b-');
plot(PNew2,w0New2,'bo');
plot(Pfit_NewConsts0,w0fit_NewConsts0,'k-');
hold off

title('Measured deflections and model fit');
xlabel('Pressure [Pa]');
ylabel('Deflection [m]');
legend('Comsul fit','Comsul','Run 1+2 fit','First Run fit' ... 
    'First Run','Second Run fit','Second Run',... 
    '1+2 fit with s0 = 230 MPa','Location','SouthEast');

fig2 = figure(2);
hold on
plot(P_COMSOL./1e6,w0_COMSOL./1e-6,'m+', 'LineWidth',2);
plot(PNew1./1e6,w0New1./1e-6, 'go', 'LineWidth',2);
plot(PNew2 ./1e6,w0New2 ./1e-6, 'bo', 'LineWidth',2);
plot(Pfit_New ./1e6,w0fit_New ./1e-6, 'c-', 'LineWidth',2);
plot(Pfit_NewConsts0 ./1e6,w0fit_NewConsts0 ./1e-6, 'k-', 'LineWidth',2);
hold off
title('Measured deflections and model fit', ' FontWeight','bold ');
xlabel('Pressure /[MPa]', ' FontWeight','bold ');
ylabel('Deflection /[\mu m]', ' FontWeight','bold ');
legend('Comsol ','First Run ',' Second Run ','Run 1+2 fit ', ...'
'Run 1+2 fit with s0 = 230 MPa','Location','SouthEast');

%% Print values
disp('Printing values...')
tx = sprintf('s0 = %3.3f MPa',fittedValues_New(1)/1e6);
disp(tx);
tx = sprintf('E = %3.3f GPa',fittedValues_New(2)/1e9);
disp(tx);
end

H.1.2. membraneFitError2

1 function MSEfinal = membraneFitError2(guesses,P,w0,nu,
 thickness,shortwidth)
2  % MSEfinal = membraneFitError(guesses,P,w0,nu,thickness,
 shortwidth)
3  % This function calculates the error between the theoretical 
values of the
4  % deflection based on the guesses and the experimental values 
of the
5  % deflection
6
7  %% Calculating and initializing values
8  % built in stress
9  s0 = guesses(1);
10
11  % in-plane strain
12  Eps = guesses(2)/(1-nu^2);
13
14  % dimensionless form
15  s0bar = (s0*(shortwidth/thickness)^2)/Eps;
16
17  % Number of experimental points
18  datapoints = length(P);
19
20  % mean squared error of the fit
21  MSE = 0;
22
23  %% Fitting to each datapoint
24  oldopts = optimset('fsolve');
25  optionsF = optimset(oldopts,'Display','off');
26  for i = 1:datapoints
27    % dimensionless pressure (from experimental value)
28    Pbar = P(i)*(shortwidth/thickness)^4/Eps;
29
30    % dimensionless deflection (from experimental value)
31    w0bar = w0(i)/thickness;
32
33    % start guess H(sbar) set to (pi^2)/2 (from "Fracture Properties of Silicon Nitride Thin Films from the Load-deflection of Long Membranes)
34    start_solve = s0bar + (w0bar^2*pi^2)/4;
35
36    % finds the sbar which minimizes the transcendental function
37    sbar_sol = fsolve(@(x) membraneMinimizeStrain(x,s0bar,w0bar),...
38      start_solve,optionsF);
39
40    % calculates the sum of the squared errors (MSE) by calculating the deflection of the membrane based on the sbar_solution and finding the difference with the experimental value
41    MSE = MSE+(Pbar*G(sbar_sol)*thickness-w0(i))^2;
42  end
43  MSEfinal = MSE;
44 end

H.1.3. membraneMinimizeStrain

1 function sbarDifference = membraneMinimizeStrain(sbar,s0bar,w0bar)
2  % This function is used to fit the strain to the experimental values
3
4 sbarDifference = -sbar + s0bar + (1/2)*w0bar^2*H(sbar);

H.1.4. G

function out = G(sbar)
2
3 xbar = 0;
4
5 out = (((1)/(2*sbar))*(((1)/(4)) - xbar^2) - ((cosh(sqrt(3*sbar))...)
6 - cosh(2*xbar*sqrt(3*sbar)))/(4*sqrt(3*sbar^3)*sinh(sqrt(3*sbar))));

H.1.5. H

function out = H(sbar)
2
3 out = (4*(8 + 4*sbar)*sinh(sqrt(3*sbar))^2 - 6*sbar -...
4 3*sqrt(3*sbar)*sinh(2*sqrt(3*sbar)))/(4*sqrt(3*sbar)^3*...
5 sinh(sqrt(3*sbar))*4*sinh((sqrt(3*sbar))/(2))/(2)^(2))^(2));

H.1.6. membraneFitError3

function MSEfinal = membraneFitError3(guesses,P,w0,nu,
10 thickness,shortwidth)
11 % MSEfinal = membraneFitError(guesses,P,w0,nu,thickness,
12 % This function calculates the error between the theoretical
13 % deflection based on the guesses and the experimental values
14 % of the
15 % deflection
16
17 % calculating and initializing values
18 % built in stress
19 s0 = guesses(1);
20 s0 = 230e6;
21
22 % in-plane strain
23 Eps = guesses(2)/(1-nu^2);
24 Eps = guesses(1)/(1-nu^2);
25 % dimensionless form
s0bar = (s0*(shortwidth/thickness)^2)/Eps;

% Number of experimental points
datapoints = length(P);

% mean squared error of the fit
MSE = 0;

%%% Fitting to each datapoint
oldopts = optimset('fsolve');
optionsF = optimset(oldopts,'Display','off');
for i = 1:datapoints
    % dimensionless pressure (from experimental value)
    Pbar = P(i)*(shortwidth/thickness)^4/Eps;

    % dimensionless deflection (from experimental value)
    w0bar = w0(i)/thickness;

    % start guess H(sbar) set to (pi^2)/2 (from "Fracture Properties of Silicon Nitride Thin Films from the Load-deflection of Long Membranes")
    start_solve = s0bar + (w0bar^2*pi^2)/4;

    % finds the sbar which minimizes the transcendental function
    sbar_sol = fsolve(@(x) membraneMinimizeStrain(x,s0bar, w0bar),...
        start_solve,optionsF);

    % calculates the sum of the squared errors (MSE) by calculating the deflection of the membrane based on the sbar_solution and finding the difference with the experimental value
    MSE = MSE+(Pbar*G(sbar_sol)*thickness-w0(i))^2;
end
MSEfinal = MSE;
H.2. Holography of Graphene

These scripts were used to analyze the holograms taken of graphene.

H.2.1. grapheneHolography

```matlab
function [holo,points] = grapheneHolography

startScript;

%% Setup
dir = '..\TEM & SEM\d120725 - Holography of Multi-layer Graphene';

holo = struct('name',{},...
'phase',{},...
'amp',{},...
'rms',{},...
'std',{},...
'newPhase',{},...
'newPhaseX',{},...
'newPhaseY',{},...
'meanX',{},...
'minMeanX',{},...
'difX',{},...
'maxDifX',{},...
'slopeX',{},...
'interceptX',{},...
'slopeXError',{},...
'meanY',{},...
'minMeanY',{},...
'difY',{},...
'maxDifY',{},...
'slopeY',{},...
'interceptY',{},...
'slopeYError',{});

%% Hologram A3
%H1

c = 1;
holo(c).name = 'A3-H1-10-320000X-holo-phase';
holo(c).phase = imread(fullfile(dir,holo(c).name '.tif'));
```
holo(c).amp = imread([dir ' A3-H1-10-320000X-holo-amplitude'.tif]);

%H2
c = 2;
holo(c).name = 'A3-H2-13-670000X-holo-phase';
holo(c).phase = imread([dir ' holo(c).name'.tif]);

%H3-14
c = 3;
holo(c).name = 'A3-H3-14-320000X-holo-phase';
holo(c).phase = imread([dir ' holo(c).name'.tif]);

%H3-15
c = 4;
holo(c).name = 'A3-H3-15-320000X-holo-phase';
holo(c).phase = imread([dir ' holo(c).name'.tif]);

%H4-17
c = 5;
holo(c).name = 'A3-H4-17-320000X-holo-phase';
holo(c).phase = imread([dir ' holo(c).name'.tif]);

%H4-18
c = 6;
holo(c).name = 'A3-H4-18-320000X-holo-phase';
holo(c).phase = imread([dir ' holo(c).name'.tif]);

%H5
c = 7;
holo(c).name = 'A3-H5-22-320000X-holo-phase';
holo(c).phase = imread([dir ' holo(c).name'.tif]);

%H6
c = 8;
holo(c).name = 'A3-H6-25-320000X-holo-phase';
holo(c).phase = imread([dir ' holo(c).name'.tif]);

%H7-34
c = 9;
holo(c).name = 'A3-H7-34-410000X-holo-phase';
holo(c).phase = imread([dir ' holo(c).name'.tif]);
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78  \%H7-35
79  c = 10;
80  holo(c).name = 'A3-H7-35-410000X-holo-phase';
81  holo(c).phase = imread(['dir' '/' holo(c).name '.tif']);
82
83  \%H7-36
84  c = 11;
85  holo(c).name = 'A3-H7-36-410000X-holo-phase';
86  holo(c).phase = imread(['dir' '/' holo(c).name '.tif']);
87
88  \%H8-38
89  c = 12;
90  holo(c).name = 'A3-H8-38-410000X-holo-phase';
91  holo(c).phase = imread(['dir' '/' holo(c).name '.tif']);
92
93  \%H8-39
94  c = 13;
95  holo(c).name = 'A3-H8-39-410000X-holo-phase';
96  holo(c).phase = imread(['dir' '/' holo(c).name '.tif']);
97
98  \%\% Hologram A4
99
100 \%H1-41
101  c = 14;
102  holo(c).name = 'A4-H1-41-320000X-holo-phase';
103  holo(c).phase = imread(['dir' '/' holo(c).name '.tif']);
104
105 \%H2-43
106  c = 15;
107  holo(c).name = 'A4-H2-43-320000X-holo-phase';
108  holo(c).phase = imread(['dir' '/' holo(c).name '.tif']);
109
110 \%\% Hologram A5
111
112 \%H1-59
113  c = 16;
114  holo(c).name = 'A5-H1-59-255000X-holo-phase';
115  holo(c).phase = imread(['dir' '/' holo(c).name '.tif']);
116
117 \%H2-61
118  c = 17;
119  holo(c).name = 'A5-H2-61-255000X-holo-phase';
120  holo(c).phase = imread(['dir' '/' holo(c).name '.tif']);
MATLAB Scripts

%H3 -63
121 c = 18;
122 holo(c).name = 'A5-H3-63-255000X-holo-phase';
123 holo(c).phase = imread([dir '\ holo(c).name '.tif']);

%H4 -65
127 c = 19;
128 holo(c).name = 'A5-H4-65-255000X-holo-phase';
129 holo(c).phase = imread([dir '\ holo(c).name '.tif']);

%H5 -67
133 c = 20;
134 holo(c).name = 'A5-H5-67-255000X-hole-holo-phase';
135 holo(c).phase = imread([dir '\ holo(c).name '.tif']);

%H6 -69
138 c = 21;
139 holo(c).name = 'A5-H6-69-255000X-hole-holo-phase';
140 holo(c).phase = imread([dir '\ holo(c).name '.tif']);

%H7 -72
142 c = 22;
144 holo(c).name = 'A5-H7-72-255000X-hole-holo-phase';
145 holo(c).phase = imread([dir '\ holo(c).name '.tif']);

%H8 -76
147 c = 23;
149 holo(c).name = 'A5-H8-76-255000X-holo-phase';
150 holo(c).phase = imread([dir '\ holo(c).name '.tif']);

%H8 -77
152 c = 24;
154 holo(c).name = 'A5-H8-77-255000X-holo-phase';
155 holo(c).phase = imread([dir '\ holo(c).name '.tif']);

%%% Image Processing
158 for i = 1:c
159
160 % blur and truncate data
161 holo(i).rms = rms(holo(i).phase(:)); % root-mean square
162 holo(i).std = std(holo(i).phase(:)); % standard deviation

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filterSize = floor(6*holo(i).std);
if mod(filterSize,2) == 0
    filterSize = filterSize + 1;
end
if filterSize < 3
    filterSize = 5;
end
filterSize = double(filterSize);
blur = fspecial('gaussian',[filterSize filterSize],...
    double(holo(i).std));
holo(i).newPhase = imfilter(holo(i).phase,blur,'same');
holo(i).newPhase = min(max(holo(i).newPhase, ...
    holo(i).rms-3*holo(i).std),holo(i).rms+3*holo(i).std) ;

if i<16
    % remove charging in x-direction
    holo(i).meanX = mean(holo(i).newPhase);
    holo(i).difX = diff(holo(i).meanX);
    [y,holo(i).maxDifX] = max(holo(i).difX(5:(...
        size(holo(i).meanX,2)-100)));
    [P,S] = polyfit(5:(holo(i).maxDifX-20),...
        holo(i).meanX(5:(holo(i).maxDifX-20)),1);
    Error = sqrt(diag(inv(S.R)*inv(S.R')).*S.normr.^2./S.
        df);
    holo(i).slopeXError = Error(1);
    holo(i).slopeX = P(1); % slope
    [y,holo(i).minMeanX] = min(holo(i).meanX(5:holo(i).
        maxDifX));
    % y = ax+b
    % b = y-ax
    holo(i).interceptX = y - holo(i).slopeX*holo(i).
        minMeanX;
    for m = 1:size(holo(i).newPhase,1)
        for n = 1:size(holo(i).newPhase,2)
            holo(i).newPhaseX(m,n) = holo(i).newPhase(m ,...
                n)-(holo(i).slopeX*n+holo(i).interceptX);
        end
    end

    % remove charging in y-direction
    holo(i).meanY = mean(holo(i).newPhaseX(:,:,:)}
5: (holo(i).maxDifX - 20)), 2);
[P2, S] = polyfit(1: size(holo(i).newPhaseX, 2), holo(i).
meanY', 1);
Error = sqrt(diag(inv(S.R) * inv(S.R')) * S.normr.^2 ./ S.
df);
holo(i).slopeYError = Error(1);
holo(i).slopeY = P2(1);
tt = max(holo(i).meanY, 0);
for k = 1: length(holo(i).meanY)
    if tt(k) == 0
        tt(k) = max(holo(i).meanY(:));
    end
end
[y, holo(i).minMeanY] = min(tt);
holo(i).interceptY = y - holo(i).slopeY * holo(i).
meanY;
for m = 1: size(holo(i).newPhaseX, 1)
    for n = 1: size(holo(i).newPhaseX, 2)
        holo(i).newPhaseXy(n, m) = holo(i).newPhaseX(n ,... 
m) - (holo(i).slopeY * n + holo(i).interceptY);
    end
end
% set vacuum to ~ zero
globalMin = mean(mean(holo(i).newPhaseXy(:, ... 
5: (holo(i).maxDifX - 20)));)
if globalMin > 0
    holo(i).newPhaseXy = holo(i).newPhaseXy - 
globalMin;
else
    holo(i).newPhaseXy = holo(i).newPhaseXy + 
globalMin;
end
else
% remove charging in x-direction
holo(i).meanX = mean(holo(i).newPhase);
holo(i).difX = diff(holo(i).meanX);
[y, holo(i).maxDifX] = max(holo(i).difX(... 
100: (size(holo(i).meanX, 2) - 5)));
[P, S] = polyfit((holo(i).maxDifX + 20):( ... 
size(holo(i).meanX, 2) - 5), holo(i).meanX(...
(holo(i).maxDifX+20):(size(holo(i).meanX,2)-5))
   ,1);

Error = sqrt(diag(inv(S.R)*inv(S.R'))).*S.normr.'^2./S.
df);
holo(i).slopeXError = Error(1);
holo(i).slopeX = P(1); %slope
[y,holo(i).minMeanX] = min(holo(i).meanX(...
   (holo(i).maxDifX):(size(holo(i).meanX,2)-5))));
%y = ax+b
%b = y-ax
holo(i).interceptX = y - holo(i).slopeX*holo(i).
   minMeanX;
for m = 1:size(holo(i).newPhase,1)
   for n = 1:size(holo(i).newPhase,2)
      holo(i).newPhaseX(m,n) = holo(i).newPhase(m,n
   )...-
   -(holo(i).slopeX*n+holo(i).interceptX);
end
end

% remove charging in y-direction
holo(i).meanY = mean(holo(i).newPhaseX(:,...
   (holo(i).maxDifX+20):(size(holo(i).meanX,2)-5))
   ,2);
[P2,S] = polyfit(1:size(holo(i).newPhaseX,2),holo(i).
   meanY','1);
Error = sqrt(diag(inv(S.R)*inv(S.R'))).*S.normr.'^2./S.
df);
holo(i).slopeYError = Error(1);
holo(i).slopeY = P2(1);
tt = max(holo(i).meanY,0);
for k = 1:length(holo(i).meanY)
   if tt(k) == 0
      tt(k) = max(holo(i).meanY(:));
   end
end
[y,holo(i).minMeanY] = min(tt);
holo(i).interceptY = y - holo(i).slopeY*holo(i).
   minMeanY;
for m = 1:size(holo(i).newPhaseX,1)
   for n = 1:size(holo(i).newPhaseX,2)
      holo(i).newPhasexy(n,m) = holo(i).newPhaseX(m
   ,m)...
272 \(-(\text{holo}(i).\text{slopeY} \cdot n + \text{holo}(i).\text{interceptY});\)
273 end
274 end
275
276 \%set vacuum to ~zero
277 \text{globalMin} = \text{mean(\text{mean}(\text{holo}(i).\text{newPhasexy}(;,...
278 (\text{holo}(i).\text{maxDifX}+20):(\text{size(\text{holo}(i).\text{meanX},2)-5))));}
279 if \text{globalMin} > 0
280 \text{holo}(i).\text{newPhasexy} = \text{holo}(i).\text{newPhasexy} - \\
281 \text{globalMin};
282 \text{else}
283 \text{holo}(i).\text{newPhasexy} = \text{holo}(i).\text{newPhasexy} + \\
284 \text{globalMin};
285 \text{end}
286 end
287
288 \text{play} = 0;
289
290 if \text{play} > 0
291 if \text{(i>15) \&\& (i<19)}
292 \text{figure}
293 \text{subplot}(2,2,1);
294 \text{imagesc(\text{holo}(i).\text{phase});}
295 \text{set(gca,'YDir','normal');}
296 \text{set(gca,'XDir','normal');}
297 \text{title(sprintf('Original: %s',\text{holo}(i).\text{name}));}
298 \text{colormap('jet');}
299 \text{axis image}
300 \text{subplot}(2,2,2);
301 \text{hist(\text{holo}(i).\text{phase},100);}
302 \text{title(sprintf('Histogram of original',\text{holo}(i).\text{name}))}
303 ;
304 \text{axis square}
305 \text{subplot}(2,2,3);
306 \text{imagesc(\text{holo}(i).\text{newPhase});}
307 \text{set(gca,'YDir','normal');}
308 \text{set(gca,'XDir','normal');}
309 \text{title(sprintf('Blurred and truncated: %s',\text{holo}(i).\text{name}));}
310 \text{colormap('jet');}
311 \text{axis image}
312 \text{subplot}(2,2,4);
311    hist(holo(i).newPhase,100);
312    title(sprintf('Histogram of truncated',holo(i).name));
313    axis square
314
315    figure
316    subplot(2,2,1);
317    imagesc(holo(i).newPhase);
318    set(gca,'YDir','normal');
319    set(gca,'XDir','normal');
320    title(sprintf('B&T: %s',holo(i).name));
321    colormap('jet');
322    axis image
323    subplot(2,2,2);
324    plot(mean(holo(i).newPhase),'r-');
325    title(sprintf('Mean of B&T (x-dir)',holo(i).name));
326    axis square
327    subplot(2,2,3);
328    imagesc(holo(i).newPhasex);
329    set(gca,'YDir','normal');
330    set(gca,'XDir','normal');
331    title(sprintf('X-corrected: %s',holo(i).name));
332    colormap('jet');
333    axis image
334    subplot(2,2,4);
335    plot(mean(holo(i).newPhasex),'b-');
336    hold on
337    plot(mean(holo(i).newPhase),'r-');
338    hold off
339    title(sprintf('Mean of x-corrected',holo(i).name));
340    axis square
341
342
343    figure
344    subplot(2,2,1);
345    imagesc(holo(i).newPhasex);
346    set(gca,'YDir','normal');
347    set(gca,'XDir','normal');
348    title(sprintf('X-corrected: %s',holo(i).name));
349    colormap('jet');
350    axis image
351    subplot(2,2,2);
352    plot(mean(holo(i).newPhasex,2),'r-');
MATLAB Scripts

```matlab
353 title(sprintf('Mean of X-corrected (y-dir)', holo(i).name));
354 axis square
355 subplot(2,2,3);
356 imagesc(holo(i).newPhasexy);
357 set(gca,'YDir','normal');
358 set(gca,'XDir','normal');
359 title(sprintf('X and Y-corrected: %s', holo(i).name));
360 colormap('jet');
361 axis image
362 subplot(2,2,4);
363 plot(mean(holo(i).newPhasexy,2),'b-');
364 hold on
365 plot(mean(holo(i).newPhasex,2),'r-');
366 hold off
367 title(sprintf('Mean of y-corrected', holo(i).name));
368 axis square
369 end
370 end
371 end
372
373 %% Fitting Fringes
374 x1 = 124;
375 y1 = 209;
376 x2 = 149;
377 y2 = 199;
378
379 % find a line to estimate fringe spacing
380 [fringesLine,xTop,yTop,xBottom,yBottom] = ...
381     weightedLineProfile(holo(1).newPhasexy,x1,y1,x2,y2,50,
382     false);
383 % find spacing with autocorrelation
384 fringeSpacing = max(xcorr(fringesLine));
385 % determine x and y displacement
386 a = (y2 - y1)/(x2 - x1);
387 xDisp = floor(fringeSpacing) + 1;
388 yDisp = floor(a*fringeSpacing) + 1;
389
```
%% Data Processing

to be used

A3-H2-13 = 2
A3-H3-14 = 3
A3-H4-17 = 5
A3-H4-18 = 6
A3-H5-22 (skidt) = 7
A3-H6-25 (-||-) = 8
A3-H8-38 (-||-) = 12
A3-H8-39 (-||-) = 13

A5-H1-59
A5-H3-63
A3-H2-13

points = struct ('val',{},'name',{},'error',{}

play = 0;

i = 2;
x1 = 1;
y1 = 420;
x2 = 235;
y2 = 420;
spread = 20;
row = [175 255 317 244];
col = [408 340 422 480];
row = [67 74 152 143];
col = [142 239 221 130];
pCount = 1;
[points(pCount).val, points(pCount).error, points(pCount).
  name] = ...
  ghScript1(holo(i).newPhasexy,holo(i).name,x1,y1,x2,y2,
    spread,...
  play,row,col,xDisp,yDisp,holo(i).slopeX,holo(i).
    interceptX,...
  holo(i).slopeXError,holo(i).slopeY,holo(i).interceptY,...
  holo(i).slopeYError);

i = 3;
y1 = 233;
x2 = 177;
y2 = 233;
row = [146 182 205 182];
col = [227 179 234 280];
row = [116 121 245 205];
col = [340 494 495 355];
pCount = 2;

[points(pCount).val, points(pCount).error, points(pCount).name] = ...
  ghScript1(holo(i).newPhasexy, holo(i).name, x1, y1, x2, y2, spread, ...
  play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).interceptX, ...
  holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
  holo(i).slopeYError);

i = 5;
y1 = 173;
x2 = 239;
y2 = 173;
row = [137 189 265 281 229 123];
col = [235 232 278 335 389 331];
pCount = 3;

[points(pCount).val, points(pCount).error, points(pCount).name] = ...
  ghScript1(holo(i).newPhasexy, holo(i).name, x1, y1, x2, y2, spread, ...
  play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).interceptX, ...
  holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
  holo(i).slopeYError);

i = 6;
y1 = 173;
x2 = 239;
y2 = 173;
row = [127 203 274 259 223 133];
col = [238 235 283 358 389 328];
pCount = 4;

[points(pCount).val, points(pCount).error, points(pCount).name] = ... 
ghScript1(holo(i).newPhasexy, holo(i).name, x1, y1, x2, y2, spread,...
play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).interceptX,...
holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY,...
holo(i).slopeYError);

i = 7;
y1 = 250;
x2 = 250;
y2 = 250;
row = [239 346 383 341 244];
col = [193 182 251 338 281];
pCount = 5;

[points(pCount).val, points(pCount).error, points(pCount).name] = ... 
ghScript1(holo(i).newPhasexy, holo(i).name, x1, y1, x2, y2,
spread,...
play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).interceptX,...
holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY,...
holo(i).slopeYError);

i = 8;
y1 = 250;
x2 = 260;
y2 = 250;
row = [275 370 410 340 271];
col = [187 184 254 314 260];
pCount = 6;

[points(pCount).val, points(pCount).error, points(pCount).name] = ... 
ghScript1(holo(i).newPhasexy, holo(i).name, x1, y1, x2, y2,
spread,...
MATLAB Scripts

505      play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).
           interceptX, ...
506      holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
507      holo(i).slopeYError);
508
509      i = 12;
510      y1 = 313;
511      x2 = 295;
512      y2 = 313;
513      row = [261 310 320 270];
514      col = [274 283 347 335];
515
516      pCount = 7;
517
518      [points(pCount).val, points(pCount).error, points(pCount).
           name] = ...     
519      ghScript1(holo(i).newPhase, holo(i).name, x1, y1, x2, y2,        
           spread, ...,        
520      play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).        
           interceptX, ...
521      holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
522      holo(i).slopeYError);
523
524      i = 13;
525      y1 = 313;
526      x2 = 295;
527      y2 = 313;
528      row = [276 321 315 275];
529      col = [307 311 374 362];
530
531      pCount = 8;
532
533      [points(pCount).val, points(pCount).error, points(pCount).
           name] = ...     
534      ghScript1(holo(i).newPhase, holo(i).name, x1, y1, x2, y2,        
           spread, ...,        
535      play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).        
           interceptX, ...
536      holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
537      holo(i).slopeYError);
538
539      %A4
540      %high
i = 14;
x1 = 80;
y1 = 48;
x2 = 358;
y2 = 334;
row = [167 499 501 443 172];
col = [290 154 21 13 268];
pCount = 9;

[points(pCount).val, points(pCount).error, points(pCount).name] = ...
    ghScript1(holo(i).newPhase, holo(i).name, x1, y1, x2, y2, spread, ...
    play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).interceptX, ...
    holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
    holo(i).slopeYError);

% medium
i = 14;
x1 = 80;
y1 = 48;
x2 = 358;
y2 = 334;
row = [237 498 498 237];
col = [307 254 176 281];
pCount = 10;

[points(pCount).val, points(pCount).error, points(pCount).name] = ...
    ghScript1(holo(i).newPhase, holo(i).name, x1, y1, x2, y2, spread, ...
    play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).interceptX, ...
    holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
    holo(i).slopeYError);

% low
i = 14;
x1 = 80;
y1 = 48;
x2 = 358;
y2 = 334;

row = [120 500 500 120];
col = [350 350 500 500];
row = [402 483 484 447 413];
col = [502 502 472 453 474];
pCount = 11;

points(pCount).val, points(pCount).error, points(pCount).name = ghScript1(holo(i).newPhasexy, holo(i).name, x1, y1, x2, y2, spread,...
play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).
interceptX,...
holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY,...
holo(i).slopeYError);

% high
i = 15;
x1 = 80;
y1 = 48;
x2 = 358;
y2 = 334;
row = [139 499 502 379 132]; %x
col = [247 97 16 10 224]; %y
pCount = 12;

points(pCount).val, points(pCount).error, points(pCount).name = ghScript1(holo(i).newPhasexy, holo(i).name, x1, y1, x2, y2, spread,...
play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).
interceptX,...
holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY,...
holo(i).slopeYError);

% medium
i = 15;
x1 = 80;
y1 = 48;
x2 = 358;
y2 = 334;
row = [147 499 500 150];
col = [278 218 124 257];
pCount = 13;

[p, p.error, p.name] = ghScript1(holo(i).newPhasex, holo(i).name, x1, y1, x2, y2, spread, ...
play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).interceptX, ...
holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
holo(i).slopeYError);

% low
i = 15;
x1 = 80;
y1 = 48;
x2 = 358;
y2 = 334;
row = [120 500 500 120];
col = [350 350 500 500];
row = [374 435 438 401 377];
col = [462 465 432 411 437];
pCount = 14;

[p, p.error, p.name] = ghScript1(holo(i).newPhasex, holo(i).name, x1, y1, x2, y2, spread, ...
play, row, col, xDisp, yDisp, holo(i).slopeX, holo(i).interceptX, ...
holo(i).slopeXError, holo(i).slopeY, holo(i).interceptY, ...
holo(i).slopeYError);

% play = 1;
% A5
i = 16;
x1 = 450;
y1 = 317;
x2 = 198;
y2 = 321;
% row = [297 52 77 385];
% col = [478 489 32 35];
row = [107 210 200 155 138 85 67 72];
col = [430 415 381 388 320 278 332 393];
pCount = 15;

[row] = [107 210 200 155 138 85 67 72];
[col] = [430 415 381 388 320 278 332 393];
pCount = 15;

[i = 18;
x1 = 396;
y1 = 301;
x2 = 175;
y2 = 297;

[row] = [242 54 161 326];
[col] = [496 496 21 35];
row = [108 219 211 155 111];
col = [334 279 241 247 262];
pCount = 16;

[i = 18;
x1 = 396;
y1 = 301;
x2 = 175;
y2 = 297;

[row] = [242 54 161 326];
[col] = [496 496 21 35];
row = [108 219 211 155 111];
col = [334 279 241 247 262];
pCount = 16;

% Phase Amplitude stuff

%% Phase Amplitude stuff

phaseImg = holo(1).newPhasexy;
ampImg = min(max(holo(1).amp, rms(holo(1).amp)) - 3*std(holo(1).amp(:)), ...
    rms(holo(1).amp) + 3*std(holo(1).amp(:)));

x1 = 45;
y1 = 360;
x2 = 160;
y2 = 360;
spread = 50;

[ampLine, xTop, yTop, xBottom, yBottom] = ...
    weightedLineProfile(ampImg, x1, y1, x2, y2, spread, false);
[phaseLine, xTop, yTop, xBottom, yBottom] = ...
    weightedLineProfile(phaseImg, x1, y1, x2, y2, spread, false);

ampLineModif = max(ampLine) - ampLine;

% figure
% subplot(1,2,1);
% imagesc(phaseImg);
% set(gca,'YDir','normal');
% hold on
% plot(xTop, yTop, 'r--','LineWidth',2);
% plot([x1 x2],[y1 y2], 'r-', 'LineWidth', 2);
% plot(xBottom, yBottom, 'r--','LineWidth',2);
% hold off
% title('Phase');
% axis image
% subplot(1,2,2);
% imagesc(ampImg);
% set(gca,'YDir','normal');
% hold on
% plot(xTop, yTop, 'r--','LineWidth',2);
% plot([x1 x2],[y1 y2], 'r-', 'LineWidth', 2);
% plot(xBottom, yBottom, 'r--','LineWidth',2);
% hold off
% title('Amplitude');
% axis image
% figure
% subplot(1,2,1);
% plot(phaseLine, 'LineWidth',2);
% title('Phase - Line profile');
% axis square
subplot(1,2,2);
plot(ampLineModif,'LineWidth',2);
title('Amplitude - Line profile inverted');
axis square

% figure
plot(ampLineModif,phaseLine,'r*')
title('Phase vs amplitude')
xlabel('Amplitude');
ylabel('Phase');
axis square

%% Verification of slope charging
A5-H6-69 : 21
c = 21;
figure
imagesc(holo(c).newPhase);
set(gca,'YDir','normal');
colormap('gray');
hold on

area 1
a1x = [400 400 450 450 400];
a1y = [5 350 350 5 5];
plot(a1x,a1y,'r-');

area 2
a2x = [180 180 275 275 180];
a2y = [295 330 330 295 295];
plot(a2x,a2y,'g-');

area 3
a3x = [300 300 380 380 300];
a3y = [241 196 196 241 241];
plot(a3x,a3y,'b-');

area 4
a4x = [380 380 460 460 380];
a4y = [5 350 350 5 5];
plot(a4x,a4y,'y-');
hold off
axis image

figure
subplot(1,4,1)
```matlab
imagesc(holo(c).newPhase(5:350,400:450));
set(gca,'YDir','normal');
axis image
subplot(1,4,2)
imagesc(holo(c).newPhase(295:330,180:275));
set(gca,'YDir','normal');
axis image
subplot(1,4,3)
imagesc(holo(c).newPhase(196:241,300:380));
set(gca,'YDir','normal');
axis image
subplot(1,4,4)
imagesc(holo(c).newPhase(5:350,380:460));
set(gca,'YDir','normal');
axis image
figure
subplot(1,4,1)
plot(mean(holo(c).newPhase(5:350,400:450)),'LineWidth',2);
axis square
ylim([2.95 3.35])
title('Area 1')
subplot(1,4,2)
plot(mean(holo(c).newPhase(295:330,180:275)),'LineWidth',2);
axis square
ylim([2.95 3.35])
title('Area 2')
subplot(1,4,3)
plot(mean(holo(c).newPhase(196:241,300:380)),'LineWidth',2);
axis square
ylim([2.95 3.35])
title('Area 3')
subplot(1,4,4)
plot(mean(holo(c).newPhase(5:350,380:460)),'LineWidth',2);
axis square
ylim([2.95 3.35])
title('Area 4')

[profile,xTop,yTop,xBottom,yBottom] = ...
weightedLineProfile(holo(c).newPhase,100,358,435,185,10,
true);
figure
```
plot(profile, 'LineWidth', 2)
axis square
disp('X')
X = 400:450;
Y = mean(holo(c).newPhase(5:350, 400:450));
[P1, S] = polyfit(X, Y, 1);
Error = sqrt(diag(inv(S.R)*inv(S.R'))).*S.normr.^2./S.df;
P1(1)
Error(1)
X = 180:275;
Y = mean(holo(c).newPhase(295:330, 180:275));
[P2, S] = polyfit(X, Y, 1);
Error = sqrt(diag(inv(S.R)*inv(S.R'))).*S.normr.^2./S.df;
P2(1)
Error(1)
X = 300:380;
Y = mean(holo(c).newPhase(196:241, 300:380));
[P3, S] = polyfit(X, Y, 1);
Error = sqrt(diag(inv(S.R)*inv(S.R'))).*S.normr.^2./S.df;
P3(1)
Error(1)
X = 380:460;
Y = mean(holo(c).newPhase(5:350, 380:460));
[P4, S] = polyfit(X, Y, 1);
Error = sqrt(diag(inv(S.R)*inv(S.R'))).*S.normr.^2./S.df;
P4(1)
Error(1)
disp('Y')
X = 5:350;
Y = mean(holo(c).newPhase(5:350, 400:450), 2)';
[P1, S] = polyfit(X, Y, 1);
Error = sqrt(diag(inv(S.R)*inv(S.R'))).*S.normr.^2./S.df;
P1(1)
Error(1)
X = 295:330;
Y = mean(holo(c).newPhase(295:330, 180:275), 2)';
[P2, S] = polyfit(X, Y, 1);
Error = sqrt(diag(inv(S.R)*inv(S.R'))).*S.normr.^2./S.df;
P2(1)
Error(1)
X = 196:241;
Y = mean(holo(c).newPhase(196:241,300:380),2)';
[P3,S] = polyfit(X,Y,1);
Error = sqrt(diag(inv(S.R)*inv(S.R')).*S.normr.^2./S.df);
P3(1)
Error(1)
X = 5:350;
Y = mean(holo(c).newPhase(5:350,380:460),2)';
[P4,S] = polyfit(X,Y,1);
Error = sqrt(diag(inv(S.R)*inv(S.R')).*S.normr.^2./S.df);
P4(1)
Error(1)
figure
subplot(1,4,1)
plot(mean(holo(c).newPhase(5:350,400:450),2),'LineWidth',2);
axis square
ylim([3.02 3.35]);
title('Area 1')
subplot(1,4,2)
plot(mean(holo(c).newPhase(285:340,180:275),2),'LineWidth',2)
axis square
ylim([3.02 3.35]);
title('Area 2')
subplot(1,4,3)
plot(mean(holo(c).newPhase(196:241,300:380),2),'LineWidth',2)
axis square
ylim([3.02 3.35]);
title('Area 3')
subplot(1,4,4)
plot(mean(holo(c).newPhase(5:350,380:460),2),'LineWidth',2);
axis square
ylim([3.02 3.35]);
title('Area 4')

H.2.2. weightedLineProfile

function [profile,xTop,yTop,xBottom,yBottom] = weightedLineProfile(...
    img,x1,y1,x2,y2,width,plotOn)
profile = 0;
xTop = 0;
6  yTop = 0;
7  xBottom = 0;
8  yBottom = 0;

9  if x1 == x2 || y1 == y2
10     %% Straight
11     if x1 == x2 && y1 == y2
12         profile = 0;
13     else if y1 == y2
14         profile = mean(img((y1-width):(y1+width),... 
15                     min(x1,x2):max(x1,x2)),1);
16         xTop = [x1 x2];
17         yTop = [y1+width y2+width];
18         xBottom = [x1 x2];
19         yBottom = [y1-width y2-width];
20     if plotOn
21         figure
22         imagesc(img);
23         set(gca,'YDir','normal');
24         colormap('gray');
25         hold on
26         plot(xTop,yTop,'r--');
27         plot([x1 x2],[y1 y2],'r-');
28         plot(xBottom,yBottom,'r--');
29         hold off
30         axis image
31     end
32  else if x1 == x2
33      profile = mean(img(min(y1,y2):max(y1,y2),... 
34                     (x1-width):(x1+width)),2);
35      xTop = [x1+width x2+width];
36      yTop = [y1 y2];
37      xBottom = [x1-width x2-width];
38      yBottom = [y1 y2];
39      if plotOn
40         figure
41         imagesc(img);
42         set(gca,'YDir','normal');
43         colormap('gray');
44         hold on
45         plot(xTop,yTop,'r--');
46         plot([x1 x2],[y1 y2],'r-');
47         plot(xBottom,yBottom,'r--');
48     end

hold off
axis image
end
end
end
end

else

%% Inclined

%% Finding slop and intercept for primary and perpendicular line
slope = (y2-y1)/(x2-x1);
perpendicularSlope = -1/slope;
% intercept = y1 - slope*x1;
perpendicularIntercept = y1 - perpendicularSlope*x1;

%% Calculating begining x-coordinates for width parameter
xWidthPoints = (x1-width):(x1+width);
% line from x1,y1 along the perpendicular
% calculate the end coordinates at width distance from x1,y1
% floor and create list
%0 = (1 + a2^2)*x2^2 + (2*a2*b2 - 2*x1 - 2*a2*y1)*x2 + x1^2
% + b2^2 + y1^2 - d^2 - 2*b2*y1
a = (1 + perpendicularSlope^2);
b = (2*perpendicularSlope*perpendicularIntercept - 2*x1 -
  2*perpendicularSlope*y1);
c = x1^2 + perpendicularIntercept^2 + y1^2 - width^2 -
  2*perpendicularIntercept*y1;
d = b^2-4*a*c;

%first solution
s1 = (-b+sqrt(d))/(2*a);

%second solution
s2 = (-b-sqrt(d))/(2*a);

%creating x-coordinates and corresponding y-coordinates
%these are the begining x and y for the parallel lines width
distance from
%the primary line
perpendicularXPoints = min(round(s1),round(s2)):max(round(s1),round(s2));

perpendicularYPoints = perpendicularSlope*
    perpendicularXPoints +...
    perpendicularIntercept;

xPoints = min(x1,x2):max(x1,x2);
profile = struct('points',{});

if plotOn
    figure
    imagesc(img);
    set(gca,'YDir','normal');
    axis image
    colormap('gray');
    hold on
    plot([x1 x2],[y1 y2],'r-');
    hold off
end

%% Calculating weighted profile for each line
for i = 1:length(perpendicularXPoints)
    if x2 > x1
        tempXPoints = perpendicularXPoints(i):(perpendicularXPoints(i)... + length(xPoints) - 1);
    else
        tempXPoints = (perpendicularXPoints(i) - length(xPoints)... + 1):perpendicularXPoints(i);
    end
    tempYPoints = slope*tempXPoints + perpendicularYPoints(i)
    ...
    - slope*perpendicularXPoints(i);

%stay within the image (truncate to positive integers)
t1 = tempXPoints;
t2 = tempYPoints;
tempXPoints = zeros(1,length(t1(t1>=1)));
tempYPoints = zeros(1,length(t1(t1>=1)));
count = 1;
for m = 1:length(t1)
    if t1(m)>=1 && t2(m)>=1
tempXPoints(count) = t1(m);
tempYPoints(count) = t2(m);
count = count + 1;
end
done

if plotOn
  if i == 1
    xTop = tempXPoints;
yTop = tempYPoints;
    hold on
    plot(xTop,yTop,'r--');
    hold off
  else if i == length(perpendicularXPoints)
    xBottom = tempXPoints;
yBottom = tempYPoints;
    hold on
    plot(xBottom,yBottom,'r--');
    hold off
  end
end

% interpolate the value
% the line passes through two y-coordinate matrix indices
% the percentage of the line in each box is used to weigh the
% contribution to the value used. For a slope of 1 only 1 matrix
% indices is passed through and this is used
profile(i).points = zeros(size(tempXPoints));
for j = 1:length(tempXPoints)
  if floor(tempYPoints(j)) == tempYPoints(j)
    profile(i).points(j) = img(tempYPoints(j),
    tempXPoints(j));
  else
    up = img(ceil(tempYPoints(j)),tempXPoints(j));
down = img(floor(tempYPoints(j)),tempXPoints(j));
    profile(i).points(j) = ((ceil(tempYPoints(j))... - tempYPoints(j)))*up + (tempYPoints(j)... - floor(tempYPoints(j)))*down)/1;
  end
%% Averaging the results of the profiles

tprofile = zeros(size(profile(1).points));
for i = 1:length(profile(1).points)
    c = 0;
    for j = 1:length(profile)
        c = c + profile(j).points(i);
    end
    tprofile(i) = c/length(profile);
end
profile = tprofile;

H.2.3. scaleToPercent

function output = scaleToPercent(input)
output = input(:) - min(input(:));
output = output / max(output(:));

H.2.4. rms

function b = rms(a)
b = sqrt(sum(a(:).*conj(a(:)))/length(a(:)));
Glossary

**Silicon Nitride (SiN<sub>x</sub>)**
A low-stress and strong membrane material made from a Si-rich recipe, giving a non-stoichiometric silicon nitride. 5, 6, 8, 10–14, 33, 34, 39–42, 45, 46, 48, 62, 67–69, 71, 79–84, 87–90, 93, 95–99, 101–108, 111, 114, 116, 117, 120, 123–125, 128, 129, 131, 141, 145, 153, 156, 169, 171, 172, 175, 192, 217

**Silicon Oxide (SiO<sub>2</sub>)**
A naturally occurring mix of oxygen and silicon. Silicon oxide is also the main component in glass.. 8, 10, 12, 33, 34, 81, 116–118, 121

**7-up bath (7-up)**
A chemical cleaning process involving sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). This is not to be confused with the soft-drink of the same name.. 41

**Amorphous Silicon (amorph-Si)**
Amorphous silicon. This silicon is completely amorphous with no significant crystal structures. 76, 99, 107, 110–113, 117–119, 141, 175

**Reactive Ion Etch (RIE)**
An advanced etching technique using a charged plasma of ions accelerated towards the surface with a potential drop. The etch is part physical and part chemical. This etching method uses alternating etching and passivation steps to protect the sidewalls and allow for high aspect ratio etching.. 81, 87, 99, 107, 108, 175

**gold (Au)**
A pliable chemically inactive metal. 5–9, 34, 58–61, 68, 71, 81, 92, 93, 128, 167

**Buffered Hydrofluoric Acid (BHF)**
A mixture of ammonium fluoride (NH<sub>4</sub>F) and hydrofluoric acid (HF) used to etch oxides. The HF is buffered in the NH<sub>4</sub>F to reduce the etch rate. 41

**cleanroom**
A clean environment where the particle density in the air is extremely low. A
class 100 cleanroom has 100 particles of diameter 0.5 µm or less per cubic foot of air. There are no or extremely few particles which are larger. 33, 34, 39, 40, 45, 48, 81, 98, 107, 116

**Coefficient of Thermal Expansion (CTE)**
The measure of volume increase as a function of temperature. 34, 40

**Electron beam (e-beam)**
The electron beam is, in this work, the beam of coherent, focused electrons generated by an electron-optics setup in a scanning electron microscope or a transmission electron microscope. iii, 9, 20, 29, 52, 55

**Electro-chemical scanning-electron-microscopy cell (EC-SEM cell)**
A special setup for a scanning electron microscope. This setup allows direct imaging of the liquid inside the setup with the electron microscope. It also allows electrical connection to the liquid. The liquid can be exchanged easily. iii, 6, 13–15, 20, 23–33, 39, 44, 45, 49, 53–55, 58, 60–62, 67, 71

**Electron microscopy (EM)**
A method using electrons to image micron and sub-micron scale objects. 6, 20

**Environmental Scanning Electron Microscope (ESEM)**
A variant of the Scanning Electron Microscope which uses differential pumping and a gaseous detection device to detect the secondary or backscattered electrons and image the sample. 6, 13, 19, 62

**Environmental Transmission Electron Microscope (ETEM)**
A variant of the Transmission Electron Microscope which uses differential pumping to separate the sample from the electron source, optics and detection. 6, 13, 19, 75

**Focused Ion Beam (FIB)**
A tool for imaging and milling in samples in the SEM. A focused ion beam accelerates heavy ions onto the substrate and measures the result, much like the SEM. The damage with FIB is much more extensive and it is frequently used to mill patterns in samples or to remove enough of the sample so it can be used in TEM. 14, 15, 65, 68, 69, 71

**Hexadimethyldisilazane (HMDS)**
Also called bis(trimethylsilyl)amine, is a surface treatment which makes the surface hydrophobic and improves adhesion of resist. Chemical formula: $\left[\text{(CH}_3\text{)}_3\text{Si}\right]_2\text{NH}$. 40
Potassium Hydroxide (KOH)
An anisotropic silicon etch. This etch has different etch rates on different crystal planes. On a <100> wafer this means that a square will create a pyramid depression. 8, 11, 14, 15, 34–41, 76, 79–81, 83–85, 87–90, 93, 97–100, 102, 107, 108, 110, 111, 114, 120–123, 141, 146, 157, 171, 172

Low Pressure Chemical Vapour Deposition (LPCVD)
An advanced deposition technique similar to PECVD, but performed at low pressure. 40, 87, 111

Nanoparticles (NPs)
A small solid particles with a diameter between 1 nm and 100 nm. 8–10, 12, 16, 81, 92, 93, 95, 128

Polydimethylsiloxane (PDMS)
An easy to use polymer which can be moulded to various structures and with various stiffness. The chemical formula is $\text{CH}_3[\text{Si(CH}_3)_2\text{O}]_n\text{Si(CH}_3)_3$ where $n$ is the number of monomers. 13, 24, 26, 27, 29–31, 44, 71

Poly-crystalline Silicon (poly-Si)
Poly-crystalline silicon. This silicon consists of multiple grains each with a separate crystal orientation. 14, 81, 82, 84, 93, 96, 98, 99, 103, 105–108, 113, 117, 119, 120, 122–124, 141

Platinum (Pt)
A noble metal. 6, 13, 16, 34, 42, 58, 59, 71, 114, 146, 160

RCA clean (RCA)
A multi-step chemical cleaning process designed to remove metallic and organic contaminants. The process uses water (H$_2$O), hydrogen peroxide (H$_2$O$_2$), ammonium hydroxide (NH$_4$OH), hydrochloric acid (HCL) and, optionally buffered hydrofluoric acid (HF). Werner Kern developed it while working for the Radio Corporation of America. 40

Reactive Ion Etch (RIE)
An advanced etching technique using a charged plasma of ions accelerated towards the surface with a potential drop. The etch is part physical and part chemical. 40, 87, 90, 120

Scanning Electron Microscope (SEM)
An electron microscope which operates by sending electrons into the sample and measuring the resulting secondary electrons. The sample is scanned in a
raster scan to create an image. iii, 2–5, 11, 13, 14, 19, 20, 23, 24, 26, 27, 29, 

**Silicon (Si)**
A common microfabrication material. 6, 11, 14, 15, 34, 39–41, 82, 84, 87, 88, 
90, 92, 97, 104, 107, 111, 116, 120, 145, 153, 169, 192

**transmission electron microscope (TEM)**
An electron microscope which operates by sending electrons through the sample. 
iii, 2, 3, 6–12, 14, 16, 20, 33, 75–81, 84, 90, 92, 93, 95–97, 105, 106, 110, 111, 
113, 120, 121, 125, 129, 131, 141, 142

**Titanium (Ti)**
An extremely strong metal. 114
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