Wet-Chemical Etching of Silicon

MicroChemicals

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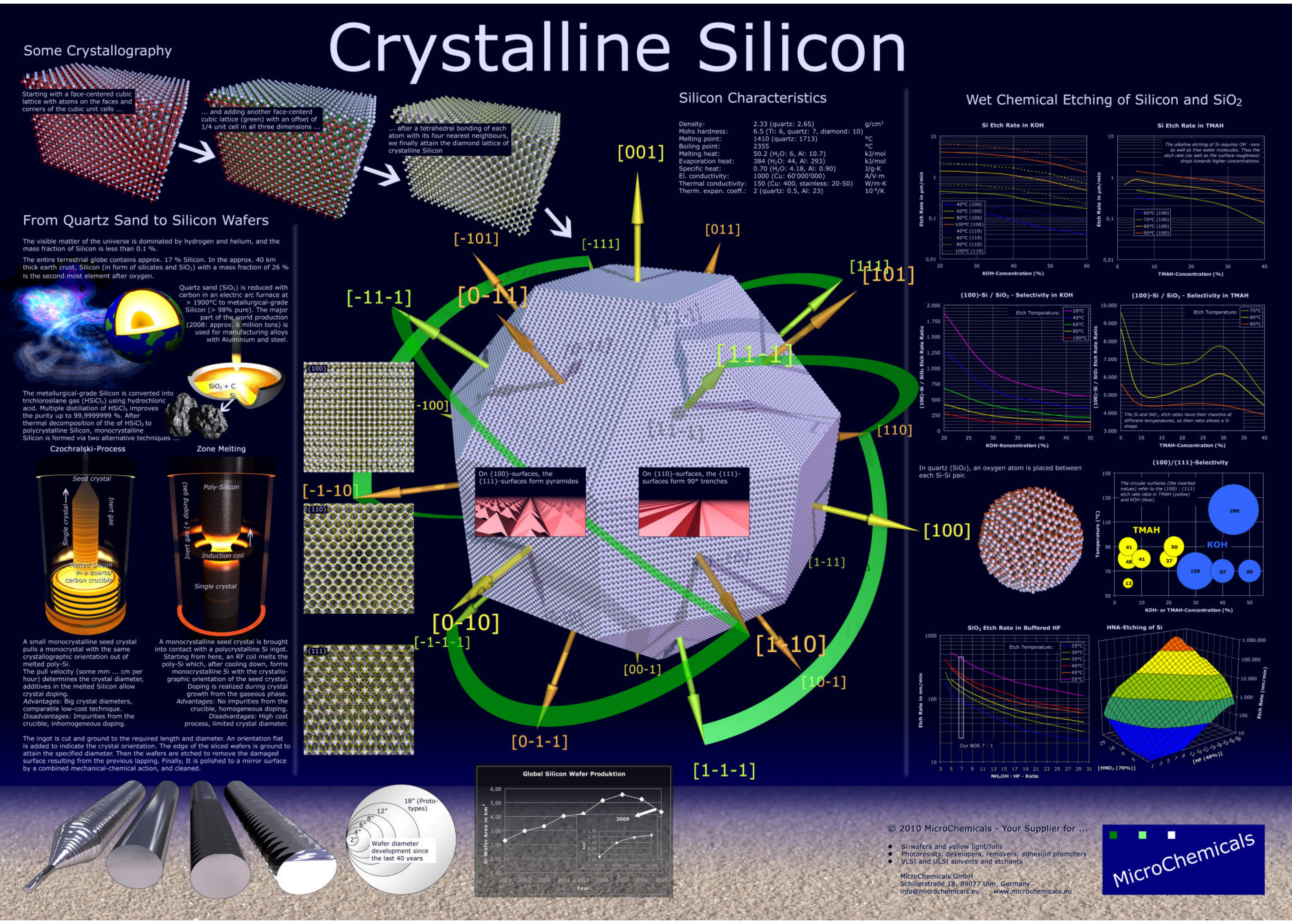
Our Poster „Crystalline Silicon"

Crystallography, etch rates of Si (isotropic and anisotropic) and SiO_2, Si-wafer production, summarized on a DIN A0 Poster ... Interested? Gladly we send you one or more posters for free (only valid for Europe)! Just send us a short e-mail: info@microchemicals.de



Crystalline Silicon

Some Crystallography

Starting with a face-centered cubic lattice with atoms on the faces and corners of the cubic unit cells ...

... and adding another face-centerd cubic lattice (green) with an offset of 1/4 unit cell in all three dimensions ...

... after a tetrahedral bonding of each atom with its four nearest neighbours, we finally attain the diamond lattice of crystalline Silicon

From Quartz Sand to Silicon Wafers

The visible matter of the universe is dominated by hydrogen and helium, and the mass fraction of Silicon is less than 0.1 %.

The entire terrestrial globe contains approx. 17 % Silicon. In the approx. 40 km thick earth crust, Silicon (in form of silicates and SiO_2) with a mass fraction of 26 % is the second most element after oxygen.

Quartz sand (SiO_2) is reduced with carbon in an electric arc furnace at > 1900°C to metallurgical-grade Silicon (> 98% pure). The major part of the world production (2008: approx. 6 million tons) is used for manufacturing alloys with Aluminium and steel.

The metallurgical-grade Silicon is converted into trichlorosilane gas ($HSiCl_3$) using hydrochloric acid. Multiple distillation of $HSiCl_3$ improves the purity up to 99,9999999 %. After thermal decomposition of the of $HSiCl_3$ to polycrystalline Silicon, monocrystalline Silicon is formed via two alternative techniques ...

Czochralski-Process

A small monocrystalline seed crystal pulls a monocrystal with the same crystallographic orientation out of melted poly-Si.
The pull velocity (some mm ... cm per hour) determines the crystal diameter, additives in the melted Silicon allow crystal doping.
Advantages: Big crystal diameters, comparable low-cost technique.
Disadvantages: Impurities from the crucible, inhomogeneous doping.

Zone Melting

A monocrystalline seed crystal is brought into contact with a polycrystalline Si ingot. Starting from here, an RF coil melts the poly-Si which, after cooling down, forms monocrystalline Si with the crystallographic orientation of the seed crystal. Doping is realized during crystal growth from the gaseous phase.
Advantages: No impurities from the crucible, homogeneous doping.
Disadvantages: High cost process, limited crystal diameter.

The ingot is cut and ground to the required length and diameter. An orientation flat is added to indicate the crystal orientation. The edge of the sliced wafers is ground to attain the specified diameter. Then the wafers are etched to remove the damaged surface resulting from the previous lapping. Finally, It is polished to a mirror surface by a combined mechanical-chemical action, and cleaned.

Silicon Characteristics

Density:	2.33 (quartz: 2.65)	g/cm³
Mohs hardness:	6.5 (Ti: 6, quartz: 7, diamond: 10)	
Melting point:	1410 (quartz: 1713)	°C
Boiling point:	2355	°C
Melting heat:	50.2 (H_2O: 6, Al: 10.7)	kJ/mol
Evaporation heat:	384 (H_2O: 44, Al: 293)	kJ/mol
Specific heat:	0.70 (H_2O: 4.18, Al: 0.90)	J/g·K
El. conductivity:	1000 (Cu: 60'000'000)	A/V·m
Thermal conductivity:	150 (Cu: 400, stainless: 20-50)	W/m·K
Therm. expan. coeff.:	2 (quartz: 0.5, Al: 23)	10^{-6}/K

On {100}-surfaces, the {111}-surfaces form pyramides

On {110}-surfaces, the {111}-surfaces form 90° trenches

Wet Chemical Etching of Silicon and SiO_2

The alkaline etching of Si requires OH^--ions as well as free water molecules. Thus the etch rate (as well as the surface roughness) drops towards higher concentrations.

The Si and SiO_2 etch rates have their maxima at different temperatures, so their ratio shows a S-shape.

In quartz (SiO_2), an oxygen atom is placed between each Si-Si pair.

The circular surfaces (the inserted values) refer to the (100) : (111) etch rate ratio in TMAH (yellow) and KOH (blue).

Wafer diameter development since the last 40 years

Our Si Wafer Stock List: Si-Wafers.

Since 2010, we supply our customers - beside photoresists, solvents, and etchants - also with c-Si wafers (2 - 8 inch, one- and double-side polished, optionally with SiO_2 and Ni_3N_4). Therefore, we are happy to provide you with technical support also in this field of microstructuring.

Thank you for your interest!

Anisotropic Silicon Etching

Strong alkaline substances (pH > 12) such as aqueous KOH- or TMAH-solutions etch Si via

$$Si + 4\,OH^- \rightarrow Si(OH)_4 + 4e^-.$$

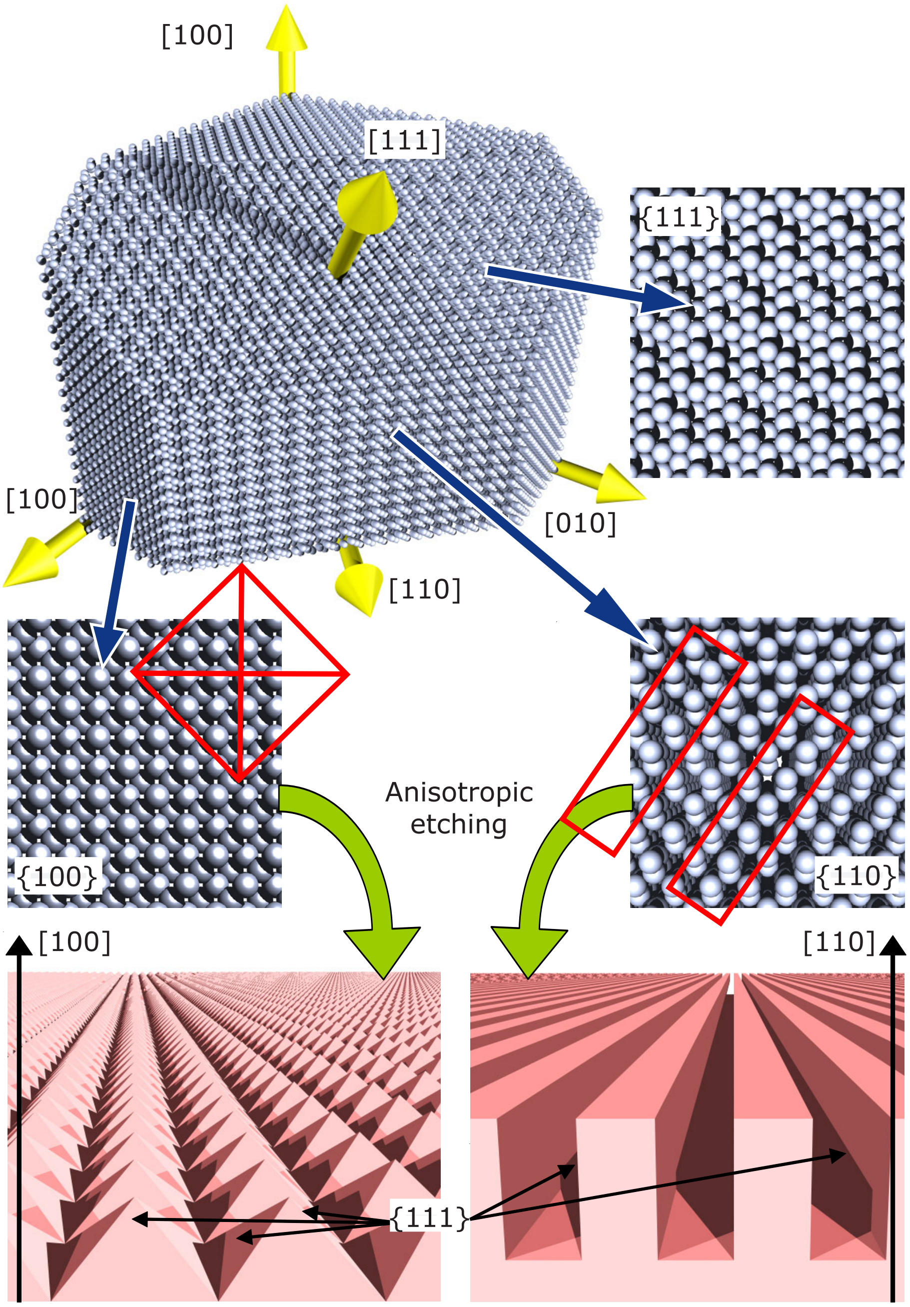
Since the bonding energy of Si atoms is different for each crystal plane, and KOH/TMAH Si etching is not diffusion- but etch rate limited, Si etching is highly anisotropic: While the {100}- and {110}-crystal planes are being etched, the stable {111} planes act as an etch stop:

(111)-orientated Si-wafers are almost not attacked by the etch.

(100)-orientated wafers form square-based pyramids with {111} surfaces. These pyramids are realised on c-Si solar cells for the purpose of reflection minimization.

(110)-orientated wafers form perpendicular trenches with {111} side-walls, used as e. g. microchannels in micromechanics and microfluidics.

The degree of anisotropy (= etch rate selectivity between different crystal planes), the etch rates, and the etching homogeneity depend on the etching temperature, atomic defects in the silicon crystal, intrinsic impurities of the Si crystal, impurities (metal ions) by the etchant, and the concentration of Si-atoms already etched.



The doping concentration of the Si to be etched also strongly impacts on the etching: 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}.

The following table lists etch rates of Si and the hard masks Si_xN_y and SiO_2, and etch selectivity between different crystal planes as a function of the etchant.

Isotropic Etching of Silicon and SiO$_2$

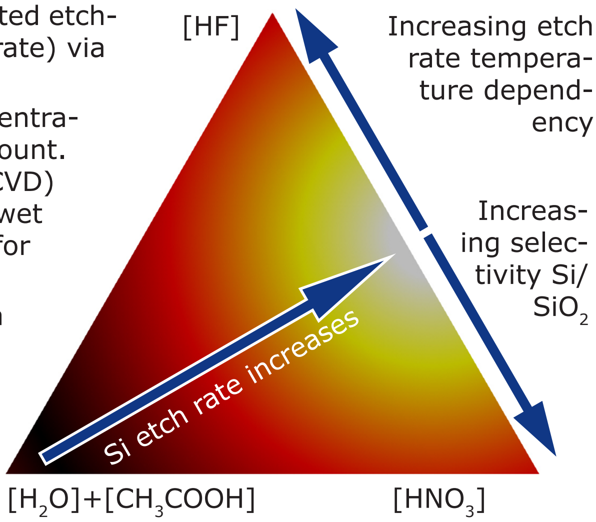
Etchant	Etch rate ratio		Etch rate (absolute)			Advantages (+) Disadvantages (-)
	(100)/(111)	(110)/(111)	(100)	Si$_3$N$_4$	SiO$_2$	
KOH (44%, 85°C)	**300**	**600**	1.4 µm/min	<1 Å/min	14 Å/min	(-) Metal ion containing (+) Strongly anisotropic
TMAH (25%, 80°C)	**37**	**68**	0.3-1 µm/min	<1 Å/min	2 Å/min	(-) Weak anisotropy (+) Metal ion free
EDP (115°C)	**20**	**10**	1.25 µm/min	1 Å/min	2 Å/min	(-) Weak anisotropy , toxic (+) Metal ion free, metallic hard masks possible

The following chemical reactions summarize the basic etch mechanism for isotropic silicon etching (steps 1-4), and SiO$_2$ (only step 4) using a HF/HNO$_3$ etching mixture:

(1) NO$_2$ formation (HNO$_2$ always in traces in HNO$_3$): $HNO_2 + HNO_3 \rightarrow 2\,NO_2 + H_2O$
(2) Oxidation of silicon by NO$_2$: $2\,NO_2 + Si \rightarrow Si^{2+} + 2\,NO_2^-$
(3) Formation of SiO$_2$: $Si^{2+} + 2\,(OH)^- \rightarrow SiO_2 + H_2$
(4) Etching of SiO$_2$: $SiO_2 + 6\,HF \rightarrow H_2SiF_6 + 2H_2O$

In conclusion, HNO$_3$ oxidises Si, and HF etches the SiO$_2$ hereby formed.

Fig. right-hand: High HF : HNO$_3$ ratios promote rate-limited etching (strong temperature dependency of the etch rate) of Si via the oxidation (1) - (3), while low HF : HNO$_3$ ratios promote diffusion-limited etching (lower temperature dependency of the etch rate) via step (4). HNO$_3$-free HF etches do not attack Si.



The SiO$_2$ etch rate is determined by the HF-concentration, since the oxidation (1) - (3) does not account. 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 oxide for the same reason.

An accurate control of the etch rate requires a temperature control within ± 0.5°C. Dilution with acidic acid improves wetting of the hydrophobic Si-surface and thus increases and homogenizes the etch rate.

Doped (n- and p-type) silicon as well as phosphorus-doped SiO$_2$ etches faster than undoped Si or SiO$_2$.

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We assume no liability for any hazard for staff and equipment which might stem from the information given in this brochure.

Generally speaking, it is in the responsibility of every staff member to inform herself/himself about the processes to be performed in the appropriate (technical) literature, in order to minimize any risk to man or machine.