Simulation of silicon etching with KOH

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Anisotropic chemical etching of monocrystalline silicon in KOH aqueous solution is investigated. The atomic scale model proposed is based on the influence of the OH group on chemical bonds. Etch rate and activation energies are calculated and extended to the complete etch rate polar diagram and compared to available experimental data. Finally, an analytical description of etch rate ratios is proposed. © 1997 Elsevier Science Ltd.

1. Introduction

Recent years have seen important progress in the construction of micro-electromechanical structures with technologies derived from integrated circuit fabrication. Anisotropic chemical etching is one of the key techniques for technological elaboration of 3D microstructures leading to micromechanical devices and micro-systems [1, 2]. Single crystal silicon is chemically etched using strong bases such as KOH, EDP, TMAH, etc. through silicon oxide or nitride masks realized with the classical lithographic process.

These processes are very complicated and the results are not always accurately predictable. Thus, the successful design and implementation of such microstructures depend to a large degree on 'experience' or on the diligence used in a trial-and-error approach. To build complicated micro-dynamical systems good predictive CAD tools become a necessity. Some attempts have been carried out to simulate the etching process using geometrical rules [3–7].

The general problem, taking into account all crystallographic directions, is very complex. For concave corners, the 3D shape will be defined by slowest etch rates and facets can disappear. In contrast, for a convex corner, the 3D shape will be defined by fastest etch rates, and new facets can appear. In order to know when and which a new facet will appear, the time step inside the simulator has to be determined and adapted first. At present, this kind of modelling is valid only in some particular cases. Some other simulators take into account a number (three or four) of crystallographic directions to avoid this high CPU method to research when a new facet will appear and which one. The risks are missing the right orientation of facets and describing imperfectly the 3D shape. For these reasons, the geometrical surface construction program requires complete etch rate information for all possible directions. This is also true for simulation based on the model equivalent of the solid on solid model. Minima and maxima of the etch rate polar diagram have to be known in direction and modulus.
etch rates are highly dependent on the crystalline orientation, concentration of etching solution, temperature and doping concentration of etched substrates (especially P⁺ doping). EDP is an interesting etchant because of its anisotropy and selectivity with several materials. The decrease of etching rate with boron concentration in silicon is abrupt. Nevertheless, its high level of toxicity is a great handicap. KOH is without doubt the most useful etchant for implementation. The anisotropy is quite high but the decrease of etching rate with boron concentration is more smooth. The selectivity with silicon oxide makes it a poor candidate for long time etching. Therefore, for some applications, TMAH is used. The selectivity with silicon oxide is higher, but the anisotropy lower. Unfortunately, not enough information has been published to describe the complete etch rate diagram. Generally, etch rates have been measured and published only for a few materials and some etchants in some selected directions: the two or three principal crystallographic planes [8–11]. In addition, values of etching rate and activation energies for TMAH, EDP and KOH are scattered. The most complete work on KOH (values for TMAH are too scattered) is due to Tellier et al. [11]. In this paper, we shall refer to Tellier and Seidel [10] for experimental values.

To obtain physically plausible etch rate diagrams, we have developed a simplified atomic scale model of the etching process.

2. Atomic model

As we shall see later, this modelling is consistent with the electrochemical approach developed by Seidel et al. The etching process in KOH solution can be described by the following global reaction:

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

and summarized for our purpose by the following steps:

- first, binding of the hydroxide ion to the unpaired electron of the surface dangling bonds through the Helmoltz layer. The ionization energy of this surface state is weak (near 0.35 eV) and thus this reaction occurs very rapidly.

- secondly, breaking of the Si–Si backbonds which proceeds by electron transfer into the conduction band and successive binding of hydroxide ions which weaken the backbonds’ strength. This event is thermally activated.

According to the previous assumption, the major kinetic event that governs the etching process is the breaking of chemical bonds. The result of successive breakings of the chemical bonds is the subtraction of atoms from the surface. The surface diffusion is neglected since we are dealing with low temperature condition. The arrival of OH on etching surface is assumed to have a probability equal to one, due to the low energy associated with this step, and, in the case we do not take into account stirring effects. Experiments shows that this assumption is true for KOH but not for TMAH. Also, this model does not take into account explicitly the nature of different etching solutions such as EDP or TMAH. The etchant is taken into account by adapting the set of microscopic activation energies for each etchant. At present, this work has just been done for KOH. The influence of the doping level has been studied in detail by Seidel et al. as concentration effects. If our model does not take into account doping effects, experiments have shown that a variation of concentration does not change the macroscopic activation energies and thus the concentration can be introduced as a pre-exponential factor in the calculation of probabilities.

The model supposes that the probability for breaking a non-dangling bond is governed by an Arrhenius law whose activation energy depends
on the number of OH groups bounded to these atoms [12]. We assume that if the number of OH groups attached to the two atoms surrounding a chemical bond increases, the strength of this bond decreases, which leads to an increase of the probability for breaking it. The probability for breaking a bond, \( P_{i,j} \) is:

\[
P_{i,j} = l \exp \left( \frac{E_{i,j}}{kT} \right)
\]

where \( l \) stands for the vibrational frequency of the crystal lattice, \( k \) Boltzmann's constant and \( T \) temperature. \( E_{i,j} \) is the microscopic activation energy associated with the configuration \((i,j)\) where \( i \) and \( j \) are the number of non-dangling bonds of the two neighbouring atoms. In silicon, the atom lies at the centre of a tetrahedron, thus numbers \( i \) and \( j \) are equal to four minus the number of attached OH groups. The time of breaking associated with \( P_{i,j} \) is given by:

\[
T_{i,j} = -\ln(z)/P_{i,j}
\]

where \( z \) is a random number evenly distributed between 0 and 1. At the first pass, the simulator checks each configuration and computes the corresponding probability and the associated time. After that, at each pass, when all the surface is checked, the configuration with the least time is removed. The number of OH groups of neighbouring configurations is changed and their new probabilities and new times are calculated. The operator can choose crystal orientation, temperature of etching, size of the crystal samples, periodic conditions for the lateral faces of the samples or design facilities for the creation of a mask.

In a previous model, described in Ref. [13], atoms were removed by taking into account the number of bonds of each atom independently of the state of the neighbouring atoms. To find the experimental anisotropic ratio \( R_{(100)}/(100) \), it was necessary to change the microscopic activation energy of three bonded atoms for each crystal orientation. Let us see bonding situations for the three main low-index crystal planes. For the \((100)\) plane, an atom has two dangling bonds and two bonds with atoms which have four bonds. Thus two bonds have to be broken to remove an atom. For the \((111)\) plane, which corresponds to the lowest etch rate, the atom has one dangling bond and three bonds with atoms which have four bonds. So, three bonds have to be broken to remove one atom from the etching surface. In the case of the \((110)\) plane, atoms at the surface have one dangling bond, two bonds with atoms which have three bonds and one bond with an atom which has four bonds. In this case, three bonds also have to be broken, but two of them are connected to three bound atoms instead of four bound atoms as in the \((111)\) plane. These two bonds are certainly weaker. It can be explained by the number of OH groups.

In this model, the number of OH groups attached to an atom can vary from zero to three. So the total number of configuration is 16. Two are useless: 4—4 is a chemical bond between two atoms in the substrate and 1—1 is a chemical bond between two atoms in the solution. By symmetry consideration, we have eight different configurations (see Table 1). They can be roughly classified into five cases depending on the total number of OH groups.

![Table 1](image)

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TABLE 1 List of configurations and probabilities used: Δ represents an OH attached group and \( i/j \) the number of bonds for the two atoms surrounding a bond

<table>
<thead>
<tr>
<th>Probabilities</th>
<th>Attached OH groups</th>
<th>((i/j)) configurations</th>
<th>Used probabilities</th>
</tr>
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<tr>
<td>( P_{1A} )</td>
<td>Δ—</td>
<td>3/4, 4/3</td>
<td>( P_{\Delta} )</td>
</tr>
<tr>
<td>( P_{2A} )</td>
<td>ΔΔ—</td>
<td>2/4, 4/2</td>
<td>( P_{2\Delta} )</td>
</tr>
<tr>
<td>( P_{2A} )</td>
<td>ΔΔ—</td>
<td>3/3</td>
<td>( P_{2\Delta} )</td>
</tr>
<tr>
<td>( P_{3A} )</td>
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<td>( P_{3\Delta} )</td>
</tr>
<tr>
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<td>ΔΔΔ—</td>
<td>1/4, 4/1</td>
<td>( P_{3\Delta} )</td>
</tr>
<tr>
<td>( P_{4A} )</td>
<td>ΔΔΔΔ—</td>
<td>1/3, 3/1</td>
<td>( P_{4\Delta} )</td>
</tr>
<tr>
<td>( P_{4A} )</td>
<td>ΔΔΔΔ—</td>
<td>2/2</td>
<td>( P_{4\Delta} )</td>
</tr>
<tr>
<td>( P_{5A} )</td>
<td>ΔΔΔΔ—Δ</td>
<td>1/2, 2/1</td>
<td>( P_{5\Delta} )</td>
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</tbody>
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with an increasing probability for breaking (from $P_{1\Delta}$ to $P_{5\Delta}$). We make no distinction for the different configurations in the case of three and four OH groups considering that the effects will be of the second order due to the small difference of calculated probabilities. But a distinction is made for the case of two OH attached groups. It is known that the influence of radicals on a bound is not the same in these two configurations ($\Delta\Delta^{-}$; $\Delta^{-}\Delta$). The relative differences between $E_{i,j}$ yields the anisotropy between different breaking probabilities. The smaller the deviation is, the more isotropic etching becomes. This particular point has been verified.

3. Results

3.1 Time dependence

In Fig. 1 the variations of the etch rate versus time for (100) and (111) ideal surfaces is reported. We can observe that etch rate varies very rapidly at the beginning of the etching process for (100) orientation and reaches a steady state value. In order to explain this behaviour, we have studied the evolution of the surface morphology. The decrease of the etching rate is due to the appearance of $P_{2\Delta}$ bonds on the (100) surface. On the contrary, for a (111) orientation, we observe the increase of the etching rate. This is due to the appearance of $P_{2\Delta}$ bonds on the (111) surface. In both cases, if the simulation is performed until the removal of 600,000 atoms, the variation of the steady state etching rate is less than 1%. From this observation, we can consider that: (i) to calculate an etch rate by considering only theoretical ideal surfaces can introduce some mistakes; (ii) the etch rate is closely related to the specific roughness of each orientation.

3.2 Etch rate and activation energies

Our simulations are not able to calculate absolute value of etch rates; but a feature of general interest for many practical applications of anisotropic silicon etching is the ratio of the etch rates which determine the type of 3D shapes after etching. From experiments, for KOH solution, (110) planes are etched faster than (100) planes, with nearly identical macroscopic activation energies of 0.60 and 0.595 eV, respectively. The macroscopic activation energy for (111) planes is approximately 0.74 eV with the slowest etch rate. It can be seen that the slower the etch rate is, the higher the macroscopic activation energy is. As a consequence, the etch rate ratio of (110):(100):(111) increases from 50:30:1 near the boiling point of the solution to 160:100:1 at room temperature. Our simulation found an anisotropic ratio of 60:47:1 at boiling point and 1300:750:1 at room temperature. This is a consequence of a too low etch rate for (111), but the ratio between (110) and (100) is still in good agreement. However, we can read in the literature different values for (111) etch rate and activation energy.
Some experimental values for more complex orientations are also available in the literature. The anisotropic ratio \( R_{(hkl)/(100)} \) has been calculated and compared with the experimental data for different crystal orientations at 80°C. Figure 2 shows the experimental and simulated ratio \( R \) for \((hkl)\) perpendicular to \((100)\) planes (from \((100)\) to \((001)\), for example). Dots represent experimental data and the line simulated data. The agreement between experimental data and simulated data is quite good.

Macroscopic activation energies have also been calculated around the same zone axis \((hkl)\) (Fig. 3). We find a continuous variation from 0.61 eV for \((100)\) to 0.60 eV for \((110)\) with a minimum of 0.565 eV for \((120)\), which is the fastest orientation with our model. The macroscopic activation energy of \((111)\) is 0.85 eV, higher than the experimental one.

With the same set of \( E_{ij} \), we have extended calculations to more complex orientations. Figure 4 shows simulated etch rate obtained for \((hhl)\) planes (from \((110)\) to \((001)\)). Figure 5 shows results for orientations from \((140)\) to \((100)\). In these two figures, dots are simulated data and lines extrapolated data. The positions of maxima, minima and etch ratios in these two cases are quite good. Table 2 summarizes the results. Tellier et al. have developed a tensorial model to predict the value of slowness function with a modulus inverse to the etch rate. The dissolution slowness surface can be described by the end of a vector \( L \), a function of \( \Theta \) and \( \Phi \) which characterizes a crystalline orientation \((hkl)\). The modulus can be developed as a function of \((n_1, n_2, n_3)\), the components of the normal vector for each orientation, and written as:

\[
L = D_0 + D_1 n_1 + D_2 n_2 + D_3 n_3 + D_4 n_1 n_2 + D_5 n_1 n_3 + D_6 n_2 n_3 + \ldots
\]

The number of parameters \( D \) can be reduced because of silicon crystal symmetries. To determine all the \( D_{ijkl}, \ldots \), we have carried out a simplex fit to simulated data. After the reduction, the number of parameters is 31 and the maximum tensor rank is 18. The advantage of such a description is to interpolate between some orientation in order to reduce the number of simulations, and to provide an analytical description of the etching polar diagram usable for simulation tools.
Fig. 4. Normalized etch rates as a function of orientation from (001) to (110): simulated data (dots) and extrapolation (line).

Fig. 5. Normalized etch rates as a function of orientation from (140) to (001) simulated data (dots) and extrapolation (line).
TABLE 2 Experimental and simulated data about minima and maxima of complete etch rate diagram. Angles are in degrees and etch rate \( V \) normalized to \( V_{(100)} \)

<table>
<thead>
<tr>
<th></th>
<th>Maximum</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Minimum</th>
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<td>90</td>
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<td>45</td>
<td>62</td>
<td>90</td>
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<td>1.64</td>
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<td>1.64</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>( 110 )</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>( \Theta_{\text{exp}} )</td>
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<td>63</td>
<td>90</td>
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<td>( \Theta_{\text{sim}} )</td>
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<td>( V_{\text{sim}} )</td>
<td>1.52</td>
<td></td>
<td>1.4</td>
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<tr>
<td>( 140 )</td>
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<td>1.55</td>
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3.3 Surface morphology
The surface morphology has been investigated at 80°C in the case of \( 100 \) and \( 111 \) oriented surfaces. Figures 6 and 7a,b illustrate a 3D view for two planes near the beginning of the etching. The simulated surface is a square of 100Å \( \times \) 100Å. The darker (whiter) the pixel, the lower (higher) it is. It can be observed that each surface presents a different aspect. The \( 100 \) planes show a faceted structure distributed over the whole layer when the \( 111 \) planes show a more flat surface containing cavities and/or islands. After the first removal of an atom on a \( 111 \) flat surface, a cavity is created and its surface increases because atoms at the ledge and at the kink sites exhibit one or two backbonds.

Fig. 6. Simulated \( 100 \) etched surface.
and are removed more easily than atoms on a flat surface which have three bonds. After some time, cavities coalesce and form a terrace. Inside a cavity, an atom with three bonds can also be removed and form another cavity which will grow rapidly. This explains that the (111) surfaces are very smooth and flat. On the other hand, a (100) oriented surface is constituted by faceted structure with a predominance of (111) oriented facets. A simple microscopic mechanism has not be established for the (100) surface due to its complexity. The microscopic roughness seems to increase and has to be simulated for a longer time.

4. Conclusion

An atomic scale simulator based on the influence of hydroxide groups has been presented. It allows one to calculate etch rate and macroscopic activation energy for all crystal orientations in order to describe the etch rate polar diagram. Further improvements of the model are under development in our laboratory. More than 30 etch rates and 14 macroscopic activation energies have been calculated and compared to experimental result in the case of anisotropic chemical etching of silicon with KOH at 80°C. The agreement is good enough to reach an analytical
description of the etch rate polar diagram. The surface morphology has been investigated for the (100) and (111) orientations. The result is qualitatively good in comparison with experience.

References


