



Influence of nanoscale surface roughness on flow behaviour in fluidic microchannels



Master thesis report

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Abstract

Microsieve is largely used in the area of filtration and selective gas permeation. Such applications can benefit from a microsieve with a low flow resistance. The flow resistance is usually achieved by reducing the thickness of the microsieve, however, at the mean time microsieve membrane strength becomes low. To solve this dilemma, a microsieve has to be thick enough to withstand high pressure or forces while at the same keep its resistance remaining the same as a very thin membrane. The conductance difference for thick and thin microsieve membranes is caused by the rough surface of microsieve channel. Therefore, it is postulated that a microsieve with extremely smooth channel surface would prevent the influence on total resistance from the channel wall roughness.

A silicon microsieve with smooth channel surface is designed and fabricated to examine the influence of surface roughness on flow conductance. DRIE is applied to drill holes through the wafer, which will create microscale roughness. The circular holes will be getting a post processing with KOH wet etching: a rhombus shaped channel is fabricated with smooth surface. By measuring the flux through the microsieve with nanoscale roughness and comparing this with the microsieve with micro roughness, the influence of surface roughness on flow flux or flow conductance is determined.

The experiment results show the flow conductance of the microsieve with smooth channel surface is almost the same as that of the microsieve with rough channel surface, which means most gas molecules are reflected diffusively by the channel walls. The silicon surface property is analyzed and dry nitrogen and HF treatment is applied to prevent the influence from water molecules. Larger gas molecules SF_6 are also tried. Both of these two experiment results show the same diffusive reflection behaviour. Therefore, it is concluded that the diffusive reflection is not only caused by large scale surface roughness, but also highly depended on the surface solid atoms arrangement as well as gas molecule size and shape. Specular reflection can occur on the condition that gas molecule can be treated as sphere and its size is larger than the distance between solid atoms, while at the same time the solid atoms at surface have to be regularly patterned and closely packed. Such kinds of surface can be achieved by graphane or boron nitride (BN) coating.

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Chapter 1 Introduction

1.1 Micro-mechanical electrical systems

Microelectromechanical systems (MEMS) refer to devices that have characteristic length of less than 1 mm but more than 1 micron. MEMS combining electrical and mechanical components are fabricated using the process in the microelectronics industry, which is also called micromachining. The fabrication technologies include the lithography, wet etching (KOH, TMAH), dry etching (RIE, DRIE), deposition (LPCVD, PECVD) and other technologies capable of manufacturing small devices. Silicon is the most common use material in MEMS. It can be chemically etched into various shapes, and associated thin-film materials as polysilicon, silicon nitride and aluminum can be micromachined in batches into a vast variety of mechanical shapes and configurations. Nanodevices (some say NEMS) further push the envelope of electromechanical miniaturization.

MEMS are finding increased applications in a variety of industrial and medical fields, with a potential worldwide market in the billions of dollars. Accelerometers for automobile airbags, keyless entry systems, dense arrays of micromirrors for high-definition optical displays, scanning electron microscope tips to image single atoms, micro-heat-exchangers for cooling of electronic circuits, reactors for separating biological cells, blood analyzers and pressure sensors for catheter tips are a few of current usage. Microducts are used in infrared detectors, diode lasers, miniature gas chromatographs and high frequency fluidic control systems. Micropumps are used for ink jet printing, environmental testing and electronic cooling. Potential medical applications for small pumps include controlled delivery and monitoring of minute amount of medication, manufacturing of nanoliters of chemicals and development of artificial pancreas.[1]

There has been great interest in microfluidic devices during the last few decades in various research fields such as instrumentation and medical application. Microsieve is largely used in the area of filtration and selective gas permeation. With a functionalised coating, microsieve can become bio compatible and thus it can be used for medical application in hospitals.

Many filtration applications can benefit from a microsieve with a low flow resistance. These low flow resistance microsieves can be realized by using silicon micromachining techniques. In 1995, C. van Rijn *et al* [2] reported a 1 µm thin silicon nitride microsieve with perforations of 4um diameter by using conventional lithographic techniques. After that, various different micromaching techniques were used for the fabrication of micro- or nano-sieve. Kuiper *et al* [3] made a silicon nitride microsieve membrane with pore size Φ =65nm by using laser interference lithography, reactive ion etching and KOH wet chemical etching. Besides circular pores, he also tried to make microsieve with slit-shaped pores on a <110> silicon wafer. In order to get extremely low flow resistance, the thickness of microsieve keeps going down. Unnikrishnan *et al*[4] reported a thin nanosieve membrane (45nm thick and pore size 120nm) by using laser interference lithography and thin film transfer techniques.

1.2 Problem statement

As discussed above, high fluxes (high conductance) through the microsieve membrane require the membrane thickness to be extremely low, while on the other hand, the microsieve membrane strength is getting low because it is directly proportional to the thickness of microsieve[3]. This always causes a dilemma situation to us. One solution is to apply a specifically designed strong support underneath, but this will cause extra fabrication effort. Another solution is to make a microsieve thick enough to withstand high pressure or forces while at the same keep its resistance remaining the same as a very thin membrane. The conductance difference for thick and thin microsieve membranes is caused by the rough surface of microsieve channel. Therefore, it is postulated that a microsieve with extremely smooth channel surface would prevent the influence on total resistance from the channel wall roughness.

A silicon microsieve with smooth channel surface is designed and fabricated to examine the influence of surface roughness on flow conductance. DRIE is applied to drill holes through the wafer, which will create microscale roughness. The circular holes will be getting a post processing with KOH wet etching: a rhombus shaped channel is fabricated with smooth surface. By measuring the flux through the microsieve with nanoscale roughness and comparing this with the microsieve with micro roughness, the influence of surface roughness on flow flux or flow conductance is determined.

1.3 Outline

This report is focusing on the fabrication of a microsieve with smooth channel surface. After fabrication, gas flow through the microsieve is measured to examine the influence of surface roughness on flow conductance. The content of this report is arranged as follows:

Chapter 2 Theory: Gas flow conductance in capillary. In this chapter, a detailed discussion about gas flow conductance through capillary and microsieve is given in the viscous regime. Influence of gas molecule and solid interface interaction on determining the flow conductance is analyzed as well.

Chapter 3 Microfabrication techniques. In this chapter, important micromaching techniques deep reactive ion etching and KOH wet anisotropic etching are introduced. Surface roughness reduction methods are given at the last of the chapter: KOH etching, hydrogen annealing and sacrificial thermal oxidation.

Chapter 4 Microsieve fabrication process. In this chapter, a brief description of experiment is given, including process outline all the equipment used.

Chapter 5 Microsieve fabrication process results and discussion. This chapter focuses on the experiment results and discussions about the results. Special discussions are about SU 8 lithography, DRIE etching recipe, surface roughness after KOH etching and hydrogen annealing.

Chapter 6 Characterization. In order to measure the mass flow through the microsieve, it is firstly bonded to the glass tube then measured in home-made flow measurement system. The experiment results are compared with the theoretical results according to the formulas in Chapter2.

Chapter 7 Conclusion and Outlook. In this chapter, an overall conclusion is given for this master thesis project. And future work to improve this experiment is also discussed.

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Chapter 2 Theory: Gas flow conductance in capillary

In this chapter, firstly the three flow regimes are described and flow conductance in viscous regime is introduced. In the following, slip effect and gas-solid interaction are discussed. Finally, different kinds of silicon surface are analyzed.

2.1 Knudsen Number

The principle parameter in gas flow conductance theory is the Knudsen number (Kn), which distinguishes the different flow regimes. The Knudsen number is defined as the ratio of mean free path λ over by the characteristic dimension of the gas flow *d*, i.e., the capillary diameter when gas flow through a long capillary.



Figure 2.1 flow regimes according to different Kn[2]

Considering the value of the Knudsen number, we can divide the gas flow into three regimes (Figure 2.1): viscous, transition and free-molecular flow. In the viscous flow regime (Kn < 0.01), the mean free path is small compared to the characteristic dimension of the channel, the collisions between molecules occur more frequently than collisions of molecules with the channel walls. Consequently, intermolecular collisions predominate in determining the characteristics of the flow. The flow in this regime is treated as a continuous medium. In the free-molecular or Knudsen Flow regime (Kn > 1), the mean free path is very large compared to the characteristic length scale and the intermolecular collision probability is quite low. The flow is limited by the collisions with the walls of the channel. In the transition flow regime (0.01 < Kn < 1), both types of collisions (intermolecular collision and collision with channel wall) are influential in determining the flow characteristics. There are only empirical equations to describe flow behavior in this regime. This division of the regimes of flow is very important because the methods used for calculation of the gas flows essentially depends on the regime. To calculate the Knudsen number, we have to know the mean free path, which absolutely cannot be measured directly. Therefore, we have to use the following formula to calculate the mean free path [2]:

$$\lambda = \frac{kT}{\sqrt{2\pi}d_{mol}^2 P} \tag{2.2}$$

Where the k is the Boltzmann constant and d_{mol} is the diameter of the gas molecule. For most gases, the mean-free-path at atmospheric pressure and room temperature is around 50-100nm.

2.2 Flow conductance in viscous regime

In this viscous flow regime, the flow is described by the famous Hagen-Poiseuille's law [3] (Eq.2.3) which was formulated in 1840 by observation of human blood flow in vessels and water flow in tiny tubes. This law describes the slow viscous incompressible flow through a constant circular cross-section. Poiseuille's experiment gave the evidence to the correct boundary condition (no slip) for a laminar incompressible flow at a solid boundary. Hagen-Poiseuille's law can be used to model the biological flow, such as blood flow and flow through the endothelial layer. It can also be used in porous media and filters.

$$Q_{vol-vis-tube} = \frac{\pi r^4}{8\eta L} * \Delta P \tag{2.3}$$

Where $Q_{vol-vis-tube}$ is the volumetric flow rate $[m^3/s]$, η is the dynamic viscosity $[Pa^*s]$, $\Delta P = P_{entrance} - P_{exit}$ [Pa] the pressure drop across the tube, L the tube length [m], the r its radius [m]. We can adjust equation 2.3 to incorporate compressible flow by introducing the mass flow $Q_{mass} = Q$. The transformation is using the ideal gas law PV = NRT (with N the number of molecules and R the universal gas constant):

$$Q_{vis-tube} = \frac{P_a}{RT} * \frac{\pi r^4}{8\eta L} * \Delta P$$
(2.4)

Where $Q_{vis-tube}$ is the mass flow rate [mol/s], $P_a = (P_{entrance} + P_{exit})/2$ the arithmetic mean pressure.

Electricity was originally understood to be a kind of fluid. Both Poiseuille's law and Ohm's law illustrate the transport phenomena. Therefore, the flow conductance can be derived by analogy with electrically resistance. Poiseuille's law corresponds to Ohm's law for electrical circuits ($\Delta V = I^*R$), where the pressure drop ΔP is analogous to the voltage ΔV and flow rate Q is analogous to the current I. Then the flow resistance or its reciprocal flow conductance is:

$$F_{vis-tube} = \frac{1}{R} = \frac{Q}{\Delta P} = \frac{P_a}{RT} * \frac{\pi r^4}{8\eta L}$$
(2.5)

The Hagen-Poiseuille's law is based on some assumptions: The gas flow is laminar and is fully developed——thus the flow velocity profile is constant through the tube length, which means ignorance of the entrance and exit effect. Besides, the flow velocity at the wall is assumed to be zero, thus non-slip. In 1891, Sampson [4] solved the Stoke's stream function for the viscous flux through a circular hole in a very thin wall with the assumption of zero velocity at the wall (eq.2.5&2.6).

$$Q_{vis-orifice} = \frac{P_a}{RT} * \frac{r^3}{3\eta} * \Delta P$$
(2.6)

$$F_{vis-orifice} = \frac{P_a}{RT} * \frac{r^3}{3\eta}$$
(2.7)

Chapter 2 Gas flow conductance in capillary

Now, we consider the gas flow through a tube with arbitrary length. In figure 2.2, there are actually two parts which contribute to the total flow transport, Poiseuille's and Sampon's flow. Therefore, the resistance from these two contributions is in series (conductance in parallel). The total flow conductance can be considered as addition of these two conductances. A general formula for conductance through tubes with arbitrary length in viscous regime is given [5]:

$$F_{vis} = \frac{F_{vis-orifice} * F_{vis-tube}}{F_{vis-orifice} + F_{vis-tube}} = \frac{P_a}{RT} * \frac{r^3}{3\eta} * \left(1 + \frac{8L}{3\pi r}\right)^{-1}$$
(2.8)



Figure 2.2 Top: schematic of total flow consist of sampon's effect and poiseuille's law. Bottom: resistance series and conductance parallel configuration.

When the single orifice or tube is replaced by a microsieve with a hexagonal array of orifices or tubes, the total transport can be simply add all contributions from the individual orifice or tube. However, the entrance and exit flow of a single orifice or tube will influence flow through its neighbouring ones. This influence is caused by the movement of molecules on the microsieve surface. This influence on the flow flux rate is corrected by Tio and Sadhal [6] with a correction factor $(1 - f(k))^{-1}$, and f(k) is given in eq. 2.9 with k the porosity of the microsive:

$$f(k) = \frac{2H_3}{3\pi^{5/2}} \left(\frac{\sqrt{3}}{2}k\right)^{3/2} + \frac{6H_5}{5\pi^{7/2}} \left(\frac{\sqrt{3}}{2}k\right)^{5/2} + \frac{18H_7}{7\pi^{9/2}} \left(\frac{\sqrt{3}}{2}k\right)^{7/2} + \frac{56H_9}{9\pi^{11/2}} \left(\frac{\sqrt{3}}{2}k\right)^{9/2} \dots$$
(2.9)

The numerical values of the various H_i are: H_3 =11.0342, H_5 =6.76190, H_7 =6.19524, H_9 =6.05695. Therefore, for a microsieve with hexagonal arrays of orifices, using the summation of individual orifice concept, the flow conductance can be given:

$$F_{vis-orifice-sieve} = F_{vis-orifice} * \frac{Ak}{\pi r^2} * (1 - f(k))^{-1} = \frac{ArkP_a}{3\eta\pi RT} * (1 - f(k))^{-1}$$
(2.10)

Where A is the effective area of the microsieve and k is the porosity of the microsieve. Similarly, for for a microsieve with hexagonal arrays of tubes: the conductance is given:

$$F_{vis-tuve-sieve} = \frac{ArkP_a}{3\eta\pi RT} * \left(1 - f(k) + \frac{8L}{3\pi r}\right)^{-1}$$
(2.11)

It is noticed that the viscous mass flow is direct proportional to the mean pressure and differential pressure. For the flow conductance in the molecular and transition regime, see appendix A&B.

2.3 Slip flow and Interaction between molecules and wall

The Hagen-poseuille's law is based on the boundary condition of zero velocity (non-slip) at the wall surface. However, researches [7] show that there exists a non-zero velocity (slip) at the wall surface. The slip effect becomes very important for the micro/nano-scale flows as the characteristic length decreases.

In 1879, Maxwell studied the interaction at gas-solid interface and proposed a slip model for gases over a solid interface based on kinetic theory [8]. In 1909 Knudsen did the first experiment and confirmed the Maxwell slip model [1]. In the following decades the Maxwell model was demonstrated to be valid for gases over solid surfaces by the Boltzmann transport theory [9-11] and experimental measurements [12-15]. The Maxwell model has been widely used in rarefied gas dynamics and gas microfluidics.



Figure 2.3 schematic of specular reflection and diffusion reflection

In Maxwell's theory of gas molecules interaction with solid surface, there are two models of gas molecule reflection: specular and diffuse (figure 2.3). The specular reflection model assumes that the incident molecules reflect on the body surface as the elastic spheres reflect on the entirely elastic surface, i.e., the normal to the surface component of the relative velocity reverses its direction while the parallel to the surface components remain unchanged. The diffusive reflection model assumes that the gas molecules strike the surface and are reflected in all directions with equal probability.

For a normal surface, Maxwell considered treating the surface as something intermediate between a perfectly specularly reflecting (specular) and perfectly diffusively reflecting surface. He assumed that in every unit of the surface, a portion of f diffusively reflects the incident molecules, while *1-f* portion specularly reflects the incident molecules. It is clear that if all the molecules are

reflected diffusively, f=1, while if all the molecules are reflected specularly, f=0. It is frequently assumed in theoretical and numerical works that the gas is fully diffusively reflected at the wall (i.e., f=1).

In practice, the diffuse model (fully accommodation f=1) is applicable. The surfaces processed by usual industrial means at normal atmospheric temperature and with not too high incident energy of the oncoming flow, the diffuse reflection model can serve as fairly good approximation of the interaction of molecules with the body surface. Some people explain diffuse reflection as that the gas molecules are adsorbed near the wall for a *certain time* and totally forget the incident information. Thus, they will leave the wall and re-emitted to the free space above the wall in all angles [7]. However, this explanation is lack of evidence for how long the "*certain time*" is and why would the gas molecules be absorbed. And if this is true, then specular reflection cannot exist. Because even for a perfectly flat surface, the incoming gas molecules into the surface will be adsorbed rather than directly reflected. In this report, we guess it is the roughness which probably causes the diffusive reflection (Figure 2.4). Five molecules strike the surface in a parallel direction. But they meet the surface in the different orientation with respect to the normal direction of the meeting point on the surface. As a result, when the molecules are reflected from



Figure 2.4 incoming gas molecules reflected isotropically

the surface, they will scatter in different directions. Therefore, we postulate that, if the surface roughness is largely reduced, fewer molecules will be reflected diffusively, and on the other hand, more gas molecules will be reflected specularly from the surface. This hypothesis will be tested in the following experiment of this report.

For a validation of our hypothesis, an experiment is designed in Chapter 4. Silicon is employed as the surface material, because it is convenient to make devices with silicon due to its high developed micromachining techniques. Before going to the experiment, an inside view of silicon surface made by different techniques is discussed in below.



Figure 2.5 Left: DRIE fabricated silicon surface; Right:silicon surface after KOH treatment.

In figure 2.5, it is shown a rough surface fabricated by using DRIE technique. Due to the larger scale roughness on the surface fabricated by DRIE, the surface will produce diffusive reflection. After a KOH treatment, the surface roughness can be largely reduced to the nano scale.

As discussed above, the surface roughness might play an important role in flow bahivor through tubes. To eliminate the influence from the surface roughness, one way is to make the tubes extremely thin, e.g., a thin orifice. Because the length of orifice is so short and even shorter than the mean free path of the gas molecules, gas molecules will directly go through the orifice without any collision with the walls. Experiment is done by Uniniksrishnan et al [16] in this group: an ultra-thin (45nm) nanosieve is used to examine the flow behavior at different pressures (thus different flow regime). Experiment results show that conductance in transition regime is the superimposition of viscous and molecular flow fluxes due to absence of gas-wall collisions. In this report, another method is proposed. Instead of making the tube extremely short, we try to make extremely smooth (ideally atomically smooth) channel surface for a microsieve. If most of the gas molecules are reflected specularly from this smooth surface as what we postulated, the channel wall has no contribution to total resistance or conductance, because there is no momentum loss along the motion direction during the gas molecule-wall collisions. Therefore, conductance for a tube or a microsieve is independent of its length, and is only related to the entrance and exit effect (just like an orifice). The formula for viscous flow conductance through a microsieve with atomically smooth surface is then reduced to:

$$F_{vis-smoot\ h} = \frac{ArkP_a}{3\eta\pi RT} * \left(1 - f(K)\right)^{-1}$$
(2.12)

Chapter 2 Gas flow conductance in capillary

The flow conductance is believed to be much larger than that for a microsieve with the same length but a relatively rough surface. The ratio of flow conductance for smooth and rough surface is written as:

$$C = \frac{F_{vis-smoot h}}{F_{vis-roug h}} = \frac{\frac{ArkP_a}{3\eta\pi RT} * (1 - f(K))^{-1}}{\frac{ArkP_a}{3\eta\pi RT} * (1 - f(k) + \frac{8L}{3\pi r})^{-1}} = \frac{1 - f(k) + \frac{8L}{3\pi r}}{1 - f(K)} = 1 + \frac{8L}{3\pi r(1 - f(k))}$$
(2.13)

Where f(k) is the correction factor. If we have a microsieve with aspect ratio (L/r) of 20, C is around 20 according to eq. 2.13(For the value of f(k), k is given at 43.67% in chapter 6 and f(k) is 0.885). Therefore, if our hypothesis is true, during the experiment, compared with that through microsieve with rough surface a much larger flow flux (or conductance) through the microsieve with smooth surface will be observed.

Later on, the experiment results will show this hypothesis is not correct due to lack of consideration on atomic roughness on the surface and gas molecule shape. More details will be given in Chapter 7.

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Chapter 3 Microfabrication techniques

In the micromachining techniques, etching is basically divided into two groups: wet chemical etching and dry (plasma) etching. Wet chemical etching was important technique for the integrate circuit manufacturing in 1960s. It can provide low cost and high selectivity between substrate and mask. Later on in the early 1970s, dry etching was widely adopted for anisotropic etching. It can offer the possibility of vertical etch rate which greatly exceeds the horizontal etch rate. From then on, more and more research came into dry or plasma etching. In this chapter, both of these two techniques will be discussed in detail. The first part is about wet chemical anisotropic etching. The principle of etching mechanism will be discussed here. Detailed discussion about KOH anisotropic etching is introduced as well. In the second part, a general introduction about dry plasma etching is given. Special discussion focuses on deep reactive ion etching, especially on Bosch process.

3.1 Wet chemical anisotropic etching

Wet chemical anisotropic etching is one of most important techniques for bulk silicon micromachining. The anisotropic feature of etching silicon allows us to precisely control the etching shape and dimensions of structures. This technique is commonly used for making pressure or acceleration sensors. Furthermore, some complicated 3D structures, such as ink-jet printing devices and other microfluidic systems, are also fabricated with this technique. The possibility of batch processing by using wet chemical etching could largely reduce the production cost, which makes devices more competitive on the market.

3.1.1 Silicon crystal structure

The anisotropy of silicon etching is dominated by the silicon planes. Therefore, before we discuss the etching mechanism, a general introduction of silicon crystal structure is given in the following [1].

A crystal structure is formed by placing a collection of atoms (also called basis) at each point of the lattice. The lattice is defined as the periodic arrangement of atoms, which can be described by three translational vectors, a, b, c, in 3-D structures. The arrangement of atoms in the crystal looks the same when viewed from the point \mathbf{r} as when viewed from \mathbf{r} ` translated by an integral multiple of vector:

$$\mathbf{r} = \mathbf{r} + u_1 \mathbf{a} + u_2 \mathbf{b} + u_3 \mathbf{c} \tag{3.1}$$

Here, the u_1 , u_2 , u_3 , are arbitrary integers. The lattice is called the primitive lattice if any two points from which the atomic arrangement looks the same always satisfy eq.1 with a correct choice of the integers.

There are three most common basic crystal structures: Simple Cubic, Body-centered cubic, and Face-centered cubic. They are shown in figure 3.1.



Figure 3.1 three basic crystal structures

Silicon has a diamond crystal structure. The lattice of this structure is face-centered cubic, and the basis has two identical atoms at coordinates (000), (1/4, 1/4, 1/4) located at each point of the Face-Centered Cubic lattice, as shown in figure 3.2. From the figure, we can see that each atom has 4 nearest neighbors. The diamond structure is relatively empty: the volume filled by the hard spheres is only 34% of the total available volume.



Figure 3.2 Left: atomic positions projected on the cube face in a cube of diamond structure. Fractions denote heights above the base in unit of cube edge. Right: Silicon crystal structure shows the tetrahedral arrangement.[1]

Different planes or directions in the crystal are usually identified by a set of integers h, k, and l, which are also called Miller indices. For a specific crystal face, the Miller indices are given by (hkl) for the plane and [hkl] for the crystal orientation (vector perpendicular to the plane). Three fundamental planes are shown in silicon crystal structure in Figure 3.3.





Figure 3.3 Top: fundamental planes in silicon crystal. Bottom: side view of silicon crystal structure of three fundamental planes.[2]

The family of faces, like (100), (010), (001) are all equivalent and called $\{100\}$ planes. Similarly, the direction [100], [010], [001] are marked as a set of <100> directions. Usually, in micromaching, <100> and <110> orientation wafers are the most two common used wafers.

3.1.2 KOH etching

KOH is the most commonly used etchant for wet chemical anisotropic etching. It is much less dangerous than other etchant, easy to prepare and etches fast. Although it is incompatible with IC industry due to the metal contamination, it is still can be used for industrial use in micromaching.

The first detailed study of KOH etching was done by Price in 1973[3]. He used not only KOH solutions but also KOH+Isopropyl alcohol. He found the KOH solution at a concentration of 10%-15% (weight percent) had the fastest etch rate. When the isopropyl alcohol was added, the fastest etch rate occurred at a concentration of 30%. Roughly speaking, the addition of alcohol would decrease the etch rate. He also found that the etching was not diffusion limited because the solution stirring had no influence on the etch rate. On <100>silicon wafers, Price observed an etch ratio of 35:1 for $\{100\}/\{111\}$ crystal planes. Later on Kendall [4] reported that the etch rate of $\{110\}$ crystal planes was at least 400 times faster than that on the $\{111\}$ crystal planes using 44% concentration KOH solutions at 85°C. In his study, he also showed the relationship between the etch rate and the degree of crystal misalignment. His results were shown in Figure 3.4.



Figure 3.4 Left: Disorientation θ between {110} and {111} planes. Right: The undercutting to depth ratio (etch rate of {111} / etch rate of {110}) for a series of grooves at various disorientation angles. [4]

The chemical reaction during the etching process was investigated by Palik[5,6,7]. He monitored the reaction process by Raman spectroscopy. It was pointed out in his study that both hydroxide (OH) and wafer (H_2O) were involved with the etching. He proposed a chemical reaction equation:

$$Si + 2H_2O + 2OH^- \rightarrow Si(OH)_2O_2^{-2} + 2H_2$$

In a later work, he took the energy level into consideration and said that the reaction transferred an electron form OH^- into the silicon surface bond and then back to the etch products. However, Raley [8] *et al* assumed that there were four electrons which were transferred into the conduction band by an initial oxidation reaction and the electrons will be consumed in a following reduction step. His chemical reaction equations are:

$$Si + 20H^{-} \rightarrow Si(0H)_{2}^{+2} + 4e^{-}$$

 $Si(0H)_{2}^{+2} + 4e^{-} + 4H_{2}O \rightarrow Si(0H)_{6}^{-2} + 2H_{2}$

In order to find the etching rate of different crystal planes, Seidal [9] suggested a wagon wheel pattern mask (Shown in figure 3.5). When the {111} crystal planes meet at concave corners,



Figure 3.5 Left: wagon wheel pattern mask. Lateral underetch rates as a function of orientation when using a 50% KOH solution at a temperature 78° C of <100> wafer (middle) and <110> wafer (right)[9].

etching effectively stops. However, at the convex corners, the etch rate is quite fast and lateral undercut occurs. Corner compensation (adding mask materials to the convex corners) will slow down the etch rate at these corners.

For decades, people attempt to explain the different etch rate on different crystal planes. Generally, the etch rate follows the sequence $\{110\} > \{100\} > \{111\}$. Some people [3,6] try to explain this using the reaction kinetic of the surface atoms. They argued that the {111} planes have a higher density of surface atoms to the etchant than that to $\{100\}$ planes. The etch rate would eventually decrease due to the increase in shielding by surface bonded OH or oxygen. However, this cannot explain why the etch rate of {110} planes is higher than the other two planes since the {110} planes have an even higher density of surface atoms. Another explanation was given by Price[3]. He indicated that the etch rate was related to the available bond density of different crystal planes. The surface of crystal planes with highest available bond density had the fastest etch rate. However, the ratio of available bond density for the crystal planes $\{110\}$; $\{100\}$; $\{111\}$ is 1.41:2:1.15. This obviously cannot explain that the etch ratio for {110}:{111} can achieve 400:1 since the density varies by a factor of less than two. Kendall[4] also proposed that {111} planes get oxidized rapidly and thus this {111} plan could be protected by a thin oxidation layer immediately after immersion into the KOH solution. But the oxidation rate of {110} is still faster than that of {111} plane. In a more reasonable model, Palik [5-7] assumed that the anisotropy was caused by the differences in activation energy, backbond geometry and reaction probability. We have already known that the ratio of available bond density for the crystal planes {110}:{100}:{111} is 1.41:2:1.15. But the ratio for backbonds follows the sequence of 1:2:3. So in order to etch away one silicon atom form a {111} plane, three backbonds have to be broken, while for the {100} plane only two backbonds. Therefore, if the probability of breaking one backbond is 1% (just an assumption), then the probability of breaking two backbonds from {100} planes is 100 times smaller. And at the same time, for the three backbonds, the probability is 10000 times smaller. The probability would be even smaller because occupied bonds will lower the bond energy of the backbonds left [2].

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3.1.3 {111} planes related orientation dependent etching

In the silicon crystal, eight {111} planes form an octahedron. The wafer orientation determines how the octahedron is located in the wafer with respect to the wafer flats. Different etching shapes can be achieved due to the restriction of very slow etch rate on {111} planes in KOH solutions. Figure 3.6 shows the octahedron of {111} planes and how it is located in the <100> and <110> wafers.



Figure 3.6 Position of the octahedron limited by {111} planes in differently oriented silicon wafers

The most common applications are to fabricate V-groove and U-groove. To achieve this, a mask with a rectangular opening is used. For the V-groove on the <100> wafers (figure 3.7), the mask is aligned parallel to the prime flat of wafer. The etch proceeds downward until $\{111\}$ planes are reached. In the V-groove, the $\{111\}$ planes intersects with $\{100\}$ planes at an angle of 54.7°.



Figure 3.7 Left: mask alignment parallel to the prime flat. Right: V-groove with 54.7° {111} planes.



Figure 3.8 Left: mask alignment parallel to the prime flat. Right: U-groove with 90° {111} planes

However, the angle will slightly vary because the etch rate of {111} is not zero and the alignment of wafer surface and wafer flat is not perfect with crystal orientation. For a U-groove (Figure 3.8), the mask is aligned parallel to the prime flat. The etch process continues until the two {111} planes intersect with each other. The lateral etch is restricted by {111} planes.

One of the extensive applications of the octahedron feature of silicon crystal is to fabricate the rhombus shaped microchannel [10]. The cross-section of this octahedron with the (110) plane is a rhombus with interior angles of 70.53° and 109.47° . This rhombus is marked in Figure 3.9 in dotted lines. The octahedron is extended along the [110] direction, as shown in the Figure 3.9 in order to give a clear view.



Figure 3.9 The {111} octahedron (a) and its extended form (b) for visualization of microchannels in silicon.[10]

However, a direct wet KOH etching of these channels is not possible because two {111} planes will lead to etch stop at the channel bottom. In order to etch through the limiting {111} planes, the crystal structure has to be damaged along the etch path. This usually can be done by laser beam or deep reactive ion etching. (Figure 3.10)



Figure 3.10 channels through the wafer and <1 1 0> silicon (left). The right picture shows the final shape with crystal damage.[11]

With these techniques, various kinds of microchannels can be fabricated on wafers with different orientations (Figure 3.11).



Figure 3.11 Schematic view of possible microchannels in silicon formed by intercepting the extended octahedron with the surfaces of (a)<110>, (b)<110>, (c)<100>, and (d)<111> silicon wafers, respectively.[10]

3.2 High aspect ratio DRIE with profile control

While wet chemical etching was successfully used in the early days of integrated circuit manufacturing, it has been largely replaced by plasma or dry etching due to two main reasons. The first reason is that very reactive chemical species are produced in plasma, which can often etch more vigorously than species in a nonplasma environment. The second reason is that vertical etching—to minimize underetching—is possible with plasma etch systems. So far, plasma etching can be divided into three groups: (1) chemical plasma etching (PE); in such an etching system, there are pure chemical plasma Etching is achieved by pure chemical reaction and few ion bombardments. (2) Physical plasma etching (or ion beam etching); In this case, patterning is fulfilled by sputtering a layer with high energetic flux. However due to no chemical etchant, the etch rate is quite low. (3) The reactive ion etching (RIE or more precisely reactively assisted ion beam etching). The RIE can provide directional etching due to the combination of chemical and physical plasma etching. Details about RIE will be discussed in the following [2,12,13,14].

3.2.1 The principle of plasma etching

The principle of plasma etching is simple[2]: use a gas glow discharge to dissociate and ionize relatively stable molecules forming chemically reactive and ionic species, and choose the chemistry such that these species react with the solid to be etched to form volatile or gaseous products. Electrical discharges have commonly been used to generate plasma in the laboratory using a glass tube in which two metal electrodes are installed (Figure 3.12a). The plasma is accomplished by evacuating the discharge tube to a pressure range between 10^{-5} to 10^{-3} atmosphere and applying a voltage between the two electrodes. As the voltage gradually increases, only a very small electrical current flows. However, when the voltage has reached a few hundred volts, electric current through the tube shows an abrupt increase, and the tube begins to emit visible orange–red light. This condition in the discharge tube is called plasma and is caused by



Figure 3.12. (a) A simple DC source system with two parellel-plate electrodes. (b) RIE system with RF source.

the relaxation of excited particles, which are created by electron impact. The gas becomes

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electrically conductive due to ionization; the process is also caused by electron impact in which an atom is fragmented into an ion while liberating an extra electron. Because the extra electrons formed by ionization will also convert electrical energy into kinetic energy—which will produce even more electrons—the electrical fields are quite effective in creating plasma.

In the modern lab, a more common configuration is to use a RF source (figure 3.12b) instead of a DC one. A basic system is the so-called Capacitive coupled plasma reactor (CCP). The RF power will generate electric field which will force the electrons to the positive electrodes. In their way, they will collide with the feed gas to generate gas phase etching environment which contains photons, neutrons, electrons, ions, and phonons. Electrons can track the RF electric field due to its larger mobility compared with ion's. Therefore, after the ignition of the plasma electrodes acquire a negative charge whereas the plasma becomes positively charged. Only the electrons very nearby the electrodes will reach the electrodes during the RF cycle. A thin region depleted from electrons will be developed close to the electrodes, which is called the sheath region. Because there are no electrons in this region to generate photons, this region is dark and therefore has another name: dark space. The rest of plasma is called glow region. Both regions are separated by a boundary layer.

In such a CCP RIE system, a typical etching process can be roughly divided into following four steps.

- 1. Production of active gas species. The RF source can generate the plasma (reactive species). It is accomplished by electron dissociation and ionization process.
- 2. Transport of the active species from the bulk plasma to the wafer surface. This occurs mainly by diffusion, which sometimes limits the etch rate for a particular structure such as a deep trench.
- 3. Reaction steps. The reactive species, usually F radicals, are firstly adsorbed on the surface. This process could be strongly enhanced by the ion bombardment, because the ion bombardment will create the active etching spots through surface modification or chemical products removal on the surface. Then chemical reaction will happen between the adsorbed active species and the materials to be etched. In case of Fluorine-based etching of silicon, the chemical products would be either volatile species SiF₄ or their precursors SiF₁, SiF₂, SiF₃.
- 4. Pump out of the volatile chemical products.

As discussed above, in the CCP reactor, the RF source is capacitively coupled with the plasma. In order to get high density plasma, the RF power needs to be high; however, this high power RF would lead to a high DC bias. Therefore, an alternative to use inductively coupled plasma reactor (ICP) is introduced to create high density plasma with low DC bias [15]. In an ICP reactor, the coil is wrapped around the discharge chamber in which the electrical fields are generated. The ICP reactor is working at a frequency of 13.56MHz with a power of several hundred watts to thousand watts. Figure 3.14 shows a dual-source RIE system.



Figure 3.14 A dual source RIE system [13]

3.2.2 Deep reactive ion etching (DRIE)

The etch depth distinguishes DRIE from RIE. Deep reactive-ion etching (DRIE) is a highly anisotropic etching process used to create deep, steep-sided holes and trenches in wafers, with aspect ratios of 20:1 or more. It was developed for microelectromechanical systems (MEMS), but is also used to produce trenches for high-density capacitors for DRAM. Two technologies, including Bosch process and cryogenic process, are mainly used for the protection of sidewall and to enable the fabrication of micro/nanostructures with vertical walls. The Bosch process alternately repeats the process between etch/deposit modules: removal of substrate and passivation of a chemically inert material. During the etch step, the directional ion will sputter the exposed surface in the bottom of the microstructures. Passivation layer is then coated and protects the side-wall from further etch. Each etch/deposition cycle lasts for several seconds and is repeated many times. In cryo-DRIE, the wafer is cooled down to -110 °C. The low temperature slows down the chemical reaction that produces isotropic etching. Ions continue to bombard the surfaces and remove them away to yield vertical sidewalls.

The difference between these two techniques lies in the way of adding inhibitor gases into plasma which will form the passivation layer during the etching process. In cryo-DRIE process, the inhibitor gas is added at the same time the etch gas enters ——thus also called mixed mode DRIE. In Bosch process, the inhibitor gas and etch gas are added in a sequence —— thus also called pulsed mode DRIE. The inhibitor gas in the former method is usually oxygen and the wafer is often cryogenically cooled to strengthen the inhibitor. In the latter method, the inhibitor is usually fluorocarbon gases which can perform strong polymer building [15]. See details in the figure 3.16.



Figure 3.16 Top: Cross sectional view of trenches etched in both mix and pulsed mode. Bottom: flow rate versus etch time during the etching process.

In the pulsed mode, during the etch step a shallow trench is formed in the silicon substrate, with an isotropic profile characteristic of fluorine-rich glow discharges. During the passivation cycle, a protective fluorocarbon film is deposited on all surfaces. In the subsequent etch step, ion bombardment promotes the preferential removal of the film from all horizontal surfaces, allowing the profile to develop in a highly anisotropic fashion (Figure 3.16 top right). In a typical configuration SF_6 is flowed during the etching cycle and C_4F_8 or CHF_3 during the sidewall protection cycle. Compared to the mixed mode, the etch rate of pulsed mode is lower due to the paasivation layer deposition. In order for the directional etching to proceed, higher ionic impact should be applied to clean the bottom of the etching structures due to the thicker passivation layer. This also leads to a lower selectivity between mask and substrate. It is also shown one of the intrinsic features of pulsed mode DRIE in the figure—the scallops (figure 3.16 top right). This scalloping effect is caused by the etch/deposit cycle.

3.2.3 High aspect ratio trench etching

High aspect ratio trench (HART) etching is one of the most important applications of DRIE. Profile control is extremely important during the HART etching. In the following parts, different effects in the profile control are discussed. These effects include RIE lag, bowing, bottling, and tilting [13,15,16].

There are two kinds of particles which are the main source for the etching in DRIE: ions and radicals. Ions are etching the passivating layer and controlling the profile by their direction. Radicals are necessary for etching the silicon. Normally, for an ion-inhibitor DRIE process, the high-density plasma has to wait for the incoming ion bombardment before it is able to remove silicon atoms. Therefore, the ion transportation from bulk plasma to the silicon surface is crucial to understand the etching process.

A molecule is hit by a fast moving electron and is ionized. This ion diffused with random thermal velocity to the plasma boundary (boundary between the bulk plasma and the sheath). The boundary distortion will influence the electric field and then influence the moving direction of ion which is entering the sheath region. When the ion passes the sheath region, it will collide with other particles. Therefore, due to the collision and thermal motion, the ion flux will disperse. This effect can be described by the ion angular or energy distribution function. After this the ion is entering the trench in which the ion deflection occurs because the electric field, from the conducting sample charging, will change the ion's motion. The ion will end at the sidewall or the bottom of trench. Depending on the energy and collision angle it will reflect, etch, or just stay at the sidewall or trench bottom. A detailed discussion about different effects is as follows:

- Tilting is caused by boundary distortion or local difference in radical density. Boundary
 distortion is found when sample geometry is greater than the thickness of sheath region.
 Lower the system pressure can increase the thickness of the sheath region and thus
 prevent this effect. Radical density difference will cause the radical flow from the high
 density area to the low density area, which will result in a non-vertical radical flux with
 respect to the silicon wafer surface. This can be minimized by making mask layout more
 uniform.
- 2. Bowing effect: This effect occurs in conducting samples. Ions in the trench will deflect due to the image force. Increasing the sidewall passivation or the energy of incoming ions before entering the trench would help to reduce this effect. This could be achieved in the cryogenic cooling condition or putting more passivation gas into the plasma.
- 3. Bottling effect: This effect is often confused with bowing effect. It is caused by ion shadowing or off-normal ions when ions are traveling down to the trench. In higher regions of the trench, ions are coming from a wide range of angles and there will be strong lateral undercut depending on the ion energy. However in the lower region, the sidewall etching will stop because ions will fail due to ion shadowing and ion depletion. To prevent this effect, there are two ways:1) sharpen the ion angular distribution function by decreasing the dark space thickness;2) decrease the ion energy distribution function by

the way of dc self-bias.

4. RIE lag: This effect can be explained in considering the amount of ions which exist during their travel in the trench. During the travel ions will deflect due to negative charged walls. Therefore, the ions will be captured by the walls. So the mount of ions reaching the bottom will be smaller. For smaller trenches, ion depletion is reached sooner than that of wider trenches because the flux/area ratio is smaller after certain etch depth. Another reason for this effect is the radical depletion. The radical flux is isotropic when entering the trench, but radical etching will cause decreasing of radicals to the bottom of trench. For smaller trenches, this is more pronounced after a certain depth.

3.2.4 Equipment

The DRIE system in the experiment is Adixen AMS 100SE DRIE system. This system can provide both the cryogenic and Bosch process with a temperature range between -180° C and $+50^{\circ}$ C. Feed gases include O₂, SF₆, CHF₃, C₄F₈, Ar and will be converted into high density plasma by ICP on the top. To direct the ionic species toward the substrate, a CCP is connected to the system. Important qualification factors of such a DRIE system include ICP power, throttle position, SF₆ flow, passivation gas flow, substrate holder distance, CCP power, temperature, and helium backside pressure. Etch rate and etch profile can be controlled by tuning the above parameters. In addition, the selectivity between the mask material and substrate is also influenced by these parameters. In the following, a general description [15,17]is given about the above parameters:

- 1. The ICP could influence the etch rate by creation of radical from feed gas in the plasma. At the same time, higher ICP power would create higher pressure in the chamber for the same amount of multi-atomic gas (SF₆, CHF₃, and C_4F_8). As the dark space width is direct proportional to the reciprocal of pressure, the lateral etching, caused by ion-gas collision during travel through dark space, could be influenced by ICP power.
- 2. Increasing etch gas flux can increase the etch speed due to more etch radicals in the plasma. However, for a certain ICP power the etch speed does not increase linearly with gas flux. It will increase till it reaches a maximum, then decreases.
- 3. Inhibitor gas is used to protect the sidewalls from etching. An increase in inhibitor gas flow decreases the etch-speed but results in better etch-profile anisotropy due to better side-wall passivation.
- 4. The throttle valve is related with the chamber pressure. The chamber pressure is increased by closing the exhaust throttle valve. An increased chamber pressure will have a bad effect on the etch-profile due to the increase in non-directional (lateral) etching.
- 5. CCP power is used to generate electric power, which accelerates the ions from the plasma glow straight towards the substrate. The directional etch rate will increase due to more ion bombardment to remove the inhibitor layer. However, this results in low selectivity between the mask and substrate.
- 6. Substrate holder distance is the distance between the substrate and the plasma source.

When it decreases, the etch rate increases due to high probability for the substrate to expose to the high density radical.

- 7. Wafer temperature has a big influence on the inhibitor's passivation ability. The inhibitor layer formation is stronger in lower temperature, thus resulting in a better anisotropic etch-profile. However, in cryogenic condition, special attention has been paid to the crack of the mask material.
- 8. Wafer loading influences the etch rate because of depletion of radicals. Higher wafer loading consumes more radicals, which means lower the density of radicals, thus results in a decreasing of etch rate. Higher wafer loading also increases the wafer temperature.

In this experiment, it is designed to find the right DRIE recipe for wafer through etching (380um for (110) wafer) with a straight side wall and a good mask selectivity. The requested aspect ratio is 19:1. The tuning parameters in the recipe include the temperature, the CCP setting, and etching time, while other parameters are fixed. The etching mode is pulsed mode. Wafers are patterned with microsieve mask which has circular holes (Φ : 20-um) with a hexagonal pattern. Silicon loading is around 10% of a 100mm wafer (22.67% for the patterned area).

3.3 Surface roughness reduction

As discussed above, DRIE has become one of the most important processes in MEMS fabrication. The Bosch process is commonly used for vertical deep trench etching. Nevertheless, the Bosch process has its own drawbacks. One of them is the vertical sidewall roughness due to the periodical etching and deposition steps during process. A lot of efforts are made to reduce the surface roughness. Especially in the area of optical mirror techniques, because when the vertical is used as an optical mirror, the smooth sidewall is crucial to minimize the light scattering and maintain the collimated light beam. As reported in the literature [18-25], there are three main methods to reduce the sidewall roughness caused by Bosch process: 1. KOH wet anisotropic etching; 2. Hydrogen annealing; 3.thermal oxidation. In this report, the first two methods will be discussed.



Figure 3.17 SEM pictures of scalloping effect.

3.3.1 KOH treatment

The scallops on the morphology of etched structures during DRIE can be removed by KOH wet anisotropic etching. Due to the high selectivity between {100}/{111} or {110}/{111} planes, etch will be very fast for {100}-and{110}-planes, while it is so slow for {111} planes as if it stops on this plane. As a result, etch will self-align with the restriction of {111} planes. Therefore, the sidewall smoothness of etched structures is mainly determined by the smoothness of the slowly etched {111} planes. A lot of studies have been done to investigate the surface morphology of different planes in etched structures in KOH solutions. Tellier [18] made a theoretical analysis about dependence of surface roughness on silicon crystal orientation. Later on, Sato [19] proposed an experimental proof for the relationship between surface roughness and crystal orientation. He performed his experiment by etching silicon spheres in the KOH solution. In his study the roughness of {111} planes is less than 100nm. He also showed that an increase in KOH concentration will improve the surface smoothness.

Vertical structures with smooth sidewalls can be fabricated on <110> silicon wafers with the mask align to the [111] crystal orientation. In the literature, a lot of studies on fabrication of



Figure 3.18 SEM pictures of the vertical sidewall measured in side view with respect to process time of KOH crystalline etching after DRIE[20].

vertical optical mirror for MEMS devices [20-22] have been reported. In Yun's study [20], the vertical mirror was made by using DRIE process and a successive KOH etching of a <110> SOI wafer. He also tried to improve the etching conditions for KOH solution. In his study, the optimal etching condition for KOH was found to be 45% wt concentration and 70°C temperature.

3.3.2 Hydrogen annealing

The hydrogen annealing has a great influence on the surface morphology of silicon substrate. Silicon atoms migration on the surface is enhanced by hydrogen at high temperature around 1000° C. Based on this feature, atomically smooth or regular arranged steps on <100> or <111> wafers can be achieved. This hydrogen-enhanced surface atom migration not only influences the surface morphology but also can change the global profile if the surface migration length is larger than or comparable to the structure dimensions. Previous experiment has reported to produce round corners and various voids by using hydrogen annealing in bulk silicon [23].

The mechanism of atom migration in hydrogen annealing can be explained by surface diffusion theory. As the silicon is annealed in the hydrogen environment, the silicon surface will be terminated by H atoms. The global profile transformation is modeled as atom motion on an isotropic continuum (The transport of silicon atoms is actually determined by atomistic nature of crystals and is affected by the crystalline structure). The surface transport is dominated by surface diffusion and evaporation-condensation in the isotropic medium. However, for the annealing temperature less than 1100°C, surface diffusion has the main influence on the atom migration. Figure 1 shows a schematic of surface diffusion of silicon atoms. From figure 3.19, we can see that the atoms tend to leave the convex corners and accumulate at the concave corners.



Figure 3.19 Top: Schematic illustrating atom migration on surface. Bottom: cross section of a line and space pattern etched on bulk silicon; left:before annealing right:after annealing[24].

In the literature, Mullins` theory of thermal grooving is used as the model to simulate the profile development.

$$v = \gamma * \Omega^2 * n * \frac{D}{kT} * \frac{\partial^2 K}{\partial s^2}$$

Where the v is the profile developing speed, γ is the surface tension of the substrate, Ω is the molecular volume, n is the atom density, D is the diffusion coefficient, T is the temperature, K is the surface curvature, and s is the arc length along the profile. The diffusion coefficient is determined by the temperature and pressure. Sato [23] explored this relationship with a trench evolution. He found the relationship as shown in figure 3.20. M. Lee [24] reported that the relationship between diffusion coefficient and temperature actually followed the Arrhenius equation. The pressure may only affect the activation energy of diffusion coefficient.



Figure 3.20 Time and pressure dependence of trench transformation. X and Y are defined as the long and short axis of the trench

Hydrogen-enhanced surface diffusion can effectively reduce the surface roughness. Therefore, it is possible to use this technique to reduce the scalloping effect in the Bosch process. M. Lee demonstrated sidewall scalloping was dramatically reduced by applying the hydrogen annealing [24].



Figure 3.21 sidewall roughness caused by DRIE.(a) before and (b) after annealing[24]. The wafer was then annealed in pure hydrogen at 1100° C, 10 torr for 10 min.

Sacrificial thermal oxidation is another way to remove the surface roughness. The patterned structure is first oxidized then followed by an oxidation removal procedure. If necessary, these two steps can be repeated a few times to further reduce the surface roughness. However, it will not be used in this experiment because it will consume a lot of silicon and may also cause stress problems.

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Chapter 4 Microsieve fabrication process

The fabrication of microsieve is done in the cleanroom of MESA+ institute of nanotechnology. Our aim is to make a rhombus shaped microsieve with smooth surface. The process starts with <110> wafers which are patterned with 20 µm circular holes in a hexagonal pattern. After this, pulsed mode DRIE is applied to drill holes into the silicon. The aspect ratio after wafer-through etching for the 20 µm holes is 19:1. After DRIE, there are periodical rough structures (so-called scallops) on the channel surface. This roughness is caused by the pulsed process and will be removed in a post-etch procedure using an anisotropic etch solution like KOH. During the KOH etch of the scalloped microsieve, most of the silicon planes are etching fast until the much more chemically stable {111} planes are reached. As a result, the originally circular channels become rhombus shaped channels with nano-scale smooth sidewalls.

4.1 Mask design

The mask is designed using the software CleWin3.0 from PhoeniX Software. The 5-inch mask has a design area of 10cm*10cm. Our pattern is located in a 8cm*8cm square centered at (0,0). Because the mask is designed for SU-8, a negative photoresist, the blue holes area is covered with chromium. For negative photoresist, photoresist from the non-exposed area will dissolve in the developer. The mask has a hexagonal pattern with hole`s diameter of 20um and the distance between the holes is 40um. The porosity of patterned area is 22.67% and the wafer loading is around 18.48%. The mask design is shown in figure 4.1.



Figure 4.1 schematic view of the mask design.

4.2 Process Outline

The main process steps are shown in the following as well as a brief description of each step. Detailed discussion is made in the following paragraphs. For a detailed process, see the appendix C.

Step	Process description	Cross-section of wafer
1	Substrate selection:<110> DSP wafers (p type) 380um±10um	
2	A thin layer of 50nm silicon rich nitride (SiRN) is deposited on both sides of the wafer (LPCVD). It is used as the mask for KOH etching.	
3	5um thick of SU-8 is spin-coated on top of the SiRN followed with a soft bake procedure. This SU 8 layer is used as mask for DRIE	
4	Standard photo lithography is used to pattern the SU-8. Post-exposure bake is applied before development. After that, RER 600 is used to develop the photo resist for 3.5 minutes followed by 2-hour hardbake.	
5	100nm of chromium is sputtered on the backside of the wafer in order to prevent the backside helium leakage during the last few minutes of DRIE.	
6	DRIE process is applied to etch away the unprotected area. Circular channels are created. Etch will stop at the chromium layer.	
7	Chromium is removed away.	
8	SU 8 is removed by Piranha solution. Cleaning time is about 30min. After this, wafer is oxidized at 800°C for 30min to remove fluorocarbon.	
9	Before KOH etching, a HF 1% is applied to lift off the fluorocarbon and to remove silicon oxide. Wafer is put in KOH solution for 2hours. After the SiRN removal, our final device is ready.	
	Si SiRN	SU8 Cr

Table 4.1 process outline of microsieve fabrication

Equipment used in the experiment.

Name	Usage
Tempress LPCVD G3	SiRN deposition
Plasmos Ellipsometer	SiRN thickness measurement
S üssMicroTec Spinner Delta 20	SU 8 coating
Electronic Vision Group 620 Mask Aligner	lithography
TCO Spray Developer	SU 8 development
Nikon Microscope	Optical microscopic inspection
Veeco Dektak 8	Surface profile measurement
Sputterke	Cr spputering
Adixen 100SE	DRIE process
Furnace B3	Dry oxidation
KOH wet bench	KOH wet etching

Another surface roughness reduction is performed by hydrogen annealing. The system used for hydrogen annealing is shown in figure 4.2



Figure 4.2 H_2 annealing system

Chapter 5 Microsieve fabrication results and discussions

5.1 Lithography with SU 8 mask

SU-8 is a negative, epoxy type, near-UV photoresist that has been originally developed and patented by IBM. Due to its low optical absorption in UV range, this photoresist can form very thick film. The SU-8 resist contains a few percent of photoacid generator that will produce a strong acid when a photochemical transformation takes place upon absorption of a photon. This photoacid acts as a catalyst in the subsequent crosslinking reaction that takes place during post exposure bake (PEB), that is, crosslinking occurs only in regions that contain acid catalyst and mainly during PEB. This high-aspect-ratio resist, SU-8, leads itself well to MEMS applications.

In this experiment there are two types of SU 8: SU 8-5 and SU 8-2005 from Microchem. We apply the same procedure for both of them. The procedure is as follows: (for detailed process flow, see the appendix C)

Step	Description	Cross section
1	Substrate-(100) wafers	
2	Standard cleaning	
3	Dehydration bake @120°C for 10min	
4	Spin coating with delta20 program 5	
5	Softbake start @ 25°C; 1 min @ 50°C; 1 min @ 65°C 3 min @ 95°C; finish at 25°C.	
6	Exposure using hard contact mode 10sec	
7	Postbake start @ 25°C; 1 min @ 50°C; 1 min @ 65°C 2 min @ 80°C; finish at 25°C.	
8	Development in RER 600 for 3:30min followed by RER 600 and IPA rinse	
9	Optical microscope check cracks in SU 8 layer	
10	Hardbake @120°C for 2 hours	
11	Optical microscope check cracks in SU 8 layer	
12	Veeco Dektak 8 check thickness of SU 8	
	Si SU8	

Table5.1 SU 8 process outline

SU 8-2005 is an upgraded version of SU 8-5 according to datasheet from the MicroChem Company. It is said that SU 8-2005 shows significantly improved wetting, faster drying and clean edge bead removal, which is also proved in our experiment. SU 8-5 is used as a substitute for SU 8-2005 due to SU 8-2005 supplement problem in the lab.

The first problem came across in the experiment is that part of SU 8 stuck on the mask when doing the exposure with the mask aligner. It happens almost on every wafer with SU 8-5 if the wafer is directly transferred from step 5 to step 6 in the above procedure (Table 5.1). However, after pre-exposure baking (softbake), if the wafers are kept in the room temperature for about 20 hours, the sticking problem occurs much less often. And if the wafers are kept for even longer time, i.e. more than 60 hours, the sticking problem will hardly happen. It turns out after a long time, the top surface layer of SU 8-5 transforms from liquid phase to solid phase and it is strong enough to withstand the force during the hard contact of exposure. For the wafers with SU 8-2005, sticking problem is not observed. To certain extent, this can prove that SU 8-2005 dries faster than the SU 8-5. Although the sticking problem happens not all over the wafer but only on small areas, it still has huge influence on the following DRIE experiment. The area without of SU 8 protection, due to the sticking problem, is much larger than the characteristic dimension of our structures (Φ : 20um). Therefore, this area has a much faster etch rate than the area with the patterns (in our experiment: 20um holes) due to the aspect ratio effect on etch rate. This area without SU 8 protection will be etched through the wafer quite fast and then backside helium leakage would make the process to be terminated before it reaches to the end of the process. After the post-exposure bake, development of SU 8 is done with Spray-gun by using RER 600



Figure 5.1 Left column is SU8 before hardbake. There are cracks on SU8 layer. Right Column is SU 8 after hardbake. Cracks are gone. Top row is SU 8-5 while bottom row is SU 8-2005.

chemicals for 3:30 min, followed by 5sec RER 600 solution rinse and 5sec IPA rinse. After development, there are cracks on SU 8 layer under microscope (Figure 5.1). This effect can be largely reduced by a following hardbake procedure.

Chapter 5 Microsieve fabrication results and discussions

The thickness of the photoresist is measured by using Veeco Dektak 8. The results are showing in Table 5.2.

Postion	1	2	3	4	5
SU 8-5	5114.78nm	5060.52nm	5034.89nm	5148.93nm	5078.85nm
SU 8-2005	5717.03nm	5676.23nm	5625.08nm	5747.51nm	5645.51nm

Table5.2 Thickness of SU 8	e5.2 Thickness of SU	8
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From table 5.2, we can see the thickness of photoresist is around $5 \,\mu$ m. The thickness of SU 8-2005 is slightly thicker than that of SU 8-5, which is caused by the difference of viscosity between them.

The side view of development results are shown in figure 5.2 for both SU 8-5 and SU 8-2005. In general, both types of SU 8 offer the straight vertical structure.



Figure 5.2 Cross section of vertical SU 8 structure

5.2 DRIE with 908-35 mask

Before using SU 8 as a mask, a positive photoresist Olin908-35 with a typical thickness of 3.5um is chosen as the mask. The lithography process is done by a technician in TST group.

Previous DRIE experiment with the same type photoresist——Olin907-12 has been done by Jansen and Unnikrishnan [1, 2]. In their experiments, the main process parameters in a pulsed-mode DRIE are discussed, such as: ICP power (for plasma generation), etch gas flow rate, inhibitor gas flow rate, exhaust throttle valve position (indirectly chamber pressure), CCP power (to create an electric field between plasma and the wafer for directional ion bombardment), wafer holder distance from plasma source (SH-position), wafer chuck temperature, and loading of the masked pattern (which is the amount of unmasked area exposed to plasma for etching). All these parameters have different effects on the etch-speed and etch-profile. The etch recipe including all the parameters mentioned above is shown in table 5.3.

Parameters	Value
SF_6 flow(etch gas)	400 sccm
CHF ₃ flow(inhibitor gas)	200 sccm
SF ₆ pulsing time	48
CHF ₃ pulsing time	0.5s
ICP power	2500 w
CCP _{LF} power	50 w(10ms on- 90 ms off)
Substrate distance from source(SH)	110mm
Throttle vale position	15% (i.e. chamber pressure = 10 Pa)
Helium wafer backside cooling pressure	10mbar
Wafer chuck temperature	-120°C

Table 5.3 DRIE etch recipe for microsieve fabrication

The etch results from Ref [2] are shown in table 5.4. Different kinds of effects (e.g. lateral undercut, bottling, tapering, RIE lag etc.) are shown in the etch profile and methods to solve the problems has been well discussed in Ref. [1-3].

Exp. #	1	2	3	4	5	6	7	8	9
Τ[℃]	0	0	0	-40	-40	-80	-80	-120	-120
CCP LF [W]	20	20	20	20	20	20	20	20	20
CCP On-Off[ms]	10-90	10-90	20-80	20-80	20-80	20-80	20-80	20-80	20-80
CHF ₃ flow[sec]	1⁄2	1	1	1	1	1	1	1	1⁄2
Etch Time [min]	3	3	3	3	15	15	20	20	15
Etch profile of a micro hole	J	Į							
Etch Depth [um]	21	22	24	26	74	76	90	58	95

Table5.4 results of wafers with 5umΦ holes, hexagonal pattern[2]

The starting recipe based on the recipe in Table 5.3 is customized for the requested HARTs. As the silicon should be etched through the wafer of 380um, both a good selectivity between the mask and substrate and a thick photoresist layer are needed. The CCP power is tuned to 50w to increased the directional etch speed. Meanwhile, due to the increased ion bombardment, the erosion of mask material is also increased. The experiment results are shown in the table 5.5. The wafer A and B are etched at -120°C for 10min and 25min respectively. The sidewall is quite straight. The average etch rate of wafer B is lower than wafer A because of the RIE lag. However, a lot of photoresist cracks are observed due to the very low temperature. Cracks are also observed on wafer C and D. In order to prevent the cracks, temperature is increased. At -100°C, cracks are still there. But at -80°C, the cracks are gone. However, due to the higher temperature the bottling effect—i.e. lateral undercut in the upper level of the trench—is more severe. This is clearly shown by the wafers G and H. Even worse, the photoresist is gone after 46min etching with an etch depth of only 162um. The bottling effect is caused by the insufficient passivation. Therefore the inhibitor is changed into C_4F_8 which is a stronger inhibitor due to the higher CF₂ production than the CHF₃ inhibitor.

XXI C		D		D	Г	Г		TT
water	A	В	C	D	E	F	G	H
Diameter[um]	10	10	20	20	10	10	10	10
T[°C]	-120	-120	-120	-120	-120	-100	-80	-80
CCPLF [W]	50	50	50	50	50	50	50	50
CCP 0n-off [ms]	10-90	10-90	10-90	10-90	10-90	10-90	10-90	10-90
CHF ₃ flow [sccm]	200	200	200	200	200	200	200	200
Etch Time [min]	10	25	30	15	25	20sec	46	25
P.R etched [um]	0.4	2	1.7	0.7	1.9	0	3.5	2.2
Etch Depth [um]	82	154	244	144	154	NA	162	132
Etch profile								

Table5.5 etch results	s with 908-35 mas	k
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 C_4F_8 is found to have an extremely strong blocking capacity, for only very small amounts of gas are needed to block etching. CHF₃ and C_4F_8 show the identical etch profile when the flow of C_4F_8 is about 1/30 of the flow of CHF₃. Another advantage is for C_4F_8 the inhibitor is present even up to the room temperature.

In the experiment with C_4F_8 as inhibitor, the temperature is set to -40° C to minimize the change of crack forming due to thermal shock. This experiment is focusing on the flow flux and CCP onoff time. The experiment results are shown in Table 5.6. Wafer I and J show that as the etching time increasing from 15min to 30min, the bottling effect appears. This effect is due to insufficient passivation. To reduce the effect, the C_4F_8 flux is increased. However the sidewall is getting quite rough (black silicon appears) in wafer L. This effect is reduced by tuning the CCP on-off time from 10-90 to 10-40, which increases the amount of ionic species. However after 45min etching, the photoresist is gone due to the higher mask erosion rate. Further increasing C_4F_8 flux does not give much improvement on the etch profile.

Wafer	Ι	J	K	L	М	Ν	0	Р
Diameter [um]	20	20	20	20	20	20	20	20
T[°C]	-40	-40	-40	-40	-40	-40	-40	-40
CCPLF [W]	50	50	50	50	50	50	50	50
on-off [ms]	10-90	10-90	10-90	10-90	10-40	10-40	10-20	10-40
C ₄ F ₈ flow [sccm]	50	50	80	150	150	150	250	250
Etch Time [min]	15	30	15	15	15	45	15	15
P.R. etched [um]	0.9	1.9	0.7	0.1	1	3.5	2	0.8
Etch Depth. [um]	141	226	142	123	137	286	134	135
Etching profile								

Table5.6 Further	experiments re	sults with 908-35
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In the two groups of experiments, temperature plays an important role in the profile control. The reason is that the inhibiting capacity of inhibitor increases conveniently while lowering the temperature.

In pulsed etching mode (SF₆/CHF₃ or SF₆/C₄F₈ at 2500w) with Olin 908-35 as etching mask, the maximum etch rate is 18um/min for 10% loading while the average etch rate in this experiment is round 9.5um/min. Due to the RIE lag, the deeper the trench goes, the lower the etch rate is. The mask erosion is acceptable at the lower bias—around 0.05um/min at -120°C with CCP on-off time of 10-90. However none of the recipe shows perfect profile for wafer through etching with the straight sidewall. At the lower temperatures (<80°C) the silicon etch profile is fine, but the Novolack resin suffers for cracks due to thermal shock. Cracks are prevented when etching at higher temperature (>80°C). But now the etch profile is suffering from the bottling effect. Therefore, the Olin 908-35 is not a qualified candidate for mask material during the etching.

5.3 DRIE with SU 8 mask

The etching results of first experiment are shown in table5.7.Experiments start with wafer A, etch profile shows vertical and smooth sidewall. As to the mask selectivity, etch rate of SU 8 is about 4um per hour. Wafer B has a deep but slightly positive tapered channel. This is caused by lack of ionic species as the etching proceeds. Wafer C and D are designed to reproduce the results of Wafer B. There are some areas on Wafer C where is not covered by SU 8 mask. Therefore, a silicon ring is used to protect that specific area from etching. In this case, etch rate is lower due to higher Si loading. Increasing the CCP on-off time can improve the profile but also lead to higher mask erosion. In order to find a balance between the etch profile and mask erosion, a two-step process is applied. Recipes are as follows: on-off time for wafer E: 45min 10-90 and 15min 10-40; wafer F: 30min 10-90 and 30min 10-40; wafer G: 30min 10-40 and 30min 10-90.

Wafer	А	В	С	D	Е	F	G	Н
Diameter [um]	20	20	20	20	20	20	20	20
T[°C]	-120	-120	-120	-120	-120	-120	-120	-120
CCP LF [W]	50	50	50	50	50	50	50	50
on-off [ms]	10-90	10-90	10-90	10-90	10-40	*	*	*
Etching time [min]	15	60	60	60	60	60	60	60
CHF ₃ flow [sccm]	200	200	200	200	200	200	200	200
SU 8 etched [um]	0.97	3.08	3.57	2.5	>5	3.57	>5	>5
Etch depth [um]	150	417	374	433	360	418	400	429
Etch profile								

Table 5.7 Etch results of first experiment with SU 8 mask

The etching time and CCP setting for each step still needs further investigation due to the unsatisfactory results. Another problem is that sidewall roughness appears at the middle and bottom part of the trench. Figure 5.3 shows the sidewall roughness of wafer D, F, G, H.



Figure 5.3 Sidewall roughness during the etching with SU 8 as the mask.

The position where the sidewall roughness starts is 287um, 257um, 218um, and 239um for wafer D, F, G, H respectively. The sidewall roughness is created due to ionic species trapped by the image force. This force can capture ions, which causes attack to the sidewall. During the travelling from the top to the bottom of the trench, the ionic species lose their energies. The deeper the ionic species travel, the more energy they lose and the easier they are captured. At certain point, the ionic species do not have enough energy to escape from the image force capture. And then they are trapped on the sidewall and start to attack the sidewall. This effect can be reduced by increasing the energy of ionic species by increasing the CCP power in the following experiment.

So far, it is suggested that the CCP setting plays an important role in etching profile. It can be explained as follows: There are two parameters in the CCP setting: power and on-off time. The power determines the energy of ionic species while the on-off time controls the directional ionic species flux. Increasing the on-off time can reduce the positive taper effect at the bottom. At the mean time, increasing the power could possibly reduce the sidewall roughness. The former has been verified by the experiment (wafer E table 5.7) and the later will be verified in the future experiment.

Although the SU 8 has some problems during the exposure and development, it still provides almost perfect profile compared with Olin 908-35. The problems occurring during the exposure and development can be overcome by using another type of SU 8—SU 8-2005. In the following experiments, two problems needed to be solved: 1) reduce sidewall roughness 2) decrease mask erosion rate (improve selectivity). Further experiment results are shown in table 5.8:

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The experiment started with Wafer A, which is used as the reference wafer during this experiment. After 1 hour etch with the recipe described in table 5.8, the profile showed the almost the same result with the previous experiment (Wafer D in table5. 7). It was positive tapering at the bottom part of the channel, which was caused by the RIE lag. The sidewall attack begins at the depth of about 252um. In order to find out the relationship between the sidewall attack position and the etch time, we reduce the etch time to 45min (Wafer B). There is no sidewall attack in the whole channel and only slightly positive tapering could be seen at the bottom. To further investigate when the positive tapering effect occurs, Wafer C and Wafer D are etched for 30min and 15min respectively.

Wafer	А	В	C	D	E	F	G*
Diameter[um]	20	20	20	20	20	20	20
T[°C]	-120	-120	-120	-120	-120	-120	-120
CCP _{LF} [W]	50	50	50	50	75	50	50
CCP 0n-off [ms]	10-90	10-90	10-90	10-90	10-90	10-40	10-90
CHF ₃ flow [sccm]	200	200	200	200	200	200	200
Etch time [min]	60	45	30	15	60	30	30
SU 8 etched [um]	2.6	2.2	1.4	0.7	>5	2.8	1.4
Etch depth [um]	429	335	251	152	415	254	246
Position** [um]	252	NA	NA	NA	289	NA	NA

Table 5.8 Etch results of second experiment with SU 8 mask

The result shows no tapering. Back to the sidewall attack effect, we increase the CCP power to 75w to see the relationship between the CCP power and the position of sidewall attack. The etch profile shows that there is only slightly sidewall attack at the depth of 289 um. However the SU 8 is fully removed due to the higher CCP power—thus more ion bombardment. It testifies our hypothesis that the sidewall roughness position would be deeper as the CCP power increased, because the ionic species have higher energy. Meanwhile, compared with Wafer A, the positive tapering effect is also reduced. The etch profile of wafer F is compared with the wafer E in table 5.7. The top part of the channel in wafer F seems perfect. But compared with Wafer C, the channel is widened, which is caused by changing the on-off time setting (To simplify the tuning of on-off time, in the following experiments, we fix the on-time at 10ms and only off-time changes). The Wafer G is deposited with SiRN on both sides. The thickness of SiRN was 59.46nm (Measured by Ellipsometer). The etch profile and the etch rate are identical with the results of Wafer C, which indicates there is influence on the etch results caused by SiRN.

Further experiments are performed to tune the parameters in table 5.9. Multiple-step of DRIE process is applied. In the beginning of etching, low CCP low is applied. As etching goes on, CCP power changes to higher value. This can reduce the RIE lag effect, at the same time, it is hoped that the sidewall attack would also be eliminated. Experiment starts with a 50w+75w combination (wafer A) with each step of 30min. The etch profile is vertical and straight, but the sidewall attack still occurs. A six-step process is therefore applied, which changes from 20w to 70w with a step of 10w (wafer B). The ugly etch profile indicates that the etch process stops during the first step because of too much inhabitation, which is further proved by experiment of Wafer C. Whether the etch stop is caused by the Adixen 100se is checked by experiment using wafer D and E. Their etch results show identical etch profiles with previous experiments. Without satisfying experiment results in the current CCP power and on-off time setting, we go for higher CCP power and lower on-off time setting. Wafer F is set at CCP power 100 w and on-off time 10-140. The etch depth and selectivity are satisfying. Although the etch profile is slightly positive tapering, it is improved compared previous experiments. In the experiment of wafer F, higher CCP power is used to reduce the positive tapering effect. Etch Profile is straight and vertical while the sidewall attack still happens. Wafer H tries to further lower the on-off time setting in order to get rid of sidewall attack. However, the etch profile again shows positive tapering and sidewall attack.

Wafer	А	В	C	D	Е	F	G	Н
Diameter[um]	20	20	20	20	20	20	20	20
T[°C]	-120	-120	-120	-120	-120	-120	-120	-120
CCP LF [W]	50+75	20-70	20	75	75	100	115	115
CCP on-off [ms]	10-90	10-90	10-90	10-90	10-90	10-140	10-140	10-190
CHF ₃ flow [sccm]	200	200	200	200	200	200	200	200
Etch time [min]	30+30	60	10	53	55	60	60	60
SU 8 [um]	NA	5.45	5.59	NA	NA	3.5	4	1.8
Etch depth [um]	406	97.03	96.52	370	390	414	408	440

Table 5.9 Etch results of third experiment with SU 8 mask

In the following experiment, we examine the influence of CCP power and on-off time on etch profile separately (table 5.10). The CCP power of wafer A, B, C is fixed at 50w. The on-off time is 10-40, 10-70, and 10-90, respectively. As the off-state time of CCP power in one pulse cycle decreases, the sidewall attack reduces. However, we have to notice that the selectivity of mask is dramatically decreased due to the amount of ion bombardment. Wafer C, D, E is fixed at the same on-off time: 10-90. The CCP power is increased from 50w, 75w to 100w. Higher CCP power generates ions with higher kinetic energy—thus high ion bombardment. Compared with these three etch profiles, it is found that as CCP power increases, the positive tapering effect is largely reduced, while the mask selectivity is dramatically decreased. To solve this problem, we postulate that a combination of higher CCP power and lower on-off time setting can offer good mask selectivity for the same etch profile.

Wafer	А	В	С	D	Е
Diameter[um]	20	20	20	20	20
T[°C]	-120	-120	-120	-120	-120
CCP LF [W]	50	50	50	75	100
CHF ₃ flow [sccm]	200	200	200	200	200
CCP on-off [ms]	10-40	10-70	10-90	10-90	10-90
Etch time [min]	60	60	60	60	60
SU 8 etched [um]	5.6	4.14	3.2	5.6	5.6
Etch depth [um]	360	407	428	415	391

Table 5.10 etch profile versus CCP power and on-Off time

Further experiments to find appropriate combination of CCP power and on-off time are shown in Table 5.11. The maximum CCP power of the system can afford is 200w and the maximum off time is set as 190ms. Among all the results, it is clearly seen that wafer G gives the best etch profile and reasonable mask selectivity.

Wafer	А	В	C	D	Е	F	G
Diameter[um]	20	20	20	20	20	20	20
T[°C]	-120	-120	-120	-120	-120	-120	-120
CCP LF [W]	115	115	125	150	175	200	175
CCP on-off [ms]	10-165	10-190	10-190	10-190	10-190	10-190	10-165
CHF ₃ flow [sccm]	200	200	200	200	200	200	200
Etch time [min]	60	60	60	60	60	60	60
SU 8 [um]	2.8	2.6	1.8	3.3	3.1	3.2	4.3
Etch depth [um]	426	440	420	422	427	413	402

Table 5.11 Etch results of fourth experiment with SU 8 mask

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Combined with the previous experiments, all the recipes which can offer relatively perfect etch profile are summarized in table 5.12. The first two recipes (wafer A and B) have very low mask selectivity (all the SU 8 is etched way), besides wafer A does not have enough etch depth. For the last two recipes (wafer C and D), they both have good mask selectivity and relatively perfect etch profile. However, recipe D has a slightly smoother sidewall than recipe C. Therefore, we conclude recipe D as the final etch recipe for the microsieve fabrication.

Wafer	А	В	C	D	E	F
Diameter[um]	20	20	20	20	20	20
T[°C]	-120	-120	-120	-120	-120	-120
CHF ₃ flow [sccm]	200	200	200	200	200	200
CCP _{LF} [W]	50	100	115	175		
CCP 0n-off [ms]	10-40	10-90	10-140	10-165		
Etch time [min]	60	60	60	60	60	60
SU 8 etched [um]	5.6	5.6	3.3	4.3		
Etch depth [um]	360	391	415	402		
Etch profile						

For a 380um <110> wafer, the etching time is approximately 57 min. The reason for a 60min etching is explained as follows: DRIE on the wafer scale shows non-uniformity which is possibly due to the local depletion of etch radicals by the etching silicon surface. This depletion was stronger at the wafer center than at the wafer edge (the so-called edge effect or Bull's eye effect.)



Figure 5.4 Non-uniformity etching due to bull's eye effect

Figure 5.4 shows a faster etch rate in the edge than that in the center. To prevent this effect, 3min extra etching is applied to guarantee everywhere on the wafer is etched through and stops at the backside chromium protection layer. Figure 5.5 shows the DRIE etch result. The etched channel shows almost identical profile from the top to the bottom. As the etch proceeds, etch rate is going down and the number of scallops per unit length is increasing while the roughness of scallops is decreasing.



Figure 5.5 SEM pictures of circular channels after DRIE. Top: sidewise of the channels. Bottom: left top part of channel; middle: middle part of channel; right: bottom part of channel

The bottom of channel is wider than the rest, which is possibly caused by the notching effect. As discussed before, There silicon wafer is double side deposited by SiRN. At the end stage of the etching, ions will be deflected by this SiRN layer, because SiRN layer is insulator and will be

Chapter 5 Microsieve fabrication results and discussions

charged during the etching. The deflected ions will attack the sidewall, which will lead to the lack of protection for sidewall. Fluorine-radicals come in and lateral etch occurs where the sidewall is without inhibitor protection.

The roughness of scalloping effect is on the micrometer scale depending the etch rate. HRSEM pictures show a close view of sidewall roughness.



Figure 5.6 HRSEM of sidewall roughness after DRIE.

5.4 Sidewall roughness reduction in KOH bath

After DRIE, patterned silicon wafer is put into Cr etchant for 15min to remove the backside chromium protection layer. The remaining SU 8 layer on top is cleaned in Pirahna solution for 30min. After this, a 30min dry oxidation process is applied to burn off fluorocarbon layer on the channel surface, which is from the DRIE process. Before KOH wet etching, a 1% HF dip is done to remove the silicon oxide layer which grows during dry oxidation process. Finally, KOH wet chemical etching is applied. KOH concentration is 25% wt and etch temperature is 75°C. The etch time is around 2hours and etch rate of SiRN mask is less than 0.6nm per hour. After KOH, SiRN mask is removed in 50% HF solution. The etching results are shown in figure 5.7&5.8.



Before KOH bath (SiRN as a mask) Af

After 2hr KOH bath

Strip SiRN mask

Figure 5.7 The top three pictures show the development from circular channel to rhomboid channel in KOH bath.



Figure 5.8 SEM pictures of top view of rhombus channel after KOH etching.

Figure 5.7 gives a top view of how the rhombus channel develops. From the middle picture in Figure 5.7, we can clearly see the radius of inscribed circle in the rhombus is larger than the original circular pattern, which is possibly caused by slowly etched {111} planes. The etch rate of {111} planes depends on the angle intersecting with {110} planes. The angle for the left (111) plane is 35.3° and 144.7° for the right (111) planes. Etch rate for these two cases are $12.5nm^*min^{-1}$ and $37.5nm^*min^{-1}$, respectively. In this experiment, four {111} planes are vertical to the <110> wafer, the etch rate is around 20nm*min⁻¹ which is reasonable in between above two values. The surface roughness is checked by HRSEM. It is shown in figure 5.9



Figure 5.9 HRSEM of channel surface roughness.

From figure 5.9, we can see that the channel surface is not really atomically smooth. A close view in figure 5.10 shows that there are even small islands or pits on the surface (nano scale). The pits defect can be explained as follows: Oxygen atoms, dissolved in the silicon during crystal growth, will occupy interstitial positions in the lattice. Precipitation due to heat treatment of the wafer causes a chemical reaction of silicon and interstitial oxygen to solid silicon dioxide. Since silicon dioxide is approximately two and a half times larger than pure silicon in volume, which results in mechanical stress in the lattice. To release this stress, interstitial silicon atoms are generated. Subsequently, the interstitial silicon atoms gather in extrinsic stacking faults. This process depends on the mobility of atoms, which again depends on temperature. The shape of the stacking faults is determined by thermodynamics and can be anything from irregular to circular or

triangular. The stress fields around these stacking faults give rise to a locally increased etch rate of the silicon, thus creating pits on the surface. The islands defect will be caused by contaminated residuals.





5.5 Hydrogen annealing

Hydrogen annealing is done in the CMP group. The experiment parameters are listed in table 5.13.

Parameters	Value
Temperature(°C)	950
H ₂ Pressure(mbar)	6
Time(min)	30

Table 5.13 Hydrogen annealing experiment

The equipment is shown in Chapter 4 figure4.2. First, the sample is fixed on the sample holder and then vacuum pump is turned on. After that, Hydrogen is turned on. Temperature is set at 950°C. Experiment result is shown in the figure5.11. From the figure, the scallops are still visible and almost as the same as they are before hydrogen annealing. This is probably caused by the relatively low annealing temperature since in most of literatures hydrogen annealing is done at around 1100°C. The surface atom migration highly depends on the diffusion coefficient and the relationship between diffusion coefficient and temperature follows the Arrhenius equation. Therefore, 150°C difference would lead to a dramatic change to the diffusion coefficient. The surface atom migration speed is so low that the surface morphology seems to stay in the same fashion. The reason why the results are not satisfying as the literature showed is still under investigation.



Figure 5.11 SEM pictures of microsieve channel before (left) and after (right) hydrogen annealing.

5.6 Conclusion

After a series of test, an optimized process for SU 8 is found. DRIE recipe for wafer through etching is chosen as shown in table 5.14. Surface roughness reduction is tried by both KOH wet chemical etching and hydrogen annealing. The results of KOH etching show that the surface roughness is largely reduced. The roughness scale is down from micrometer-scale to nanometer-scale. On the other hand, hydrogen annealing does not reduce the surface roughness.

Table 5.14 Final DRIE etch recipe

Parameters	Value
SF ₆ flow(etch gas)	400 sccm
CHF ₃ flow(inhibitor gas)	200 sccm
SF ₆ pulsing time	4s
CHF ₃ pulsing time	0.5s
ICP power	2500 w
CCP _{LF} power	175 w(10ms on- 165 ms off)
Substrate distance from source(SH)	110mm
Throttle vale position	15% (i.e. chamber pressure = 10 Pa)
Helium wafer backside cooling pressure	10mbar
Wafer chuck temperature	-120°C

Reference:

- 1. Jansen, H.V. de Boer, M.J. Unnikrishnan, S. Louwerse, M.C. and Elwenspoek, M.C. 'Black silicon method X: a review on high speed and selective plasma etching of silicon with profile control: an in-depth comparison between Bosch and cryostat DRIE processes as a roadmap to next generation equipment.' Journal of micromechanics and microengineering, 19 (3) 2009
- 2. Unnikrishnan ,S.' Micromachined Dense Palladium Electrodes For Thin-Film Solid Acid Fuel Cells' PHD thesis University of Twente 2009
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Chapter 6 Characterization

After the finishing the fabrication process, the microsieve is first bonded to a glass tube for easy characterization. Gas flow through the glass tube and microsieve is measured with a home-made experiment setup. Experiment data will be compared with theoretical value and analyzed in this chapter.

6.1 Glass tube bonding



Figure 6.1 Schematic view of glass tube bonded on microsieve

The bonding process is done in an oven in TST group. First, the microsieve is placed on the ceramic plate of the oven and then a glass tube with inner radius of 3mm is put on top of the microsieve (Figure 6.1). The oven is gently and slowly closed to prevent the glass tube from falling down due to the air flow turbulence. The oven is turned on and set at the temperature 790°C. After 20min heat treatment, oven is turned off and the sample is cool down to room temperature. Finally, the glass tube is firmly bonded to the microsieve. During the measurement, the tube bonded on the microsieve can stand high pressure without any damage. A final device is shown in figure 6.2.



Figure 6.2 microsieve bonded with glass tube

6.2 Theoretical estimation of mass flow through microsieve

The gases used in the experiment are compressed air, dry nitrogen and SF_6 . Related parameters are listed in table 6.1.

Parameters	Values	Accuracy
Ambient temperature T	294k	0.4%
Effective area of microsieve A_m	$7.07*10^{-6} \text{ m}^2$	6%
Porosity of microsieve k	43.67%	10%
Side length of rhomboid <i>l</i>	2.66*10 ⁻⁵ m	2.5%
Viscosity of air at 294k	1.841*10-5 Pa*s	0.2%
Viscosity of nitrogen at 294k	1.789*10-5 Pa*s	0.2%
Viscosity of SF6 at 294k	1.555*10-5 Pa*s	0.3%
Length of microsieve channel	3.8*10 ⁻⁴ m	2.6%
Flow conductance	NA	24.7%

Table 6.1 Parameter values used for flow conductance calculation

Experiment error occurs when doing the experiment measurement. It could be caused by experiment apertures, environment conditions, measurement methods, and even the experimenter. Some aspects which produce errors are listed in the following:

- 1. The ambient temperature is measured by the temperature sensor in the cleanroom, and it has the accuracy of $\pm 1^{\circ}$ C.
- 2. Effective area of the microsieve $A_m = \pi r^2$. The bonded radius of glass tube will enlarge during the glass-silicon bonding due to edge curving because of surface tension of soft glass. The diameter has an error of ±0.1mm.
- 3. The error of L (the thickness of (110) wafer) is 380um±10um according to the wafer supplier.
- 4. The viscosity η varies with the ambient temperature T. The data is listed in table 6.2.

Temperature	Air	N ₂	SF ₆
293k	1.836*10 ⁻⁵ Pa*s	1.785*10 ⁻⁵ Pa*s	1.550*10 ⁻⁵ Pa*s
294k	1.841*10 ⁻⁵ Pa*s	1.789*10 ⁻⁵ Pa*s	1.555*10 ⁻⁵ Pa*s
295k	1.845*10 ⁻⁵ Pa*s	1.794*10 ⁻⁵ Pa*s	1.561*10 ⁻⁵ Pa*s

Table 6.2 Visc	ousity versus	temperature f	or different	gases
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5. Error from the microscope, the measured channel diameter or rhomboid side length has an error of ± 0.1 um.

Accuracy for other parameters is related to the above five aspects and the accuracy for all the parameters are listed in Table 6.1 in percentage. The accuracy of flow conductance F can be determined by eq. 6.9: $Error(F)=error(A_m)+error(k_{rhom})+error(1)+error(\eta)+error(P_a)+error(T)+error(1)+error(L)=6\%+10\%+2.5\%+0.2\%+0.5\%+0.4\%+2.5\%+2.6\%=24.7\%$



Figure 6.3 Schematic top view of microsieve channel

The porosity of microsieve is calculated as follows for both before and after KOH etching.

As shown in figure 6.3(left), the porosity of microsieve with hexagonal pattern holes is defined as total hole (blue) areas over by the total patterned area. To simplify the calculation, we can choose the smallest repeating unit: a triangle as shown in the figure 6.3 (middle). In this unit, parts of the blue circles (stand for the holes) are overlapped with the triangle, and the porosity is defined as the overlapped area divided by the area of triangle. The area of overlapped part is given:

$$S_{overlap} = \frac{60^o}{360^o} * \pi r^2 = \frac{1}{6}\pi r^2$$
(6.1)

The area of the triangle is given:

$$S_{tri} = \frac{1}{2} * a * a * sin60^{o} = \frac{\sqrt{3}}{4}a^{2} = 4\sqrt{3}r^{2}$$
(6.2)

Therefore, the pososity for the microsieve with circular holes is given:

$$k = \frac{area \ of \ overlaps(3 * S_{overlap})}{area \ of \ triangle(S_{tri})} = \frac{3 * \frac{1}{6}\pi r^2}{4\sqrt{3}r^2} = 0.227$$
(6.3)

After the KOH etching, circular channel cross-section transforms to rhomboid shape. The porosity of microsieve with rhomboid channels is still defined as the area of rhombus channel over by total patterned area. Therefore the porosity is given (figure 6.3 right):

$$k_{rhom} = \frac{\text{total area of rhomboid}}{\text{total patterned area}} = \frac{\text{area of rhomboid}}{\text{area of holes}} * \frac{\text{area of holes}}{\text{total patterned area}}$$
$$= \frac{\text{area of rhomboid}}{\text{area of holes}} * k = \frac{l * l * \sin 70^{\circ}}{\pi r^{2}} = 0.4367$$
(6.4)

Where the *l* is the side length of rhomboid.

As discussed in Chapter 2, the formulas (eq. 2.3-eq. 2.11) are only valid for circular tubes or microsieve with circular channels. For flow conductance through microsieve with rhombic channel, we can calculate by adapting these formulas (eq. 2.3-eq. 2.11) by introducing two parameters the hydraulic diameter D_H and cross section shape factor K_{shape} . The hydraulic diameter is defined as:

$$D_H = \frac{4A}{H} = \frac{4l^2 \sin 70^o}{4l} = l \sin 70^o = 0.94l$$
(6.5)

Where the *A* is the cross section area and *H* is the perimeter. The shape factor is discussed in Ref. 1-2. For a microsieve with rhombic cross section, the shape factor K_{shape} is given 14.046 (with the smaller angle 70°). The viscous flow conductance for a single channel with rhombic cross section is given:

$$F = \frac{P_a}{RT} * \frac{D_H^2 A}{2K_{shape} \eta L} = \frac{(0.94l)^2 * l^2 sin70^o}{2\eta * 14.046 * L} = 0.030 * \frac{l^4}{\eta L}$$
(6.6)

Where the l is the side length of rhomboid, L is the length of channel. For a microsieve, the conductance can be written as summation of all the individual channels:

$$F_{1} = \frac{P_{a}}{RT} * \frac{D_{H}^{2}A_{m} * k_{rhom}}{2K_{shape} \eta L} = \frac{P_{a}}{RT} * \frac{(0.94l)^{2} * A_{m} * k_{rhom}}{2\eta * 14.046 * L} = 0.031 * \frac{A_{m}kl^{2}}{\eta L} \frac{P_{a}}{RT}$$
(6.7)

Where the A_m is the total area of bonded microsieve, k is the porosity.

For the conductance from entrance and exit effect as well as the influence from neighborhood, it can be achieved using eq. 2.10 by introducing the hydraulic diameter D_H and cross section shape factor K_{shape} .(f(k)=0.0395 when k=0.4367)

$$F_{vis-orifice-sieve} = \frac{ArkP_a}{3\eta\pi RT} * \left(1 - f(k)\right)^{-1}$$
(2.10)

$$F_2 = \frac{A_m D_H k_{rhom} P_a}{2K_{shape} \eta \pi RT} * \left(1 - f(K)\right)^{-1} = 0.034 * \frac{A_m kl}{\eta} \frac{P_a}{RT}$$
(6.8)

Therefore, the total flow conductance through a microsieve is given:

$$F = \frac{F_1 F_2}{F_1 + F_2} = \frac{A_m k_{rhom} l}{\eta} \frac{P_a}{RT} \left(\frac{1.060l}{31l + 34L}\right)$$
(6.9)

The flow conductance is believed to bemuch larger than that for a microsieve with the same length but a relatively rough surface. The ratio of flow conductance for smooth and rough surface is written as:

$$C = \frac{F_2}{F} = \frac{\frac{A_m D_H k P_a}{2K_{shape} \eta \pi R T} * (1 - f(K))^{-1}}{\frac{A_m k l}{\eta} \frac{P_a}{R T} (\frac{1.060 l}{31l + 34L})} = \frac{17(31l + 34L)}{530l}$$
(6.10)

For a microsieve with l=26.6 um, L=380 um, C is around 17. Therefore, if our hypothesis is true, conductance through the microsieve with smooth surface will be 17 times of that through microsieve with rough surface.

6.3 Flow measurement setup

The schematic of the gas flow set-up used for characterization is illustrated in figure 6.4. Experiments are performed by flowing gases at 294 K, at varying mean pressures and at fixed differential pressure across the microsieve. The pressure of incoming compressed air or dry nitrogen is set at desired value (4bar) by the pressure regulator. Gas flux is controlled by a mass flow meter (Bronkhorst High-Tec, error margin 0.5 % on readout and 0.1 % on full scale 1000sccm). A pressure sensor (Sensortechnics, error margin 0.5% on full scale) is placed between mass flow meter and sample holder, and it reads the absolute pressure above the ambient pressure before the sample. A differential pressure sensor (Sensortechnics GmbH, error margin 0.2% on full scale 0.344bar) reads the pressure drop over the sample. The absolute pressure and pressure drop over the sample can be adjusted by the mass flow controller and needle valve.



Figure 6.4 Schematic representation of the gas flow measurement set-up.

6.4 Procedure of measurement

At first, the influence of connection plastic tubes and glass tube on the total flow flux is measured. A glass tube without the microsieve is placed at the sample holder. Flow flux through the whole system is measured at varying differential pressures and absolute pressures. The conductance is calculated and compared later on with the sample with the microsieve. It turns out that the conductance of connection tubes and glass tube is so large that its contribution to the total conductance can be ignored.

Second, the compressed air used during the experiment is not filtered and the microsieve can act as a filter. This could reduce the total mass flow through the microsieve during the measurement due to the dust particle accumulation. To check this, the mass flow is monitored for a continuous measurement for about 60min. The mass flow is roughly remaining the same within the noise error during the measurement.

At the start of the measurements, the flow controller is completely closed. The needle valve now is fully open. To measure the mass flow through the sample at varying differential pressures, firstly the compressed air supply is switched on and is set to a fixed value (4bar) using the pressure regulator. After this, the mass flow controller is slowly open and set at a certain value. Slowly turn the needle valve until the required absolute pressure is achieved. In this way we can record the varying differential pressures, while the absolute pressure is kept constant. To do the same experiment at higher absolute pressures, at first the flow flux is increased by open the mass flow controller and subsequently the needle valve is adjusted till the desired absolute pressure is achieved. To measure the mass flow through the microsieve at varying absolute pressures, while keeping the differential pressure across the microsieve constant, we adopt a similar procedure as mentioned above. The only difference is that the here the flow controllers are readjusted to always maintain a constant differential pressure across the microsieve. During the measurement, the more the needle valve is open, the lower the absolute pressure is and the larger the differential pressure is.

6.5 Experiment results and discussion

Mass flow through the microsieve is measured at varying mean pressures: 2bar, 3bar, and 4bar as well as different differential pressures: 20mbar, 40mbar, 60mbar and 80 mbar. The Knudsen number is $1.4*10^{-3}$, $9*10^{-4}$, and $7*10^{-4}$. Therefore, flow is in the viscous regime. The theoretical values of flow conductance at different mean pressures are given in figure 6.5 according to eq. 6.9 with upper and lower limit (These limits come from the errors listed in table 6.1). Experiment data is plotted in figure 6.6&6.7.



Figure 6.5 Flow conductance versus mean pressure with errors.



Figure 6.6 Mass flows versus differential pressure. Gas: Compressed air



Figure 6.7 Mass flows versus mean pressure. Gas: Compressed air

From the figures above, we can clearly see that a linear increasing trend in the total mass flow flux, which is directly fit with the viscous behaviour. These two graphs give the first indication that flow through the microsieve is in the viscous regime and it is linearly proportional to the mean pressure and differential pressure. The conductance is then compared with the theoretical value in Figure 6.8.



From the figure 6.8, the experimental flow conductance matches the theoretical value within the error. However, the conductance is much smaller than the value from eq. 6.8, which contradicts

Figure 6.8 Comparison of theoretical and experimental flow conductance at differential pressure of 20mbar.

with what we expect. In our expectation, the flow conductance should be much higher than theoretical value from both eq. 6.9, and it should be close to the value derived from eq.6.8. One possible explanation for figure 6.8 would be: There is always a thin native oxide (SiO_2) layer on silicon surface. This oxide layer makes the silicon surface hydrophilic, which will attract water molecules from compressed air or ambient environment. Gas molecules will interact with the water molecules on surface and cause them to lose kinetic energy. This can be removed by hydrogen fluoride solutions.

In order to eliminate the influence from water molecules and native silicon oxide, we change the gas from compressed air into dry nitrogen supplied in cleanroom. Before the measurement, microsieve is put into 1%HF to remove the native oxide layer. The hydrophilicity of the channel surface can withstand for 15min after 1%HF dip. The experiment results are plotted in figure 6.9.



Figure 6.9 mass flow fluxes through microsieve before and after HF dip. The differential pressure is fixed at 20mbar.

In figure 6.9, the results demonstrate almost identical flow flux at the same mean pressure for microsieve before HF dip and after HF dip. The HF treatment will make the silicon surface atoms covalently bonded with hydrogen atoms—hydrogen terminated silicon surface. The roughness on the surface is caused by hydrogen and silicon bond on the scale of angstrom Å. The distance between two silicon atoms is about 4 Å. Figure 6.10 shows a hydrogen terminated silicon surface surface and a schematic view of surface roughness.



Figure 6.10 hydrogen terminated silicon surface (111) a nanometer sized area of bare silicon (circled area is 1nm by 1nm bare silicon) (left); schematic view of surface roughness (right)

In the following experiment, SF_6 with a diameter of around 6.8Å is used as the test gas (the largest gas molecule in our lab). HF dip is also applied before measurement. The results are shown in figure 6.11.



Figure 6.11 mass flow fluxes through microsieve using SF_6 and N_2 . The differential pressure is fixed at 20mbar.

The slopes of flow flux-mean pressure curve through the microsieve by using SF_6 and N_2 are approximately the same. The gas molecule size is still comparable with the surface roughness, in other words, gas molecules are still reflected diffusively.

*All the flow measurement data are shown in appendix D

6.6 Discussions

A microsieve with smooth channel surface is used to examine the influence of surface roughness on flow behaviour in viscous regime. Flow flux is measured at different conditions during the experiment. It is widely accepted the hagen-poiseuille's law can adequately describe the flow behaviour through tubes or porous media in the viscous regime based on the diffusive reflection assumption. However, in our case, we believe if the surface roughness is largely reduced, more gas molecules will be reflected specularly. Our experiments demonstrate the results matched with the formulas based on the diffusive reflection assumption. The reason why gas molecules are reflected diffusively at the solid smooth surface could be explained as follows:

First of all, the gas molecules and solid atoms at surface are considered as hard elastic spheres. Supposing there is a solid atom standing still (yellow sphere) and gas molecules (blue sphere) are moving towards all directions as shown in figure 6.12 (A). Any gas molecules with a velocity Vy < 0 will have a chance to collide with the solid atom. During the collision, the solid atom is assumed to so large that it will stand still, and the gas molecules will be reflected. The gas molecule moving direction is isotropic after reflection. As shown in Figure 6.12 (B), the reflection direction depends on where the gas molecule strikes on the solid atoms. Therefore, in general a gas molecule with given velocity in direction and magnitude, strikes a fixed elastic hard sphere, its velocity after reflection may be in any direction with equal probability — the reflection direction is isotropic. Now let's place a number of such solid atoms spread over the surface and they are so far apart from each other that no solid atom is protected by its neighbour atoms from the impact of collision with gas molecules as shown in figure 6.12 (C). The surface layer is so deep that no molecules can pass through it without collisions with one or more solid atoms. Every gas molecules approach to the surface and must strike one or more solid atoms at the surface. After that, the gas molecule's motion becomes isotropically — the so called diffusive reflection.



Figure 6.12 A) gas molecule and the solid atoms are considered as hard spheres and the gas molecule approaches the solid atom in all directions (Vy < 0). B) gas molecule strikes the solid atom at different positions and after reflection, its velocity becomes isotropical. C) gas molecules strikes a solid surface


Figure 6.13 Left: gas molecule size larger than the distance between solid atoms. Right: densely packed solid When the size of gas molecule is larger than the distance between two solid atoms or the solid atoms are so densely packed that the solid atom is protected by its neighbor atoms from the collision with gas molecules (Figure 6.13). In this case, there is a larger probability for gas molecules to strike the surface solid atom at its pole position than at its equator position. The larger the incident angle (included angle between incident direction and normal direction to the surface) is, the greater probability of gas molecules will be to strike the solid atom near its pole position. The velocity direction of reflected molecules will not equally distribute in all directions this time, but there is a greater probability of its tangential part of velocity being the same as before its collision and the normal part of velocity being the opposite to the normal part before collision——thus the specular reflection.

Two extreme situations are shown in figure 6.14 the normal incidence and glancing incidence. Now suppose we have a surface with high densely packed solid atoms and larger size of incoming gas molecules (much larger than the distance between two solid atoms). At the normal incidence condition, gas molecules will reflect diffusively and at the glancing incidence condition, gas molecules will reflect specularly.



Figure 6.14 Left:gas molecules comes to the surface in any direction. Middle: Gas molecules come with normal angle with respect to the surface. Right: gas molecules come with glancing angle.

Chapter 6 Characterization

In above discussions, the gas molecules are treated as the hard spheres. However, gas molecules have various different shapes other than spheres. The three gas molecules used in this experiment, He, N_2 and SF_6 molecule shapes are shown in figure 6.15



Bottom: different molecules strike surface atoms.

The monatomic helium molecule can be treated as hard sphere, while the nitrogen molecule is formed by triple bond of two nitrogen atoms. Its shape is like a bar, which will cause the diffusive reflection even the nitrogen atoms strike the surface with closely packed atoms at glancing incidence. For a larger molecule SF_6 , its shape is like a six-ray star and it will have the same diffusive reflection behavior as N₂.

In a conclusion, the diffusive reflection is not only caused by large scale surface roughness, but also highly depended on the surface solid atoms arrangement as well as gas molecule size and shape. Specular reflection can occur on the condition that gas molecule can be treated as sphere and its size is larger than the distance between solid atoms, while at the same time the solid atoms at surface have to be regularly patterned and closely packed.

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Chapter 7 Conclusion and Future scope

7.1 Overall conclusion

A microsieve with smooth channel surface is designed and fabricated on a 4-inch double side polished <110> wafer. A 5um thick negative photoresist SU 8 is chosen as the mask material. It is patterned with 20 µm circular holes in a hexagonal pattern. The advantage of SU 8 is that it can provide straight vertical profile. During the DRIE process, 5um SU 8 is thick enough to withstand. Even at -120° C in the cryogenic DRIE process, SU 8 can still provide good protection. A pulsedmode DRIE process is applied to etch through the whole <110> wafer (380um). DRIE can provide fast etch rate and high aspect ratio trench etching. After a series of test experiments, an optimal recipe for the wafer through with straight vertical profile etching is found. A protection layer of 100nm chromium is deposited on the backside of the wafer to prevent the Notching effect. The experiment results show only slightly notching effect (small lateral undercut at the channel bottom). After DRIE, chromium is etched away in the Cr etchant. SU 8 is removed in piranha solutions for 30min. A following dry oxidation process successfully burn off the fluorocarbon layer on the channel surface. Double side SiRN layer is deposited as the KOH etch mask. The surface roughness produced by DIRE process is dramatically reduced by this KOH wet chemical etching. After 2hours etching, a microsieve with smooth rhombus channel surface is made.

This microsieve is used to test the influence of surface roughness on the viscous flow behavior in porous media. Flow flux through the microsieve is measured by using a home-made experiment setup. Different gases, mean pressures and differential pressures are applied during the experiment. It is assumed that the microsieve with smooth channel surface will have a higher flow conductance due to the specular reflection. However, the experiment results show the flow conductance of the microsieve with smooth channel surface is almost the same as that of the microsieve with rough channel surface, which means most gas molecules are reflected diffusively by the channel walls. The silicon surface property is analyzed and dry nitrogen and HF treatment is applied to prevent the influence from water molecules. Larger gas molecules SF_6 are also tried. Both of these two experiment results show the same diffusive reflection behaviour. Therefore, it is concluded that the diffusive reflection is not only caused by large scale surface roughness, but also highly depended on the surface solid atoms arrangement as well as gas molecule size and shape. Specular reflection can occur on the condition that gas molecule can be treated as sphere and its size is larger than the distance between solid atoms, while at the same time the solid atoms at surface have to be regularly patterned and closely packed. Such kinds of surface can be achieved by graphane or boron nitride (BN)coating.

7.2 Future scope

Future work will focus on the fabrication of atomically smooth surface. There are two kinds of materials which are promising for this application.

Graphene is a one-atom-thick planar sheet of sp2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice (Figure 7.1). It can be visualized as an atomic-scale chicken wire made of carbon atoms and their bonds. Graphene exhibits a wealth of unique electronic transport properties. However, it is not only interesting in terms of electrical transport, but it is also the building block of the most common macroscopic solid lubricant graphite. The pseudo-twodimensional sp2-bonding in graphite yields one of the most effective solid lubricants. The individual 2D graphene planes are weakly bonded in the third dimension by van der Waals forces, which can be used to explain the excellent lubricating properties of graphite. Research shows that graphene films can largely reduce the friction between solid interfaces. Graphene films have been technically used as low-friction antiwear coating for SiC surfaces. To produce atomically smooth surfaces, Silicon carbide is heated to high temperature (>1100°C) and reduced to the single grapheme layer.



Figure 7.1 A single suspended sheet of graphene shows individual carbon atoms (yellow) on the honeycomb lattice.

Another material would be boron nitride, which is a chemical compound with chemical formula BN, consisting of equal numbers of boron and nitrogen atoms. BN is isoelectronic to a similarly structured carbon lattice and thus exists in various crystalline forms. The hexagonal form corresponding to graphite is the most stable and softest among BN polymorphs, and is therefore used as a lubricant and an additive to cosmetic products. It can work as a lubricant at high temperature up to 900°C.

Both the above two materials have the hexagonal flat atomic structure. Although they are mostly used as solid lubricate, we postulate that it may work for gas too due to its atomically smooth surface structure.

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Appendix

Appendix A

Flow conductance in free molecular regime

Although the Hagen-Poiseuille law forms a firm basis when treating the fluid as a continuum, it is far off when considering free-molecular behavior as found in 1829 by Thomas Graham. Graham found that the rate of escape of a gas is inversely proportional to the square root of the mass of its molecules. Later on, Knudsen started a series of experiments to establish the theory about how the molecular flow depending on the tube dimensions and the physical gas properties. For a tube with a length of L, a radius of r, a cross section of A_{tube} and a perimeter of H, and Q is mass flow rate. The formula deduced by Knudsen is given:

$$Q = \frac{1}{RT} * \frac{4v\Delta P}{3\int_0^L \frac{H}{A_{tube}}^2 dl}$$
(A1)

Where v is the mean molecular speed, which can be derived by using Maxwell-Boltzmann distribution:

$$v = \int_0^\infty v * 4\pi v^2 (m/2\pi kT)^{3/2} \exp[(-mv^2/2kT)] dv = (\frac{8kT}{\pi m})^{\frac{1}{2}} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$
(A2)

For a long tube with uniform circular cross section, eq. A1 is given:

$$Q = \frac{1}{RT} * \frac{4\left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}}{3\int_{0}^{L}\frac{2\pi r}{(\pi r^{2})^{2}}dl} * \Delta P = \frac{8\pi r^{3}}{3L} * \sqrt{\frac{1}{2\pi MRT}} * \Delta P$$
(A3)

$$F_{mol-tube} = \frac{Q}{\Delta P} = \pi r^2 * \left(\frac{3L}{8r}\right)^{-1} * \sqrt{\frac{1}{2\pi MRT}}$$
(A4)

For the conductance through an orifice or short tubes, we can derive the formulas as follows: Consider an isothermal vessel containing gas at pressure P_1 , and there is an orifice on the vessel wall. Through this orifice, gas molecules can effuse into an adjacent vessel, where the pressure is $P_2(P_2 < P_1)$. O. Meyer showed that the number of molecules of a gas at rest as a whole that strike a certain surface with area *A* is given by the relation:

$$\frac{dN}{dt} = \frac{1}{4}vA(n_1 - n_2)$$
(A5)

Where the N is the number of gas molecules, n_1 is the number density (N/V) of gas corresponding

to the pressure P_1 , n_2 is the number density corresponding to P_2 . Using the ideal gas law, PV=NkT, n=N/V=P/kT, the flow rate is given:

$$Q = \frac{1}{4}vA(P_1 - P_2) * \frac{1}{kT} = \frac{1}{4}vA * \Delta P * \frac{1}{kT}$$
(A6)

Therefore, formula of molecular conductance for an orifice:

$$F_{mol-orifice} = \pi r^2 * \frac{1}{\sqrt{2\pi MRT}}$$
(A7)

It was pointed out that the formula A3 was only valid when the diameter of the orifice was comparable or much less than the mean free path under certain pressure. Ideally, the orifice can be treated as "no length".

Dushman took into account of the entrance and exit effect of a tube with circular cross section, and used the electrical analogy concept to add inversely the conductance of corresponding parts:

$$F_{mol-long} = \frac{\pi r^2}{\sqrt{2\pi MRT}} \left(1 + \frac{3L}{8r}\right)^{-1}$$
(A8)

However, later on in 1932, Clausing argued that Dushman's formula was only valid for long tubes not for short ones. Meanwhile, he developed the concept of transmission probability using probability functions and provided a procedure for more accurate evaluation in long and short tubes. In the same year, Kennard found a more accurate formula for short tubes:

$$F_{mol-short} = \frac{\pi r^2}{\sqrt{2\pi MRT}} \left(1 + \frac{L}{2r}\right)^{-1} \tag{A9}$$

Similar to the viscous flow, molecular flow conductance for a microsieve with hexagonal arrays of tubes or orifices can also be derived by addition all individual ones.

Appendix B

Flow conductance in transition regime

The transition from molecular flow to viscous flow was another main subject in Knudsen's experiment. When the mean free path is comparable with the characteristic dimensions of the tube, intermolecular collisions compete with the purely molecule-wall interaction. Knudsen treated the conductance in the transition regime as a combination of viscous flow and molecular flow conductance. Based on the Maxwell's law of velocity distribution in conjunction with a straightforward theory of the interaction of gas molecules with a solid wall, he found:

$$F = aP + \frac{b(1+C_1P)}{1+C_2P}$$
(B1)

With *a* representing Poiseuille's expression and *b* the coefficient of molecular flow, C_1 , C_2 are two empirical parameter. In his experiment, Knudsen found a minimum when he plotted the

curve for conductance versus the pressure. He postulated that this effect would be caused by the influence of the wall roughness.

Pollard and Present examined the concept of self-diffusion in transition regime and obtained a qualitative explanation of the Knudsen minimum. They suggested, at least at low pressures, the total transport can be described by the superposition of the diffusive transport computed in their paper and a drift component. Their paper discussed the pressure dependence of self-diffusion in a capillary but they only proposed the idea of superposition as a qualitative explanation for the Knudsen minimum. Lund and Berman (1966) presented a useful model describing transport



Figure B1 (a) Volume **flux** $Q/\Delta p$ as a function of mean pressure for CO₂ flow through a long capillary. **R** = 0.0033 cm, **L** / **R** = 613.2 (from Knudsen 1909), **L** = 2.042 cm. (b) Flow of gases through capillaries of various length to radius ratio. A, He: **L** / **R** = 0.319; B, Xe: **L** / **R** = 11.84; C, He: **L** / **R** = 11.84; **D**, CO₂: **L** / **R** = 613.2. Points show experimental results; lines fitted model equation (from Lund and Berman 1966). The pronounced minimum only for sufficiently long tubes.

under a partial pressure gradient (self-diffusion) as well as under a total pressure gradient in capillaries of arbitrary L/ R and covering pressures from free molecule to continuum regimes. Comparison with experimental data suggested that surface effects and slip contributions needed to be taken into account. Experimental results from Lund and Berman (1966) are shown in figureB1

Appendix C

Process document

Step	Process		Comment
1	Substrate selection - Silicon <110> DSP (#subs010)	CR112B / Wafer Storage Cupboard Supplier: Orientation: <110> Diameter: 100mm \pm mm Thickness: 380 μ m \pm 10 μ m Polished: Double side polished (DSP) Resistivity: 5-10 Ω cm Type: p	
2	Cleaning Standard (#clean003)	CR112B / Wet-Bench 131 HNO ₃ (100%) Selectipur: MERCK HNO ₃ (69%) VLSI: MERCK • Beaker 1: fumic HNO ₃ (100%), 5min • Beaker 2: fumic HNO ₃ (100%), 5min • Quick Dump Rinse <0.1µS • Beaker 3: boiling (95°C) HNO ₃ (69%), 10min • Quick Dump Rinse <0.1µS • Spin drying	
3	Etching HF (1%) Native Oxide (#etch027)	CR112B / Wet-Bench 3-3 HF (1%) VLSI: MERCK 112629.500 • Etch time: >1min • Quick Dump Rinse <0.1µS • Spin drying	native oxide removal
4	LPCVD SiRN - uniform thickness (#depo002)	CR125C / Tempress LPCVD G3 Program: SiRN01 • SiH ₂ Cl ₂ flow: 77,5 sccm • NH ₃ flow: 20 sccm • temperature: $820/850/870$ °C • pressure: 150 mTorr • N2 low: 250 sccm • deposition rate: ± 4 nm/min • N _f : ± 2.18 • check validation site for material properties	thickness:50nm
5	Ellipsometer Measurement (#char007)	CR118B / Plasmos Ellipsometer	check the thickness of SiRN
6	Lithography - Dehydration bake SU-8 (#lith062)	CR112B / Hotplate • Dehydration bake (120°C): 10min	

7	Lithography - Coating SU-8 5 (Delta20)	CR112B Microche Manufac	/ S üssl em NA turer Sj	MicroTec Spi NO SU-8 5 pecs:	nner Delta 20	program 5
	(#lith063)	program	ר (Γhickness μm)		
		4	7	7		
		Experime	ental R			
		Spin program	rpm	Thickness (µm)		
		1	1000	13.6		
		2	1500	8.4		
		3	2000	7.4		
		4	2500	6.0		
		5	3000	5.2		
		6	3500	4.6		
		7	4000	4.1		
8	Lithography - Softbake SU-8 5 (#lith064)	CR112B or CR117B / Hotplate For spin programs 4-7 start @ 25 C 1 min @ 50 C 1 min @ 65 C 3 min @ 95 C finish at 25 C.		program the hotplate and leave the wafer for three nights and two days(prevent sticking		
		8				problem)
9	Lithography - Alignment & Exposure SU-8 5 (#lith065)	CR117B Electroni • Exposu	CR117B / EVG 620 Electronic Vision Group 620 Mask Aligner • Exposure time 10sec			
10	Lithography - Post Exposure Bake SU-8 5 (#lith066)	CR112B For spin • Start @ • 1 min • 2 min • 5 °C/2m	CR112B or CR117B / Hotplate For spin program 4-7: • Start @ 25 °C • 1 min @ 50 °C • 1 min @ 65 °C • 2 min @ 80 °C • 5 °C/2min down to 25 °C			
11	Lithography - Development SU-8 5 (#lith067)	CR102A / Wet-Bench 9 TCO Spray Developer Developer: PGMEA (RER600, ARCH Chemicals) • Time 3:30 min with spray-gun • Time: 5sec rinse with PGMEA bottle • Time: 5sec rinse with IPA • Spin drying				

12	Optical microscopic inspection - Lithography (#char001)	CR112B / Nikon Microscope			check cracks on su 8 layer	
13	Lithography - Hard bake SU-8 (#lith068)	CR112B or Cl • 2hr @ 120	R117B / Hotp ℃	blate		
14	Optical microscopic inspection - Lithography (#char001)	CR112B / Nik	CR112B / Nikon Microscope			
15	Surface profile measurement (#char005)	CR118B / Vee	CR118B / Veeco Dektak 8			check the thickness of SU 8(~5um)
16	Sputtering of Cr (Sputterke) (#depo017)	Eq.Nr. 37 / Sputterke Cr Target (gun #: see mis logbook) • Electrode temp.: water cooled electrode • Ar flow: app. 80 sccm, pressure depending! • Base pressure: < 1.0 e-6mbar • Sputter pressure: 6.6 e-3mbar • power: 200W • Depositionrate = 15 nm/min			sputtering Cr for back protection in DRIE	
17	Plasma etching of Si A-pulsed-CHF3 (#etch069)	CR 125c/Adix Application: S wafer through	ten SE Silicon pillars,	/Si high load/	trenches,	1 hr
		Parameters	Etch	Deposition (pulsed)		
		Gas	SF ₆	CHF ₃		
		Flow (sccm)	400	200		
		Time (sec)	4	0.5		
		Priority	2	1		
		APC %	15	15		
		ICP (Watt)	2500	2500		
		CCP (Watt)	nvt	20		
		Pulsed (msec)	nvt	20on/180off		
		Pulsed (msec) SH (mm)	nvt 110	20on/180off 110		
		Pulsed (msec) SH (mm) Electrode temp.	nvt 110 -120	20on/180off 110 -120		
		Pulsed (msec) SH (mm) Electrode temp. He (bar)	nvt 110 -120 10	20on/180off 110 -120 10		

		60 min postbake	
18	Optical microscopic inspection - Lithography (#char001)	CR112B / Nikon Microscope	check the etch profile
19	Etching of Cr Wet (#etch034)	CR116B / Wet-Bench 2 Chromium etch LSI Selectipur: MERCK 111547.2500 • Quick Dump Rinse <0.1µS • Spin drying Etchrates = 100nm/min	remove Cr
20	Cleaning "Piranha" (H ₂ SO ₄ /H ₂ O ₂) (#clean008)	CR112B / Wet-Bench 130 H ₂ SO ₄ (96%) VLSI, BASF H ₂ O ₂ (31%) VLSI, BASF	su 8 removal
		 Only use the dedicated wafer carriers and rod! H₂SO₄:H₂O₂ (3:1) vol% • add H₂O₂ slowly! to H₂SO₄ be carefull exothermic process • adjust the hotplate at 85 ℃, the temperature will increase to 130 ℃ • Cleaning temperature: 130°C • cleaning time 10-15min • Quick Dump Rinse <0.1µS • Spin drying 	
21	Dry Oxidation at 800 °C of Silicon (#depo026)	CR112B / Furnace B3 Standby temperature: 800 °C • Program: DOX-800 • Temp.: 800°C • Gas: O ₂ • Flow: 41/min	do fluro carbon removal
22	Etching BHF (1:7) SiO ₂ (#etch024)	CR112B / Wet-Bench 3-3 HF/NH ₄ F(1:7) VLSI: BASF • Quick Dump Rinse $<0.1\mu$ S • Spin drying Etchrate thermal SiO ₂ = 60-80nm/min Etchrate PECVD SiO ₂ = 125/nm/min Etchrate TEOS SiO ₂ = 180/nm/min	lift off flurocarbon and remove oxide
23	Etching of Silicon by KOH - standard (#etch038)	CR102B / KOH KOH: MERCK 105019.500 KOH:DI = (1:3) 25wt% KOH: 500g KOH pellets in 1500ml DI water • Temp.: 75°C • Stirrer	2hours

		• Quick Dump Rinse $<0.1\mu$ S • Spin drying Etchrates: Si $<100> = 1 \mu$ m/min Si $<111> = 12.5$ nm/min SiO ₂ (thermal) = 180nm/hr SiRN < 0.6 nm/hr	
24	Etching HF (50%) LPCVD SiN or Thermal oxide (#etch029)	CR112B / Wet-Bench 3-3 HF (50%) VLSI: MERCK 100373.2500 • Quick Dump Rinse $<0.1\mu$ S • Spin drying Etchrate SiRN = 5nm/min Etchrate SiO ₂ = 1 µm/min	
25	Cleaning RCA-2 (HCL/H ₂ O ₂ /H ₂ O) (#clean007)	CR112B / Wet-Bench 130 HCL (36%) Selectipur, BASF H ₂ O ₂ (31%) VLSI, BASF Only use the dedicated wafer carriers and rod! HCL:H ₂ O ₂ :H ₂ O (1:1:5) vol% • add HCL to H ₂ O • add H ₂ O ₂ when mixure at 70 °C • temperature 70-80 °C • cleaning time 10-15min • Quick Dump Rinse < 0.1μ S • Spin drying	

Appendix D

Flow measurement data

Compressed air as test gas.

Absolute pressure(bar)	ΔP(mbar)	fluxΦ(sccm)	Mean pressure(bar)	F
1	10.59	121	2	8.45515E-07
1	18.4	207	2	8.325E-07
1	24.47	273	2	8.25582E-07
1	33.1	367	2	8.20483E-07
1	42.81	469	2	8.10698E-07
1	65.52	667	2	7.53327E-07
1	82.76	852	2	7.61817E-07
2	8.075	137	3	1.25548E-06
2	23.27	387	3	1.23068E-06
2	32.64	537	3	1.21746E-06
2	44.56	715	3	1.18739E-06
2	56.95	889	3	1.15515E-06
3	6.443	148	4	1.69983E-06
3	17.98	397	4	1.63393E-06
3	26.45	575	4	1.6087E-06
3	44.61	914	4	1.51616E-06
0.56	20.02	176	1.56	6.50549E-07
1.4	20.08	268	2.4	9.87649E-07
2.31	20.09	368	3.31	1.3555E-06
2.91	20.09	433	3.91	1.59492E-06
3.56	20.11	500	4.56	1.83988E-06
0.44	39.97	315	1.44	5.83187E-07
0.75	40	382	1.75	7.067E-07
1.07	40.02	450	2.07	8.32084E-07
1.36	40.09	512	2.36	9.45074E-07
1.77	40.05	596	2.77	1.10122E-06
0.28	60.04	415	1.28	5.11492E-07
0.54	59.92	491	1.54	6.06375E-07
0.86	59.96	592	1.86	7.3062E-07

1.2	60.04	694	2.2	8.55363E-07
1.62	60.02	813	2.62	1.00237E-06
0.3	80.09	546	1.3	5.04482E-07
0.56	80.06	648	1.56	5.98951E-07
0.83	80.07	754	1.83	6.9684E-07
1.11	79.99	855	2.11	7.90974E-07
1.39	80.05	953	2.39	8.80974E-07

Dry nitrogen as test gas

Absolute pressure(bar)	$\Delta P(mbar)$	$flux\Phi(sccm)$	Mean pressure(bar)
Before HF dip			
0.74	20.02	200	1.74
1.64	20	300	2.64
2.26	20.04	371	3.26
3	19.96	449	4
3.47	19.98	499	4.47
After HF dip			
0.75	19.97	200	1.75
1.62	20	302	2.62
2.3	19.99	376	3.3
2.89	19.98	442	3.89
3.42	20	501	4.42

SF₆ as test gas

Absolute pressure(bar)	$\Delta P(mbar)$	fluxΦ(sccm)	Mean pressure(bar)
SF ₆			_
0.66	19.95	199.4695	1.66
0.82	20.01	216.1804	1.82
0.97	20.01	229.7082	1.97
1.12	20.01	243.5013	2.12
1.24	19.99	252.5199	2.24
N2			
0.67	19.99	199	1.67
1.5	20.01	299	2.5
2.16	20.01	377	3.16
2.99	20.01	472	3.99
3.38	20.01	516	4.38

Influence of connection tubes and bonded glass tube

Absolute pressure(bar)	$\Delta P(mbar)$	fluxΦ(sccm)
1	1.16	629
1	1.295	683
1	1.648	771
1	2.078	863
1	2.456	938
2	0.8152	660
2	1.032	749
2	1.358	858
2	1.677	946
3	0.7286	715
3	1.061	873
3	1.401	998