**WET-CHEMICAL ETCHING OF SILICON AND SiO\(_2\)**

Silicon is the most common substrate material used in microelectronics and micro-mechanics. It is used not only as a passive substrate, but also as an active material in electronic or mechanical components. The necessary patterning can also be achieved by means of wet-chemical etching methods, as described in this chapter.

**Anisotropic Etching of Silicon**

**Etching Mechanism**

Strongly aqueous alkaline media such as KOH-, NaOH- or TMAH-solutions etch crystalline silicon via

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

Because the Si atoms of the different crystal planes have different activation energies for the etching reaction and the KOH etching of Si is not diffusion-limited but etching-rate-limited, the etching process takes place anisotropically: The \{100\} and \{110\} planes are much more rapidly etched than the stable \{111\} plane that act as etch stops.

**(111)-oriented Wafers**

(111)-oriented Si wafers are hardly attacked by alkaline solutions, since here the entire wafer surface forms an etch stop. Because the real orientation of wafers is usually tilted to a few 0.1° against the ideal crystal plane, with nominally (111)-oriented wafers, an etching attack in the form of very shallow steps also occurs.

**(100)-oriented Wafers**

(100)-orientated wafers in alkaline etchants form square-based pyramids with \{111\} surfaces. These pyramids can be realised on mono-crystalline silicon solar cells for the purpose of reflection minimisation.

**Etch Rates**

The anisotropy, the absolute etch rates and the homogeneity of the etching depend on both defects in
the silicon as well as contamination of the etching by metal ions and already etched Si ions in addition to etching temperature. Also the doping of Si plays an important role:

During etching, boron-doped Si forms borosilicate glass on the surface which acts as etch stop if the boron doping concentration exceeds \( (> 10^{19} \text{ cm}^{-3}) \).

Fig. 120 and Fig. 121 show the temperature and concentration-dependent etch rates of (100)- and (110) planes in KOH- and TMAH-solutions (Fig. 119), as well as the selectivity of the SiO\(_2\) etching (Fig. 120 and Fig. 121), which is often used as masking.

**Typical Etching Mixtures**

We supply 25% TMAH and 44% KOH in VLSI quality. Because these media only attack SiO\(_2\) to a very small extent, the (native) SiO\(_2\) film must be removed before the anisotropic Si etching in diluted or buffered hydrofluoric acid.

**Suitable Etching Masks**

The high pH values and temperatures required for the anisotropic etching of silicon attack even heavily cross-linked negative resists in a short time, so that photoresist masks do not come into question for this purpose. Instead, hard masks usually made of silicon nitride, SiO\(_2\) or alkaline-stable metal films such as chromium are used, which in turn can be structured using photoresist masks.
Isotropic Etching of Silicon with HF/HNO₃

Etching Mechanism

The basic etching mechanism in the isotropic etching of Si is divided into the oxidation of silicon using nitric acid and the etching of the oxide constantly formed on the surface from this with hydrofluoric acid:

1. Formation of NO₂ from nitric acid: \[ 4 \text{HNO}_3 \rightarrow 4 \text{NO}_2 + 2 \text{H}_2\text{O} + \text{O}_2 \]
2. Oxidation of silicon by NO₂: \[ 2 \text{NO}_2 + \text{Si} \rightarrow \text{SiO}_2 + 2 \text{NO} \]
3. Etching of SiO₂: \[ \text{SiO}_2 + 6 \text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2 \text{H}_2\text{O} \]

with the formula of the overall reaction:

\[ 4 \text{HNO}_3 + 2 \text{Si} + 12 \text{HF} \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O} + \text{O}_2 + 2 \text{H}_2\text{SiF}_6 \]

The resulting hexafluorosilicic acid (H₂SiF₆) is stable in aqueous solution.

Etching Rates of Silicon

Fig. 122 shows the rate of etching of crystalline silicon in different HF : HNO₃ mixtures at room temperature.

The etch rate drops towards zero when either the HF or HNO₃ concentration becomes very low, since in pure HF no SiO₂ forms which can be etched in HF, and HNO₃ only oxidises the Si without etching it.

An accurate control of the etching rate requires temperature accuracy within ±0.5°C. A dilution with acetic acid improves the wetting of the hydrophobic Si-surface and thus increases the spatial homogeneity of the etch rate.

Doped (n- and p-type) silicon exhibits a higher etching rate than undoped silicon.

Etch Selectivity of Si : SiO₂

As the etching triangle in Fig. 123 shows, high HF : HNO₃ ratios promote rate-limited etching (strong temperature dependency of the etch rate) of Si via the oxidation step.

Low HF : HNO₃ ratios promote diffusion-limited etching (lower temperature dependency of the etch rate). Pure HF does not attack silicon, pure HNO₃ only results in an oxidation of its surface.

The SiO₂ etch rate is determined by the HF-concentration, since the oxidation does not play a role.

Etching of SiO₂ with HF or BHF

Hydrofluoric Acid

Hydrofluoric acid (HF) is the only wet-chemical medium with which SiO₂ can be isotropically etched at a reasonable rate. Due to the high toxicity of concentrated HF, one has to consider the concentration that is really required for each individual application. 1 % HF is sufficient for re-
moving native SiO₂ in a so-called HF-Dip, and even 200 - 300 nm oxide can be etched in 10 % HF or buffered HF in a reasonable amount of time. We supply 1 %, 10 % and 50 % HF in VLSI-quality.

**Buffered Hydrofluoric Acid**
The etching of Si and SiO₂ consumes F-ions via the reaction SiO₂ + 4 HF → SiF₄ + 2 H₂O. HF buffered with ammonia fluoride (BHF = NH₄F + H₂O + HF):

- maintains the free F⁻ ion concentration via NH₄F + H₂O → H₃O⁺ + F⁻ + NH₃ allowing a constant and controllable etch rate as well as spatial homogeneous etching,
- an increase in the etch rate (factor 1.5 - 5.0) by highly reactive HF₂⁻ ions and
- an increase in the pH-value (→ minor resist underetching and resist lifting).

Despite the increased reactivity, strongly buffered hydrofluoric acid has a pH-value of close to 7 and therefore may not be detected by chemical indicators. We offer buffered HF (BOE 7: 1 = AF 87.5 - 12.5) in 2.5 L containers in VLSI quality optionally with or without surfactant for improved wetting and etching homogeneity.

**Etch Rates of SiO₂ in HF or BHF**
Compared to thermal oxide, deposited (e.g. CVD) SiO₂ has a higher etch rate due to its porosity; wet oxide a slightly higher etch rate than dry (thermal) oxide for the same reason, i.e. thermally via O₂ produced SiO₂. Phosphorus-doped SiO₂ etches faster than undoped SiO₂.

**Etching of Glasses**
Unlike SiO₂, glasses with various compositions show a strong dependency between their etch rate and additives in the etch. Such additives (e.g. HCl, HNO₃) dissolve surface films formed on the glass during etching, which are often chemically inert in HF and would stop or decelerate glass etching with pure HF. Therefore, such additives allow a continued etching at a constant and high rate. This allows one to increase the etch rate at a reduced HF-concentration (= increased stability against resist peeling).
### Our Photoresists: Application Areas and Compatibilities

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<th>Positive Applications</th>
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<th>Resist Film Thickness</th>
<th>Recommended Developers</th>
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<td>AZ® 1505</td>
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<td></td>
<td>AZ® 1512 HS</td>
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<td></td>
<td>AZ® 1514 H</td>
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<td></td>
<td>AZ® 1518</td>
<td>1.5 - 2.5 µm</td>
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<td>3 - 5 µm</td>
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<td>AZ® 4562</td>
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<td></td>
<td>AZ® P4330</td>
<td>3 - 5 µm</td>
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<td></td>
<td>AZ® P4620</td>
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<td>Dip coating</td>
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<td>AZ® PL 177</td>
<td>6 - 8 µm</td>
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<tr>
<td></td>
<td>AZ® 4999</td>
<td>1 - 15 µm</td>
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</table>

### Inorganic Developers (Typical demand under standard conditions approx. 20 L developer per L photoresist)

**AZ® Developer** is based on sodium phosphate and -metalsilicate, is optimized for minimal aluminum attack and is typically used diluted 1:1 in DI water for high contrast or unidiluted for high development rates. The dark erosion of this developer is slightly higher compared to other developers.

**AZ® 351B** is based on buffered NaOH and typically used diluted 1:4 with water, for thick resists up to 1:3 if a lower contrast can be tolerated.

**AZ® 400K** is based on buffered KOH and typically used diluted 1:4 with water, for thick resists up to 1:3 if a lower contrast can be tolerated.

**AZ® 303** specifically for the AZ® 111 XFS photoresist based on KOH / NaOH is typically used diluted 1:3 - 1:7 with water, depending on whether a high development rate, or a high contrast is required.

**Metal Ion Free Developers (TMAH-based) (Typical demand under standard conditions approx. 5 - 10 L developer concentrate per L photoresist)**

**AZ® 326 MIF** is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water.
Our frequently updated wafer stock list can be found here: [www.microchemicals.com/products/wafers/waferlist.html](http://www.microchemicals.com/products/wafers/waferlist.html)

Our Silicon-, Quartz-, Fused Silica and Glass Wafers

Specifications

Common parameters for all wafers are diameter, thickness and surface (1- or 2-side polished). Fused silica wafers consist of amorphous SiO₂, the so-called JGS2 wafers have a high transmission in the range of ≈ 280 - 2000 nm wavelength, the more expensive JGS1 wafers at ≈ 220 - 1100 nm.

Glass wafers, if not otherwise specified, are made of borosilicate glass.

Further Products from our Portfolio

Electroplating

Plating solutions for e.g. gold, copper, nickel, tin or palladium: [www.microchemicals.com/products/electroplating.html](http://www.microchemicals.com/products/electroplating.html)

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... [www.microchemicals.com/products/solvents.html](http://www.microchemicals.com/products/solvents.html)

Acids and Bases (MOS, VLSI, ULSI)

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, ... [www.microchemicals.com/products/etchants.html](http://www.microchemicals.com/products/etchants.html)

Etching Mixtures

for e.g. chromium, gold, silicon, copper, titanium, ... [www.microchemicals.com/products/etching_mixtures.html](http://www.microchemicals.com/products/etching_mixtures.html)
Further Information


Our Photolithography Book and -Posters

We see it as our main task to make you understand all aspects of microstructuring in an application-oriented way. At present, we have implemented this claim with our book Photolithography on over 200 pages, as well as attractively designed DIN A0 posters for your office or laboratory. We will gladly send both of these to you free of charge as our customer (if applicable, we charge shipping costs for non-European deliveries):

www.microchemicals.com/downloads/brochures.html
www.microchemicals.com/downloads/posters.html
Thank you for your interest!

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