Chapter – 3
Chapter 3

Anisotropic Etching

3.1 Introduction

Anisotropic etching of silicon refers to the direction-dependent etching of silicon, usually by alkaline etchants like aqueous KOH, TMAH and other alkaline hydroxides like NaOH and LiOH. Due to the strong dependence of the etch rate on crystal direction and on etchant concentration, a large variety of silicon structures can be fabricated in a highly controllable and reproducible manner. Hence, anisotropic etching of silicon using aqueous KOH solution has been used widely and for long to easily fabricate a variety of devices and 3-D MEMS structures at a low cost. These include V-grooves for VMOS transistors, small holes for ink jets and diaphragms for MEMS pressure sensors. The actual reaction mechanism has not been fully understood for long and a comprehensive physical model for the process has not yet been developed. With increasing numbers of MEMS applications, interest has grown for process modelling, simulation and software tools useful for prediction of etched surface profile.

Chemical etching of silicon depends on crystal orientation, temperature and concentration of the etchant. Geometry of the area to be etched also influences the etch rate owing to the different crystal planes encountered during the etching process. In order to prepare an accurate physical model, experimental data under varying conditions are required. Therefore, anisotropic etching of (100) silicon has been carried out at varying temperatures and concentrations at CEERI, Pilani. In order to minimize the influence of other chemicals on the etching mechanism and therefore obtain more accurate results, pure KOH solution has been preferred over a number of mixtures with moderators like Ethylene Diamine Pyrocatechol (EDP) and Isopropyl Alcohol (IPA). Also, since the boiling point of a moderator like IPA is just 82.5 °C, the use of pure KOH solution
enables the temperature of the etch solution to be raised up to its boiling point. The results obtained by experimentation have been used in order to understand and postulate a physical model for anisotropic etching.

During etching, bubbles of hydrogen gas are generated as a by-product of the reaction between Si and KOH. The quality of the surface generated after etching is largely determined by the size and properties of these bubbles. This is because when the hydrogen bubbles adhere to the silicon surface, they act as temporary localized etch masks. This masking effect tends to produce hillocks bounded by four (111) facets when etching of (100) is carried out. The bubbles tend to adhere more strongly to a silicon surface that is hydrophobic. It has been observed that the surface roughness depends on the hydrophilic or hydrophobic nature of the silicon surface. This in turn depends upon the KOH solution concentration. Hence, the data gathered at different KOH concentrations and temperatures for etch rate is also useful to determine surface quality. Surface quality was determined using Atomic Force Microscopy (AFM) on the etched surface samples.

In this chapter, the experimental data, results, relevant details of the experiment and theoretical background have been discussed.

3.2 Wet Etching Fundamentals

Isotropic etching

Wet etching of silicon is used for cleaning, shaping, polishing and characterizing structure and compositional features. Wet chemical etching provides higher degree of selectivity than dry etching techniques. Wet etching is often faster. More recently though, with ECR dry etching, etch rates of up to 6 microns /minute were achieved. Modification of wet etchant and /or temperature can alter the selectivity and specially when using alkaline etchants to crystallographic orientations. Etching proceeds by reactant transport to the surface.
Isotropic etchants, also polishing etchants, etch in all crystallographic directions at the same rate; they usually are acidic, such as HF/HNO₃/CH₃COOH (HNA), and lead to rounded isotropic features in Si. They are used at room temperature slightly above (<50°C). Some alkaline chemicals etch anisotropically, i.e., they etch away crystalline silicon at different rates depending on the orientation of the exposed crystal plane.

Uses of Isotropic Etchants: When etching silicon with aggressive acidic etchants, rounded isotropic patterns form. The method is widely used for:

- Removal of work damaged surfaces.
- Rounding of sharp anisotropically etched corners (to avoid stress concentration).
- Removing of roughness after dry or anisotropic etching.
- Creating structures or planar surfaces in single crystal slices (thinning).
- Patterning single crystal, polycrystalline, or amorphous films.
- Delineation of electrical junctions and defect evaluation (with preferential isotropic etchants).

For isotropic etching of silicon, the most commonly used etchants are mixtures of nitric acid and hydrofluoric acid.

Anisotropic Etching

Anisotropic etchants etch desired structures in crystalline materials when carried out properly. Anisotropic etching results in geometric shapes bounded by perfectly define crystallographic planes since the rate of etching is direction dependent. A wide variety of etchants have been used for anisotropic etching of silicon, including aqueous solutions of KOH, NaOH, LiOH, CsOH, NH₄OH and quaternary NH₄OH with the possible addition of alcohol. Alkaline organics such as ethylenediamine, choline or hydrazine with additives such as pyrocatechol and pyrazine are employed as well.
Wet Anisotropic Etching Using Aqueous KOH Solution

The existence of selective and anisotropic etching for Si and SiO2 has formed the basis of many of the initial micromachining investigations. There are two classes of etchants: the KOH-based etchants and the ethylene diamine based etchants. Both types show highly anisotropic behavior; etching <111> Si planes at a much slower rate than other planes. Both etchants show a doping dependence, with etch rates slowing considerably as the Si becomes more than $3 \times 10^{19}$ cm$^{-3}$ p-type with boron doping.

In order to calculate the angle between two crystallographic planes with known Miller Indices in case of a cubic lattice as of silicon, following well-known relation is used:

$$\cos (h_1k_1l_1; h_2k_2l_2) = \frac{1}{\sqrt{h_1^2 + k_1^2 + l_1^2} \cdot \sqrt{h_2^2 + k_2^2 + l_2^2}}$$

In case of <100> and <111> planes, the above takes the following form:

$$\cos \langle 100 \rangle : \langle 111 \rangle = \frac{1}{\sqrt{3}} = 0.5774$$

$$\cos ^{-1} (0.5774) = 54.74^\circ$$

Thus a V-groove will be formed as a result of wet etching of Si<100> making an angle of $54.74^\circ$ between the <100> and the<111> plane. (The angle between the planes is an important parameter for the necessary calculations for designing the mask layout). The making of angle is shown in the Figure 3.1.
According to [1], the overall etching reaction in KOH solution may be given by the equation:

\[
\text{Si} + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 2\text{H}_2
\]

It is the H\(_2\) produced in this reaction that is seen as bubbles escaping from the reaction vessel. The Orthosilicic acid \{\text{Si(OH)}_4\} produced is soluble in the solution.

KOH is one of the most commonly used silicon etch chemistry for micromachining of silicon wafers. Ethylene diamine – based etchants (e.g. ethylene diamine-pyrocatechol, EDP) are a potential carcinogenic material so not commonly used. KOH etching depends not only on the crystallographic orientations of the wafers but also on the operating temperature and its concentration [2]. KOH etching is usually performed at 75°C to 80°C, though the etch rate is slower. This because at higher temperature (above 120°C) it is found that \text{Si}_3\text{N}_4 layer which is used as a mask also starts etching. Also at higher temperature near boiling point due to the aggressive etching process delicate features in the device may get damaged.
3.3 Experimental Methodology

In order to gather the data necessary to be able to postulate a model for etching of silicon by KOH, several samples of (100) silicon wafer were prepared. Silicon (100) samples have been prepared starting with device grade chemical cleaning of the wafer. Thermal oxidation of 0.5-micrometer thickness was grown using wet-dry-wet sequence at 1100 °C, in a horizontal quartz furnace. LPCVD silicon nitride was deposited over that layer, at 780 °C for a thickness of 0.15 micrometer in a horizontal quartz furnace reactor. The combination of silicon dioxide and silicon nitride provides stable masking action in KOH solution at elevated temperatures. Square windows of 2.0 mm size were delineated in an array using photolithography. Dry etching was used to selectively remove silicon dioxide and silicon nitride. The samples were used for KOH etching in a reflux condenser equipped with a magnetic stirrer to maintain KOH concentration, as shown in Figure 3.2. The wafers were etched at various temperatures and concentrations of KOH for a period of one hour each. No additives other than DI water for dilution were used in all experimentation in order to be able to develop a model based on data uninfluenced by the reactivity of other chemicals. Also, data could be gathered at higher temperatures since the addition of low BP impurities like isopropanol (B.P. 82.5 °C) has been avoided. The etch depth was measured by an indirect method using an optical microscope. This method makes use of the fact that the angle between the (100) and (111) planes in a silicon crystal is always 54.74°.
With the help of the scale provided with the optical microscope lens, the length $x$ was measured under 50X magnification. The actual etch depth $y$ was then estimated using the relationship: $y = x \tan 54.74^\circ$. Etch rate was then evaluated as the etched depth per unit time ($\mu m/min$).

Figure 3.2. Reaction container for KOH etching at CEERI, Pilani.
3.4 Surface Roughness due to KOH Etching

The origin of pyramid formation during etching may be attributed to the adhesion of H$_2$ bubbles to the silicon surface, as shown in Figure 3.3. The purity of the etchant and of the water used is also crucial for achieving smooth surfaces. Surface roughening has also been attributed to the etching conditions and surface inhomogeneities. Poor bubble detachment from the surface results in the formation of micro-pyramids and pits, as shown in Figure 3.3.

![2M KOH](image)

**Figure 3.3.** Schematic representation of hydrogen bubble formation on a masked Si (100) surface (left) and the resulting hillock formed by H$_2$ attachment, leading to a truncated pyramid (right).

Etching under ultrasound conditions in the presence of additives usually employed in micromachining baths leads to smooth and defect-free surfaces. The significant improvement in surface finish under these conditions indicates that hydrogen bubbles, which are temporarily attached during the etch process, are one of the main origins of surface roughness [3]. The AFM image of the sample surface shown in Figure 3.4, is further shown in Figure 3.5, but under ultrasound condition.
Figure 3.4. AFM image of a Si (100) surface etched in KOH solution at 60° C for 60 min.

Figure 3.5. AFM image of a Si (100) surface etched in KOH solution at 60° C for 60 minutes but under ultrasound condition.
The formation of large hydrogen gas bubbles depends on the adhesion between the KOH solution and the silicon wafer. If the surface is hydrophilic, only small bubbles are formed and roughness is reduced and if the surface is hydrophobic, large bubbles and hence large hillocks are formed as shown in Figure 3.6. Concentrated KOH solutions tend to adhere more to Si surfaces, resulting in smaller bubbles and less roughness. These bubbles cause temporary localized etch stops equivalent to etch masks. Surface roughening in the form of hillocks can be observed and the resulting morphology is governed by the anisotropic etch rates producing pyramids made of four \{111\} facets.

Figure 3.6. Schematic representation of hydrogen bubble formation for hydrophobic (left) and hydrophilic (right) silicon surfaces.

After studying the AFM images of the etched surfaces, shown in Figure 3.7, which are etched at 10 wt % and 20 wt % concentration of KOH at the same temperature (80°C), we conclude that with increasing concentration the surface quality improves (roughness decreases). This would suggest that at higher KOH concentrations, the silicon surface is more hydrophilic. This may be understood from the fact that due to the higher KOH concentration, the Si atoms at the crystal surface are OH\(^-\) terminated instead of being H terminated. Silicon surface, that is OH\(^-\) terminated, is more hydrophilic due to the presence of charge on the OH\(^-\) radical and the fact that water is a polar solvent.
The significant improvement in surface finish under ultrasound conditions indicates that hydrogen bubbles, which are temporarily attached during the etch process, are one of the main origins of surface roughness. Enhancement of surface finish by the addition of isopropanol and oxidation agents or etching under positive potentials can be related to a decrease in the liquid/solid contact angle $\Theta$, favouring bubble detachment.

Improvement in surface finish on application of a positive potential also points to OH$^-$ termination of the surface. The positive potential attracts negatively charged OH$^-$ ions and leads to greater Si-OH termination. This in turn increases the hydrophilic nature of the surface, favouring faster bubble detachment and improved surface finish.
3.5 Physical Models for KOH Etching

According to [4], it is believed that the etch rate is related not only to the macroscopic process, but also to the microscopic ones, which are denoted here by the temporary states. According to the above chemical process, for an atom on a \{1 0 0\} plane, the possible microscopic states during the etching process are shown in the Figure 3.8. To distinguish them clearly, digits have been marked on the corresponding microscopic state in the Figure3.8.

![Figure 3.8](image)

**Figure 3.8.** Diagram of possible existing microscopic states for \{1 0 0\} crystal planes during anisotropic etching in KOH.

With the macroscopic reaction, microscopic states will be transferred into other states. The transfer relation of the microscopic states is shown in Figure 3.9. It is known that the chemical reaction is a dynamic process and the chemical balance is a dynamic equilibrium. From the macroscopic viewpoint, for the atoms participating in the reaction, when the number of the reacted atoms is equal to that of the produced ones, the reaction will reach the dynamic balance. It is just the same for the microscopic states. For one microscopic state, when the produced number is equal to the reacted number, the dynamic equilibrium will appear.
Because the etch rate is related to time, a main equation which is widely used in chemicophysics is adopted here. The main equation related to the transfer probability between different states is a kind of differential equation. It is distinctive and convenient to describe the chemical reaction using this equation. The important parameter in the main equation is the transfer probability. Once it is fixed, the main equation will be listed.

The microscopic states listed in the Figure 3.8 may be transferred into other states. The transform is not arbitrary, certainly. It follows the macroscopic reaction. For example, for state 6, it should transfer into orthosilicic acid Si(OH)₄. A hydroxyl ion can be combined into state 6, so it will transfer into state 7. At the same time, two hydroxyl ions can be combined with state 6, too. So, state 6 can be changed into state 8. The two transforms can both occur and their possibilities will determine the possible result. Corresponding to the microscopic states listed in the Figure 3.8, the possible transfer relation of the states is illustrated in the Figure 3.9, in which the transform possibilities
are shown using arrows. The number of the microscopic state during the reaction is assumed to be \( n_i \), where \( i \) stands for the marked number shown in the Figure 3.8. The transfer probability from state \( i \) to state \( j \) is \( P_{ij} \). The main equations that describe the reactions shown in the Figure 3.9 are listed below:

\[
\frac{dn_1}{dt} = -P_{12}n_1 + P_{21}n_2
\]
\[
\frac{dn_2}{dt} = P_{12}n_1 + P_{32}n_3 - P_{21}n_2 - P_{23}n_2
\]
\[
\frac{dn_3}{dt} = P_{23}n_2 + P_{43}n_4 + P_{53}n_5 + P_{63}n_6 - P_{32}n_3
\]
\[
- P_{34}n_3 - P_{55}n_5 - P_{66}n_6
\]
\[
\frac{dn_4}{dt} = P_{34}n_3 + P_{34}n_5 + P_{64}n_6 - P_{43}n_4 - P_{45}n_4 - P_{46}n_4
\]
\[
\frac{dn_5}{dt} = P_{45}n_4 + P_{55}n_5 + P_{75}n_7 - P_{54}n_5 - P_{65}n_6 - P_{57}n_5
\]
\[
\frac{dn_6}{dt} = P_{56}n_6 + P_{46}n_4 + P_{76}n_7 + P_{86}n_8 - P_{66}n_6
\]
\[
- P_{64}n_6 - P_{57}n_6 - P_{68}n_6
\]
\[
\frac{dn_7}{dt} = P_{57}n_8 + P_{57}n_5 + P_{67}n_6 - P_{78}n_7 - P_{75}n_7 - P_{76}n_7
\]
\[
\frac{dn_8}{dt} = P_{78}n_7 + P_{88}n_6 - P_{87}n_8 - P_{86}n_8.
\]

The transfer probability \( P_{ij} \) obeys the Boltzmann distribution:

\[
P_{ij} = \lambda \exp \left( \frac{E_i - E_j}{kT} \right)
\]

Where \( E_i \) and \( E_j \) stand for the microscopic activation energies of states \( i \) and \( j \), respectively, \( \lambda \) is the vibrational frequency of the crystal lattice, \( K \) is the Boltzmann constant and \( T \) is the temperature [5]. Once the activation energy is fixed, the above equation will be dissolved.
3.6 Results and Inferences

The experimental results for the etch rate of KOH in silicon substrate varying with etching temperatures and etchant concentration have been shown in the Figure 3.10 and 3.11.

![Figure 3.10](image1.png)

Figure 3.10. Shows variation in etch rate (experimentally) with increasing temperature.

![Figure 3.11](image2.png)

Figure 3.11. Shows variation in etch rate (experimentally) with KOH concentration.
The calculated results for the etch rate of KOH in silicon substrate varying with etching temperatures and etchant concentration have been shown in the Figure 3.12 and 3.13.

**Figure 3.12.** Shows variation in etch rate (by calculation) with increasing temperature.

**Figure 3.13.** Shows variation in etch rate (by calculation) with etchant concentration.
The high degree of correlation between the expected values obtained by calculations (based on the model proposed) and the experimentally observed results validates the model.

In the experiments conducted at CEERI, the Arrhenius relationship postulated in the model proposed in [2, 4, 5] has been verified. This is seen clearly in the graph shown in Figure 3.14, for etching using 30- wt % KOH solution.

Figure 3.14. Shows variation of etch rate with temperature showing Arrhenius relationship.

Figure 3.15 shows the result obtained by experimentation at CEERI for the variation of etch rate of (100) Si with concentration at the temperatures of 50 °C, 60 °C and 70 °C. Concentration of the KOH solution was varied by adding the required amount of DI water to a standard 45 wt % solution.
The graph shown in Figure 3.15 indicates that variation of etch rate with concentration is less pronounced at lower temperatures like 50 °C and 60 °C than at 70 °C, since the etch rate itself at these temperatures is less. The variation in etch rate at 70 °C shows first an increase with concentration and then a decrease. An explanation provided by research conducted much earlier suggested a model where both OH\textsuperscript{−} and H\textsubscript{2}O participate in the reaction with Si as follows:

\[
\text{Si} + 2\text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Si(OH)}_4 + \text{H}_2
\]

Such a reaction would proceed at a lower rate in the absence of any one of the reactants H\textsubscript{2}O and OH\textsuperscript{−}. Since at low KOH concentration, OH\textsuperscript{−} is in low concentration, and at high KOH concentration, H\textsubscript{2}O is available in low concentration; the reaction
would slow down at both high and low KOH concentrations. However, this is not a comprehensive explanation capable of explaining all the experimental results obtained.

Figure 3.16 shows the result obtained by experimentation at CEERI for the variations in etch rate with temperature for 45-wt % KOH solution.

![Graph showing etch rate vs temperature for 45-wt% KOH solution.](image)

**Figure 3.16.** Shows variation of etch rate with temperature for 45-wt % KOH solution.

A steep increase in etch rate is seen with temperature. Plots of etch rate versus 1/T (where T is absolute temperature) have shown a straight-line Arrhenius relationship between etch rate and temperature in Figure 3.14.

Figure 3.17 shows the result obtained by experimentation at CEERI for the variation of etch rate of (100) Si with concentration at the temperatures of 80 °C, 90 °C
and 100 °C. The boiling point of the KOH solution increases almost linearly with concentration. The boiling point sets the upper limit of the maximum temperature allowed for a given concentration.

Figure 3.17. Variation in etch rate with concentration at temperatures of 80 °C, 90 °C and 100 °C.

The etching rate shows a peak for each temperature curve that is shifted towards lower concentration with increasing temperature. At 80 °C, a maximum etching rate of 1.5 μm/min is obtained for 25 wt % KOH solution. For temperatures above 80°C, the peak of the maximum etch rate is shifted to 15 wt % KOH solution. At 100 °C the maximum etch rate is about 3.0 times of that at 80 °C.
From the observations taken at CEERI, faster etching rate with smooth silicon surface has been observed at higher temperatures in low KOH concentration solutions. Higher KOH concentrations improve etched surface finish. Etch rate for a particular concentration increases with temperature.
References


