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

$$Si + 2\,OH^- + 2\,H_2O \rightarrow Si(OH)_4 + H_2 \rightarrow SiO_2(OH)_2^{2-} + 2\,H_2$$

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.

(110)-oriented Wafers

(110)-orientated wafers in alkaline etchants form perpendicular trenches with {111} side-walls, used as e.g. micro-channels in micro-mechanics and micro-fluidics.

Etch Rates

The anisotropy, the absolute etch rates and the homogeneity of the etching depend on both defects in

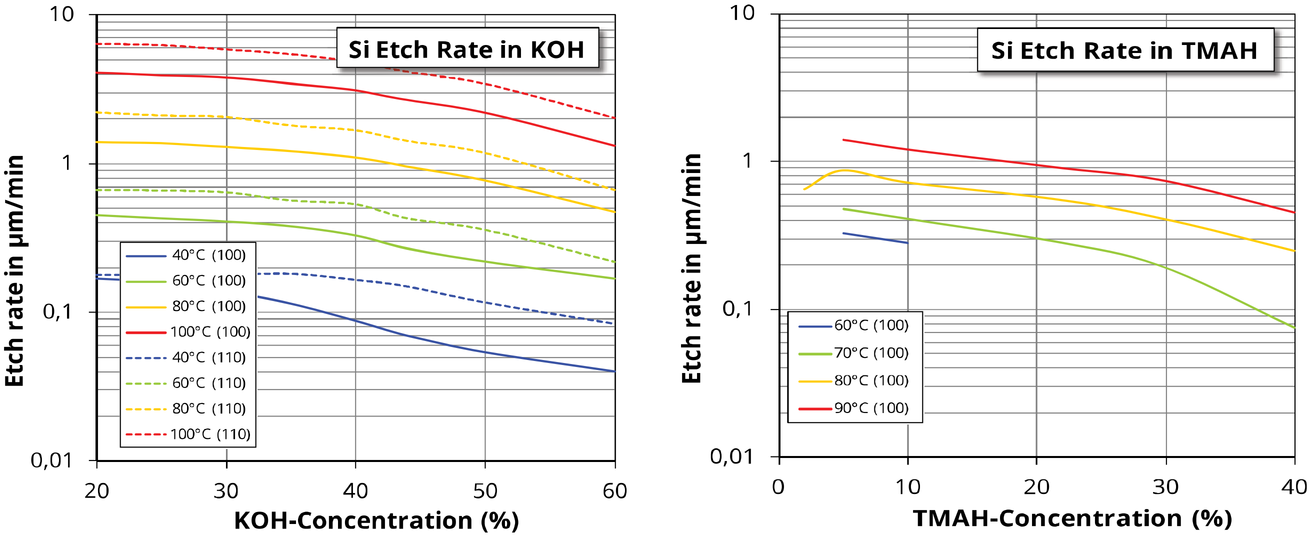


Fig. 119: The concentration and temperature-dependent etching rate of (100) and (110) planes of crystalline silicon in KOH (left graph) and TMAH (right graph). The alkaline etching of Si requires in addition to OH- ions, free water molecules. Therefore, the etching rate, but also the surface roughness of the etched silicon surface, decreases to stronger alkaline solutions.

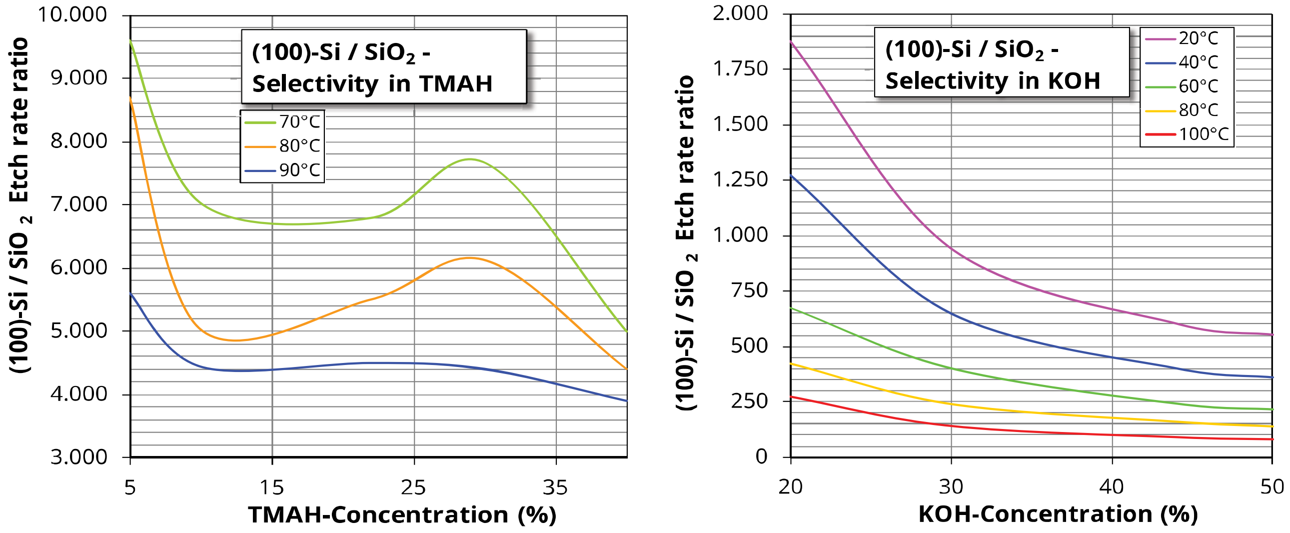


Fig. 120: The concentration and temperature-dependent selectivity of the etching rate of (100) - Si and SiO_2 in TMAH (left graph) and KOH (right graph). In TMAH, the etch rates of Si and SiO_2 have their maximum at different TMAH concentrations, which is why their ratio shows a local minimum.

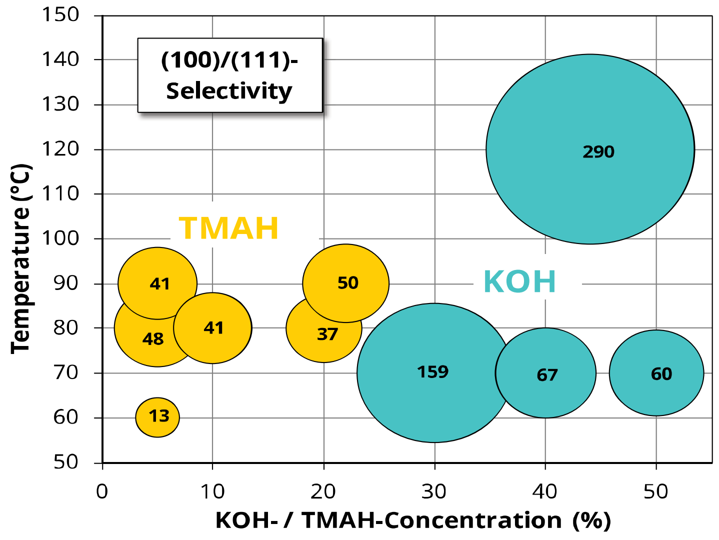


Fig. 121: The ratio of the etching rates of silicon in (100) to the (111) direction in TMAH- (orange circular areas) and KOH-solutions (blue-green) as a function of the respective concentration and temperature

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} 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/HNO_3

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 NO_2 from nitric acid: $4\ HNO_3 \rightarrow 4\ NO_2 + 2\ H_2O + O_2$
(2) Oxidation of silicon by NO_2: $2\ NO_2 + Si \rightarrow SiO_2 + 2\ NO$
(3) Etching of SiO_2: $SiO_2 + 6\ HF \rightarrow H_2SiF_6 + 2\ H_2O$

with the formula of the overall reaction:

$$4\ HNO_3 + 2\ Si + 12\ HF \rightarrow$$
$$4\ NO + 6\ H_2O + O_2 + 2\ H_2SiF_6$$

The resulting hexafluorosilicic acid (H_2SiF_6) is stable in aqueous solution.

Etching Rates of Silicon

Fig. 122 shows the rate of etching of crystalline silicon in different HF : HNO_3 mixtures at room temperature.

The etch rate drops towards zero when either the HF or HNO_3 concentration becomes very low, since in pure HF no SiO_2 forms which can be etched in HF, and HNO_3 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.

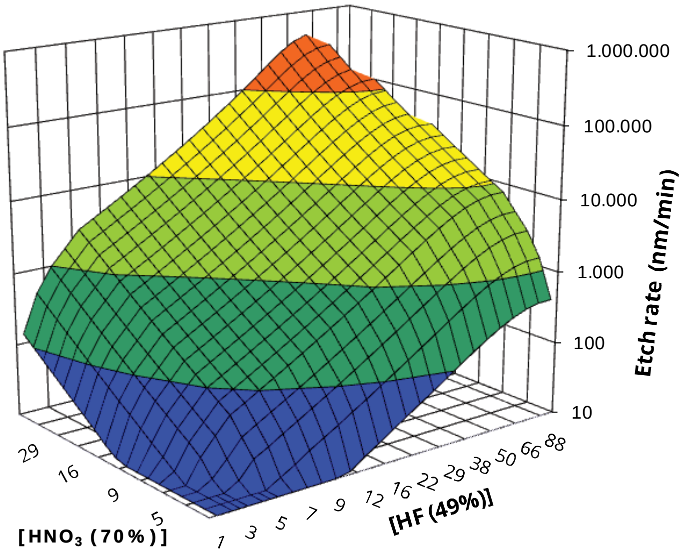


Fig. 122: The etching rate of silicon as a function of the HNO_3 and HF concentration of the etching mixture at room temperature.

Etch Selectivity of Si : SiO_2

As the etching triangle in Fig. 123 shows, high HF : HNO_3 ratios promote rate-limited etching (strong temperature dependency of the etch rate) of Si via the oxidation step.

Low HF : HNO_3 ratios promote diffusion-limited etching (lower temperature dependency of the etch rate). Pure HF does not attack silicon, pure HNO_3 only results in an oxidation of its surface.

The SiO_2 etch rate is determined by the HF-concentration, since the oxidation does not play a role.

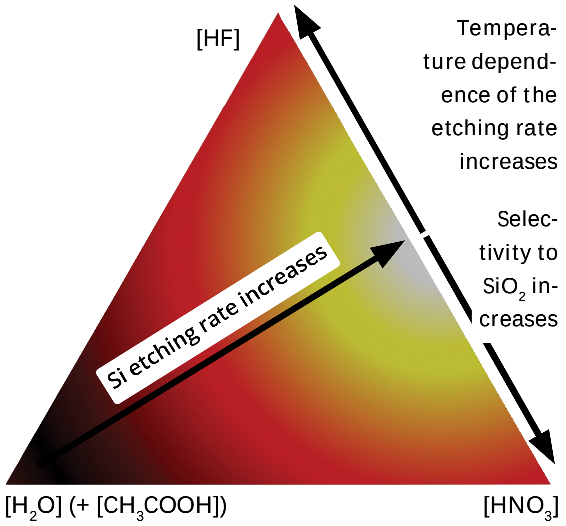


Fig. 123: The etching triangle for silicon shows the principal dependence of the etching rate on the composition of the etchant.

Etching of SiO_2 with HF or BHF

Hydrofluoric Acid

Hydrofluoric acid (HF) is the only wet-chemical medium with which SiO_2 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 removing native SiO_2 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 SiO_2 consumes F-ions via the reaction $SiO_2 + 4\ HF \rightarrow SiF_4 + 2\ H_2O$. HF buffered with ammonia fluoride ($BHF = NH_4F + H_2O + HF$) :

- maintains the free F^- ion concentration via $NH_4F + H_2O \rightarrow H_3O^+ + F^- + NH_3$ 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 HF_2^- 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 SiO_2 in HF or BHF

Compared to thermal oxide, deposited (e.g. CVD) SiO_2 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 O_2 produced SiO_2. Phosphorus-doped SiO_2 etches faster than undoped SiO_2

Etching of Glasses

Unlike SiO_2, glasses with various compositions show a strong dependency between their etch rate and additives in the etch. Such additives (e.g. HCl, HNO_3) 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

Recommended Applications[1]		Resist Family	Photoresists	Resist Film Thickness[2]	Recommended Developers[3]	Recommended Removers[4]
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls	AZ® 1500	AZ® 1505	≈ 0.5 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
			AZ® 1512 HS	≈ 1.0 - 1.5 µm		
			AZ® 1514 H	≈ 1.2 - 2.0 µm		
			AZ® 1518	≈ 1.5 - 2.5 µm		
		AZ® 4500	AZ® 4533	≈ 3 - 5 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
			AZ® 4562	≈ 5 - 10 µm		
		AZ® P4000	AZ® P4110	≈ 1 - 2 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
			AZ® P4330	≈ 3 - 5 µm		
			AZ® P4620	≈ 6 - 20 µm		
			AZ® P4903	≈ 10 - 30 µm		
		AZ® PL 177	AZ® PL 177	≈ 3 - 8 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Spray coating	AZ® 4999		≈ 1 - 15 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Dip coating	MC Dip Coating Resist		≈ 2 - 15 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® ECI 3000	AZ® ECI 3007	≈ 0.7 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
			AZ® ECI 3012	≈ 1.0 - 1.5 µm		
			AZ® ECI 3027	≈ 2 - 4 µm		
		AZ® 9200	AZ® 9245	≈ 3 - 6 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	
			AZ® 9260	≈ 5 - 20 µm		
	Elevated thermal softening point and high resolution for e. g. dry etching	AZ® 701 MiR	AZ® 701 MiR (14 cPs)	≈ 0.8 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
			AZ® 701 MiR (29 cPs)	≈ 2 - 3 µm		
Positive (chem. amplified)	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® XT	AZ® 12 XT-20PL-05	≈ 3 - 5 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
			AZ® 12 XT-20PL-10	≈ 6 - 10 µm		
			AZ® 12 XT-20PL-20	≈ 10 - 30 µm		
			AZ® 40 XT	≈ 15 - 50 µm		
		AZ® IPS 6050		≈ 20 - 100 µm		
Image Reversal	Elevated thermal softening point and undercut for lift-off applications	AZ® 5200	AZ® 5209	≈ 1 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF	TechniStrip® Micro D2 TechniStrip® P1316 TechniStrip® P1331
			AZ® 5214	≈ 1 - 2 µm		
		TI	TI 35ESX	≈ 3 - 4 µm		
			TI xLift-X	≈ 4 - 8 µm		
Negative (Cross-linking)	Negative resist sidewalls in combination with no thermal softening for lift-off application	AZ® nLOF 2000	AZ® nLOF 2020	≈ 1.5 - 3 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® NI555 TechniStrip® NF52 TechniStrip® MLO 07
			AZ® nLOF 2035	≈ 3 - 5 µm		
			AZ® nLOF 2070	≈ 6 - 15 µm		
		AZ® nLOF 5500	AZ® nLOF 5510	≈ 0.7 - 1.5 µm		
	Improved adhesion, steep resist sidewalls and high aspect ratios for e. g. dry etching or plating	AZ® nXT	AZ® 15 nXT (115 cPs)	≈ 2 - 3 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
			AZ® 15 nXT (450 cPs)	≈ 5 - 20 µm		
			AZ® 125 nXT	≈ 20 - 100 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® P1316 TechniStrip® P1331 TechniStrip® NF52 TechniStrip® MLO 07

Our Developers: Application Areas and Compatibilities

Inorganic Developers

(typical demand under standard conditions approx. 20 L developer per L photoresist)

AZ® Developer is based on sodium phosphate and –metasilicate, is optimized for minimal aluminum attack and is typically used diluted 1 : 1 in DI water for high contrast or undiluted 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 diluted 1 : 3 - 1 : 7 with water, depending on whether a high development rate, or a high contrast is required

Metal Ion Free (TMAH-based) Developers

(typical demand under standard conditions approx. 5 - 10 L developer concentrate per L photoresist)

AZ® 326 MIF is 2.38 % TMAH- (<u>T</u>etra<u>M</u>ethyl<u>A</u>mmonium<u>H</u>ydroxide) in water.

---

[1] In general, almost all resists can be used for almost any application. However, the special properties of each resist family makes them specially suited for certain fields of application.

[2] Resist film thickness achievable and processable with standard equipment under standard conditions. Some resists can be diluted for lower film thicknesses; with additional effort also thicker resist films can be achieved and processed.

[3] Metal ion free (MIF) developers are significantly more expensive, and reasonable if metal ion free development is required.

AZ® 726 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development)

AZ® 826 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development) and other additives for the removal of poorly soluble resist components (residues with specific resist families), however at the expense of a slightly higher dark erosion.

Our Removers: Application Areas and Compatibilities

AZ® 100 Remover is an amine solvent mixture and standard remover for AZ® and TI photoresists. To improve its performance, AZ® 100 remover can be heated to 60 - 80°C. Because the AZ® 100 Remover reacts highly alkaline with water, it is suitable for this with respect to sensitive substrate materials such as Cu, Al or ITO only if contamination with water can be ruled out..

TechniStrip® P1316 is a remover with very strong stripping power for Novolak-based resists (including all AZ® positive resists), epoxy-based coatings, polyimides and dry films. At typical application temperatures around 75°C, TechniStrip® P1316 may dissolve cross-linked resists without residue also, e.g. through dry etching or ion implantation. TechniStrip® P1316 can also be used in spraying processes. For alkaline sensitive materials, TechniStrip® P1331 would be an alternative to the P1316. Nicht kompatibel mit Au oder GaAs.

TechniStrip® P1331 can be an alternative for TechniStrip® P1316 in case of alkaline sensitive materials. TechniStrip® P1331 is not compatible with Au or GaAs.

TechniStrip® NI555 is a stripper with very strong dissolving power for Novolak-based negative resists such as the AZ® 15 nXT and AZ® nLOF 2000 series and very thick positive resists such as the AZ® 40 XT. TechniStrip® NI555 was developed not only to peel cross-linked resists, but also to dissolve them without residues. This prevents contamination of the basin and filter by resist particles and skins, as can occur with standard strippers. TechniStrip ® NI555 is not compatible with GaAs.

TechniClean™ CA25 is a semi-aqueous proprietary blend formulated to address post etch residue (PER) removal for all interconnect and technology nodes. Extremely efficient at quickly and selectively removing organo-metal oxides from Al, Cu, Ti, TiN, W and Ni.

TechniStrip™ NF52 is a highly effective remover for negative resists (liquid resists as well as dry films). The intrinsic nature of the additives and solvent make the blend totally compatible with metals used throughout the BEOL interconnects to WLP bumping applications.

TechniStrip™ Micro D2 is a versatile stripper dedicated to address resin lift-off and dissolution on negative and positive tone resist. The organic mixture blend has the particularity to offer high metal and material compatibility allowing to be used on all stacks and particularly on fragile III/V substrates for instance.

TechniStrip™ MLO 07 is a highly efficient positive and negative tone photoresist remover used for IR, III/V, MEMS, Photonic, TSV mask, solder bumping and hard disk stripping applications. Developed to address high dissolution performance and high material compatibility on Cu, Al, Sn/Ag, Alumina and common organic substrates.

Our Wafers and their Specifications

Silicon-, Quartz-, Fused Silica and Glass Wafers

Silicon wafers are either produced via the Czochralski- (CZ-) or Float zone- (FZ-) method. The more expensive FZ wafers are primarily reasonable if very high-ohmic wafers (> 100 Ohm cm) are required.

Quartz wafers are made of monocrystalline SiO_2, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO_2. 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.

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

Specifications

Common parameters for all wafers are diameter, thickness and surface (1- or 2-side polished). Fused silica wafers are made either of JGS1 or JGS2 material, for quartz wafers the crystal orientation needs to be defined. For silicon wafers, beside the crystal orientation (<100> or <111>) the doping (n- or p-type) as well as the resistivity (Ohm cm) are selection criteria.

Prime- ,Test-, and Dummy Wafers

Silicon wafers usually come as „Prime-grade“ or „Test-grade“, latter mainly have a slightly broader particle specification. „Dummy-Wafers“ neither fulfill Prime- nor Test-grade for different possible reasons (e. g. very broad or missing specification of one or several parameters, reclaim wafers, no particle specification) but might be a cheap alternative for e. g. resist coating tests or equipment start-up.

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

Our frequently updated wafer stock list can be found here: è www.microchemicals.com/products/wafers/waferlist.html

Further Products from our Portfolio

Plating

Plating solutions for e. g. gold, copper, nickel, tin or palladium: è www.microchemicals.com/products/electroplating.html

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... è www.microchemicals.com/products/solvents.html

Acids and Bases (MOS, VLSI, ULSI)

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, … è www.microchemicals.com/products/etchants.html

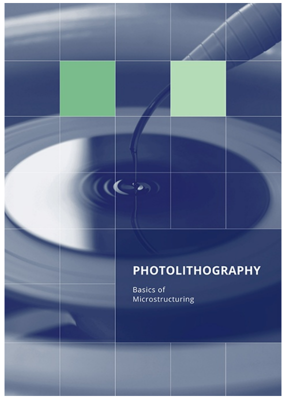
Etching Mixtures

for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

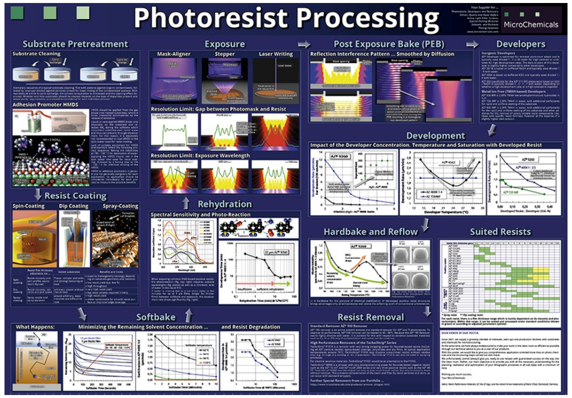
Further Information

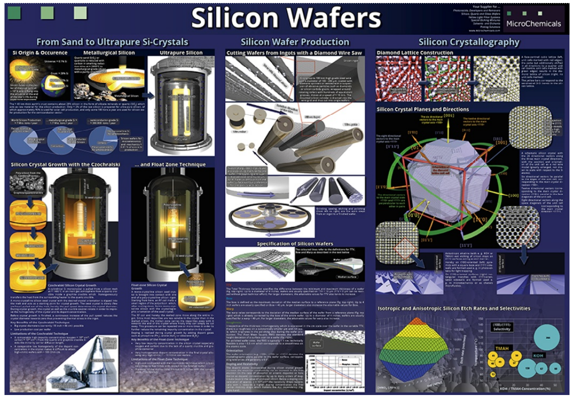
Technical Data Sheets:	www.microchemicals.com/downloads/product_data_sheets/photoresists.html
Material Safety Data Sheets (MSDS):	www.microchemicals.com/downloads/safety_data_sheets/msds_links.html

Our Photolithography Book and -Posters


PHOTOLITHOGRAPHY

Basics of Microstructuring


Photoresist Processing


Silicon Wafers

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!

Disclaimer of Warranty & Trademarks

All information, process descriptions, recipes, etc. contained in this document are compiled to the best of our knowledge. Nevertheless, we can not guarantee the correctness of the information. Particularly with regard to the formulations for chemical (etching) processes we assume no guarantee for the correct specification of the components, the mixing conditions, the preparation of the batches and their application.

The safe sequence of mixing components of a recipe usually does not correspond to the order of their listing. We do not warrant the full disclosure of any indications (among other things, health, work safety) of the risks associated with the preparation and use of the recipes and processes. The information in this book is based on our current knowledge and experience. Due to the abundance of possible influences in the processing and application of our products, they do not exempt the user from their own tests and trials. A guarantee of certain properties or suitability for a specific application can not be derived from our data. As a matter of principle, each employee is required to provide sufficient information in advance in the appropriate cases in order to prevent damage to persons and equipment. All descriptions, illustrations, data, conditions, weights, etc. can be changed without prior notice and do not constitute a contractually agreed product characteristics. The user of our products is responsible for any proprietary rights and existing laws.

Merck, Merck Performance Materials, AZ, the AZ logo, and the vibrant M are trademarks of Merck KGaA, Darmstadt, Germany