Anisotropic Etching of Crystalline Silicon in Alkaline Solutions

I. Orientation Dependence and Behavior of Passivation Layers

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ABSTRACT

The anisotropic etching behavior of single-crystal silicon and the behavior of SiO₂ and Si₃N₄ in an ethylenediamine-based solution as well as in aqueous KOH, NaOH, and LiOH were studied. The crystal planes bounding the etch front and their etch rates were determined as a function of temperature, crystal orientation, and etchant composition. A correlation was found between the etch rates and their activation energies, with slowly etching crystal surfaces exhibiting higher activation energies and vice versa. For highly concentrated KOH solutions, a decrease of the etch rate with the fourth power of the water concentration was observed. Based on these results, an electrochemical model is proposed, describing the anisotropic etching behavior of silicon in all alkaline solutions. In an oxidation step, four hydroxide ions react with one surface silicon atom, leading to the injection of four electrons into the conduction band. These electrons stay localized near the crystal surface due to the presence of a space charge layer. The reaction is accompanied by the breaking of the backbonds, which requires the thermal excitation of the respective surface state electrons into the conduction band. The step is considered to be rate limiting. In a reduction step, the injected electrons react with water molecules to form new hydroxide ions and hydrogen. It is assumed that these hydroxide ions generated at the silicon surface are consumed in the oxidation reaction rather than those from the bulk electrolyte, since the latter are kept away from the crystal by the repulsive force of the negative surface charge. According to this model, monosilicic acid Si(OH)₄ is formed as the primary dissolution product. All anisotropic silicon etchants. The anisotropic behavior is due to small differences of the energy levels of the back-bond surface states as a function of the crystal orientation.

Anisotropic etchants for crystalline silicon have been known for a long time (1-3). Their first applications included the etching of V-grooves on <100> silicon or U-grooves on <110> silicon, in order to fabricate MOS transistors for high power and high current densities (4). Increasing attention has been paid to this etching technology, after recognizing its unique capabilities for micromachining three-dimensional structures (5-9). Due to the strong dependence of the etch rate on crystal orientation and on dopant concentration, a large variety of silicon structures can be fabricated in a highly controllable and reproducible manner. Typical structures include thin membranes, deep and narrow grooves, and cantilevers with single or double sided suspension. Important fields of application include the fabrication of passive mechanical elements, sensors, and actuators, as well as micro-optical components (8, 10). Among the best known examples are sensors for pressure (8), acceleration (11), and flow (12), as well as ink jet nozzles (13), connectors for optical waveguides (14), and major components of a gas chromatograph (15).

All anisotropic etchants are aqueous alkaline solutions, where the main component can be either organic or inorganic. The first organic system was proposed in 1962 and consisted of hydrazine (N₂H₄) and water with the addition of pyrocatechol (C₆H₄(OH)₂) (16). It was shown that pyrocatechol is not a necessary component, and might well be omitted (2). Experiments were made with iso-2-propyl alcohol as a third component, which was shown to act as a moderator (3). In a later work, hydrazine was substituted by ethylenediamine (NH₂(CH₂)₂NH₂), which is more stable and less toxic than the former (2).

Purely inorganic aqueous solutions of KOH and NaOH have been known to etch silicon anisotropically for a long time (1). A different system with improved etching behavior was obtained by the addition of isopropyl alcohol (17).
In general, all aqueous solutions containing hydroxides of other alkali metals, like LiOH, and CsOH (18) perform in a similar manner. Aqueous solutions of ammonium hydroxide (NH₄OH), were also reported to etch anisotropically (19). The same type of solution with the addition of H₂O₂ is frequently employed for the cleaning of silicon wafers (20). More complicated derivatives of ammonium hydroxide, e.g., so-called quaternary ammonium hydroxides like tetramethylammonium hydroxide (N(CH₃)₄OH) and choline ((CH₃)₃N(CH₂CH₂OH)OH) can also be used as anisotropic etchants (21).

**General Considerations**

Solutions consisting of ethylenediamine, water, and pyrocatechol (EDP) are among the most widely employed. Many essential results concerning the composition of this system and its crystal orientation dependence were reported in the work done by Finne and Klein (2). They found that pyrocatechol can be omitted, so that in its most primitive form, the etchant solely consists of ethylenediamine and water. With nonaqueous ethylenediamine no etching was achieved, indicating that water is an active and necessary component. The maximal etch rate occurred at an ethylenediamine to water molar ratio of approximately 1.2. By the addition of pyrocatechol, a strong increase of the etch rate by a factor of three was found, saturating at a concentration of approximately 4 mole percent (m/o). For the three main silicon crystal orientations <100>, <110>, and <111>, Finne and Klein found an etch rate ratio of 17:10:1.

The effects of further additives were studied by Reisman et al. (22). They found that when exposing the EDP solution to oxygen, 1,4-benzoquinone and other products are formed, leading to an increase of the etch rate and a darkening of the solution. This effect can be avoided by continuously purging the etching apparatus with an inert gas (2, 22). They also found that trace quantities of pyrazine (C₄H₇N₂) lead to an increase of the etch rate. However, similar to pyrocatechol, this effect nearly saturates at a concentration of 5g pyrazine per liter ethylenediamine. Since commercially available ethylenediamine usually contains an unknown trace amount of pyrazine, Reisman et al. (22) proposed to intentionally add enough pyrazine to the solution so that the saturation level is reached.

For the ethylenediamine-water-pyrocatechol system, several recipes were proposed. Reisman et al. developed two specific solutions optimized for use where either a high etch rate was required ("F") or where lower etch rates and/or lower temperatures are desired ("S") (22). Their specific compositions are listed in Table I, together with a recipe used by Finne and Klein ("T") (2) and another one proposed by Bosasss ("B") (23).

For both solutions suggested by Reisman et al. (22) an activation energy of 0.36 eV on <100> silicon was found, which is considerably smaller. These results indicate that diffusion processes influence the silicon dissolution rate considerably.

The work of Abu-Zeid et al. (26) showed that, for ethylenediamine-based solutions, the silicon etch rate can be increased considerably by stirring. They also showed that the etch rate depends on the effective silicon area being exposed to the solution and its geometry. An increase can be observed, when the area of the active region gets smaller.

A chemical analysis of the residues showed that they consisted mainly of SiO₂ with additional trace amounts of reaction products.

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For hydrazine water solutions a very similar behavior to the one observed in EDP solutions was found (3, 27, 28). At a temperature of 118°C, an etch rate ratio of 16:9.1 for the (100):(110):(111) planes was determined, which is comparable to EDP (26). When underetching convex corners, (211) was identified as an etch bordering plane with a very high etch rate (3, 27).

Among the inorganic solutions, the one most frequently used is based on KOH. The first detailed study on a ternary mixture of KOH, water, and isopropyl alcohol was given by Price in 1973 (17). His major observations were the following: the maximal etch rate occurred at a KOH concentration of 10-15 weight percent (w/o) when no alcohol was added, and around 30% KOH with alcohol. In general, the addition of isopropyl alcohol leads to a decrease of the etch rate. On <100> silicon the activation energy was found to be between 0.52 and 0.69 eV. He found no effect of stirring on the etch rate, indicating that the reaction is not diffusion limited. Under optimum conditions, Price observed an etch rate ratio of 35:1 for the (100):(111) crystal planes (17). A much higher anisotropy ratio of up to 500:1 for the <110> to <111> etch rates in a highly concentrated 55% KOH solution was reported by Kendall (29, 30). Further data on the etch rates of <110> and <111> silicon as well as SiO₂ were given by Clark and Edell (31). For KOH solutions with a concentration between 9 and 34 w/o, they found the following ranges of activation energies: 0.8-0.9 eV for <110> and 0.4-0.9 eV for <111>, and 0.8-1.0 eV for SiO₂.

In a work done by Pakis et al. (32) the etching process of KOH on silicon was monitored in situ by Raman spectroscopy. From these experiments the main reaction species was determined to be OH⁻. They proposed SiO₂(OH)₂⁻ to be the primary etching product with subsequent polymerization. The following overall gross reaction was suggested by them (33).

\[
\text{Si} + 2 \text{H}_2\text{O} + 2 \text{OH}^- \rightarrow \text{Si(OH)₄}^- + 2\text{H}_2
\]
participate chemically in the reaction. In a later work (34), Palik et al. included energy level considerations, stating that the etching reaction transfers an electron from \( \text{OH}^- \) into the silicon surface bond and then back to the etch products.

A more detailed break down of the reaction equations, including the transfer of charge was suggested by Bailey et al. (24). They assumed that four electrons are injected into the conduction band by an initial oxidation reaction, which are later consumed in a reduction step

\[
\text{Si} + 2 \text{OH}^- \rightarrow \text{Si(OH)}_2^{++} + 4e^- \quad [4]
\]

\[
\text{Si(OH)}_2^{++} + 4e^- + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_6^{6-} + 2\text{H}_2\text{O} \quad [5]
\]

In the literature published to date several attempts were undertaken to explain the anisotropic behavior of these etchants. Price indicated that a correlation between the available bond density of different crystal planes and the etch rate could exist (17). However, it is difficult to explain etch rate ratios of about 100:1 when the bond density only varies by a factor of two. Another proposal was made by Kendall who argues that [111] planes get oxidized more rapidly than others and therefore could be covered with a thin oxide layer immediately after immersion into the etchant (29). Palik et al. assume that the anisotropy might be attributable to differences in activation energies and in backbond geometries on different surfaces (33).

In this paper, experimental results on the orientation dependence of the etch rate for several solutions as a function of composition and temperature will be given. An attempt will be made to give a model valid for all anisotropic silicon etchants, explaining the underlying mechanism. Furthermore, results on the etch behavior of the most widely used passivation layers SiO\(_2\) and Si\(_3\)N\(_4\) will be reported.

The effects of dopants on the silicon etch rate will be discussed in an accompanying paper (35).

**Experimental**

In the experiments, n- and p-type Czechralski grown 3 in. wafers with <100> and <110> orientation were used. The resistivities were 1-10 \( \Omega \cdot \text{cm} \), corresponding to an impurity concentration of approximately \( 1 \times 10^{13} - 1 \times 10^{14} \text{ cm}^{-3} \). For passivation, these wafers were either thermally oxidized or a CVD silicon nitride layer was deposited.

In order to obtain detailed data on the crystal orientation dependence of the etch rate, a fan shaped or wagon wheel shaped masking pattern was employed, consisting of radially divergent segments with an angular separation of one degree (36-40). This pattern was transferred to the passivation layer. Thus, alternating segments of bare silicon and regions covered with silicon dioxide or silicon nitride were obtained. The size of a chip containing one such pattern was 16 - 16 mm\(^2\). In order to achieve a more accurate angular resolution, particularly in the neighborhood of [111] planes, where the etch rate is a very sensitive function of the angular orientation, a second pattern with segments and spaces differing by an angle of 0.1° and with a total angular spread of 4° was used.

For etch rate studies on passivation layers, wafers covered with thermal SiO\(_2\) (1000°C, wet), CVD-SiO\(_2\) (SiH\(_4\), N\(_2\)O, 800° and 900°C) and CVD-Si\(_3\)N\(_4\) (SiH\(_4\) and NH\(_3\), 900°C) were prepared and diced to the same chip size mentioned above.

The samples were etched in an oil-heated, double-walled glass vessel. The temperature was varied between 20° and 115°C and was controlled with an accuracy of ±0.2°C. In order to keep the composition of the etchant constant, the vapors were recondensed in a water cooled reflux condenser. In the case of EDP solutions, an additional nitrogen purge was applied, in order to prevent changes of the etch properties due to contact with atmospheric oxygen (2, 12).

The inorganic etchants employed in the experiments were KOH, NaOH, and LiOH with concentrations in the range of 10-60, 24, and 10%, respectively, where all values are in weight percent. In some experiments, isopropyl alcohol was added to a 20% KOH solution according to the following recipe: 1 liter H\(_2\)O, 312g KOH, 250 ml isopropyl alcohol. The only organic etchants used were EDP solutions, among which a composition type “S” introduced by Reisman et al. was employed most frequently (Table I). This choice was made because it is applicable in a wide temperature range which is important for obtaining reliable data on activation energies.

After etching the chips masked with a wagon wheel pattern, a blossom-like figure developed. This phenomenon is due to the total underetching of the passivation layer in the vicinity of the chip center, leaving an area of bare exposed silicon. The radial extension of this area depends on the crystal orientation of the individual segments, leading to a different amount of lateral underetching. The pattern developed on a <100> test sample etched in an EDP solution is shown in Fig. 1.

Visual inspection of such blossom-like patterns was only used for a qualitative evaluation of the anisotropy. In order to obtain quantitative results, the lateral etch rates were determined by measuring the width \( w \) of the overhanging passivation layer with an optical linewidth measurement system (LEITZ Laitem). This is illustrated in Fig. 2, showing a schematic cross section of the test chip after etching. Additionally, the depth \( d \) of the etch grooves and the orientation of the etch bordering planes were determined by means of a mechanical stylus profiler and laser reflection methods, respectively (41). Similar measurements were performed on chips with the 0.1° pattern.

To evaluate the etch rate of the passivation layers, their thicknesses were measured by ellipsometry before and after etching.

**Results**

**Morphology of the etched silicon surfaces.**—After etching a partially masked silicon surface, two regions of interest arise. One is the bottom surface obtained from vertical etching, the other consists of the laterally under-etched sidewalls developing along the edges of a masking pattern.

When using EDP solutions, the surfaces generally tend to be quite smooth, particularly on etched bottom surfaces of <100> wafers. Also, the laterally under-etched sidewalls of the passivated segments are generally smooth. However, as indicated in Fig. 3, a certain waviness can be observed on fast etching sidewall crystal planes.

On etched surfaces of <110> wafers with relatively large areas exposed to the etchant, a linearly textured structure develops which can be recognized with the naked eye. When viewed under a scanning electron microscope, as shown in Fig. 4, these textured surfaces appear to be bounded by well-defined, slanted crystal planes.

As has been observed in numerous previous studies, [111] crystal planes form perfectly smooth lateral sidewalls, both on <100> and on <110> wafers, and for all etchants investigated (5, 6).

In case of alkaline etchants like KOH, the vertically etched bottom surfaces of <100> and <110> wafers turn out to be relatively smooth. However, when using a solu-

Fig. 1. Etch pattern emerging on a masked test wafer with the orientation <100> after etching in an EDP solution type S. The residual oxide at the center is due to the finite resolution of the mask.
tion of low concentration (below 30%), a tendency for the formation of pyramids can be observed on <100> wafers. The laterally underetched sidewalls of the masked segments generally appear to be fragmented, as demonstrated in the micrographs of a <110> wafer shown in Fig. 5a and b. Both pictures show a steep-walled mesa rising over a more gently sloped shoulder. Within this formation patches with smooth {111} surfaces can be observed. They are surrounded by jagged surfaces which could not be identified as any particular crystal plane.

Etch limiting crystal planes.—By means of laser reflection measurements, as indicated in Fig. 2, the crystal orientation of the planes bounding the laterally underetched segments was determined for the case of EDP etchants. These planes are shown in Fig. 6 for <100> and <110> wafers in the form of stereographic projection diagrams. For both wafer orientations they can be characterized by the Miller indexes \{hhk\} where \(h\) and \(k\) are integers with \(h \geq k\). This was found for all EDP compositions and temperatures applied.

As mentioned above and indicated in Fig. 4, a linearly textured structure develops on bottom surfaces of etched <110> wafers. The crystal orientation on the long steps in this texture was found to be close to (331). On the basis of these results, it is surprising to observe the formation of smooth, laterally underetched {111} surfaces on <100> wafers, when using EDP solutions. A similar surprise is the formation of smooth, flat-etched bottoms when etching narrow grooves bounded by vertical {111} planes on <110> wafers. This phenomenon is probably attributable to the different geometrical situation of a flat, large surface, as compared to a small sidewall bounded by concave corners.

For silicon surfaces etched by KOH, the resulting crystallography depends on the composition of the etchant. Furthermore, as mentioned above, only a limited number of crystal planes can be identified. For relatively high KOH concentrations, exceeding 35%, these planes are shown in the stereographic projection diagrams in Fig. 7. In contrast to EDP solutions, vertical (100) planes emerge on <100>-wafers (Fig. 7a) when a masking pattern with an angle of 45° to the flat is used (39). When misaligning such a pattern by a few degrees with respect to this 45° line, the vertical smooth sidewall remains, but an inclined shoulder begins to form in the corner. When misalignment exceeds a few degrees, a similar situation as shown in Fig. 5a develops.

The crystal planes marked in the central region of the <110> diagram, Fig. 7b, correspond to the slanted shoulders depicted in Fig. 5b. The vertical (111) planes on <110> wafers rise over an inclined shoulder of {311} planes. Such a shoulder does not arise when using EDP solutions.

Lateral etch rate as a function of crystal orientation.—As mentioned above, it was found for EDP solutions that etch bordering crystal planes develop, which are characterized by the indexes \(\{hkk\}\) where \(h \equiv k\). The lateral underetch rates of these planes on <100> and <110> wafers for a temperature of 95°C are shown in the polar coordinate diagrams in Fig. 8. Apart from the sharp absolute minima at (111) planes, relative minima occur at (110). The maximal lateral etch rate is observed for (311) planes.

The differences of the lateral underetch rates of crystal planes occurring several times on the same diagram, e.g., in Fig. 8b, are due to different slanting angles of these planes. The immediate result of the measurement is the projection of the etch rate onto the surface of the wafer. The true etch rate can be calculated by multiplying the apparent lateral underetch rate, as measured by the overhanging film of the passivation layer, by the sine of the inclination angle \(\theta\). This factor can be given as a function of the lateral alignment angle \(\phi\) in the wafer plane. When the <110> direction, which corresponds to the intersecting line of the (100) wafer plane and the resulting etch bordering (111) plane, is taken as \(\phi = 0°\), the following formula applies

\[
\sin \theta = \sqrt{1 - \frac{1}{\tan^2 (45° - \phi) + 2}}
\]

For <110> wafers again with the <110> direction taken as \(\phi = 0°\), which in this case corresponds to the intersecting line of the (110) wafer plane and the (111) planes with an inclination angle of 33.3°, the correction factor is given by

\[
\sin \theta = \frac{\tan \phi + 1}{\sqrt{2} \tan^2 \phi - 2 \sqrt{3} + 3}
\]
When an angular correction is applied according to these equations, the etch rates of the same crystal planes with different inclinations nearly coincide. The result of such a transformation on a <110> wafer is shown in Fig. 9.

For KOH solutions, similar polar coordinate diagrams for <100> and <110> wafers are shown in Fig. 10. These results are in general agreement with the KOH data of de Guet et al. (42). In comparison to the results obtained with EDP (Fig. 8), it is remarkable that the peak etch rates are far more pronounced. However, since the sidewalls are not particularly flat, the resulting etch rates can be attributed to specific crystal planes only for some orientation angles. All other etch rates are average values for surfaces composed of many different crystal planes.

The lateral etch rate in the vicinity of (111) crystal planes is extremely sensitive to small angular misalignments. This can be seen from high resolution measurements, the results of which are shown in Fig. 11 for EDP and KOH solutions. The etch rate increases by about a factor of two for a misalignment of 1° on a <100> wafer. On a <110> wafer, this effect is even more pronounced due to the faster variation of crystal planes as a function of misalignment (29). Thus, in practical applications where large aspect ratios are important, precise alignment is crucial.

Temperature dependence of the etch rates.—The temperature dependence of the vertical etch rate on <100> wafers for various EDP and KOH solutions is shown in Fig. 12. For an EDP solution type S an activation energy of 0.40 eV was determined. For KOH solutions, values between 0.57 and 0.62 eV were found. On <110> surfaces, the results were 0.33 eV for EDP and again between 0.57 and 0.62 eV for KOH solutions.

The activation energies $E_a$ and pre-exponential factors $R_o$ were determined according to the Arrhenius law $R = R_o \cdot \exp(-E_a/kT)$. The experimental results obtained on <100> and <110> wafers are listed in Table II for <100> and <110> wafers for all etchants investigated.

A feature of general interest for many practical applications of anisotropic silicon etching is the ratio of the etch rates of the main crystal planes {100}, {110}, and {111}. The {100} and {110} rates were determined by vertically etching <100> and <110> wafers. The <111> etch rate was determined by laterally underetching segments on <100> or <110> wafers with an angular separation of 0.1°. The results for an EDP solution type S are shown in Fig. 13. It can be seen that the slower the etch rate, the higher is the activation energy. As a consequence, the etch rate ratio of <110>/<111> as well as <100>/<111> increases from 30:1.
Fig. 7. Stereographic projection diagrams of crystal planes bounding the etch front when laterally underetching a masking pattern on (a, right) <100> and (b, left) <110> wafers in a KOH solution with a concentration exceeding 30%.

near the boiling point of the solution to about 150:1 and 100:1, respectively, at 50°C. A similar behavior can be observed for KOH solutions. <110> etches about 60% faster than <100>, with nearly identical activation energies of 0.61 and 0.59 eV, respectively. The activation energy of <111> is approximately 0.7 eV. The etch rate ratio of <110>:<100>:<111> was found to vary from 50:30:1 at 100°C to about 160:100:1 at room temperature. These results show that the anisotropy ratios are roughly comparable between EDP and KOH. However, as mentioned earlier, the exact values of these etch ratios depend on the effective area exposed to the solution, especially in EDP solutions (26).

The temperature dependence for the lateral etch rates of different crystal planes on <100> wafers was measured for an EDP solution type S. The results are shown in the Arrhenius diagram in Fig. 14 where the parameter of the different curves refers to the polar alignment angle of the edge of the masking pattern with respect to the <110> direction. As can be seen from this diagram, the activation energy is higher on crystal planes with a lower etch rate. This situation is indicated in more detail in Fig. 15a, and b, where the activation energy and the pre-exponential factor are shown as a function of orientation angle, corresponding to specific crystal planes. The activation energies vary between 0.25 and 0.52 eV.

KOH etchants reveal a similar behavior. However, in this case the orientation angle cannot always be correlated to a specific crystal plane, as mentioned above. The activation energies were found to vary between 0.58 eV and approximately 0.7 eV, which is in good agreement with earlier reports of 0.51-0.64 eV (30) and 0.57-0.71 eV (31) for <100> and <110> at low and high KOH concentrations, respectively.

Influence of etchant composition and concentration.—For very high KOH concentrations exceeding 15 w/o the silicon etch rate decreases when raising the concentration further, as indicated in Fig. 16. It was found that for very high concentrations the data could best be fitted by assuming a proportionality to the fourth power of the molar water concentration. For the full range of concentrations investigated, the best fit for the etch rate R was obtained by taking $R \propto [H_2O]^4 [KOH]^{1/4}$.

When isopropyl alcohol is added to a KOH solution, a general decrease of the etch rates can be observed, which is about 20% for <100>, but almost 90% for <110>. This is shown in Fig. 17 for a 20% KOH solution with. and without the addition of 250 ml isopropyl alcohol per liter water. As a result of the much stronger decrease of the etch rate on a <110> surface, the etch rate ratio of <100>:<110> is reversed.

Fig. 8. Lateral underetch rates as a function of orientation on (a, left) <100> and (b, right) <110> silicon wafers when using an EDP solution type T at a temperature of 95°C.
An increased tendency for the formation of white residues appearing on the silicon surface was found for KOH etchants with a concentration below 15%. This is in agreement with the observation by Reisman et al. (22) for EDP solutions, where they also found a similar effect when increasing the water concentration.

**Diffusion effects.**—In agreement with the observations by Abu-Zeid et al. regarding the effect of stirring (26), we have also found that diffusion plays a major role for EDP solutions. The lateral etch rate of {111} planes was found to depend on the geometry of the actively etching surfaces. As an example, when etching a V groove, the etch rate of the sidewalls is small as long as a flat actively etching {100} bottom surface is still present, and increases after the completion of the V groove. Another example appears when etching a laterally confined geometry on a wafer. In this case an increased etch rate can be observed along the periphery of a masked large area etching surface as compared to that of the central region.

Diffusion effects are far less pronounced when KOH is used. However, some depletion effects are observable. As an example, when very deep and narrow grooves are etched on <110> silicon, the vertical etch rate decreases gradually (29).

**Etch rates of passivation layers.**—Passivation layers of practical interest are silicon dioxide (SiO₂) and silicon nitride (Si₃N₄). In all our experiments we could not measure
Table II. Experimental data on the activation energy $E_a$ and pre-exponential factor $R_o$ of the <100> and <110> silicon etch rates as well as of the etch rates of thermally grown silicon dioxide for different etchant compositions. $E_a$ and $R_o$ were determined according to the Arrhenius equation $R = R_o \exp (-E_a/kT)$.

20% KOH includes an isopropyl alcohol concentration of 250 ml per liter water.

<table>
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<tr>
<th></th>
<th>&lt;100&gt; Si</th>
<th></th>
<th>&lt;110&gt; Si</th>
<th></th>
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<td></td>
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<td>$R_o$ ($\mu$m/h)</td>
<td>$E_a$ (eV)</td>
<td>$R_o$ ($\mu$m/h)</td>
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<td>10% LiOH</td>
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</tbody>
</table>

The etch rate ratios between silicon and SiO$_2$ are very important for practical applications when the oxide is used as a masking layer during etching. This ratio depends strongly on the composition of the etchant and the temperature. As indicated in Fig. 20, it is about two orders of magnitude larger for an EDP solution than for KOH. For highly concentrated KOH solutions at typical temperatures used for etching, this ratio is only about 100-200, which is usually not enough when the full thickness of the wafer has to be etched through. Thus, for such applications a KOH solution with a concentration of about 20% at a lower temperature is recommendable. Then the attainable ratio is on the order of about 1000, which agrees with values reported in Ref. (30, 31).

Discussion

A central question discussed in the published literature is whether the anisotropic dissolution of silicon can be explained by a purely chemical (2, 43), or by an electrochemical model (24). Glombicki et al. (43) find that a strong argument in favor of a chemical model is the independence of the etch rate from the type and concentration of silicon dopants within wide concentration ranges. In the following we propose an electrochemical model of the etching process.
mechanism, accounting for the observed relative insensitivity of the etch rate to dopants. The general reaction mechanism for a <100> silicon surface will first be presented. Subsequently, the modifications arising from other crystal surfaces and the influence of the solution composition, as well as diffusion effects will be discussed. The effects of high dopant concentrations are discussed in an accompanying paper (35).

**Reaction mechanism.**—In the silicon crystal the electronic energy levels can be described in the usual way by the valence and the conduction band with a gap of 1.12 eV, as indicated in Fig. 21. The position of the Fermi level depends on the dopant concentration, being above midgap for n-type and below midgap for p-type silicon. The electron affinity of silicon, which is equivalent to the distance of the lower edge of the conduction band to the vacuum level, is 4.05 eV (44).

Due to the different bonding situation of atoms located near the surface of the crystal, surface states arise which are located within the forbidden bandgap. In our model, different types of surface states are considered to play an important role. They are characterized by the sequence and occupation of orbitals. In context with the following considerations we only discuss qualitatively the term scheme of those orbitals which participate in the etching process. These are the lone pairs of silicon surface atoms (A), the valence orbitals of Si—Si backbonds (B), as well as Si—O bonds in the reaction products (C). It is important to note that the relative position of the surface states with respect to the energy bandedges is independent of the type of dopant within wide concentration levels.

On the side of the electrolyte the main reactants are hydroxide ions and water molecules. This has been shown by Palik et al. (32, 33) using Raman spectroscopy and by the results of our own experiments. We propose that the redox couple H2O/OH−, plays a key role in the reaction. This was already suggested by Palik et al. (34). At zero pH this couple is defined as the normal hydrogen electrode (NHE) with a potential of −4.5 eV with respect to vacuum (45). This potential shifts towards more positive values by 59 meV/pH. For the high pH range around 14, used in our experiments, we expect an electrode potential of approximately 0.8 eV vs. NHE, amounting to −3.7 eV with respect to the vacuum.

A graphical representation of the electronic energy levels of both the solid and the electrolyte before being brought into contact is indicated in Fig. 21. The flatness of the energy bands at the surface is fictitious and was only used in order to clarify the general concepts.
A general discussion of the energy levels of redox couples can be found in the work of Memming (45). In addition to the usual density of states representation of the energy levels of the redox couple we have included a band diagram on the side of the electrolyte, being analogous to that of the solid. This will allow the inclusion of the potential distribution in the electrolyte.

After immersion of the wafer into the electrolyte, the Fermi levels on both sides of the solid/liquid interface will be brought to the same level by a transfer of electrons from the electrolyte into the silicon crystal. This will lead to a downward bending of the conduction and valence bands, which is similar for n- and p-type silicon, as indicated in Fig. 22. It is more pronounced for a p- than for an n-type semiconductor, due to the larger initial difference of the Fermi levels between the solid and the electrolyte. The extension of the resulting surface space charge layer is determined by the doping level in the semiconductor. A typical value for moderate dopant concentrations of $1 \cdot 10^{19}$ cm$^{-3}$ is 1.0 nm (44).

Similarly, the electronic states of the redox couple are influenced by the potential drop occurring at the electrolyte side of the interface. At the very high ion concentrations present at the generally used high pH values, the extension of the space charge layer on the side of the electrolyte is much smaller, on the order of 1-10 nm.

Using a molecular orbital (MO) term scheme, the electron configuration of a [100] silicon surface atom may be characterized by two $\sigma$ (Si--Si) bonding MOs (B) and two degenerate Si(3p) levels (A) occupied with two electrons, which is graphically represented in Fig. 23a.

In a first reaction step, an electron of a hydroxide ion is transferred into the orbital A of a dangling bond surface state by tunneling through the Helmholtz layer, as indicated in Fig. 23b. After this electron transfer the resulting...
OH radical can bond to the remaining unpaired electron, forming an Si—O bond at the surface corresponding to a new surface state which is characterized by the sequence of highest occupied MOs given in Fig. 23c. The reaction proceeds by thermal excitation of an electron from the highest occupied orbital A into the conduction band (Fig. 23d). The electron excitation and the formation of the Si—OH bond are uncorrelated processes, i.e., they can occur at different surface sites showing suitable electron configurations.

On a (100) surface with two dangling bonds per surface atom, two hydroxide ions can bind, as indicated in Fig. 23e, injecting two electrons into the conduction band by a positively charged silicon-hydroxide complex into the conduction band; (e) binding of second hydroxide ion leading to an increase of orbital B towards a higher energy B'.

We assume that the energy difference between the σ (Si—Si) orbitals B' and the conduction band contributes significantly to the measured activation energy in KOH solutions, being approximately 0.6 eV. Thus, this step is considered to be rate controlling for the total reaction. The smaller activation energy of 0.40 eV for the same crystal plane measured for an EDP solution is considered to be due to diffusion and solvation effects in the less alkaline electrolyte.

The oxidation half-reaction described above is in accordance with the anodic reaction of germanium in aqueous solutions, given by Turner (46). Taking both steps together (Eq. [8] and [9]), four electronic charges are required for the dissolution of one silicon atom. They are provided by two hydroxide ions and by two Si—Si binding electrons. These electrons are injected into the conduction band of the silicon crystal and stay localized near its surface, due to the potential well provided by the downward bending of the energy bands.

The silicon-hydroxide complex reacts further with two more hydroxide ions producing orthosilicic acid (47).

\[
\text{Si(OH)_4} + 2 \text{OH}^- \rightarrow \text{Si(OH)}_3^- + 2 \text{H}^+ \quad [10]
\]

It is assumed that the breaking of the backbonds described by Eq. [9] and the bonding of hydroxide ions according to Eq. [10] happen more or less simultaneously. In fact, the presence of OH⁻ ions in close vicinity to the back-bonds can actually weaken their strength.

The neutral Si(OH)_4 molecule can leave the solid surface by diffusion. In the bulk electrolyte it is unstable due to the high pH value of the solution. From silicate chemistry it is well known that for pH values exceeding 12 the following complex will be formed by the detachment of two protons (47).

\[
\text{Si}{}^{8+} + 2 \text{OH}^- \rightarrow \text{Si(OH)}_3 + \text{Si}_{\text{solid}} \quad [11]
\]

This silicate species was observed by Raman spectroscopy measurements (32).

The excess electrons in the conduction band can be transferred to water molecules which are located near the solid surface, thus producing hydroxide ions and hydrogen atoms, which recombine to molecular hydrogen.

\[
4\text{H}_2\text{O} + 4e^- \rightarrow 4\text{H}_2\text{O}^- \quad [13]
\]

In the energy diagram in Fig. 22, this step corresponds to the transfer of conduction band electrons localized near the silicon surface into the unoccupied state of the H₂O⁻ hydroxide couple, as indicated by the arrow. Therefore, it is required that an overlap between the conduction band and the upper state of the redox couple exists.

We assume that the four hydroxide ions resulting from this reduction step are the ones that are consumed in the oxidation for the dissolution of one silicon atom (Eq. [8] and [10]). Since they are generated at the silicon surface, they do not have to overcome the repulsive force of the negatively charged solid as would be the case for the hydroxide ions from the bulk of the solution. Strong support for this assumption is given by the fact that the etch rates for an EDP solution with an OH⁻ concentration of 0.034 mol/liter are nearly as large as those for KOH solutions with a hundredfold higher OH⁻ concentration of 5.10 mol/liter (compare Fig. 12).

Additional support for the involvement of four water molecules for the dissolution of one silicon atom comes from the experimentally observed correlation between the fourth power of the water concentration and the silicon etch rate for highly concentrated KOH solutions. This behavior is indicated in Fig. 16. The weak dependence of this curve on the KOH concentration indicated by the quarter power law in Fig. 16 supports the assumption that the hy-
Thus, they might play a role in facilitating the removal of the Si(OH)$_2$ complex from the crystal.

Parallel to the recombination of hydrogen atoms appearing in Eq. [14], other processes may occur. These hydrogen atoms can easily diffuse into the silicon crystal and, particularly, into the vicinity of the backbonds of the surface atoms or even into an interstitial position. It is known from amorphous silicon deposition techniques that the presence of hydrogen leads to a weakening of silicon bonds and can actually induce an "etching" effect (48, 49). Also, in crystalline silicon and in silicon dioxide, hydrogen atoms are known as structure breaking elements (50). Thus, they might play a role in facilitating the removal of the Si(OH)$_2^+$ complex from the crystal.

The overall gross reaction is summarized by the following equation

$$\text{Si} + 2 \text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2\text{(OH)$_3^-$ + 2H}_2$$  \[15\]

The driving force for this overall reaction is given by the larger Si—O binding energy of 193 kcal/mol as compared to a Si—Si binding energy of only 78 kcal/mol (51).

When the etching behavior of different inorganic solutions like KOH, NaOH, and LiOH are compared, no significant differences can be found. Thus, the role of the cations, K$^+$, Na$^+$, and Li$^+$, which do not appear in our reaction equations, can be neglected. We assume this to be true even for the more complicated cations which are present in organic solutions, like NH$_4$ (CH$_2$)$_2$NH$_4$ in the case of EDP. They only may influence the potential distribution within the inner Helmholtz layer, according to their size and specific solvation.

The role of pyrocatechol in ethylenediamine based solutions is to convert Si(OH)$_4$ into a more complex anion, increasing the solubility of the etch product. Thus, instead of the reaction described in Eq. [11] and in analogy to the etch solutions discussed in Ref. [2], the following step will occur (2, 47)

$$\text{Si(OH)$_2$} + 2 \text{OH}^- + 3\text{C}_6\text{H}_4\text{(OH)$_2$} \rightarrow \text{Si(C}_6\text{H}_4\text{O}_2)^3^- + 6\text{H}_2\text{O}$$  \[16\]

The catalytic effects of pyrazine and quinone have been described by Reisman et al. (22). They believe that in the absence of all these catalysts ethylenediamine based solutions would not etch at a significant rate. This does not agree with the results of our experiments.

When alcohol is added to an alkaline silicon etchant, it does not participate in the reaction. Its main role is to adjust the relative water concentration of the etchant. This is only important in KOH and related inorganic solutions (17), where the water concentration cannot be adjusted otherwise without severely affecting the pH value. In the case of ethylenediamine-based solutions the relative water concentration can be freely adjusted without significantly influencing the pH value, due to its incomplete dissociation.

As has been described above, the formation of residues on the silicon surface was observed for solutions with a high water concentration. In this case the rate of dissolution of silicon atoms from the crystal surface is so high that the transport of the Si(OH)$_2$ complex into the bulk electrolyte cannot keep up with its production. When the concentration of this complex on the silicon surface becomes too high, it will polymerize by the detachment of water and cover the surface. This finally results in a compound similar to SiO$_2$, which was actually observed by Wu et al. (25).

Anisotropy.—The most outstanding feature of the anisotropic behavior of alkaline etchants is the very low etch rate of [111] surfaces. The number of dangling bonds available per surface unit cell depends on the crystal orientation of the exposed silicon surface. It is lowest for a [111] surface with one dangling bond per unit cell, whereas there are two on [100] or [110] surfaces (52, 50). The areal density of dangling bonds is highest for [100] planes (52).

Thus, in the initial reaction on a (111) crystal plane, only one hydroxide ion can bind to a silicon atom

$$\text{Si} + \text{Si} \rightarrow \text{Si} + \text{Si} + \text{OH}^- \rightarrow \text{Si} \rightarrow \text{Si} + \text{OH}^- + e^- \text{cond}$$  \[17\]

In the following steps the three backbonds of the surface silicon atom have to be broken. This will happen in analogy to Eq. [9] and [10], except that in this case the transfer of three electrons into the conduction band and the subsequent binding of three hydroxide ions will be required

$$\text{Si} + \text{Si} \rightarrow \text{Si} + \text{Si} \rightarrow \text{Si} + \text{Si} + \text{OH}^- + 3\text{e}^- \text{cond}$$  \[18\]

The breaking of three Si—Si backbonds proceeds continuously by an electron transfer into the conduction band and successive binding of hydroxide ions. As soon as orthosilicic acid has been formed (Eq. [19]), the reaction will proceed as described above for a [100] surface.

Since there are three backbonds in the initial configuration of a [111] surface atom, the corresponding orbital B$^*$ is expected to be at a lower energy level than that of a [100] surface atom (compare with Fig. 23). This assumption is supported by theoretical calculations of the band structure on ideal low index surfaces of silicon (53). These calculations yield the lowest energy level for the backbond surface states on [111] surfaces, the highest on [110], and [100] in between. The absolute values from these calculations are well below the edge of the valence band. This is made for the idealized assumptions made in this calculation. More reliable data of real [111] surface states were obtained by current-imaging-tunneling spectroscopy (CIMS) by Hamers et al. (54). They obtained a value of $-1.75$ eV for the backbonds with respect to the Fermi level for highly n-doped samples. The binding of OH groups to the silicon surface lifts these backbond states to even higher values, which then presumably lie within the forbidden bandgap.

We assume that the energy difference between the backbond surface states of [100] and [111] surfaces corresponds roughly to the measured difference between the activation energies of their etch rates. In the case of KOH, we found the [111] activation energies to be approximately 0.1 eV higher than [100]. Similarly, for an EDP solution type S a consistently higher value by 0.12 eV was determined (compare with Fig. 23). This assumption is supported by theoretical calculations of the band structure on ideal low index surfaces of silicon (53).

Another argument in favor of the high etch rate is the easier penetrability of [111] surfaces for water molecules, corresponding to the main channeling direction. By this argument, it can also be understood that the observed etch rates for a [110] crystal plane actually become smaller than those for [100], when isopropyl alcohol is added to a KOH solution, as indicated in Fig. 17. Alcohol covers the silicon surface (32), so that the "channeling advantage" of [110] planes is no longer valid.

For crystal surfaces other than [100], [110], or [111] it can be assumed that, at least microscopically, they are a composition of these and possibly some other main crystal planes. In the case of surfaces etched with KOH solutions,
this composite nature can even be observed macroscopically as indicated in Fig. 5.

If the anisotropic behavior is attributable to small energy differences of the relevant surface states and if no diffusion effects were present, it can be assumed that the anisotropy would have to disappear at infinite temperature. When such an assumption is made, it can readily be calculated, that a difference of 0.12 eV between the activation energies of two different crystal planes is sufficient to cause an etch rate ratio of 100:1 at room temperature.

When the actually measured Arrhenius diagram for the lateral underetch rates of different crystal planes (Fig. 14) is extrapolated to high temperatures, it is found that the individual lines cross each other at a finite temperature. In the case of EDP they intersect at a temperature of approximately 400°C, as indicated in Fig. 24. This is due to diffusion effects which are quite noticeable for EDP solutions (26). The differences in activation energies from fast to slow etching planes for the configuration shown in Fig. 24 were indicated in Fig. 15. With 0.25 eV the maximum difference is almost twice as high as one would expect from the etch rate ratio obtained at room temperature. When diffusion effects are present, the apparent activation energy of a fast etching plane will be lowered more than for a slow etching plane, thus causing the increased differences in activation energies for different crystal surfaces that have been measured.

Etching of silicon dioxide.—For the etching of silicon dioxide we propose the following purely chemical reaction equation

\[
\text{SiO}_2 + 2 \text{OH}^- \rightarrow \text{SiO}_2(\text{OH})_2^{2-}
\]  

The experimental results indicate a linear correlation between the SiO₂ etch rate and the hydroxide concentration. This can be seen from Fig. 18, where the SiO₂ etch rates in KOH solutions exceed those in EDP by almost three orders of magnitude. Similarly, this linear correlation is found when increasing the KOH concentration up to a value of approximately 35%, as indicated in Fig. 19. For higher KOH concentrations, the etch rate decreases with the square of the water concentration, indicating that water plays a role in this reaction. Based on these observations, a numerical fit to the experimental data obtained in KOH solutions was made, the result of which is summarized in Table A-III in the Appendix.

![Fig. 24. Arrhenius diagram of the lateral etch rates on <100> silicon as shown in Fig. 14, but extrapolated to infinite temperature. Etchant used was EDP type S.](image-url)
ceeding 35% the etch rate decreases with the square of the water concentration, which is probably due to the buildup of negative charge on the solid surface.

**Acknowledgments**

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**APPENDIX**

For aqueous KOH solutions within a concentration ranging from 10-60% the following empirical formula for the calculation of the silicon etch rate \( R \) was found to be in close agreement with the experimental data

\[
R = k_c \cdot [\text{KOH}]^{0.14} \cdot e^{-E_o/k_b \cdot T}
\]

[A-1]

The values for the fitting parameters were found to be \( E_o = 0.595 \text{ eV} \) and \( k_b = 2480 \text{ Å/h (mol/liter)}^{-4.25} \) for a <100>

### Table A-I. <100> silicon etch rates in [μm/h] for various KOH concentrations and etch temperatures as calculated from Eq. [A-1] by setting \( E_o = 0.595 \text{ eV} \) and \( k_b = 2480 \text{ μm/h (mol/liter)}^{-4.25} \)

<table>
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<tr>
<th>% KOH</th>
<th>Temperature (°C)</th>
</tr>
</thead>
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<tr>
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<td>20&quot; 30&quot; 40&quot; 50&quot; 60&quot; 70&quot; 80&quot; 90&quot; 100&quot;</td>
</tr>
<tr>
<td>15</td>
<td>1.49 3.2 6.7 13.3 25.2 46 82 149 233</td>
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<tr>
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<tr>
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<td>0.74 1.0 2.2 4.5 9.5 17 31 55 105</td>
</tr>
<tr>
<td>60</td>
<td>0.60 0.8 2.2 4.4 8.4 15 27 47 78</td>
</tr>
</tbody>
</table>

### Table A-II. <110> silicon etch rates in [μm/h] for various KOH concentrations and etch temperatures as calculated from Eq. [A-1] by setting \( E_o = 0.60 \text{ eV} \) and \( k_b = 4500 \text{ Å/h (mol/liter)}^{-4.25} \)

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<th>Temperature (°C)</th>
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</tr>
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<tr>
<td>60</td>
<td>0.8 1.6 3.4 6.7 14 25 47 78 122</td>
</tr>
</tbody>
</table>

### Table A-III. Calculated etch rates of thermally grown silicon dioxide in [nm/h] for various KOH concentrations and etch temperatures. Calculation was based on best numerical fit of experimental data. The activation energy was taken to be 0.85 eV

<table>
<thead>
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<th>Temperature (°C)</th>
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</tr>
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</tr>
<tr>
<td>60</td>
<td>0.06 0.1 0.3 0.4 0.4 0.4 0.4 0.5 0.5</td>
</tr>
</tbody>
</table>
Anisotropic Etching of Crystalline Silicon in Alkaline Solutions

II. Influence of Dopants

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ABSTRACT

The etching behavior of highly boron doped silicon in aqueous solutions based of ethylenediamine, KOH, NaOH, and LiOH was studied. For all etchants, a strong reduction of the etch rate for boron concentrations exceeding approximately $2 \cdot 10^{19} \text{ cm}^{-3}$ was observed. This value is in good agreement with published data for the onset of degeneracy of p-type silicon. The reduction of the etch rate was found to be inversely proportional to the fourth power of the boron concentration. For a given high boron concentration, the etch stop effect was found to be most effective for ethylenediamine-based solutions and low concentration KOH and least effective for highly concentrated KOH. On the basis of these results, a model is proposed attributing the etch stop phenomenon to electrical effects of holes rather than chemical effects of boron. Due to the high dopant concentration the width of the space charge layer on the silicon surface shrinks drastically. Therefore, electrons injected into the conduction band by an oxidation reaction cannot be confined to the surface and rapidly recombine with holes from the valence band. The lack of these electrons impedes the reduction of water and thereby the formation of new hydroxide ions at the silicon surface. Since the transfer of four electrons is required for the dissolution of one silicon atom the observed fourth power law for the decrease of the etch rate can be explained. The reduction of the etch rate on silicon doped with germanium or phosphorus is much smaller and follows a different mechanism.

All alkaline, anisotropic silicon etchants exhibit a strong reduction of their etch rate at high boron concentrations. This feature has been widely employed for the fabrication of silicon microstructures like membranes and cantilevers in a highly controllable manner. Important application areas for such elements include the realization of masks in a highly controllable manner. Important application areas for such elements include the realization of masks in a highly controllable manner. Important application areas for such elements include the realization of masks in a highly controllable manner. Important application areas for such elements include the realization of masks in a highly controllable manner.

The first observation of an etch stop phenomenon at p-type silicon for an ethylenediamine-based solution was published by Greenwood in 1969 (7). He assumed that for this effect the presence of a p-n junction was responsible. Two years later it was found by Bogh (8), that this etch stop occurs at a boron concentration of $C_B = 7 \cdot 10^{18} \text{ cm}^{-3}$ without any preferential etch effect at a p-n junction. Later it was shown that even at higher dopant concentration levels a finite, nonzero etch rate remains (9, 10). For KOH-based solutions, Price reported a significant reduction of the dissolution rate for boron concentrations above $5 \cdot 10^{18} \text{ cm}^{-3}$ (11). For this decrease he gave the following formula

$$R = 2.5 \cdot 10^{24} C_B^{-1.3}$$

[1]