Bulk etching of silicon wafer and development of a polyimide membrane

M Aslam
Head, Electronic Materials and Processing Division
Pakistan Vacuum Society, P.O. Box 1880 Islamabad, Pakistan

E-mail: m_aslammalik@yahoo.com

Abstract. Progress in the field of engineering is always dependent on new materials. For quite some time, smart and state of the art systems are seen demanding from a modern point of view. The gas sensing devices are turned into an array of sensors than a single sensor to materialize the concept of electronic nose. The metal oxide gas sensors are actively sensitive to gas species at an elevated temperature of more than 250°C. To achieve this minimum temperature requirement, micro-heaters are developed on a certain substrate which ensures the utilization of heat energy for sensing layer of metal oxide such as tin oxide (SnO₂). In this paper, a substrate having good thermal insulation has been discussed.

1. Introduction
One of the main objectives of this research work is to produce a low heat capacity, rugged membrane support as a thin-film gas sensor substrate. An obvious candidate that is both rugged and will withstand the high temperature needed to sensitise the sensor layer is polyimide (PI) membrane. To realise this type of membrane, the supporting structure is a silicon wafer, which is bulk etched from the area of interest for membrane fabrication. A general membrane structure is as shown in figure 1.

![Figure 1. Basic bulk etched membrane.](image1)

![Figure 2. Photolithography of Cr/Au.](image2)

Silicon is an attractive material for micromachining for a number of reasons such as: it has useful, well-recognised mechanical properties and well defined processing techniques in the semiconductor industry[1, 2]. Membranes on silicon supporting structures are mostly insulating films based on oxides or nitrides (such as SiO₂ or Si₃N₄) but these membranes tend to be fragile and prone to breakage.
Several other materials apart from silicon can be used for infrastructure support such as Gallium Arsenide (GaAs) and crystalline quartz. Shearwood et al [3] and Petrini et al [4] have reported PI membrane on a GaAs substrate. According to Shearwood et al, a single layer of Probimide 7020 polyimide was spin coated onto the GaAs wafer to achieve a 7 micron thick membrane. The GaAs was then isotropically etched in NH$_3$: H$_2$O$_2$ mixture. This membrane was used to realise a micro speaker for a hearing aid application.

Petrini et al manufactured a pressure sensing structure on a PI membrane using PI2555 polyimide. The fabrication approach of Petrini et al for instance, starts with a GaAs wafer which is coated with polyimide at a spin speed of 6000 rpm for 60 seconds. After spinning, the polyimide was cured at 300 ºC for 30 minutes. The membrane thickness was 2.2 microns. The schematic diagram of the salient features of the manufacturing process is as shown in figure 2. A double alignment was used to align the backside to the upper structure of the wafer for etching. The membrane realisation on the silicon wafer was carried out using a 525 micron thick Si <100> wafer. It was spin coated using PI2575 polyimide at 1000 rpm for about 5 seconds and then at 2000 rpm for 30 seconds to achieve a thickness of 5 microns. After baking at 90 ºC for 5 minutes, a subsequent polyimide layer was spin coated again at 2000 rpm for 30 seconds to achieve a thickness of 10 microns. The polyimide was cured at 360 ºC for 30 minutes and then a photoresist mask was applied and patterned on the backside of the silicon wafer and etched in silicon etchant, generally called CP4 (3HF: 5HNO$_3$: 3CH$_3$COOH). The etch rate was about 25-30 microns/minute. When the sample was immersed in this etchant, it was observed after 10 minutes that the PI coating had come off the surface of silicon wafer.

Next, a CP4 etchant with different composition (1HF: 6HNO$_3$: 1CH$_3$COOH) was used. The etch rate of this etchant was about 5 microns/minute. A new sample was immersed in it and the same effect was observed after about 90 minutes. The PI membrane peeled off and the etchant attacked the wafer as shown in figure 3.

It was observed that the PI masks will not withstand the long etch times needed for bulk etching. The polyimide etch mask may be good for GaAs, as claimed by Shearwood and Petrini, but cannot be used for silicon. For this reason another approach was adopted, using tetra methyl ammonium hydroxide (TMAH) anisotropic etchant with silicon dioxide as an etch mask. The etching results were favourable but the membrane structure was very fragile and few membranes were intact after completion of the etching process. The author then developed another mask of Cr/Au on silicon wafer and bulk etched the wafer as shown in figure 5.

![Figure 3](image_url) Wafer etching in CP4 with PI membrane for longer time resulted in peel off the membrane.
2. Etching of silicon wafer

The wet etching of silicon plays an important role in various techniques in sensor fabrication[5]. Silicon micromachining falls into two categories; surface micromachining[1, 6] and bulk micromachining [1, 7, 8]. The purpose of bulk micromachining is to selectively remove a significant amount of silicon from a wafer in the fabrication of micromachined sensors and actuators, whereas surface micromachining is involved with the wafer surface only and usually involves sacrificial layers. Etching techniques that can be applied to the micromachining of silicon are isotropic wet etching and anisotropic wet etching, (although dry reactive ion, RI, etching is possible). In the case of isotropic wet etching, the most common etchant for silicon is ‘HNA’, a mixture of Hydrofluoric acid (HF), Nitric acid (HNO\(_3\)) and Acetic acid (CH\(_3\)COOH) [9]. The overall reaction is:

\[
Si + HNO_3 + 6HF \rightarrow H_2SiF_6 + HNO_2 + H_2O + H_2
\]  

The HNO\(_3\) drives the oxidation of the silicon, while fluoride ions from HF form the soluble silicon compound, H\(_2\)SiF\(_6\). The acetic acid has a lower dielectric constant (6.15 for CH\(_3\)COOH versus 81 for H\(_2\)O) than water, which helps to prevent the dissociation of HNO\(_3\) into NO\(_3^-\) or NO\(_2^-\), and thereby yields a higher oxidation power for the etch [10]. The acetic acid is also less polar than water and can help in achieving proper wetting of the slightly hydrophobic Si wafers. The etching chemistry is complex and the etch rate depends on chemical mixture and silicon doping.

A useful formulation for HNA is 1:3:8 (1HF: 3HNO\(_3\): 8CH\(_3\)COOH) concentration [11]. The author used this etchant at the final stage of membrane fabrication to remove the final layer of silicon beneath the polyimide membrane. This etchant was used because it does not attack the polyimide membrane at this strength over a short time period.

The anisotropic wet etching of single crystal silicon in alkaline solutions has become a key technology for micromachining. The definition of anisotropic etching is that the etch rate of silicon is highly dependent on crystal orientation. This means that the anisotropic etchant works much faster in one direction i.e., Si<100> than in another i.e., Si<111>, exposing the slower etching crystal planes over time. According to the crystalline orientation chosen, the silicon <111> planes are generally either at an angle of 54.74° to the wafer surface for silicon<100>, or perpendicular to it for silicon <110>[10].

A number of etchants, including potassium hydroxide (KOH) [6, 12-14], Ethylene-Diamine (EDP)[15, 16] and Tetra methyl ammonium hydroxide (TMAH) [17] are useful for anisotropic etching of bulk silicon. The author used TMAH to bulk etch the silicon wafer.

2.1 Silicon structure and TMAH Etching

In the anisotropic or wet etching process, it was observed that the silicon <111> is least prone to etching, and the silicon<100> and silicon<110> planes are etched with a reasonable etching rate. The etching rate depends on the etchant composition and processing temperature. The lower etch rate for silicon<111> may be due to tight packing of atoms. There may also be a reason that the energy required to remove atoms from the surface is much higher in silicon<111> as compared to silicon<100> planes.

The etching of the wafer depends both on the mask pattern and the crystal structure. The sidewalls of the developing structure are inclined at 54.74° to the surface. Figure 4 shows the structure of anisotropic etching.
Figure 4. Etched structure of silicon<100>.

From figure 4 above,

\[ \tan \theta = \frac{d}{x} \]  \hspace{1cm} (2)

Then

\[ x = \frac{d}{\tan \theta} \]  \hspace{1cm} (3)

where \( x \) is the horizontal component and \( d \) is the wafer thickness. As \( \theta = 54.74^\circ \), \( x \) can be evaluated to find the dimensions for the etching window. When designing the etch masks for backside etching, the backside window dimensions should be defined according to the following expression.

\[ W_0 = W_m - 2x \]  \hspace{1cm} (4)

or

\[ W_0 = W_m - \frac{2d}{\tan 54.74} \]  \hspace{1cm} (5)

or

\[ W_0 = W_m - \frac{2d}{\sqrt{2}} \]  \hspace{1cm} (6)

or

\[ W_0 = W_m - \sqrt{2} \times d \]  \hspace{1cm} (7)

or

\[ W_m = W_0 + 1.41 \times d \]  \hspace{1cm} (8)

where \( d \) is the wafer thickness or required etch depth. Hence, the mask window should be in accordance to equation (8). The detailed experimental work carried out during this research on wet anisotropic etching of silicon wafer and membrane fabrication is described in the next section.

3. Tetra Methyl Ammonium Hydroxide (TMAH)

This is a wet etchant based on an alkaline solution. The hydroxide etchants are generally safer and more predictable relative to other types of etchants, but they usually involve alkali metals (like Li, Na, K etc), which makes them incompatible with MOS or CMOS processing. Ammonium hydroxide (\( \text{NH}_4\text{OH} \)) is one hydroxide that is free from alkali metal, but it has a problem of ammonia, which is dissolved into water and evaporates at 90 °C from solution.
The TMAH etchant is an anisotropic etchant and it relies on the fact that alkaline solutions etch at widely different rates in various crystalline structures of silicon wafer. The anisotropic property of TMAH has been investigated by many researchers [25-28]. The first extensive investigation of TMAH was presented by O. Tabata [29] and U. Schnakenberg [30] in 1991. Highly diluted TMAH has been used in the microelectronics field as a developer for positive photoresist.

The main advantage of TMAH compared with other etchants is its relatively easy handling and CMOS compatibility. In addition, the etch rate of silicon dioxide is much slower than in KOH, making SiO$_2$ a suitable etch mask for TMAH. There is no doubt that TMAH is a very suitable etchant for anisotropic etching of silicon <100>.

It has properties somewhere between organic alkalis like ethylene diamine pyrocatecol (EDP) and metallic hydroxides such as KOH. The most negative aspect of TMAH is its price, which is much higher than KOH. However, due to its CMOS compatibility and lower toxicity, it is becoming more popular in the microelectronics field. The fabrication process is shown in figure 5.

Figure 5. Process Flow Diagram (Micromachining of silicon wafer and realisation of PI membrane).
This sample was then used for bulk etching of silicon in TMAH etchant. The experimental set up is as shown in figure 6.

![Diagram of the TMAH etching apparatus]

**Figure 6.** TMAH Etching apparatus.

The hotplate consists of an on/off and temperature control switches. The temperature of the solution can be read from a thermometer mounted inside the container. The lid of the container is equipped with a reflux condenser, which maintains the solution concentration during the long etching process. The etching rate of TMAH depends upon temperature and chemical concentration. The etch rate of TMAH at 90 °C was calculated as about 1 micron/minute. Two types of silicon wafers of different thicknesses (525 and 250 microns) were used for etching. To etch 525 microns thick wafer, it took about 8 hours and for 250 microns wafer, it was approximately four hours.

4. **Polyimide membrane fabrication**

Polyimides are an interesting group of strong, heat and chemical resistant polymers. Their strength, heat and chemical resistance is such that these materials are replacing metals and glass in many demanding industrial applications. The author has used polyimide as a substrate for a metal oxide gas sensor array due to its good thermal stability, resistance to chemicals like grease, oil and acids, and its physical strength. HDMicroSystems offers a complete product line of polyimide coatings for microelectronics, automotive and aerospace industry [35]. These coatings are formulated as a polyimide precursor in an
NMP- solvent based carrier. The curing process of polyimide precursor into a polyimide film is called imidization. An imide is a group in a molecule that has a general structure as shown in figure 7.

![An imide.](image)

When the molecule shown in figure 7 is polymerised, it becomes polyimide. Polyimides usually take one of the two forms: the first of these is a linear structure (figure 8a) where the atoms of the imide group are part of a linear chain and the second one is a heterocyclic structure where the imide group is part of a cyclic unit in a polymer chain (figure 8b) [36, 37]. Aromatic heterocyclic polyimides, shown in figure 8, are typical of the polyimides from HD MicroSystems. The detailed chemistry of polyimide materials can be found in the literature [36, 38-40]. A polymer which contains a charge transfer complex consists of two different types of monomers, a donor and an acceptor.

![Figure 8. Chemical structures of polyimides.](image)

The donor has more electrons than the acceptor, so it gives some of its electrons to the acceptor, holding them tightly together. Due to this charge transfer, the chains are stacked together with donors and acceptors very tightly, not allowing them to move around very much, thereby making polyimide so strong. The charge transfer not only occurs with the adjacent units in the polymer chain but also between the chains, making it stronger. Figure 9 shows an aromatic polyimides structure.
4.1. Experimental Work (PI Membrane)

After etching and suitable washing in DI water, the sample covered with Cr/Au on one side and etched windows on the other side, is ready for realisation of PI membrane. The process flow diagram for the membrane fabrication is as shown in figure 10. The polyimide PI2575 from HD Microsystems is supplied in a form suitable for spin coating applications. The material is a self-priming and does not require any adhesion promoter. The solution is highly viscous and it is necessary to have a short delay prior to spin to allow the polyimide to flow as far as possible and relax. This delay in spin avoids bubbles or comets in coating. The spin speed and time is determined by the film thickness required. It is observed that longer spin time improves the coating uniformity, but reduces the film thickness. The spin speed curve for PI2575 polyimide is as shown in figure 11.

- The polyimide was dispensed on the static etched-back substrate.
- The spinner started at 1000 rpm for 5 seconds. It was then accelerated to the spin speed to 2000 rpm for 30 seconds.
- The wafer was cleaned of the leached polyimide on the backside of the wafer with NMP (N-methyl-pyrrolidone) solution.
- The coated wafer was then pre-baked in oven at 90 °C for 5 minutes.
- The wafer was again spin coated with polyimide at 2000 rpm for 30 seconds. This step was repeated to increase the thickness of polyimide layer to approximately 10 microns.
- Now, the sample was baked at 120 °C for 30 minutes before final thermal curing process.

Figure 9. Aromatic heterocyclic polyimides structure[36]
After application of the polyimide, a high temperature thermal curing process is required which converts the polyamic acid to the insoluble imide form and drives out the remaining solvent. The curing process requires elevated temperatures and a controlled environment to achieve the best results. A temperature-controlled hotplate was used for curing. According to the curing profile, the sample was heated from room temperature to 360°C, with a ramp rate of 10°C/minute in nitrogen atmosphere. The sample was kept at this temperature for 30 minutes and then cooled down from 360°C to room temperature, with the ramp rate of 10°C/minute in the same environment. The colour of cured polyimide became dark brown. The sample with the cured polyimide membrane was now further processed in a 1: 3: 8 etchant (1HF(49%) : 3HNO₃ (70%) : 8CH₃COOH) until the remaining silicon layer was etched away. The sample
was then immersed in buffered HF solution to etch away the silicon dioxide layer for approximately 7.5 minutes. With this etching, the chromium film was exposed through the selective windows. The polyimide membrane was released by etching the exposed chromium and gold layers with their respective etchants. The samples were rinsed in de-ionised water and dried with slow blow dry nitrogen. The final membrane structure is as shown in figure 12. The samples with the polyimide membrane on silicon were then used to develop the micro-heater and a sensing array of four sensor elements. The samples with polyimide membranes are shown in figure 13.

4.2. SEM and AFM images
Scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM) are the techniques used to study the material morphology and surface flatness. The micromachined silicon samples with PI membrane were studied using SEM images as shown in figure 14 and figure 15.

![Figure 14](image14.png)  
**Figure 14.** SEM view of bulk etched Si<100> windows x25mag.

![Figure 15](image15.png)  
**Figure 15.** SEM cross-section of bulk etched cell x100mag.

From the SEM images, it is apparent that the etching is very smooth and very few pits can be seen on the surface of silicon wafer. The SEM cross-section shown in figure 15 is 100 times magnified image of bulk etched sample and it shows a smooth definition of etching profile and polyimide surface.

Surface irregularities were studied by using the atomic force microscopic (AFM) images. The AFM data and 3D image of the membrane surface are shown in figure 16 and figure 17 respectively.

The PI surface was scanned at three different points with a 10nm diameter stylus. The membrane surface flatness was 15nm for data line1 whereas figure 16 shows peaks of 28nm and 120nm respectively at a certain point. This was probably due to debris or particulate contamination of the surface.
5. Conclusion
In this paper, a detailed description of the fabrication of polyimide membranes is given. The paper is actually in two parts; one describing the micromachining of the silicon wafer to use it as frame for the membrane and second describing the fabrication of the polyimide membrane on top of this frame. The etching was carried out using TMAH solution at 90 ºC for 4 hours for 250 micron thick silicon wafer. The measurement of the surface flatness of the membrane was also carried out using SEM and AFM techniques. Towards the end of this chapter, a detailed description of some problems encountered, especially during the wet etching process, is discussed. The membranes fabricated by the technique described in this chapter have proved to be more robust and rugged than silicon dioxide or silicon nitride and reproducibility and repeatability is good.

References
[1] Sze S M, 1994 Semiconductor Sensors (John Wiley & Sons)
[2] Ristic L 1994 Sensor Technology and Devices (Artech House Boston-London) 65
[3] Shearwood, Birch T S and Stevens J C 1996 Microelectronics Engineering 30 547
[4] Ioana Petrini, Avramescu V, Simion G, Nitescu N, Vasilache D, Dascalu D, Knstantinidis G and Giacomozzi F 2000 Journal of Micromechanical, Micorengineering 10 218
[5] Gregory T. A. 1998 Proceedings of the IEEE 86 (8)
[6] Seidal H, Heugerger A and Baumgartel H 1990 Journal of electromechanical Society 137 3621
[7] Shikida M et al. 2000 Sensors and Actuators A 80(2) 179
[8] Rodica Iosub, 2002 Sensors & Actuators A (3277) 1
[9] Bogenchutz A F, Lochrer K H and Modreanu W 1967 Journal of Electrochemical Society: Solid State 114 (9) 970
[10] Madou M J 2002 Fundamentals of Microfabrication: The Science of Miniaturization. 2nd ed (Florida 33431: CRC Press LLC 2000 N W Corporate Blvd, Boca Raton)
[11] Peterson K E 1982 Proceedings of IEEE 70 420
[12] Zubel I 1998 Sensors & Actuators A 70 260
[13] Palik E D, Heard Jr I, Bruno P S and Tenerz L 1991 Journal of Applied Physics 70 3291
[14] Quoc-Bao Vu 1996 Journal of Electrochemical Society 143 1372
[15] Klein, 1967 Journal Electrochemical Society 114 956
[16] Reisman A, M B, Chan S A, Kaujman F B and Green D C 1979 Journal of Electrochemical Society 126 1406
[17] Tabata O et al. 1992 Sensors and Actuators A: Physical 34 (1) 51
[18] Elwenspoek M 1993 Journal of Electrochemical Society 140 2075
[19] Elwenspoek M 1996 Journal of Micromechanics and Microengineering 6 405
[20] Hesketh P J, Gowda S, Zanoria E and Danyluk S 1993 Journal of electrochemical Society 140 1080
[21] Allongue P 1993 Journal of The Electrochemical Society 140 1009
[22] Glembocki O. J, 1985 Journal of the Electrochemical Society 132 145
[23] Palik E D, 1983 Journal of Electrochemical Society 130 956
[24] Babic D, 1998 Journal of Electrochemical Society 145 4040
[25] Bassous E 1978 IEEE Transactions on Electron Devices ED-25 (10) 1178
[26] Kim C, http://www.ee.eng.hawaii.edu/mems/Han/mnc98_final.htm.
[27] Merlos A et al. 1993 Sensors and Actuators A: Physical 37-38: 737
[28] Yan G et al. 2001 Sensors and Actuators A: Physical 89 (1-2) 135
[29] Tabata O, Funbashi H and Sugiyama S 1991 Technical digest of 6th conference on Solid State Sensors and Actuators, Transducer's 91 811
[30] Schnakenberg U, Lochel B, Ullerich S and Lange P 1992 Sensors & Actuators A 25-27: 1
[31] Kloeck B, de Rooj N F and Smith R I 1998 IEEE Electron Devices 36 663-669
[32] French, Nagao M, and Esashi M 1996 Sensors and Actuators A: Physical 56 (3) 279
[33] Ashruf C M A, Sarro P M, Kazinczi R, Xia X H and Kelly J J 2000 Journal of Micromechanical Micorengineering 10 505
[34] Ashruf C M A et al. 1998 Sensors and Actuators A: Physical 66 (1-3): 284
[35] Dupont, www.hdmicrosystems.com.
[36] Mittal, 1996 Polyimide: Fundamentals and Applications (New York: Marcel Dekker)
[37] Bessonov M I, Kudryavtsev V V and Laius L A 1987 Polyimides: Thremally Stable Polymers (New York: Consultants Bureau)
[38] Kricheldorf H R 1999 Progress in Polyimide Chemistry Vol. I (Berlin, London: Springer)
[39] Mittal K L 1984 Polyimide: Synthesis, Characterisation and Applications Vol. 1,2 (New York)
[40] Adrora N A 1969 Polyimide: a new class of heat-resistant polymers (Jerusalem: I.P.S.T)