Development of Metallic Electrodes on KBr

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Contents

Abstract ix

Résumé x

Acknowledgements xi

1 Introduction 1

1.1 Introduction and Motivation ........................................ 1

1.2 Atomic Force Microscopy ........................................... 2

2 Experimental Apparatus 6

2.1 Experimental Setup ........................................... 6

2.1.1 Preparation Chamber .................................... 8

2.1.2 Main Chamber ........................................... 9

2.2 Stencil system design ........................................... 12

2.3 Mask holder design ........................................... 14

2.4 Sample holder design ........................................... 17
3 Mask Fabrication

3.1 An Introduction to Microfabrication Techniques ............... 20
3.1.1 Silicon Wafers ........................................ 20
3.1.2 Photomasks ........................................... 22
3.1.3 Chemical Etching ....................................... 24
3.1.4 Characterization ....................................... 30
3.1.5 Oxidation Furnace ..................................... 31

3.2 Stencil Mask Development ..................................... 32
3.2.1 Introduction ........................................... 32
3.2.2 Process Flow ........................................... 33
3.2.3 Etch Mask Design ....................................... 34
3.2.4 Boron Doping .......................................... 41
3.2.5 Measuring Dopant Concentrations ......................... 45
3.2.6 Silicon Membranes ...................................... 47
3.2.7 Focussed Ion Beam Milling .............................. 48

4 Metal Films .................................................. 53
4.0.8 High Vacuum Evaporation Sample Holder ................. 54

4.1 Gold on KBr .............................................. 57
4.2 Tantalum on KBr .......................................... 64

5 Conclusions .................................................. 69
5.1 Conclusions ................................................ 69
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2 Outlook</td>
<td>70</td>
</tr>
<tr>
<td>A Tylan Tube Recipes</td>
<td>72</td>
</tr>
<tr>
<td>B Mask and Sample holder Design</td>
<td>74</td>
</tr>
<tr>
<td>C Original stencil mask design</td>
<td>80</td>
</tr>
</tbody>
</table>
# List of Figures

1.1 Schematic of AFM imaging using a beam bounce detection method .

2.1 JEOL 4500A - UHV AFM, STM, SEM .

2.2 AFM cantilever holder, the clip on top holds the cantilever chip with the lower pins and side contact providing the electrical contacts to the sample. The white material below the clip is the piezo material used to oscillate the chip.

2.3 AFM tip, imaged under SEM at 18000X magnification.

2.4 Geometric considerations for evaporation through a small openings.

2.5 The mask holder with representative stencil in the middle. A approached and retracted mask with sample holder in the evaporation position are shown.

2.6 The mask holder components. a) rear part, with connection to the transfer arm, b) rails and forward piece, c) central sample holder, d) pieces assembled. The different colors denote different functional parts of the piece.

2.7 An exploded view of the sample holder.

2.8 The assembled UHV sample holder.

3.1 Positive and negative photoresist etch mask.
3.2 SEM image taken at an angle of a side mounted 525 µm thick silicon piece. Etched in 25 % TMAH timed etch, with (111) and (110) directions indicated. The wafer cross-section with cleaving marks are shown ................................................................. 25

3.3 Cleaved edge of a 100 oriented rectangular feature etched in 25% TMAH at 85 °C ................................................................. 26

3.4 20 µm silicon dry etch of large area features using trench etch recipe . 29

3.5 Stencil mask Design Process Flow .................................................. 35

3.6 Etch simulation for 100 oriented gap using ACES - white features denote the original mask file ....................................................... 37

3.7 Full wafer after membrane creation. The crosses to each side are the mask alignment marks, not the preetch alignment marks. Also shown are the snap off marks, rails, membrane hole, and chip numbering. Numbering below each chip are shallow etched rectangles to allow the chips with different size features to be distinguished . ................. 38

3.8 Micromachined silicon stencil pieces with the two stencil masks shown. a) the contact pad stencil with the 100 µm masking beam indicated and shown in side view by SEM, b) the membrane stencil with the pyramidal membrane opening shown adjacent ................................. 39

3.9 Measured dopant profiles as a function of depth for 1 h diffusion @ 1150 ° C ................................................................. 43

3.10 Measured vs theoretical dopant profiles as a function of depth for 2 h diffusion at 1150 ° C, profile measured using spreading resistance . . . 46

3.11 Silicon membranes created using boron etch stop, 2 h diffusion at 1150. Coloration due to back light, but variation in color at least partly due to different thickness in that region. ....................................................... 47

3.12 Desired features attempted on the silicon membrane using FIB. 1) Extends directly through the membrane, and overlaps the contact pads, 2) thins the membrane in the centre, 3) the nm scale features. Features are machined in this order. ....................................................... 49
3.13 500 nm thick silicon nitride membrane etched in FIB with 5 nA beam current. The machined lines are indicated, features, with 2 pairs of similar features. The lines radiating outwards are shards of the membrane, much like a pane of glass. ................................. 50

3.14 Prototypical features etched with FIB in a shallow etch on a 12 µm membrane. SEM image 54° angle of shallow structures. ............... 51

4.1 The sample holder and cleaving station for the high vacuum evaporator. Colored bands are due to layers of evaporated tantalum and gold. a) the sample holder with a KBr sample, b) the cleaving station, screws at the back, not shown, hold the sample holder in places for scribing and cleaving. .................................................. 55

4.2 The mask clamp for the high vacuum sample holder. ................. 56

4.3 The mask clamp with a silicon stencil clamped to an air cleave KBr sample .................................................. 57

4.4 SEM images of gold films 20 nm thick on KBr. All films heated up to 150 C for 1 hour, and masked with a 100 µm tungsten wire. a) 9.7 Å /min, b) 2.4 Å /min ................................. 59

4.5 AFM images of 20 nm gold films on KBr. a) 9.7 Å /min, pre-heating b) 9.7 Å /min, post-heating, c) 2.4 Å /min, pre-heating, d) 2.4 Å /min, post-heating. All samples heated up to 150 C for one hour. ............ 60

4.6 SEM of gold film deposited at 10 Å /min, but not heated following deposition. The mask clamp was used to hold a 100 µm wire to the surface. .................................................. 61

4.7 600 x 600 nm UHV AFM image of gold on KBr. The spiral and circular shapes, highlighted by the gold islands along the step, are thought to be caused by water damage to the surface. The image is taken at a low coverage region of a sample masked with a 100 µm wire. ............ 62

4.8 SEM of 5 nm tantalum film deposited at 0.8 nm/min. a) The edge of the masked region, using a 100 µm wire to mask the sample, b) Zoom of buckling region, this symmetry appears characteristic of regions where there aren’t large steps. .................................................. 65
4.9  Air AFM of 5 nm tantalum film deposited at 0.8 nm/min. a) 100x100 µm image b) 40x40 µm image 66

4.10  SEM of 2.5 nm tantalum film deposited at 0.42 nm/min masked using a silicon stencil mask, non-uniformities in the bridge region due to poorly removed residual silicon layer. a) 70 x = 1.4 mm, white feature is a part of the holding clip ,b) 3000x = 33µm, c) 2700x = 37µm 68

B.1  Central Body of the maskholder 74

B.2  Mask Rails 75

B.3  Rear part of the Mask holder 76

B.4  Ceramic insulator and wings 77

B.5  Sample holder base piece 78

B.6  Metallic clips to sample holder 79

C.1  Original features designed for the stencil mask, to be etched in RIE prior to the membrane etch from the backside 80

C.2  A partially completed example of the original etch mask features with a zoom of the area where the electrode would be, in this case only the oxide is patterned. 81
List of Tables

3.1 Measured etch rates for various silicon planes in TMAH [18] 27

3.2 RIE etch gases and reactive compounds for three common materials, reproduced in part from Fundamentals of Microfabrication: M. Madou [17] 29

3.3 Measured (100), (111) etch rates for 6 inch wafers measured in different experiments, single and double side polished 37

3.4 Calculated opening sizes and the theoretical final size given a specific etch ratio for mask openings used on the membrane photo mask 40
Abstract

A system for the deposition of metallic electrodes on KBr under ultra-high vacuum conditions has been designed and fabricated. Stencil masks and membranes 4-5 µm thick are fabricated on silicon chips have been created using wet etching in tetramethyl ammonium hydroxide (TMAH) with a boron etch stop. A holding system for UHV has been designed and built with a modified sample holder for performing electrical measurements on samples. The UHV system contains an AFM, STM, and SEM for surface examination and characterization. The growth of metals on KBr was examined using a separately constructed sample holder under high vacuum. Examination of 2.5 and 5 nm tantalum and 20 nm gold films using AFM and SEM revealed significant differences in the film growth and quality. Tantalum films appeared to be continuous, though possessing significant buckling whereas gold films have significant voids and poor edge definition around simple masks.
Résumé

Un système a été conçu et fabriqué pour permettre la déposition d’électrodes métalliques sur un substrat de KBr en Ultra-Haut Vide (UHV). Les masques gabarits et de membranes de silicium de 4-5 um sont fabriqués sur des pièces de silicium par gravure à l’eau-forte humide dans de l’hydroxyde d’ammonium tétra-méthyle (TMAH) avec un arrêt gravure à l’eau forte de Bore. Un système porteur pour UHV a été conçu et construit avec un porte-échantillon modifié pour permettre des mesures électriques sur les échantillons. Le système UHV contient un AFM, un STM et un SEM pour l’examen et la caractérisation des surfaces. La croissance de métaux sur KBr a été examinée en haut vide en utilisant un porte-échantillon construit séparément. L’examen de couches de tantale de 2.5 et 5nm et de couches d’or de 20nm par AFM et SEM ont révélé des différences significatives dans la croissance et la qualité du film. Les couches de tantale sont apparues continues bien que montrant un bouclage important, alors que les couches d’or ont des vides significatifs et une faible définition de bord autour de masques simples.
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Chapter 1

Introduction

1.1 Introduction and Motivation

The transistor is the basis for modern electronics, with a profound influence on the speed and operation of every device from digital to analog. The modern silicon based technology on which these transistors are based is rapidly approaching its technical limit. As the critical device dimensions approach the theoretical limits forced upon the system by quantum mechanics one is forced to look for alternatives to silicon transistors. As a result research groups are searching for viable alternatives which can minimize the size and power requirements for the modern transistor. The principle limitations upon transistor sizes are currently power consumption, discrete dopant effects, and electron tunneling through the gate oxide. The channel length of a transistor defines the discrete region between the drain and source controlled by the gate electrode. As this region decreases below 100 nm the gate oxide has been reduced to $< 3$ nm where tunneling creates significant leakage current and hence increased power consumption [2]. Molecular electronics offers an alternative to conventional silicon electronics where individual molecules or clusters of molecules are held between electrodes to act as individual transistors. This offers a possible solution to many of these difficulties as single molecules are nm in size, with a multitude of possible electronic configurations and nearly endless possibilities in terms of devices. Possible devices have been constructed by various research groups that contact either single
molecules or groups of molecules and exhibit non-linear current voltage characteristics, much like a modern transistor [3]. The difficulty in these experiments is a lack of reproducibility and poor agreement with theory. Relatively minor changes in the metal molecule contacts can lead to order of magnitude changes in the current voltage characteristics as the molecule to metal distance changes dramatically on an atomic scale [4].

In order to avoid these problems a knowledge of the atomic structure of the metallic contacts as well as a chemically pure surface are necessary. The focus of the work in this thesis will be a modifications to an ultra high vacuum system to deposit metallic electrodes in-situ with leads less than 50 nm wide using silicon membrane stencil masks. To do this requires modifying and redesigning the experimental apparatus to interface with this system as well as a stencil mask for the deposition of the metals. These will be discussed in the following chapters as well as preliminary results of metal deposition onto the chosen substrate. The research carried out within has taken place on a KBr substrate. This substrate can be created in vacuum with large atomically flat terraces and readily imaged. The microfabrication process to create the stencil masks will also be discussed.

KBr is an ionic crystal with a lattice constant of 6.6 Å and a cubic crystal structure like that of NaCl. Samples are prepared from a transparent single crystal block, which is cleaved in air to form a sample of the appropriate size and along the (100) direction. When properly prepared the sample surface can have atomically flat terraces which extent for microns separated by atomic steps of 3.3 Å . Both atomic and molecular resolution have been demonstrated simultaneously on the KBr substrate [5]. This gives an ideal surface to prepare electrodes in that low coverages, < 10 nm, can be used without fear of large steps causing breaks or dislocations in the traces.

1.2 Atomic Force Microscopy

In order to examine the metal electrodes in a largely insulating system one needs to be able to obtain atomic resolution on a non-conducting surface. This is achieved using an ultra high vacuum atomic force microscope (UHV-AFM). The experimental
1.2 Atomic Force Microscopy

apparatus for these experiments will be described in Chapter 2.

Atomic force microscopy is a technique first introduced by Binnig, Quate, and Gerber in 1986 [6] which employs a flexible cantilever acting as a force sensor to obtain a map of a surface via the interaction of the tip atoms with the surface. The cantilever is moved across the surface and the motion of the cantilever is typically observed through optical means to give a map of the height of the surface as a function of position as shown in Fig 1.1. In practice the actual position of the cantilever is less important than the feedback parameter used to maintain the current height, amplitude, or other variables. The position of the cantilever can be detected using a beam deflection technique as shown in the figure, optical interferometry, or other means not discussed here. Optical interferometry requires an optical fiber close to the back side of the cantilever which both emits and receives the beam. Slight variations in the distance to the cantilever are detected by the interference caused due to the change in path length. In contrast, beam bounce detection takes advantage of a reflective coating on the back side of the cantilever, and reflects the beam onto a photodiode where the shift in position is detected by the signal difference across the 4 quadrants.

To image a surface there are two principle modes, non-contact and contact mode. Contact mode imaging can have advantages but the possibility of the damaging the tip or surface are not to be risked for this experiment so only non-contact mode is to be considered.

Non-contact AFM can be either static or dynamic, with the cantilever simply moved across the surface at a fixed distance, or vibrated at or near its resonant frequency. Static imaging suffers from higher noise due to electrical or thermal noise. Dynamic mode imaging gives access to higher resolution imaging at the expense of simplicity. Frequency modulation, a particular implementation of dynamic mode imaging was introduced by Albrect and co-workers in 1991 [8] and involves oscillating the cantilever at its resonant frequency and measuring the shift in resonant frequency observed as a result of the forces acting on the cantilever. If $f_0$ is the natural resonant frequency, and $f = f_0 + \Delta f$ the frequency with the tip sample interaction. If the force gradient is constant over the oscillation amplitude then it can be simply shown that $\Delta f = \frac{f_0}{2k} k_{ts}$ by linearizing the interaction force where $k$ is the cantilever stiffness, and
1.2 Atomic Force Microscopy

Figure 1.1: Schematic of AFM imaging using a beam bounce detection method

$k_{ts}$ the gradient of the tip sample interaction. For more complicated force gradients or large amplitudes it is necessary to solve the differential equation over the full oscillation period. It has been demonstrated that this can be calculated as shown in Eqn 1.1[7] with $A$ the oscillation amplitude.

\[
\Delta f = \frac{f_0}{2k} \int_{-A}^{A} k_{ts}(z - q') \frac{\sqrt{A^2 - q'^2}}{\pi/2A^2} dq'
\]  

(1.1)

The forces responsible for the tip sample interaction have both long and short-range components. These can be summarized as van-der-waals, electrostatic, and chemical. At long range these forces are attractive, with the short range chemical repulsive forces kicking in at very small tip sample separation, less than a nm. One can simply
model these effects as shown in Eqn 1.2

\[ F_{vdW} = -\frac{A_H R}{6z^2} \]  

\[ F_{electrostatic} = -\frac{\pi \varepsilon_0 RU^2}{z} \]  

\[ F_{morse} = -E_{bond}(2\kappa e^{-\kappa(z-\sigma)} - 2\kappa e^{-2\kappa(z-\sigma)}) \]

where \( A_H \) is the Hamaker constant, \( R \) the tip radius, \( Z \) the tip sample separation, \( U \) the tip sample potential difference, \( \kappa \) the characteristic decay length of the chemical interaction, \( \sigma \) the equilibrium distance, and \( E_{bond} \) the bonding energy [7]. Van-der-Waals forces arise from the fluctuating polarization of tip and sample and is attractive. The electrostatic force is a combination of the contact potential difference of the tip and sample as well as any additional electrical potentials present. Electrostatic forces can be compensated for by applying a potential to the tip or sample to minimize the potential difference between the two, which is quadratic in \( U \). This is necessary to reduce the long range interactions and obtain the best possible resolution. Surfaces in NC-AFM are generally imaged in the attractive regime, with a tip sample separation greater than the advent of the hard repulsive chemical forces.
Chapter 2

Experimental Apparatus

2.1 Experimental Setup

The system in use for these experiments is a JEOL UHV 4500A AFM-STM-SEM. Experiments are ongoing to understand the growth characteristics of molecules and small metal clusters to this substrate in preparation for depositing electrodes.

The system has a series of two chambers, shown in Fig 2.1, as well as a loadlock for introducing the sample to vacuum. Both chambers are pumped using a separate ion and titanium sublimation pump with a turbo and roughing pump backing the loadlock for fast pump down when introducing samples. The base pressure of the main chamber is typically $2-3 \times 10^{-8}$ Pa, and $1-2 \times 10^{-8}$ Pa for the preparation chamber, measured using heated filament ion gauges. Samples are introduced by venting the loadlock to atmosphere, and pumping down with the turbo pump for at least 30 minutes to reach a pressure of $5 \times 10^{-6}$ Pa. The chambers are separated by a series of valves between the loadlock and preparation chamber, and between the preparation chamber and main chamber. Access to either chamber is controlled by means of a transfer arm with a spring clip and pin to mate with the parent holders for samples and tips. The transfer arms intersect at the turntable in the preparation chamber which has four positions for holding sample or tip boats with three of which have electrical contacts. The holders for samples and tips differ, with parent holders...
2.1 Experimental Setup

Figure 2.1: JEOL 4500A - UHV AFM, STM, SEM

capable of holding either a single sample or up to 2 tips. The AFM cantilever holder is shown in Fig 2.2. The tip is held at an angle relative to a vertically oriented sample and oscillated by the piezo element located under the chip. The STM tip holder differs in that the tip is held normal to the sample with no oscillation capability. The AFM tip holder is capable of applying a voltage to the tip through a clip isolated from the rest of the stage, separate from the voltage applied to oscillate the tip.

Samples and tips are moved from one chamber to the other using the principle transfer arm then moved from the parent holders the position on the stage via an elevator mechanism. The elevator uses a small pin to lift the sample or tip holder and linearly position it in front of the piezo or on the stage respectively.

In order to image objects on an atomic scale it is necessary to have excellent vibra-
ional stability. To this end, the microscope is located in the midst of a low vibration area housing the SEM cluster in the basement of the Wong building. The microscope itself is mounted on a vibration damping air table, with the room temperature actively controlled.

2.1 Experimental Setup

2.1.1 Preparation Chamber

The preparation chamber contains a number of deposition, characterization, and other sample preparation tools. The available tools are: Ar sputtering gun, LEED/Auger, quartz crystal microbalance, molecule evaporator, metal evaporator, sample cleaving station. The Ar sputtering gun allows for sample cleaning and material removal though has not be used for KBr samples which are soft and would be susceptible to both ionic and physical sputtering damage.

The LEED/Auger is a low energy electron diffraction and auger electron spectroscopy device [9] which can be used for looking at crystal structure and elemental composition over a small area. As this work is dealing principally with insulating materials it is difficult to accurately use LEED as the electron beam can cause significant charging and damage which obscures the crystal structure analysis.

The quartz crystal microbalance[10] is positioned on a movable bellows and can be placed in front of the sample position at an angle to calibrate the deposition rate of either the molecule or metal evaporators based on the mass deposited on the surface and the input density.

The two evaporators installed on the system both possess active water cooling during evaporation. The molecule evaporator [11] contains four separately cooled quartz pockets each capable of thermally evaporating a separate molecule at a fixed temperature. The evaporator possesses a shutter such that any individual or combination of individual pockets can be open or closed as desired. The rate is set by the evaporation temperature which is controlled by an electronic feedback unit as well as the source to sample separation. The metal evaporator however is a electron beam evaporator [12]. There are 4 separate pockets, but in this case each pocket contains a single metal rod or crucible with a nearby tungsten filament. The filament accelerates thermal
2.1 Experimental Setup

electrons to the target through a 2 keV bias voltage, causing melting and evaporation from the tip of the rod, or crucible. The evaporated material passes through a series of grids which focuses and filters the beam, allowing only neutral species to reach the target. The rate is controlled by the applied power to the filament and monitored by the ion current at the grids in conjunction with the quartz microbalance. High melting point materials like Ta and Pt can be used in rod form, lower melting point metals being placed in a crucible to avoid dripping as melting occurs.

The sample cleaving station is a simple block which can apply force to the top of a protruding sample. This allows one to create a clean surface in UHV from an externally prepared sample. For samples prepared ex-situ, it is possible to cleave the KBr block in air using a razor. The sample is first scribed to define the breaking plane, then snapped off or directly cleaved using the razor and a hammer. The sample quality depends on how well the original block is oriented and secured, the quality of the initial scribe, and the presence of any cracks or imperfections in the block. Following cleaving the sample is heated by a specially built heating holder at 1.6 A for 1 hour, reaching a temperature of 150 °C.

2.1.2 Main Chamber

The main chamber is used for imaging with AFM, STM, and SEM. Samples are transferred to clips in front of the piezo scanner where they can be accessed by spm tips, a low power optical telescope, or scanning electron microscopy (SEM). As well, the main chamber contains a low temperature cryostat for cooling samples to 30 K using liquid helium and nitrogen. The spm tips are mounted in front of the sample on a retractable stage with the laser diode and quadrant photodetector. The stage is mechanically controlled with a motorized approach mechanism and is capable of up to 400 μm travel in each direction, whereas the laser diode and mirror are moved by hand through a spring and screw system. Only the AFM capabilities will be discussed here though in principle the STM mode is identical in terms of methodology.

The piezo tube on which the sample is mounted controls the tip sample separation as well as the lateral position of the tip during scanning motion, with a maximum 1.4 μm Z range and 5 μm X and Y limits. The piezo element on the tip holder oscillates the
2.1 Experimental Setup

Figure 2.2: AFM cantilever holder, the clip on top holds the cantilever chip with the lower pins and side contact providing the electrical contacts to the sample. The white material below the clip is the piezo material used to oscillate the chip.

cantilever at its resonant frequency. To approach the sample the mechanical motors move the cantilever to a close approach. As the tip sample interaction increases close to the sample the frequency shift will increase, causing the approach to stop. All further motion is controlled by the piezo tube. The position of the cantilever is inferred in real time using the reflection of the laser off the back of the cantilever onto the photodetector. The motion of the cantilever, vertically or tortionally register as differing signals in the detector, A-B for normal motion with C-D for lateral motion. The resolution of AFM imaging is limited by the tip used. Commercially available tips are used with resonant frequencies from 150 - 300 kHz and tip radii as small as 10 nm or less. An example of these tips is shown in Fig 2.3. This image is taken with a cantilever mounted ex-situ and imaged with a high vacuum SEM.

The main chamber also houses the SEM column. Imaging with SEM involves scanning a focussed beam of electrons across the sample and collecting scattered and secondary
2.1 Experimental Setup

Figure 2.3: AFM tip, imaged under SEM at 18000X magnification

electrons at a fixed detector. The SEM is focussed upon the sample position and
is capable of 50-200000X magnification, giving a resolution down to 10 nm. The
accelerating voltage is 0.5 - 12 kV, though typically an accelerating voltage of 10 kV
is used for most applications, with a current of less than 100 uA. The principle usage
of the SEM in situ is to examine cantilevers and tips for size, defects, and tip quality.
In this work, it is also used to examine metal films on KBr, and in future to position
the AFM relative to deposited metal features. Like the LEED, while in principle it is
necessary to look at conducting surfaces with the SEM, in practice one can examine
metallic layers on these surfaces with minimal charging effects. The SEM column is
isolated from the the main chamber when not in use by a valve and pumped by a
separate ion pump at the rear of the chamber.

All UHV measurements in this system typically take place in the main chamber,
eventually to include stencil depositions as well. The design of the pieces to do these
measurements, as well as the motivation for why this route was taken are discussed
in the following section.
2.2 Stencil system design

In order to perform electrical measurements on molecules it is necessary to have an electrically isolated sample holder as well as a mechanism for approaching the stencil mask to the sample. As evaporation in UHV is a ballistic process, the geometry of evaporation through a small feature is as shown in Fig 2.4. Assuming $X \gg x$, it is simple to show that $W \approx L + (x/X)S$ and $W - w \approx L \pm (x/X)S$. For typical source sizes on the order of 1 mm, $X = 10\,\text{cm}$, $L = 100\,\text{nm}$, and $x = 1\,\mu\text{m}$ one finds that the evaporated feature size is 110 nm or 10 nm larger than projected. On the other hand with a mask to sample separation of 1 mm the evaporated feature size grows to $10.1\,\mu\text{m}$. Clearly, contact between the two must be carefully controlled to avoid spreading of the incident beam.

Figure 2.4: Geometric considerations for evaporation through a small openings
There are a number of possible solutions for performing this sort of patterning. For silicon samples it is relatively easy to pattern this sort of substrate using the microfabrication techniques to be described later. The problem is that these techniques are totally unsuitable for an ionic crystal like KBr, which would dissolve in the solutions needed. Another possibility is to use small holes in a silicon cantilever to guide the evaporation of metals on the surface [13]. The advantage of this would be that it uses the positioning capabilities already existing in the system to perform the evaporation across micron scale regions. The difficulty is that the 5 micron range of motion of the piezotube would only be sufficient to create the central features of the mask, still requiring the creation of the contact pads and traces prior to this. As well, the capability to evaporate in the main chamber would have to be added and the possibility of metals coatings affecting other sensitive parts of the system was deemed too much of a risk. What this leaves one with is to either create the desired features using some sort of evaporation mask in situ, or use a different substrate and create the features ex situ, with a cleaning process to remove contaminants. The former was chosen, partly because the capabilities currently exist to move a sample around in the system, as well as the cleaving station previously described. The mask and sample holder modifications will be described first, then in Chapter 3 the micromachining techniques to create the stencil masks themselves will be discussed.

A system for holding the mask was designed, with 2 rails for holding the mask with room to both approach and retract the mask from the sample surface. As the prep chamber already contains 2 transfer arms capable of 360° rotation and linear motion it was decided that these would provide a sufficient capability to hold a simple tool to move the sample in and out, not described here. The mask holder would be held either on the sample stage or with the transfer arm using the same holding mechanism as the current devices in system. In order to make measurements without breaking vacuum the sample holder would have to be capable of holding a sample during cleaving, having clips attached to the electrodes after evaporation, and pass a current through the sample from the connecting clips. The mask holder design will first be discussed, followed by the sample holder.
2.3 Mask holder design

The mask holder must be capable of interfacing with the transfer arm and sample stage as well as holding a silicon stencil and the sample holder. The former define the rear of the mask holder, much like the parent holders currently in use in the vacuum system, while the latter are completely redesigned. Similar to the sample holder, the piece is made from stainless steel, largely 316L, low carbon stainless. To create an insulating layer for possible future electrical contacts a Macor spacer is used. A three dimensional projection of the design is shown in Fig 2.5. The design calls for the ability to transfer the freshly cleaved sample to the mask holder using the elevator, approach the sample with the stencil mask, and evaporate using the e-beam evaporator. The mask holder is be loaded with the mask ex-situ then introduced into the vacuum chamber. The mask is approached to the sample by means of the rails, but held in place using very light copper beryllium clips. This will put the mask in direct contact with the sample and minimize distortion of the features due to separation effects. It is anticipated that in order to hold the sample away from the surface some sort of spacer, possibly 1 $\mu$m polystyrene beads, will be used. The effect on the feature size should be minimal. The minimal feature size should then be determined by the microfabrication of the stencil mask features.

The primary space constraint is the outer size of the cylindrical forward part of the sample holder, traditional parent holders for this system have an outer diameter of 18 mm. As the holder must fit through a similar opening on the turntable this is an absolute upper limit on any protruding features. A rail to rail distance of 8 mm was chosen to allow the sample space, as well as sufficient room on the stencil mask for the sample. This makes a number of tolerances relatively tight. The design schematics are shown in Appendix B. After design the first part of the piece, that which connects to the transfer mechanism, was machined in Basel along with the sample holder base. The forward parts connecting to the stencil and sample holders, including the wings and insulating disc, were machined at McGill. Due to the small feature sizes, most of the pieces must be machined by hand as the computer controlled milling machine is not suited for mm scale work in stainless. All pieces are currently complete and are shown in Fig 2.6. Tapping M1.6 or M2 holes in stainless is difficult, one is liable to easily break the taps so appropriate care must be taken in choosing the appropriate
2.3 Mask holder design

Figure 2.5: The mask holder with representative stencil in the middle. A approached and retracted mask with sample holder in the evaporation position are shown.
2.3 Mask holder design

drill size. For M1.6 holes it was found empirically that 1.4 mm or number 49 drills provide the best tap with least risk of breaking the piece or having a loose thread. The design for the central pieces and rail holders have changed several times as difficulties in machining were discovered. The main difficulty is that machining small pieces of stainless, less than 1 mm wide such as the rails, is apt to cause the pieces to bend or warp while machining. The rate at which pieces can be machined by hand is also limited by how well the piece can be cooled as a great deal of heat is generated, rapidly dulling the tool and destroying the finish of the piece. These factors need to be taken into account in machining small stainless pieces.

Figure 2.6: The mask holder components. a) rear part, with connection to the transfer arm, b) rails and forward piece, c) central sample holder, d) pieces assembled. The different colors denote different functional parts of the piece.
2.4 Sample holder design

There are several different sample holder types available within the UHV system, designed for either flat samples approximately 7 mm long and less than one mm thick, or crystalline blocks up to 2 mm thick which are cleaved in situ. The cleaving holder designed to hold the latter is entirely metal, with two set screws below the sample. The holder allows vacuum cleaving of the the KBr blocks as described above. The disadvantage with this holder is that it is impossible to make any form of electrical connection through the clips that hold the sample holder to the system. Since conductance measurements of the molecules are required one needs a way of insulating the metallic clips from the base of the sample, unless the bulk of the sample holder is constructed out of a non-conducting material. Since a significant amount of force is applied to the sample during cleaving a metal base is required with insulating ceramic spacers made of Macor [14]. The assembly is held together using H77, a vacuum compatible high temperature epoxy [15]. The glue is used to bond the base piece, to the ceramic spacer, and to the metallic clip holders. The metal clips used to connected to the sample are designed and made with copper beryllium.
2.4 Sample holder design

foils. The assembled device is shown in Fig 2.8, with an exploded view of the parts and design shown in Fig 2.7. The abrasions visible on the contact pads are due to the manufacturing process and are easily removed.

Stainless steel is used for the clip holders and body. The coloration is due to high temperature baking in air at up to 500 °C during assembly to remove the epoxy and fix a flaw in the initial assembly. The screw sizes are M1 and M1.6. The body of the sample holder was machined at the University of Basel, Switzerland, with the clips, and ceramic pieces created at McGill. The schematic diagrams are shown in Appendix B [16]. In order to contact the sample a pair of copper beryllium clips are to be used. Since the sample is cleaved in vacuum the clips will have to be attached without removing the sample holder. The space underneath the sample holder is designed to allow the clips to lock into place without touching behind the sample, and apply a small amount of force to the metallic film.

![Figure 2.8: The assembled UHV sample holder.](image)

In order to do electrical measurements the sample can either be held in the turntable
in the preparation chamber or the measurement position in the main chamber. In either region the sample is contacted by a separate isolated clip on each side through the pads on the sample holder. For making electrical measurements with a third contact it would be possible to do the measurement in the main chamber using an AFM tip as a third contact to bias the molecule.
Chapter 3

Mask Fabrication

3.1 An Introduction to Microfabrication Techniques

3.1.1 Silicon Wafers

In Chapter 2 the mask and sample holder design were discussed. To use the capabilities of these pieces to evaporate electrodes on a sample requires a thin stencil mask with openings to accommodate the rails but small enough to fit into the available space. The maximum possible dimensions are 11.5 mm horizontally, up to 16.5 mm vertically, and up to several millimeters thick. The difficulty is in creating a structure where nanometer up to millimeter size features are present and structurally stable. Standard machining tools are capable of creating metals structures as small as 10's of micrometers, however, to evaporate features less than 100 nm wide, an opening of similar order is required. This necessitates a different sort of fabrication, which naturally lies within the capabilities of silicon micromachining. The following sections will discuss silicon micromachining in order to explain the techniques and reasoning behind the design and construction of the stencil masks followed by some examples of the devices constructed.

The construction of the stencil mask requires a number of techniques first devel-
An Introduction to Microfabrication Techniques

Developed in the electronics industry for the production of silicon based microelectronics and later applied to the creation of Micro Electrical and Mechanical Systems or MEMS. These techniques are based on the processing of ultra flat silicon wafers of various widths and thicknesses, typically 4 or 6 inches in diameter and 525 $\mu m$ or 675 $\mu m$ thick respectively. Wafers are grown several different ways, one common method being the retraction of a rotating crystalline seed from a vat of high purity liquid silicon. This is known as the Czolchralski crystal pulling method [17]. The result of this process is a long single crystal silicon rod from 1-12 inches in diameter. Silicon crystals grow in a diamond lattice and the wafers are oriented along specific crystal planes. The typical wafer orientation is along the (100) plane with the flat parallel to the (110) plane. This direction is determined by the orientation of the crystalline seed used to start the process and the precise direction of the wafer dicing. Wafers along the (110) and (111) directions are also available though used less often.

Sectioning and polishing after growth produces wafers with a surface roughness of less than a micrometer on the unpolished side and less than 2 nanometers on the polished side. The purity of the wafers is generally deliberately decreased by adding dopants such as phosphorous or boron to the mix to increase the conductivity of the wafer and create either a P or N type substrate with a dopant level on the order of $10^{15}$ to $10^{16}/cm^3$. These wafers provide the basic substrate for materials ranging from electronic devices to mechanical actuators and gears.

As MEMS and silicon microelectronics require features with critical dimensions on the order of micrometers the presence of dust and other particles are a major hazard. Hence all machining of this type takes place in a clean room, where the clean room class gives the maximum number of particles greater than 0.5 $\mu m$ in size per cubic foot of air. The McGill Microfabrication facility, or microfab, has been rated as class 100 in the lithography room and 1000 in the etching and deposition room. All users in the clean room facilities are required to wear covering gear to avoid contamination due to skin flakes and take other precautions to avoid introducing contaminants into the facility. Surfaces are kept clean and a powerful air filtration system keeps the particulate count down. The tools described in the following section are all in the McGill microfab, with the exception of the focussed ion beam at the Sherbrooke and Ecole Polytechnique facilities.
3.1 An Introduction to Microfabrication Techniques

3.1.2 Photomasks

In order to create structures on a silicon wafer it necessary to transfer a pattern from software to the the silicon surface itself. The essential requirement for one to do this is to use some form of mask to protect the bulk of the wafer while selectively attacking exposed areas with chemical etchants. The method used to create the desired pattern on the wafer is to use a form of photosensitive polymer, or photoresist (PR) to mask a silicon oxide layer grown thermally on the outside of the wafer. After patterning the PR, the oxide can then be patterned and will serve as a robust etch mask for the silicon. The photoresist is exposed to 436 nm UV light through an opaque mask, then developed with a solution that will selectively remove either the exposed or unexposed resist. There are a number of photoresists in use but all fall within the two basic categories of positive and negative PR. Positive resists are insensitive to the developing solution except in the exposed areas whereas negative resists create a stable block when exposed, but are otherwise washed away. This is shown in Fig 3.1.
To create micrometer or smaller features each step in the process much keep the feature size and quality intact from the previous masking step. The photomask which exposes the PR must itself be created with preceding steps such that it contains similar quality features. At present there are two principle methods available at this facility for creating photomasks: in house photomasks created using high resolution transparencies, and outsourced masks by companies such as Adtek. The former option involves creating the mask on a standard graphics program like Adobe Illustrator and printing with a sufficiently high resolution printer, in this case 5500 dpi at a local printing company. The resolution limit of these masks is on the order of 20-30 μm. With a dot spacing of approximately 5 μm features close to the resolution limit have significant line roughness issues. The transparency is sandwiched between a quartz plate coated with chrome and positive PR, and another glass plate. This plate is exposed to UV light, then developed to remove the exposed PR. A chrome etchant then removes the chrome in the now exposed areas, and the remaining PR is removed in acetone. Alternatively, commercial masks can be created using an electron beam to selectively expose the photoresist with significantly smaller less than 100 nm features. In either case, the quartz and chrome mask can then be used to selectively expose the PR on the surface of the wafer.

Wafers must be coated with photoresist before UV exposure through the mask. Either the Spinball site coater and developer or the manual Bitek R&D spinner are used for this process and Shipley 1813 positive photoresist is currently used. The wafer is held by a vacuum chuck and PR dispensed then spun at 3950 rpm for 30s. Following this, the wafer is baked at 115 °C for 1 minute to harden the photoresist. The photoresist deposited is 1.4 μm thick, though this varies from run to run depending on the precise dispense pressure on the photoresist cannister. The thickness can vary from 13800 to 14700 Å thick though the variation is limited to ± 0.5 % on a given wafer. The quality of the PR coat decreases with very deep structures, producing streaks and non-uniformities towards the outside etch of the wafer. This will have an impact on multiple masking steps but is not an issue in this research.

The mask and wafer are positioned within several micrometers or in hard contact with each other to avoid diffraction effects. Light is passed through the mask to the photoresist coated wafer for several seconds. With the available optical exposure tool, an EVG 620, the size limitation is approximately 0.5 μm due to diffraction of
the 436 nm light used. For higher resolution it is necessary to use focussed electron beams to expose the resist. The wafers are developed by coating with the developing solution then rinsing the wafers with deionized water while spinning at several thousand revolutions per minute (rpm).

All the masks discussed in this thesis have been created on-site and as such have minimum feature sizes on the order of 30-40 \( \mu m \). For applications with large features this doesn’t pose a significant problem. The 20-30 \( \mu m \) limitation on the feature sizes with this method is partly as a result of the care taken in creating the mask. When clamping the quartz plate and transparency together even a series of relatively small bubbles can create voids where the mask will be overexposed. At smaller feature sizes this problem becomes more significant. The wavelength limitation, and mask to wafer positioning are not crucial for alignment, however, the alignment to the wafer orientation is, as will be discussed shortly.

After using the PR to pattern the oxide or other etch mask on the wafer it is relatively simple to remove, either with acetone or using an oxygen plasma in a process known as ashing. For simplicity’s sake, the openings created in the oxide will now be referred to as the mask size unless otherwise noted. For features of the size discussed here the pattern transfer from mask to oxide can be regarded as essentially perfect.

### 3.1.3 Chemical Etching

To create arbitrary structures from these wafers a series of etchants are applied. The most common methods are wet chemical etching and reactive ion etching (RIE). Common masks are thermally grown silicon oxide, photoresist, or metals. Photoresist as a polymer is not generally resistant to most wet etchants but is sufficient for some dry etch processes. Wet chemical etchants are oxidizing solutions such as KOH, tetramethyl ammonium hydroxide (TMAH), or ethylene diamine pyrocatechol (EDP). The wet etchant used at the McGill microfabrication facility for silicon is TMAH for its low toxicity and extremely low attack rate on silicon oxide etch masks [18]. For silicon oxide etching hydrofluoric acid (HF) is used.

TMAH is a highly anisotropic etchant which preferentially attacks silicon along cer-
3.1 An Introduction to Microfabrication Techniques

Figure 3.2: SEM image taken at an angle of a side mounted 525 µm thick silicon piece. Etched in 25 % TMAH timed etch, with (111) and (110) directions indicated. The wafer cross-section with cleaving marks are shown.

tain crystal planes. The relevant planes for the etch process are the ⟨100⟩, ⟨110⟩, ⟨311⟩, ⟨411⟩, and ⟨111⟩ directions. As the wafer is typically oriented along the ⟨100⟩ with the wafer flat along the ⟨110⟩ direction, any features which are perpendicular or parallel to the flat will intersect with a slow etching ⟨111⟩ direction by default. These two planes then define the bulk of the etch directionality. Of the other planes, the ⟨411⟩ and ⟨311⟩ constitute fast etching directions, which need to be taken into account for some processes where more complicated geometries are of interest such as undercutting islands to form tips. For simple geometries as are used here however it is unnecessary to consider these planes. This anisotropy in the etch process leads to structures characterized by common geometric configurations like those shown in Fig 3.2. The structure displayed is a pit formed by a long etch in TMAH at 85 ° C. The sloping sidewalls are the ⟨111⟩ planes which intersect with this opening at a 54.74 ° angle and etch significantly slower. While the oxide opening defines the etch shape,
the top of the opening will be slightly larger as a result of the non-zero (111) etch rate in TMAH. In order to obtain deep features which possess vertical sidewalls, one can either use (110) or (111) oriented wafers which will not be discussed, or align the openings with the (100) wafer direction at 45° to the wafer flat. An etch of this type is shown in Fig 3.3. As both the sides and bottom of the feature are aligned with the (100) direction they etch at the same rate outwards as down. As a result, the size of the features etched must be $W = w + 2Z$ where $w$ is the mask opening, and $Z$ the etch depth. This can pose a significant problem if etching through an entire wafer but can be advantageous for undercutting certain structures. The other disadvantage of this approach is shown as the (111) corner planes which are visible at each corner of the feature. These planes grow over time until the original feature is replaced by a (110) oriented rectangle with tapering ⟨111⟩ planes. There are techniques to compensate for the corner planes found while using this orientation [22] however it requires a significant amount of experimenting and the techniques are highly etch rate dependent.

Figure 3.3: Cleaved edge of a 100 oriented rectangular feature etched in 25% TMAH at 85 °C
3.1 An Introduction to Microfabrication Techniques

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>% TMAH</th>
<th>(100) µm/h</th>
<th>(111) µm/h</th>
<th>SiO₂ Åh</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>20</td>
<td>15</td>
<td>0.7</td>
<td>12</td>
</tr>
<tr>
<td>80</td>
<td>15</td>
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<tr>
<td>90</td>
<td>20</td>
<td>43</td>
<td>1.4</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 3.1: Measured etch rates for various silicon planes in TMAH [18]

Measured etch rates depend strongly on the solution purity, temperature, lifetime, circulation, and precise wafer orientation. In practice, wafer orientation has a tolerance of ± 1° or less depending on the manufacturer. [20]. The temperature and concentration dependence of TMAH has been measured by a number of groups [18, 23] but in practice it has been shown that it is not reliable across etch solutions and should be measured with each etch if precise etch times are required. It seems probable that the principle reason for this, assuming the etch bath is filled to a similar depth, temperature, and is fresh, is that the wafers themselves differ slightly in doping level and orientation. The 1° difference possible due to wafer growth is sufficient to cause slight variations in the etch rate due to the different planes exposed. This may also be a result of a lack of agitation in the solution, for which there are some plans to work around via magnetic stirring or some other means. For reference, in experiments with TMAH Merlos et al. have measured the rates for the (111) and (100) directions as well as thermal oxide [18] at various temperatures and concentrations and give the numbers in Table 3.1. These rates have also been measured at the McGill microfabrication facility for various etch planes [21]. The features to note are the non-zero (111) etch rates, the decreasing etch rate at higher concentration, and the decrease in (100)/(111) etch ratio at higher concentration. The etch ratio is significant as the etch ratio for KOH, on of the other most common etchants, is around 400 - 600 and the etch rate is up to 50% higher [17]. As a result, typical designs and simulations simply regard the (111) etch rate as zero, which in the case of a long TMAH etch will have significant problems. Some etch rates experimentally observed will be discussed in the following sections. The simplest and most effective procedure for measuring the etch rate of the (100) direction involves a several hour pre-etch on the pattern to be etched into the wafer. The holes etched into the silicon are then profiled and the depth used to calculate an etch rate for the sample. Another practical consideration in the current setup is the bath temperature and mixing. The TMAH bath used has
3.1 An Introduction to Microfabrication Techniques

a series of heating coils, and active cooling for recondensing the evaporated material. The temperature control unit allows temperature control to within a degree Celsius, however it is limited to a temperature of 85 °C for safety reasons. Measured etch rates will be given in the section on stencil mask design.

Silicon oxide etching with HF is simpler in that it is an isotropic etchant however the handling requires more care. HF is extremely hazardous, with significant damage to both bone and skin upon contact so full safety gear and proper rinsing is crucial. As well, HF will attack glass, metals, and some plastics. The etch rate for 10 % HF on thermally grown silicon oxide is approximately 200-250 Å /minute, with an etch rate of less than a few Å/hour on the silicon substrate. For example, a 48% HF solution at room temperature has a silicon etch rate of 0.3 Å/min [17].

The main disadvantage in wet silicon or oxide etching solutions are that it is difficult to create vertical sidewalls in features and the etch chemistry is not easily tunable. While (100) oriented features can produce vertical sidewalls, there is still the difficulty of corner planes. Reactive ion etching can get around this difficulty. As well, in a reactive ion etch chamber it is simple to selectively pattern photoresist covered oxide, in a fashion that would not be possible in HF without coating both sides of the wafer.

The full discussion of reactive ion etching, or reactive plasma etching is beyond the scope of this thesis and more information can be found in a number of sources [17][19]. The essential mechanism of the process is relatively simple. Etch gases are released at low pressure in a vacuum chamber containing the sample of interest. A plasma is created which acts to dissociate some of the chemical species into highly reactive ions and accelerate them to the surface of the wafer. At the wafer, the ionic species react in a highly anisotropic fashion giving the desired vertical sidewalls whereas the undissociated species reach the surface and diffuse to react in an isotropic fashion. The balance between the two can be controlled by the RF power applied to create the plasma, the gas flow, and the gas mixture. Common gases and the associated species used to etch the processes are shown in Table 3.2, however the precise mix is strongly recipe dependent.

The microfab contains a 4 chamber Applied Materials 5000 RIE for dry etching processes. The specific etch gases used in the recipes currently used are \( CHF_3 \), Ar,
and \( CF_4 \) for oxide etching and \( HBr, NF_3 \), and an \( He - O_2 \) mix for silicon etches. For the processes described in this research the major use of the RIE is to etch the oxide openings through a photoresist mask. The observed etch rate in the recipe used is 3900Å/min for 6 inch wafers. For smaller wafers or pieces there are significant non-uniformities, probably due to the contact between the carrier, typically a pre-etched 6 inch wafer used to hold the smaller pieces, and the instrument. As a result the outside of the wafers tends to etch significantly faster for 4 inch wafers in comparison to the center and longer etch times are necessary. The tool is designed for relatively short etches on the order of minutes which limits the ability to etch the entire 675 µm.

<table>
<thead>
<tr>
<th>Material</th>
<th>Etch Gases</th>
<th>Reactive Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Flourine or Chlorine based</td>
<td>( F, Cl, Cl_2 )</td>
</tr>
<tr>
<td>SiO₂</td>
<td>( CF_4, CHF_3, C_2F_6, C_3F_6 )</td>
<td>( CF_X )</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Chlorine Based</td>
<td>( Cl, Cl_2 )</td>
</tr>
</tbody>
</table>

Table 3.2: RIE etch gases and reactive compounds for three common materials, reproduced in part from Fundamentals of Microfabrication: M. Madou [17]

Figure 3.4: 20 µm silicon dry etch of large area features using trench etch recipe
thick wafer as the etch time would be many hours. The etch recipe currently used for silicon etching is designed for trench etches, or small area etches meant to etch deeply. In practice this translates to poor performance on larger area etches as a result of heavily loading the etch gases, redeposited material, and other effects. For an example of this refer to Fig 3.4. This recipe is designed for trench etching. When used on mm size openings it caused a significant surface roughness, tall mounds of material, and a clearly non-vertical edge. This serves as and example of how significantly one would need to adjust the recipe parameters to fully take advantage of a dry etch tool. The same recipe on narrow features, less than 10’s of microns, can produce extremely vertical trenches several micrometers deep.

3.1.4 Characterization

In order to fine tune any of the processes described above it is necessary to take advantage of the characterization tools in the microfab. The principle tools used are the profilometer, film thickness measurement tools, optical microscopy, and sheet resistance measurement probe. For profiling, a Tencor P1 profilometer with a 5 $\mu$m radius tip is used. This is a simple contact probe for profiling up to 13 or 300 $\mu$m with 1Å or 25 Å resolution respectively. In practice the surface roughness during etching can be as much as 100 Å or more even on a polished wafer so this is not a significant limitation. The film thickness measurement tools are designed for measuring the thickness of photoresist, oxide, or other thin films on silicon by spectroscopic reflectometry[24]. Given the appropriate indices of refraction of the film under examination, the tools can measure thickness down to 100 Å . In particular there are two tools: a Nanospec 2100 Film Thickness Monitor for doing single point measurements, and a Prometrix Film Thickness Mapper for doing multi point averaged measurements over a whole wafer. The former has the advantage of targeting specific areas with a beam several hundred micrometers across but is more difficult to calibrate and doesn’t give average measurements. The latter is a newer more self contained unit which allows better statistics but is less useful for wafers with numerous features or specific areas to look at. Lastly, the M-Gage 300 Sheet Resistance Monitor can be used to monitor metal film deposition, or wafer doping levels by measuring the sheet resistance of the material in a non-contact mode. Sheet resistance gives a direct measure of the doping
level of a wafer as will be discussed in more detail shortly.

### 3.1.5 Oxidation Furnace

In order to mask the wafer from the TMAH etch it is necessary to have a sufficiently thick oxide layer to withstand the full etch. Growing oxide on silicon wafers can be accomplished either by wet or dry oxidation at high temperatures. The facility contains a Tylan 4 Stack Furnace with facilities for up to 4 different processes including oxidation, boron diffusion, nitride deposition, and polysilicon. The tubes have integrated electronics to program and control the gas flows, temperatures, and mechanical movement of the wafer holder. This allows one to set the temperature ramp speed, currently set to either 5 or 10 °C/min for 4 and 6 inch wafers, and the push in and pull out rates which are on the order of 2-4 inches/min for 10 minutes. The difficulty in setting the push in and pull out rates is that they are set by calibration potentiometers on the machine which appear to be different for each tube. It has been found that a rate of 2-3 inches/min is accomplished with a software setting of 4 on the boron furnace tube and 12 on the oxidation tube. While introducing wafers the furnace is held at 625 °C for 6 inch wafers and 800 °C for 4 inch wafers to avoid warping of the wafers due to excessive temperature gradients.

Dry oxidation used a pure oxygen environment, whereas wet oxidation processes add hydrogen to the furnace tube to enhance the reaction rate. Wet oxidation times are significantly shorter and hence this is typically the process used unless very thin oxides are necessary. Native silicon oxide grows quite easily in air, a layer up to 20 Å thick can grow within several days though ceases thereafter. In order to continue growth the wafer must be at temperatures somewhere between 650 and 1250 °C. The oxidant, be it water or O\textsubscript{2} diffuses through the top layer of oxide to the surface and recombines with the silicon at the interface to form SiO\textsubscript{2}. The diffusion is limited both by the temperature and the current oxide thickness. It can be shown that the oxidation for areas greater than several hundred angstroms can be modeled by the Deal-Grove Model, with the solution given in Eqn 3.1.

\[
d = \frac{A}{2} \left[ 1 + \frac{t + \tau}{A^2/4B} \right]
\]  

(3.1)
\[ A = 2D \left( \frac{1}{ks} + \frac{1}{h} \right) \]
\[ B = \frac{2DC}{N_1} \]
\[ \tau = \frac{d_i^2 + Ad_i}{B} \]

\( t \) is the oxidation time, \( k_s \) the silicon oxidation rate constant, \( h \) the gas phase mass transport coefficient, \( D \) the diffusion coefficient, \( C \) the equilibrium oxidant concentration in the oxide, \( N_1 \) the number of oxidant molecules per unit oxide, and \( d_i \) the initial oxide thickness[19]. In the process of growing the oxide, roughly 46 % as much silicon is consumed at the interface. Prior to growing an oxide silicon wafers are highly hydrophobic, growth of any oxide on a wafer, even as small as several Å will give a wafer a hydrophilic coating. A sample oxidation recipe for 5000 Å of oxide grown at low temperatures is shown in Appendix A.

### 3.2 Stencil Mask Development

#### 3.2.1 Introduction

The goal in this work is to develop the ability to deposit metallic leads on an insulating surface in-situ. As discussed in Chapter 2, a system for holding the stencil masks in the vacuum system and positioning relative to a sample holder has been developed. The masks to deposit these metals have been developed in parallel.

The principle requirement is to create the metallic pads large enough to easily contact in vacuum but with traces small enough to be broken in order to create gaps. The stencils themselves must be part of an integrated silicon structure capable of being removed from the wafer intact and holding the stencils on the rails described in section 2.3. In order to deposit materials through a stencil mask an experimentally observed requirement from other experiments using stencil evaporation is that the aspect ratio must be < 2 or 3, feature size to membrane width [25, 26]. This means that for features less than 100 nm across, a membrane of less than 300 nm is required to avoid blocking the openings during deposition. This requires a membrane
of this order thickness and some means of fabricating the opening. It was decided to create a series of 2 masks, one with the contact pads and a gap less than 100 µm between, with the second containing a small membrane to create the smallest features. The openings in the membrane are to be created with a focussed ion beam, in a fashion demonstrated by a number of groups [13, 27, 28] for creating stencil masks for deposition. Using membrane based stencil masks for resistless deposition has been demonstrated repeatedly in recent years [13, 27, 28, 29, 30, 31]. Using FIB machined stencil masks, features as small as 70 nm or less have been demonstrated [13], and using electron beam lithography on nitride membranes features as small as 15-20 nm have been demonstrated [29]. The membranes used in the experiments referenced above are low stress silicon nitride membranes on a silicon substrate. The membranes demonstrated in this thesis have been created with a boron doped etch stop in silicon. This has the advantage of a lower stress and strain from deposited material and simpler processing but has disadvantages of stress or strain due to the boron interstitials and less control over the precise membrane thickness. For silicon membranes the electron beam etching technique would require additional, possibly destructive, steps and the necessary facilities for e-beam lithography on the substrate. It is however a possible alternative to the FIB approach in future for small size features where the FIB machining becomes limited to approximately 40 nm due to the inherent spot size and other beam effects.

3.2.2 Process Flow

Planning a MEMS device requires a detailed process flow in order to anticipate as many of the possible problems at any given step. Individually, the processes detailed in the preceding sections are simple in implementation, however initially unanticipated problems can arise when these steps are performed in conjunction with a number of other steps on a given wafer. Shown in Fig 3.5 are the basic design steps used in the creation of the stencil mask and membrane. The other stencil mask which does not require the boron doping process, described in Section 3.2.4, differs only in steps 5-8. After removing the oxide from the initial pre-etch in step 5 the wafer is immediately re-oxidized as in the latter half of step 8. For simplicity’s sake, the steps shown in the process flow are compressed from that of a typical design process flow.
3.2 Stencil Mask Development

For example step two, which is the process of patterning the wafer with the photo mask, should be broken into a series of up to three steps. In practice these would be: coating the bare silicon wafer with photoresist, exposing the photoresist to UV light through the photomask, developing exposed regions using a chemical developer. In between each step indicated on the process flow there are also necessary characterization steps to ensure the oxide thickness is as expected, to inspect for defects, to ensure that the oxide fully etches while patterning the etch mask, and that the optical exposure and develop has fully removed the photoresist from the openings. These characterizations are typically performed using an optical microscope, the nanospec measurement tool, or the prometrix film thickness monitor.

What is also not indicated on the process flow is the FIB processing step which takes place after the membrane creation. This process described separately in Section 3.2.7.

3.2.3 Etch Mask Design

Planning etch structures in anisotropic etchings can require a significant amount of simulation and planning. For designs with large scale features oriented parallel to the wafer flat and non-interacting etch planes there is relatively little need to simulate the etch, simple knowledge of the etch rate and a back of the envelope calculation will give the desired behavior. For more complicated etches, or when trying to understand how to approach the design there are tools for doing etch simulations of greater and lesser flexibility. Many of these packages are designed for industry and are not affordable for lab research or do not fit the needs of a flexible research environment creating MEMS devices. There are some simple alternatives, either design and implementing an etch simulator from scratch, or simple tools like ACES, from the University of Illinois [32].

ACES is a simple 3 dimensional simulator which allows importing of 2-dimensional mask files and will etch a surface while accounting for certain basic etch directions: (100), (110), (311), (111). Given the limited number of etch planes, results pertaining to complicated undercut structures such as tips should be treated with caution, but for simple simulations these are sufficient.

The goal for the stencil masks is to have a wafer design with snap off marks to separate the pieces, holes for the rails to support the pieces, and either a membrane
Figure 3.5: Stencil mask Design Process Flow

1. Thermally Oxidize Wafer - 5000A
2. Coat with PR, expose with photomask - pre-etch alignment marks
3. Etch oxide - 2 min in RIE
4. Strip PR in oxygen plasma, dip in HF to remove thermal oxide, etch 2 h in TMAH @ 85 C, 25%
5. Strip Oxide in HF, push in furnace @ 625 C to obtain thin (several Angstrom) oxide
6. Coat with boron impregnated film (Borofilm 100 - Emulsitone) - bake 20 min @ 200C
7. Drive in boron @ 1150 C for 2 hours - ~4-5 um deep
8. Strip film in HF, 15 minutes - thermally oxidize 950 C for 2.5 hours
9. Coat with PR, expose with photomask - aligning to the previous etch
10. Etch Oxide - 2 min in RIE
11. Strip PR in oxygen plasma, dip in HF to remove thermal oxide, etch 20+ h in TMAH @ 85 C, 25%(depends on thickness, and etch rate, check rate after 3 hours)
12. Strip oxide in HF - ~30 minutes
3.2 Stencil Mask Development

or large openings with a masking beam in the middle. The snap off, or cleaving marks, are shallow features etched into the wafer that allow the pieces to be snapped out of the wafer as a single piece. The snap off or cleaving marks are for the purpose of breaking the silicon pieces apart by hand without the need for precise cleaving of each piece. Narrow trenches etched by RIE or v-grooves etched by (110) oriented rectangles that are several hundred micrometers deep are the alternatives which have been examined. The rails holes must be approximately 1 mm across by 4 mm tall in the smallest dimension, though the top of the features will be significantly larger as discussed below. The alternative for the rails is either vertically oriented features with corner planes or rectangular features but with (111) sidewalls as shown in Fig 3.3. For the actual stencil mask, the alternative is to either put all features on a single membrane, or put small features, less than a few hundred microns, on a membrane on one chip with the larger features etched directly into a second silicon chip. The latter approach was chosen, with the former approach discussed briefly in Appendix C.

If oriented along the (110) direction, all openings must necessarily be larger than the final desired bottom opening by \( \sqrt{2} Z \left(1 - \frac{1}{R_{100/111}}\right) \) where \( Z \) is the etch depth, and \( R \) the etch ratio of the (100) to (111) direction. For a wafer 675 \( \mu m \) thick, this means an opening 954 \( \mu m \) wide is required for the final opening to be 0 \( \mu m \) wide, if one ignores the (111) etch. Shown in Table 3.3 are measured etch rates for different experiments. Etch rates as high as 30 \( \mu m/h \) have been observed with a fresh TMAH bath. Something which was not appreciated at first is that the wafers must be etched in HF for several seconds to remove any environmental oxide grown or the measured etch rates will not be representative. As shown previously, even an oxide layer of 20 Å could slow the etch for as much as an hour depending on the temperature and concentration of the solution. While there should not be time to grow these oxides between patterning and etching, the ashing process involves elevated temperatures and an oxygen plasma so it may grow a small oxide.

If the mask features are instead oriented along the (100) directions then it is easier to make small features when etching from each side, but by definition all openings will etch outwards by the wafer thickness in each direction when etching through the wafer. In particular, for the cleaving marks, this proves to be an insurmountable difficulty, as the marks must be deep enough to allow the wafer to be snapped off but
Table 3.3: Measured (100), (111) etch rates for 6 inch wafers measured in different experiments, single and double side polished

<table>
<thead>
<tr>
<th>Wafer Information</th>
<th>(100) µm/h</th>
<th>(111) µm/h</th>
<th>$R_{100/111}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSP, no HF prior to etch, 675 µm wafer</td>
<td>24.1</td>
<td>2.3</td>
<td>10.5</td>
</tr>
<tr>
<td>SSP, no HF prior to etch, 675 µm wafer</td>
<td>25.3</td>
<td>3.6</td>
<td>7.0</td>
</tr>
<tr>
<td>DSP, HF prior to etch, 628 µm wafer</td>
<td>25.3</td>
<td>2.4</td>
<td>10.1</td>
</tr>
</tbody>
</table>

in this orientation they can only be created using an RIE trench etch. This limits the depth of the cleavage marks to 10’s of $\mu m$ using RIE which has proven to be unusable.

Thus if the features in the wafer are oriented along the (110) direction then creating a small gap in the center is impossible with simple etch features as all features will etch away from openings in the oxide. However the opposite is true for (110) oriented
features as openings will etch from either side to form an arbitrarily small gap, however the cleave marks will not work as discussed above. The solution is a combination of the two. If the cleaving marks and rail holes are oriented along the wafer flat, but a diagonal or (100) oriented gap is patterned then with careful control of the etch depth an arbitrarily small gap can be created. The simulation result for a (100) oriented gap in TMAH is shown in Fig 3.6. Given that the desire is to create openings through which metals can be evaporated but with a gap in the center it is clear that the remaining beam in Fig 3.6 can be timed to give a relatively arbitrary thickness. The gap between the contact pads and traces in the original design is 50-100 \( \mu m \). The gap between the contact pads defined by the beam is anywhere from 10’s of \( \mu m \) up to several hundred micrometers. The width is designed to vary across the surface of the wafer in increments in order to give a range of possibilities depending on the

Figure 3.7: Full wafer after membrane creation. The crosses to each side are the mask alignment marks, not the preetch alignment marks. Also shown are the snap off marks, rails, membrane hole, and chip numbering. Numbering below each chip are shallow etched rectangles to allow the chips with different size features to be distinguished.
Figure 3.8: Micromachined silicon stencil pieces with the two stencil masks shown. a) the contact pad stencil with the 100 $\mu$m masking beam indicated and shown in side view by SEM, b) the membrane stencil with the pyramidal membrane opening shown adjacent.
3.2 Stencil Mask Development

size of stencil used. Calculating the size of the beam is simply a function of the width of the original feature as follows \( B = W - 2Z \) where \( W \) is the opening size in the oxide and \( Z \) the etch depth of the wafer. Calculating the size of the membrane hole is more complicated as the (111) etch rate is more variable. Not knowing the (111) etch rate for a given etch ahead of time it is only possible to estimate the opening size required. The range of opening sizes and features used are shown in Table 3.4. The membrane openings and entire chips are shown in Fig 3.7, with no actual membranes. The range of sizes of the openings are designed to accommodate the possible sizes

\[
B = W - 2Z
\]

Where \( B \) is the opening size in the oxide and \( Z \) the etch depth of the wafer.

<table>
<thead>
<tr>
<th>Information</th>
<th>Original size (( \mu m ))</th>
<th>Final Opening Size (( \mu m ))</th>
<th>( R_{100/111} = 7.0 )</th>
<th>( R_{100/111} = 10.5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane hole</td>
<td>885</td>
<td>146</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td></td>
<td>910</td>
<td>171</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td></td>
<td>935</td>
<td>196</td>
<td>154</td>
<td></td>
</tr>
<tr>
<td></td>
<td>960</td>
<td>221</td>
<td>179</td>
<td></td>
</tr>
<tr>
<td></td>
<td>985</td>
<td>246</td>
<td>204</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1009</td>
<td>270</td>
<td>228</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1034</td>
<td>295</td>
<td>253</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>761</td>
<td>719</td>
<td></td>
</tr>
<tr>
<td>Rails</td>
<td>2000</td>
<td>1261</td>
<td>1219</td>
<td></td>
</tr>
<tr>
<td>Cleave Marks</td>
<td>1540</td>
<td>801</td>
<td>759</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1640</td>
<td>901</td>
<td>859</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4: Calculated opening sizes and the theoretical final size given a specific etch ratio for mask openings used on the membrane photo mask

of the masking beam separating the contact pads evaporated with the first mask. Given the uncertainty in the etch ratio it is currently not possible to pick a specific size and say with absolute certainty what the final opening size will be. For example, the membrane opening shown in Fig 3.8 b) corresponds to the 1009 \( \mu m \) opening and has a measured size of 245 \( \mu m \), compared to an expected size of 228 to 270 \( \mu m \). The critical feature size is the final opening size, not the mask size. Two possible rail hole sizes and cleave marks were designed for similar reasons.

The wafer orientation is known at best to within a degree so assuming the photomask alignment to the nominal wafer flat is perfect there is still some uncertainty in the actual etch directions. This will not significantly affect the etch positions for most
3.2 Stencil Mask Development

The structures as they are largely self aligning, with the etch holes picking the closest crystal planes despite the mask orientation. Misalignment will have some effect on features precisely aligned with a given etch orientation, (100) for example. To avoid any possible problems, wafers have been pre-etched with a mask containing a series of rectangular alignment marks created by Xuefeng Duan [33]. As these openings etch in TMAH a series of v-groove pits are created along the appropriate directions. This allows careful alignment to the actual (110) direction on the wafer, though clearly will not correct for misalignments out of the plane. What has been described is the silicon framework for both the stencil masks. The process to create the boron doped membrane will be described next.

3.2.4 Boron Doping

In order to create a membrane one must have a means of stopping the silicon etch at the correct time. This can be done either by means of a carefully timed etch with a known or measured etch rate, silicon on insulator wafers (SOI), electrochemical etch stops, use of other materials not etched by TMAH such as silicon nitride, or an etch stop in the silicon itself.

Timed etches suffer from difficult control of the precise depth, giving a control of $\mu m$ at best with typical etch rates. Silicon on insulator wafers have an oxide layer in between two silicon parts, with the upper silicon layer typically deposited on top of the oxide. This grants an automatic etch stop as soon as the TMAH hits the oxide, but as with any deposited layer there will be inherent stress or strain due to the mismatch of the adjacent films. Electrochemical etch stops rely on the fact that the etchants do not attack the oxide. For a lightly doped silicon wafer if there exists a PN junction within the wafer, and the wafer is reverse biased with respect to a reference electrode, then when the etch reaches the N type region the circuit is suddenly forward biased, injecting holes and oxidizing the silicon. This will stop the etch. The process requires a p-type wafer with an n-type dopant at the surface, however the process examined here is a p type dopant, with n-type wafers thus this etch stop is not applicable. The most popular method is the use of a nitride membrane, which will act like the SOI wafer in that the etch will abruptly terminate at this layer. The
difficulty lies in perfecting the nitride deposition. Typically low stress silicon nitride is used (<200 MPa), but even at these stresses it can be difficult to guarantee the strength of the membrane with large etched or machined openings. A 500 nm thick low stress nitride membrane purchased commercially [34] was tested with the original etch features under an RIE etch, shown in Appendix C. Upon breaking through the membrane separated and rolled up like paper. This may have been a result of either the inherent stress in the membrane, due to stress imposed during handling, or due to the large size of the opening. It is impossible to say on the basis of a single sample and given the limited number of membranes and the cost it was not feasible to investigate further. Instead attention was focussed on developing silicon membranes.

Doping of silicon wafers can be accomplished either by high energy ion implantation and annealing, or by temperature assisted diffusion from a solid or liquid source. Both processes create a sharp change in the dopant density of the silicon wafer, which directly affects the etch rate of certain chemical etchants. Due to ease of use and low cost it was decided to use a solid boron source to dope the wafers.

Boron doping as an etch stop has been demonstrated as a feasible method of creating highly doped silicon membranes [35, 36]. The thickness of the membrane is critically controlled by the depth of the boron implant which is in turn a function of the surface concentration, temperature, and time. In order to provide an etch stop, it is necessary to have an implanted dopant concentration $> 10^{20}/cm^3$. It has been experimentally demonstrated that the etch rate of TMAH for boron implanted silicon is approximately 10 times slower at this concentration [18, 37]. The rate decreases sharply with increasing concentration concentration above a threshold, with concentrations as low as $10^{19}/cm^3$ having a negligible effect on the etch rate. In order to obtain high concentrations in the region of interest one must understand what is occurring. A boron containing solution is spun onto the wafer at high speeds to obtain a highly uniform film. In order for the film to properly adhere to the film it is necessary to first clean the wafer of any environmental oxide in HF, then create a slightly hydrophilic surface. This can be accomplished either by growing a few angstroms of oxide at high temperatures or using a chemical solution such as sulphuric acid and hydrogen peroxide 4:1 (Pirani clean). It has been found that better results are given by the former, obtained by pushing the wafers into the furnace at an oxygen ambient for a minute. The difference in results typically manifests as a large variation of the doping
Figure 3.9: Measured dopant profiles as a function of depth for 1 h diffusion @ 1150 $^\circ$ C
density of the wafer surface. Chemically treating the wafer with a Pirani solution creates a form of chemically dirty oxide, this may account for the poor film adhesion and diffusion. A point to note is that the oxide thickness cannot be large as oxide itself acts as an excellent diffusion barrier to boron with a far higher diffusion rate than bulk silicon. The wafer is baked to solidify the source and remove any residual solvent. Heating the wafer to high temperatures in a furnace will then allow the boron to diffuse from the source into the wafer itself. The recipe for this is given in Appendix A. Temperatures above 1000 °C are necessary for any sizeable effect on the dopant concentration. The limit on the concentration of the boron is actually the solubility limit of the boron at the interface between silicon and the source. If one regards the source as an infinite boron source and the solubility at the surface as the solid solubility of boron in silicon it is possible to calculate the approximate depth of the boron implantation using a simple model. The solubility limit of boron at 1150 and 1200 °C are 2.4 and 2.9 x 10^20/cm^3 respectively[37]. As the necessary concentration and the solubility limit are relatively similar, a long diffusion time is necessary to reach 10^20/cm^3 below the surface.

One can calculate the diffusion depth and profile by starting with Fick’s second law as given in Eqn 3.2

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D \frac{\partial C(x,t)}{\partial x} \right]$$

(3.2)

where C is the concentration and D the diffusion coefficient [19]. If one assumes a constant diffusion coefficient as a function of distance then the form becomes significantly simpler and can be solved in a number of cases. However this is not entirely accurate at high concentrations, where diffusion is a function of concentration. Nevertheless, it is common to apply this model even when the conditions do not particularly apply. For more complicated models there is significant work in the literature [38, 19] on taking into account electrical effects due to the dopant gradient, defects, and impurities.

There are two simply solved cases, constant source and constant dose. With a constant source the boundary condition at the surface is held fixed at some constant concentration $C_0$. Alternatively, one can hold the total dose constant, by implanting or diffusing a certain amount of the dopant and then allowing it to diffuse into the wafer. It is also possible to combine both situations, with a constant source to dope
3.2 Stencil Mask Development

the surface of the wafer followed by a constant dose diffusion for a longer time after removal of a surface film. This work is most concerned with the constant source situation. There is a well known solution to the partial differential equation in the form of the complementary error function as given by Eqn 3.3.

\[ C(x, t) = C_0 \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \]  

(3.3)

\[ \text{erfc}(z) = 1 - \text{erf}(z) \]  

(3.4)

\[ \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2)dy \]  

(3.5)

Using the solid solubilities given above and D as a function of temperature \( D = D_0 \exp(-E/kT) \) with E the activation energy, 3.5 eV in this case, and \( D_0 \) the dopant specific coefficient, 1.0 \( \text{cm}^2/\text{s} \) for boron, one can calculate the profile as a function of depth for fixed times. The calculated and experimentally observed profile for a 2 hour diffusion at 1150 °C are shown in Fig 3.10. The calculated profile clearly differs from the observed profile in both character and depth, though the observed junction depth is similar. The junction depth is given by the point at which the dopant concentration reaches the background carrier concentration. The carrier type is not shown here, though is given in Fig 3.9. As well, it is not possible with an error function, or a gaussian distribution as would be expected for constant dose diffusion, to obtain a flat concentration region as shown in the experimental data.

3.2.5 Measuring Dopant Concentrations

There are a number of methods available to measure the carrier concentration for thick doping regions, spreading resistance and differential conductivity being two common ones [19]. One can specify either the resistivity of a sample which is a bulk property, or the sheet resistance in \( \Omega/\text{square} \). The resistance of a region of material is given as \( R = \rho L/A \) where \( \rho \) is the resistivity, L the length, and A the cross sectional area. If a square area is chosen this simplifies to \( R = \rho/t \) with t the thickness, which is known as the sheet resistance of the sample. To convert between the two all that is needed is the depth of the area of interest, which can be the entire wafer if homogeneous. The advantage of a sheet resistance measurement is that it is an area independent technique.
A 4-point probe measures resistance by passing a current through two leads and measuring the resulting voltage drop across two other leads, to avoid probe effects in the current leads. The resulting voltage and current can be converted to a resistivity of the sample by $\rho = (V/I)2\pi S$ where $S$ is the probe spacing[19]. Resistivity is given in terms of $\Omega \cdot cm$, this is also often the number quoted for a particular wafer with resistivities from 1-10 $\Omega \cdot cm$ being typical for the wafers used. Differential conductivity involves measuring the sheet resistance of the surface of the wafer using a 4-point probe, removing a layer of surface material, followed by another measurement and so on. In contrast, spreading resistance measurements involve using an angled cut of the sample with a 2 point probe at different heights to build up information of the sample. Spreading resistance can be simply looked at as taking a series of resistance measurements at different depths. To reconstruct the doping profile, one takes the incremental resistivity measured at each point and uses the known dopant
3.2 Stencil Mask Development

3.2.6 Silicon Membranes

A solid source boron dopant was used a number of times to create silicon wafers with an etch stop which were then etched from the opposite side. It should be noted that even with a reduction in the rate by a factor of 10 this process can hardly be considered an etch stop. A nominal rate of 0.5 $\mu$m/min translates into an etch rate of 50 nm/min in the etch stop region, which is itself about 3 $\mu$m thick. In several experiments the majority of the membranes were either overetched or broken in handling. Due to the delicate nature of the membranes, when rinsing after chemical etches or inserting into

Figure 3.11: Silicon membranes created using boron etch stop, 2 h diffusion at 1150. Coloration due to back light, but variation in color at least partly due to different thickness in that region.

density vs resistivity curves to reconstruct the dose. This can be converted to a sheet resistance by taking each measurement as a parallel resistance and inverting to get the net sheet resistance [39].
the etch baths it was found easiest to place vertically into the fluids to avoid pressing directly on the membranes. The critical point dryer was also attempted in drying the membranes. The difficulty with this was that the dryer uses a liquid carbon dioxide and alcohol mixture to displace any remaining water from the membranes and under certain circumstances a large amount of bubbling is observed. As the wafers must lie horizontal in the tool these bubbles are very destructive to delicate membranes. It was eventually decided that drying directly with low pressure nitrogen was sufficient. Once these handling procedures were fully understood, 2 boron doped wafers were created with a TMAH etch with one shown in Fig 3.11, though the other suffered from a significant misalignment of the etch direction and is unusable for a working device. The silicon membranes in the openings are of unknown thickness when first removed from the solution, as a good method to measure the membranes non-destructively has not yet been found. By breaking and measuring the membrane cross-section in SEM an approximate thickness can be found however. This was done with some of these pieces in the FIB as discussed below.

3.2.7 Focussed Ion Beam Milling

Focussed ion beam milling is used to create the nanometer scale features on the stencil mask membrane. Instruments capable of simultaneous FIB machining are available at both the University of Sherbrooke and Ecole Polytechnique, a LEO 1540 XB and an FEI XP dual beam system respectively. Ion milling is a subtractive process, removing material from the surface by accelerating ions from a liquid metal ion source (LMIS) towards the sample. The current of the beam can vary from 1 pA up to 10’s of nA, though in the instruments used in this work a beam current of between 2 pA and 5 nA is used. The beam diameter is a function of the current used, and can vary from nm to μm in size. At pA currents the beam diameter is a minimum of a few nm, though this does not necessarily correspond to the minimum feature size achievable. The beam consists of positively charged ions accelerated towards the sample with a voltage of 30 kV. The full mechanism of ion beam machining is beyond the scope of this thesis, but the basic mechanism is important. As the positively charged ions strike the sample surface the beam causes physical sputtering, where ions elastically interact with the surface and physically eject a significant number
3.2 Stencil Mask Development

Figure 3.12: Desired features attempted on the silicon membrane using FIB. 1) Extends directly through the membrane, and overlaps the contact pads, 2) thins the membrane in the centre, 3) the nm scale features. Features are machined in this order.

of atoms. As well, secondary electrons, phonons, photons, or secondary ions are created[40]. These processes, though important, are not responsible for the bulk of the milling observed. Actual material removal rates vary greatly from sample to sample based on the doping, material, and instrument but for the two FIB’s used for this work times of $1250 \text{s/} \mu \text{m}^3$ at 1 pA are typical. The time decreases linearly with increasing current, so a 1 nA current should require 1.25 s for 1 $\mu \text{m}^3$. The implications are clear for large features where the removal of a 10 x 10 x 10 $\mu \text{m}$ block would require about 17 minutes at 1 nA. This puts constraints on the feature size of interest. As the desire is to bridge a gap of around 100 $\mu \text{m}$, with a membrane depth of at least 5 $\mu \text{m}$ it is necessary to plan the pattern accordingly. The pattern attempted in the membrane milling is shown in Fig 3.12. With a current of 5 nA, it would be sufficient to machine through a silicon membrane of 5 $\mu \text{m}$ depth in roughly 7 minutes with these features. While machining it is possible to examine the area of interest by either using an integrated SEM, or by taking low current images with the FIB. The FIB can image scattered ions from the surface and ionized surface atoms, but it is a destructive process as surface material will be removed at a rate dictated by the current. For the smallest features a beam current of 30 pA or less is typically used which gives a reasonable balance between image contrast and surface damage.

An example of a prototypical commercial silicon nitride membrane, 500 nm thick is shown in Fig 3.13 after attempted machining with the pattern shown. Prior to
3.2 Stencil Mask Development

Figure 3.13: 500 nm thick silicon nitride membrane etched in FIB with 5 nA beam current. The machined lines are indicated, features, with 2 pairs of similar features. The lines radiating outwards are shards of the membrane, much like a pane of glass.

machining the membrane was completely uniform. It is not understood why the membrane reacted so violently, though it may have been an issue of released stress or strain due to the openings created. The small lines just visible in the center of the membrane were the structures previously shown, though they do not appear to have broken through the membrane fully when examined more closely.

In order to create a working device the actual silicon membrane with the integrated chip are necessary. The two wafers with reasonably uniform silicon membranes described previously were used in the following experiments, though the etches were performed on the extra silicon membranes within the rail holes.
Chips separated from these two wafers were inserted into the FIB machine using double sided copper tape to provide an electrical path to ground. It was discovered that the thickness of the membrane was significantly larger than expected, approximately 11.89 µm measured side on using the SEM. This may be an effect of doping too deeply with boron, early removal from the etch bath, or as a side effect of the slight misalignment observed in the features. It is thought that this is an effect of non-uniform temperatures in the etch furnace tube used to dope the wafers, a problem which has since been corrected. Despite this, it was easily possible to machine shallow features in the membrane, as shown in Fig 3.14. The width of the crucial central feature was approximately 50 nm, which would be ideal and other features behaved as expected. The difficulty was in extending this etch through the entire membrane. The thickness of the membrane was found to be enough that significant redeposition effects were observed at about 7 µm depth. While milling one side of a feature, the material would be redeposited at the other side, leading to a slope in the base of the etching region. As the milling progressed this would eventually lead

Figure 3.14: Prototypical features etched with FIB in a shallow etch on a 12 µm membrane. SEM image 54° angle of shallow structures.
to a slope across the entire opening, and etching would cease. This problem can be reduced by the introduction of fluorine into the system. At the time this milling was done the gas injection system was not operational, making this impossible. This would allow milling capability for even very thick membranes, though ideally thinner membranes would be used, reducing the etch time. Another unrelated problem lies in the fact that the silicon surface is polished on the backside as well as the front, so membranes etched from the backside are effectively invisible to the electron beam which sees only a uniform surface. For membrane holes as small as 100 \( \mu m^2 \) in a chip 11.5 by 6.5 mm this becomes prohibitively difficult to locate. The only solution is to mark the backside where the features are in some fashion.

The capability to create the desired features on a highly doped silicon membrane has been demonstrated, though the desired device cannot be created until problems with the FIB are resolved.
Chapter 4

Metal Films

In order to create measurable and continuous contact leads it is necessary to understand the adhesion of metals on KBr. The most commonly used metal for modeling, transport experiments, and devices is gold, making it a logical starting material. Experiments are also underway with low coverage UHV deposition of Tantalum in this group, also making it a logical metal to examine.

The growth conditions of a metal on a substrate is as crucially important as the interaction between the substrate and metal itself. Temperature, rate, and pressure can have a significant impact on the coalescence of metallic islands into large scale grains or epitaxial films [41].

To create the metal films on the KBr surface the high vacuum evaporator[42] and sputtering systems[43] available in the department were used. The reason for using these systems rather than the UHV system is that until the availability of the stencil masks and mask holding system together it is difficult to interface with the hardware in the UHV system in a secure and sufficiently clean fashion. Due to its low melting point gold can be easily evaporated in a thermal evaporator. The base pressure for the evaporation system is on the order of $10^{-7}$ Torr. Tantalum on the other hand requires sputtering techniques for successful evaporation. Fortunately a system with the necessary high purity tantalum target is available.
To quickly examine the adhesion of these metals to KBr a simple holder was designed. The desire was to have the ability to cleave the KBr blocks ex-situ, and yet still be able to transfer the coated sample to the UHV sample holder for examination and testing in the JEOL system. This would also allow an examination of any possible macroscopic effects on the film structure due to air exposure. As well, it was desirable to be able to quickly clamp a mask in front of the sample to test the viability of the silicon stencil mask. Initially, prior to any such masks being available, the design allowed the use of a 100 µm thick wire to mask the sample.

4.0.8 High Vacuum Evaporation Sample Holder

Three pieces were designed to accommodate the sample in the evaporator system, the sample holder and cleaving stations shown in Fig 4.1 and a clamp to hold either a wire mask or the silicon stencil masks to the sample shown in Fig 4.2.

Samples are held in the holder as shown by means of a molybdenum spacer plate held in place by 2 set screws. The mask clamp is screwed to the sample holder with the wire or silicon mask held in direct contact with the sample. This can potentially cause some damage to the KBr surface but ensures a better masking of the metal. In practice the damage is minimal, and not critical for this particular application. The clamp itself is 20 mm across, with an 8 mm hole in the middle to allow for easy evaporation. Initially the samples were masked by wrapping the wire directly around the sample, but it is difficult to force the wire to lie close to the sample in this fashion, and even a gap as small as 0.5 mm would be easily sufficient to cause a significant alteration of the edge of the masked region. Screws used are M2 stainless slotted screws, with set screws to hold the sample. This piece attaches to the evaporator with a single screw into the upper plate of the evaporator.

The cleaving station is used to cleave the sample by holding the sample in place with two screws at the back with the sample resting flat against the surface as shown. The sample is then scribed with a razor blade as close as possible to the holder in order to define the cleaving plane. The sample can the be cleaved using either a razor and hammer, or by simply removing from the cleaving holder and pushing gently on the tip of the KBr block using the side of the cleaving station. The quality of the cleave
Figure 4.1: The sample holder and cleaving station for the high vacuum evaporator. Colored bands are due to layers of evaporated tantalum and gold. a) the sample holder with a KBr sample, b) the cleaving station, screws at the back, not shown, hold the sample holder in places for scribing and cleaving.

can be evaluated by eye, by looking for cracks, scratches, or an abundance of steps in the sample face. It was found empirically that the best cleave is often possible
with the latter method, possibly due to damage due to the razor or misalignment with the crystal planes using the former method. In either case, immediately after cleaving the appropriate mask must be attached using the clamp, within a minute if possible, followed by placing the sample in the evaporator. The less time the sample is exposed to air the less damage will be caused due to water and other contaminants though a precise time is not known. Typical total exposure time of the sample is on the order of 3 minutes, though even this is easily sufficient to observe water damage as will be shown.

Once in the evaporator the metal deposition rate is calibrated using crystal sensors with the sample out of the metal stream. For the thermal evaporator, the gold deposition rate is controlled by the temperature of the titanium boat on which the gold nuggets rest. For Tantalum the sputtering rate is controlled by the power applied to strip the metal ions from the target. Following deposition, the sample holder is removed and stored in a nitrogen atmosphere, in a desiccator. As soon as possible afterwards the sample is transferred to the UHV holder and system, and heated to
Figure 4.3: The mask clamp with a silicon stencil clamped to an air cleave KBr sample

150 °C for one hour within the UHV system to desorb any remaining water. Imaging is then accomplished by AFM, SEM, and an air AFM for large scan sizes depending on the sample, and the instrument availability.

4.1 Gold on KBr

Deposition rates of gold films are controlled by setting the rate using the crystal sensor prior to deposition as well as during the deposition. Achieving high rates, in the 10-100 nm/min or greater is readily achievable by heating the gold source to higher temperatures. The temperature of the gold is not however directly controlled, rather the current passed through the Ti boat is set. For a low rate evaporation a current of 120-124 A is typical though the precise rate depends strongly on the exact amount of gold in the boat. The rates used have been between 0.2 nm/min and 1 nm/min. The minimum rate however is much more difficult to control, particularly
4.1 Gold on KBr

since the gold source liquifies and begins to evaporate shortly before this point. As well, the crystal sensor measures a minimum of angstroms, making it difficult to monitor the rate realtime. Instead, measurements of the coverage for several minutes prior to deposition the initial rate. Controlling the rate during deposition involves constant tracking of the coverage. In comparison, with the e-beam evaporator the maximal rate obtained thus far is less than 2 Å /min. What is indicated by these numbers is that there is a small amount overlap possible in the rates achievable by the two systems. Since the high vacuum evaporator and sputtering machine are being used to test films in a regime close to achievable with the UHV evaporator, it is then necessary to operate close to the minimum rates with these instruments to maintain this situation.

The sample temperature during the thermal evaporation in the high vacuum system rises to 100 °C at the thermocouple just above the sample position. For higher rate evaporations it is possible to actively heat the sample in order to obtain a better grain size but this would take place at the expense of the KBr surface. Shown in Fig 4.4 are SEM images of the deposition of gold on 2 samples, after imaging the sample in the UHV AFM, then heating. The AFM images are shown in Fig 4.5 for comparison, both pre and post heating. From the SEM images it is clear that with the higher rate the film is considerably better connected, though the edge definition at the masked region is similar. The film deposited at the lower rate has considerably larger void regions, though the film still appears connected. Looking at image (c) it is clear the disconnected islands which reach into the masked region at progressively lower coverage image quite differently. Disconnected islands appear suddenly darker than the surrounding connected film. This is to be expected, as the SEM is imaging a conducting film on an insulating substrate. The film is connected to the SEM puck by means of carbon tape to provide a conducting path to ground so the only means for charge to escape are through the connected pads or through the insulating substrate. The poor edge definition at the center of Fig 4.4 a) is thought to be a result of the wire bowing out from the surface. This was the motivation for creating the mask clamp which was much more successful at holding the wire to the surface than simply wrapping the wire, as was used in the first samples shown. AFM images of the two samples support the SEM data, showing the relative connectivity of both samples. Some definition is available on the SEM images that is not clear from the
Figure 4.4: SEM images of gold films 20 nm thick on KBr. All films heated up to 150 °C for 1 hour, and masked with a 100 µm tungsten wire. a) 9.7 Å/min, b) 2.4 Å/min
AFM, though the height information observed in AFM is not visible with SEM. Using the mask clamp, another sample with a 20 nm thick film was deposited at 10 Å/min. The SEM images of the sample, in Fig 4.6 clearly show that the edge definition of the masked region is similar to that of the other samples. As well, at first glance it appears to contradict the previous measurements as it shows a large number of voids, appearing much like the lower rate sample. This however is not the case, as
Figure 4.6: SEM of gold film deposited at 10 Å/min, but not heated following deposition. The mask clamp was used to hold a 100 μm wire to the surface.
4.1 Gold on KBr

this sample was not introduced into the vacuum system and hence heated for 1 hour at 150 °C. With the previous 10 Å/min sample, it is clear from the AFM images that the sample undergoes a considerable change as a result of the heating process but only if the sample is sufficiently connected to begin with. The lower rate sample, at 2.4 Å/min does not. This is supported by the SEM images of the higher rate, unheated sample. It seems likely that the poor edge definition are largely a result of the curvature of the wire, a purely geometrical problem. Though the masked region appears to be fully 100 μm wide (not shown), in practice the 4-10 μm from either side show significant amounts of gold.

Figure 4.7: 600 x 600 nm UHV AFM image of gold on KBr. The spiral and circular shapes, highlighted by the gold islands along the step, are thought to be caused by water damage to the surface. The image is taken at a low coverage region of a sample masked with a 100 μm wire.

An examination of the KBr visible in the masked and partially masked regions of the sample show a number of spirals structures like those shown in Fig 4.7. Similar
structures have been previously been reported in the literature for NaCl crystals where the surface was partially dissolved and allowed to recrystallize [44]. The structure of the spirals and other shapes depends on whether it occurs at a screw dislocation, or atomic step, and on the amount of water present and the time. As these samples were exposed for minutes typically the structures tend to be relatively small. What is not clear is whether the presence of these features is due to the time interval between exposure to air and annealing the sample, or if they grow rapidly after exposure to air whether or not annealing is performed. The former is thought to be the case, as air cleaved samples have been used previously, with a rapid introduction into vacuum and immediate heating these are not observed.

Lastly, the resistance of the gold films was measured with a standard digital voltmeter. The film was connected and possessed a finite resistance though a definite value was difficult to obtain due to the damage induced to the film by the probes. The film is delicate enough that this brute force measurement technique cause the resistance to increase greatly as the probes mangled the surface. The main point is that both were connected, despite the large voids in the surface.

The primary conclusions drawn from this data are that even at significant thickness, gold films possess significant voids and do not grow epitaxially on KBr. Though connected, the structure of such films for narrow wires would likely be poor, particularly given that the thickness of the evaporated structures would likely have to be significantly less than 20 nm, in order to be able to actually image with AFM. The regions where the coverage decrease due to masking effects actually agree reasonably well with AFM measurements of very low coverages in UHV, where gold forms very tall, disconnected islands. More experiments would be necessary to fully examine the growth conditions of these films but this is not the principle reason for examining these films. It is also clear that for a clean UHV surface, extended exposure to air is not desirable from the perspective of water damage. While one could in principle reduce this effect by placing the sample in a nitrogen glove box, it has been observed that mobile contaminants on the surface cannot always be imaged with AFM. This would mean that a precise knowledge of either the surface or electrodes would be difficult after air exposure.
4.2 Tantalum on KBr

Less work has been done on tantalum films than gold in this work, though tantalum has been studied extensively for thin film applications in the electronics industry, for an extensive review see Westwood [45]. A possible problem is that the sputtered tantalum will have a different effect on the sample surface due to electronically, or mechanically induced damage. This effect has not be qualified, what still needs to be done is a high rate deposition of a film with the e-beam evaporator in UHV to compare the film growth. The rates needed to approach the minimum rates on the sputtering machine are at the limit of the evaporator however, and may cause the rod to be depleted prematurely and interrupt other experiments, so this test has been delayed for the time being. Several experiments have been carried out, the results of which are shown in Fig 4.8, 4.9, and 4.10. The sample shown in Fig 4.8 and 4.9 was sputtered to 5 nm thickness at 0.8 nm/min. The features to note are that the film is considerably more continuous than that of the gold film even with a quarter the thickness. At the gap where the wire masked the surface, a very different transition to that of gold is shown in Fig 4.8 a). The transition appears smooth, and near the interface the film is free of cracks and buckling. The long lines at 45 degrees are thought to correspond with crystal steps, which suggests the film is buckling preferentially at these points. In regions in between these features the film shows evidence of a 3-fold symmetry, shown in Fig 4.8 b) suggesting a (111) structure. Bulk tantalum grows in a BCC crystal with lattice constant 3.3 Å however sputtered films can have widely varying structures which typically correspond to either bulk BCC or tetragonal, in either (100) or (110) orientation[45]. It was thought that the close correspondence of the lattice constants of Ta and KBr might allow for epitaxial growth but this does not seem to be the case.

In other regions there is less buckling of the film, appearing almost as ripples in a sheet. These are all likely due to the mismatch between the film and the surface, however at the masking interface where there is a region of less coordination the strain should be relieved, as is born out in the image. It is also possible that this region of the film is partially masked due to the wire and the lower coverage is causing the effect.
Figure 4.8: SEM of 5 nm tantalum film deposited at 0.8 nm/min. a) The edge of the masked region, using a 100 \(\mu\)m wire to mask the sample. b) Zoom of buckling region, this symmetry appears characteristic of regions where there aren’t large steps.
Figure 4.9: Air AFM of 5 nm tantalum film deposited at 0.8 nm/min. a) 100x100 µm image b) 40x40 µm image
4.2 Tantalum on KBr

An examination of this sample under AFM is shown in Fig 4.9. Similar features are observed, however the onset of the gap is significantly harder to observe (not shown). The reason for this could be that the large buckling appears to be almost 200-250 nm high. This is far higher than atomic KBr steps, and given that the film is only 5 nm high seems far too high for simple warping of the film. It is possible that it is either an imaging artifact, or an effect of a poor cleave of the sample. It would explain the near invisibility of a 5 nm step. Imaging in UHV was attempted but in the KBr regions the observed structure was inconclusive. The tantalum film could not be imaged, with the images in the KBr region not understood yet.

In comparison, another experiment was performed with a 2.5 nm thick film at 0.42 nm/min. The results, using the UHV SEM in the JEOL system are shown in Fig 4.10. One of the silicon stencil masks with the central bridge was used to mask the sample, though this particular bridge had some residual silicon from prematurely stopping the TMAH etch which manifests as a poor looking feature definition as shown in Fig 4.10 a). The edge definition of the region appear similar to the previous sample, and after careful examination similar buckling and strain regions are shown in the film. The bubbling, shown in b), is not understood. It may be an air effect of the sample, either with water attacking the surface or trapped air pockets under the metallic film. What is clear is that in regions near these bubbles the stress in the film is significantly relieved, and as a result appears much more flat. In regions away from steps the 3-fold symmetry is again visible, so it seems that the film is growing in the same fashion still even with half the coverage. This would also suggest that the flat region near the masking wire on the higher coverage sample is not a coverage effect but more likely a stress relieving effect.

The tantalum films clearly grow better on the KBr surface than gold, the only concern being the warping of the film. At the gap interface this does not appear to be an issue so this is promising. The measured resistance of the 5 nm film was approximately 2.3 kΩ’s, though as with the gold films the surface was delicate enough that the contact procedure causes the film resistance to increase due to damage. As such, this can only be taken as an indication that the film is indeed fully connected. A better determination of the film structure was attempted with LEED but was unsuccessful. Given the variation between sputtered and evaporated tantalum it may not be meaningful for work in the UHV system, this remains to be seen.
Figure 4.10: SEM of 2.5 nm tantalum film deposited at 0.42 nm/min masked using a silicon stencil mask, non-uniformities in the bridge region due to poorly removed residual silicon layer. a) 70 x = 1.4 mm, white feature is a part of the holding clip, b) 3000x = 33µm, c) 2700x = 37µm.
Chapter 5

Conclusions

5.1 Conclusions

A system for the evaporation of metallic leads on the prototypical system KBr has been designed and manufactured. An examination of two possible metals for these purposes has also been conducted using high vacuum thermal evaporation and sputtering, and characterized using AFM and SEM. To evaporate the electrodes, two silicon stencil masks have been designed and fabricated with millimeter contact areas as well as 100 $\mu$m to 2 mm membranes for feature deposition. To hold these stencils a silicon chip and stainless steel rail system have been designed to work in the UHV system.

Gold and tantalum films were examined by depositing on air cleaved samples. The samples were masked using 100 $\mu$m wires or a silicon stencil mask to examine the effect of the film at the boundary of the masked region and any other possible effects. Gold films 20 nm thick at various rates proved to have differing degrees of connectivity, while the gold films have poor connectivity and definition at the edge of the masking region. All gold films examined had significant voids at even this high coverage. Tantalum films 2.5 and 5 nm thick had considerably better uniformity, though with moderate buckling of the film in certain regions. The use of tantalum for initial electrode deposition on KBr seems significantly more promising.
5.2 Outlook

To deposit the films a stainless steel mask holder and modified sample holder were designed and built. The sample holder, partially constructed at the University of Basel, was assembled at McGill and is currently complete. It possesses two electrically isolated contact pads which may be attached to the sample using copper beryllium spring clips in UHV. The mask holder is also finished, though it has yet to be tested in vacuum. Rails approximately 0.9 mm thick by 4 mm tall are in position to hold the mask close to the sample, with a 5 mm hole for evaporation through the middle.

The stencil masks have been designed and fabricated at the McGill Microfabrication Facility from 6 inch silicon wafers. The stencils are broken into 2 parts, the first of which has a (100) oriented silicon beam designed to separate the KBr surface into two contact regions for electrical measurements. The second stencil mask consists of a silicon membrane, nominally 4-5 $\mu$m thick created by etching double side polished wafers with a thermally diffused boron etch stop. These membranes have been created, though the focused ion beam tools used have only demonstrated the ability to create the desired features in principle due to equipment difficulties at the time.

In short, what has been demonstrated here are the pieces for the construction of these electrodes in an entirely UHV environment. This should allow clean measurements of the electrical properties of the molecules of interest in the near future.

5.2 Outlook

The major remaining task is to create the actual silicon stencil with FIB and attempt in situ evaporation. The capability to create structurally sound silicon membranes with an etch stop has been demonstrated. However, until the first device is created it is impossible to say how the evaporation will proceed through them. In the next iteration of the stencil masks, the main goal should be to create some means of observing the stencils from the backside of the wafer. The simplest method of doing so is simply to create small nearby features which bracket the central membrane. A shallow RIE etch would be sufficient to create these features however this would have to be done prior to the membrane etch and as such would require an entire cycle of coating the wafer, exposing, etching, and removal of the photoresist.
5.2 Outlook

The other major project to be undertaken once these metallic lines are successfully created is breaking them. As the desire is to do molecular conductance measurements on an insulating surface between electrodes, a continuous structure is neither needed nor desired. It is thought that electromigration might be sufficient to break these structures. In electromigration a current is passed through the wire and field assisted diffusion causes metal atoms to diffuse away from particular regions of the wire and a gap is suddenly created. If properly controlled this gap can be of molecular size. Alternatively, one may be able to mechanically break the wires by using an AFM tip in contact with the surface. This remains to be demonstrated. These techniques will be the goal in the near future.
Appendix A

Tylan Tube Recipes

Wet Thermal Oxidation of Silicon

Process sequence to be programmed:

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<th>O2</th>
<th>H2</th>
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-this should grow approximately 5000 A of oxide on the wafer, the temperature should not be HIGHER given that this will be a post anneal step
- initial oxygen to avoid pitting of the silicon surface under pure nitrogen
- push in speed - 12 (in software) = 2-3 inches/min

NET TIME : 04:25:00

Boron Diffusion Process

Process sequence to be programmed:

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<tr>
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<td>4000</td>
<td>125</td>
<td>0</td>
</tr>
<tr>
<td>07</td>
<td>PULL OUT (2inch/min)</td>
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<td>625</td>
<td>4000</td>
<td>125</td>
<td>0</td>
</tr>
<tr>
<td>08</td>
<td>COOL DOWN</td>
<td>00:10:00</td>
<td>625</td>
<td>4000</td>
<td>125</td>
<td>0</td>
</tr>
</tbody>
</table>

- boron diffusion depth should be on the order of 5 um, dependent on the film quality and wafer preparation
- oxygen to avoid pitting of the silicon surface under pure nitrogen
- push in speed 4 in software - 2-3 inches/min

NET TIME : 04:35:00
Appendix B

Mask and Sample holder Design

Figure B.1: Central Body of the maskholder

Angle the back here for greater strength when turning down, i.e. make back part 5mm instead of 5.5 but with a 0.5mm angled section, (or more)
Figure B.2: Mask Rails
Figure B.3: Rear part of the Mask holder
Figure B.4: Ceramic insulator and wings
Figure B.5: Sample holder base piece
Figure B.6: Metallic clips to sample holder
Appendix C

Original stencil mask design

The original design called for a membrane of several millimeters across with both nm, micron, and mm scale features on the same membrane as shown in Fig C.1. This proved impractical due to the size of membrane required and the large openings in

Figure C.1: Original features designed for the stencil mask, to be etched in RIE prior to the membrane etch from the backside
the membrane. As well, in the original design it was thought that having vertical sidewalls on the rail holes would be more important than the presence of the corner planes and rectangular symmetry. An example of this is shown in Fig C.2. As was discussed, using features at a (100) orientation has additional difficulties, particularly for the snap off marks and was abandoned in the end. The other difficulty at the time was aligning the backside membrane etch to the front side features. The ability to do front to backside alignment exists with the EVG 620, but the experience wasn’t there at the time.

Figure C.2: A partially completed example of the original etch mask features with a zoom of the area where the electrode would be, in this case only the oxide is patterned.
Bibliography

[9] Specs Scientific Instruments ERLEED system
[10] Infinicon Bakeable Crystal Sensor
[14] Macor machinable ceramic is a registered trademark of Corning Inc.
[16] created with Varicad, 2D/3D computer aided design software


[34] Silson Ltd, Northampton England.


[42] Thermionics Laboratory Inc., USA, model VE-90.

[43] Edwards Auto306 Cryo
