

# Wet chemical Etching ...

... chemical and physical Mechanisms

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MicroChemicals

This document aims for an understanding of the chemical and physical mechanism of wet etching, and hereby focuses on typical etching mixtures for metals, glasses and semiconductors.

## n Etching and Solving

While *solving* describes the overcoming of intermolecular interactions between two solids or liquids, *etching* breaks intramolecular/-atomar bonds of a solid. This document aims for an understanding how the chemical and physical properties of solvents can be explained, and which etchant is suited for your individual purpose.

## n Acids and Bases: Some Physics and Chemistry

### Acids and bases: Oxidation und Reduction

At room temperature, pure water contains approx.  $10^{-7}$  mol  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions per litre via the autoprotolysis  $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ , corresponding to a (neutral) pH-value of 7 due to the equation

$$pH = -\log_{10} [\text{H}_3\text{O}^+]$$

Due to the thermal activated autoprotolysis, the pH-value of 100°C DI- $\text{H}_2\text{O}$ , drops to approx. 6 since the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  concentrations both increase. The following table lists the pH-value of some common acids and bases:

substance	HCl (20%)	gastric juice	vinegar	$\text{H}_2\text{O}$	soap sud	KOH (1.4%)	KOH (50%)
pH-value	-1	1-3	3	7	8-12	13	14.5

Acids are proton donators and increase the  $\text{H}_3\text{O}^+$ -ion concentration in aqueous solutions via the release of protons (e.g. hydrochloric acid:  $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$ ) hereby decreasing the pH-value. The  $pK_s$ -value defines the strength (= degree of dissociation) of an acid as aqueous solution as follows:

$$pK_s = -\log_{10} \left( \frac{[\text{H}_3\text{O}^+] \cdot [\text{dissociated acid}^-]}{[\text{undissociated acid}]} \right)$$

Very strong acids such as  $\text{HClO}_4$ ,  $\text{HI}$ ,  $\text{HCl}$ , or  $\text{H}_2\text{SO}_4$  are almost completely dissociated in aqueous solutions. The following table lists the  $pK_s$ -value some acids at room temperature:

substance	Strong acids				weak acids		
	$\text{HNO}_3$	$\text{H}_3\text{PO}_4$	$\text{HSO}_4^-$	$\text{HF}$	$\text{HNO}_2$	$\text{CH}_3\text{COOH}$	$\text{H}_2\text{CO}_3$
$pK_s$ -value	-1.32	2.13	1.92	3.14	3.35	4.75	6.52

The strong trend of  $\text{H}_3\text{O}^+$  to release a proton accompanied by the assimilation of an electron explains the oxidative characteristics of acids.

Bases as proton acceptors increase the  $\text{OH}^-$ -ion concentration in aqueous solutions. Due to the law of mass action, at given temperature and pressure, the product  $[\text{H}_3\text{O}^+] \cdot [\text{OH}^-]$  always keeps constant. Therefore, with  $[\text{OH}^-]$  increasing, the  $\text{H}_3\text{O}^+$ -concentrationen drops thus increasing the pH-value. Corresponding to acids, the strength of a base as aqueous solution can be defined as follows:

$$pK_b = -\log_{10} \left( \frac{[\text{OH}^-] \cdot [\text{dissociated base}^+]}{[\text{undissociated base}]} \right)$$

The following table lists the  $pK_b$ -values of some bases at room temperature:

substance	Strong bases				weak bases		
	$\text{NaOH}$	$\text{KOH}$	$\text{S}^{2-}$	$\text{PO}_4^{3-}$	$\text{NH}_3$	$\text{HS}^-$	$\text{F}^-$
$pK_b$ -value	0.2	0.5	1.0	1.67	4.75	7.08	10.86

The strong trend of  $\text{OH}^-$  ions to release an electron explains the reductive characteristics of bases.

Chemical buffers are substances keeping the pH-value of an aqueous solution at a fixed value almost constant, despite the addition or consumption of  $\text{H}_3\text{O}^+$ - or  $\text{OH}^-$  ion (e.g. by their consumption during wet etching). This characteristics of chemicals buffers bases on their ability to bind  $\text{H}_3\text{O}^+$ - as well as  $\text{OH}^-$ -ions (or, respectively, neutralize them by releasing their conjugated acid/base), if the  $\text{H}_3\text{O}^+$ - or  $\text{OH}^-$ -ion concentration drops, and release  $\text{H}_3\text{O}^+$ - as well as  $\text{OH}^-$ -ions if their concentration drops.

Chemical buffer solutions generally are weak (= only partially dissociated) acids/bases, and their conjugated bases/ acids.

Positive Resists  
Thinner

Negative Resists  
Solvents

Image Reversal Resists  
Etching Solutions

Developers  
Process Chemicals

## Complex Formation

In order to suppress the reassembly of atoms already etched back into the solid to be etched, special **complexing agents** can be added to the etching solution. In a complex, a central atom (in most cases the etched metal) with unoccupied orbitals is surrounded by one or several ligands (atoms or molecules) offering electron duplets forming the bond between the central metal atom and the ligand. An example for complex formation is the generation of tetrachloroaurate during gold etching with aqua regia.

## Solving, Diffusion, and Convection

In order to prevent the etched material to reabsorb onto the surface of the medium to be etched, the etching solution has to be able to **sufficiently dissolve** the etched material. Our document **solvents** (available on request) focuses on this topic more detailed.

Fast and homogeneous etching requires a fast evacuation of the etched media as well as a sufficiently high replenishment with the etching solution. For this reason, two transport mechanisms have to be considered:

**Diffusion:** At room temperature, atoms have (thermal) velocities of several 100 m/s. Due to the low average free length of path in liquids, the movement of atoms results in an undirected dithering which only very slowly smoothens concentration gradients.

**Convection:** Gas formation during etching, heat evaluation by exothermic etching reactions, or mechanical agitation induces large-scale convection in the etching solution. Since diffusion alone is not sufficient, mainly this form of material transport contributes to a fast and spatiotemporal homogeneous etching.

## n Etching of Base Metals und noble Metals

### Energy, Entropy, and Enthalpy

Etching of metals can be described as the oxidation of the metal via protons donated by the  $\text{H}_3\text{O}^+$  hereby reduced to hydrogen as follows:



Concerning **base metals**, this reaction is always **exothermic**: Since base metals have a standard potential  $E^0 < 0$  which is smaller than the standard potential of hydrogen (arbitrarily set to zero), energy is released ( $\Delta U < 0$ ) when  $\text{H}^+$  ionizes the metal atom.

Oxidizing **noble metals** with  $\text{H}^+$ , however, requires energy (endothermic reaction,  $\Delta U > 0$ ). The reason why noble metals with  $E^0 > 0$  (e.g.  $E^0_{\text{copper}} = +0.34$ ) can be etched despite a required increase in the intrinsic energy is as follows: At fixed side conditions, each system tries to minimize its free enthalpy  $F = U - T \cdot S$  ( $T$  = temperature,  $S$  = entropy). Therefore, a reaction such as etching spontaneously only takes place if the change in the free enthalpy is negative ( $\Delta F = \Delta U - T \cdot \Delta S < 0$ ), which corresponds to the condition  $T \cdot \Delta S > \Delta U$ . Therefore, the nobler the metal (the higher the required energy  $\Delta U$  for etching), the higher the temperature and/or gain in entropy (e.g. by an increase of spatial degrees of freedom when changing from the solid into the liquid or gaseous state) has to be.

### Valence Electron Configuration and the Standard Potential

Both, the very reactive alkali metals (e.g. Li, K, Na) as well as many inert noble metals (such as Au, Ag, and Pt) have an s-Orbital with a single (unpaired) electron. While alkali metals very easily release this electron ( $\rightarrow$  oxidation), noble metals reveal a rather high first ionization energy ( $\rightarrow$  high positive standard potential).

The reason for this behaviour is as follows: Noble metals such as Au, Ag, or Pt with a **single electron** in the s-orbital with the quantum number  $n$  ('shell') appear to have an **completely occupied** d-orbital with the quantum number  $n-1$  (e.g. electron configuration of Gold:  $[\text{Xe}]4\text{f}^{14}5\text{d}^{10}6\text{s}^1$ ). This occupied d-orbital partially protrudes beyond the s-orbital and hereby spatially shields it against reactants. Additionally, from the point of view of the s-electron, the nuclear charge is only partially shielded from the extended d-orbital thus further increasing the bonding energy of the s-electron.

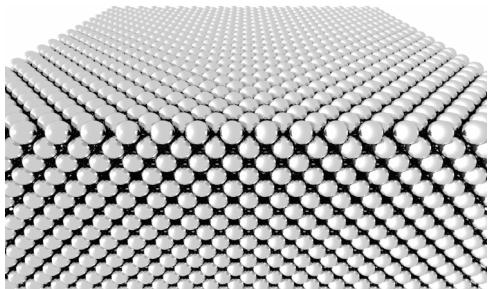
Some noble metals do not have an unpaired valence electron. Either the outer s-orbital is unoccupied (Palladium), or completely occupied with electron duplet (Iridium), both further increasing the first ionization energy and hereby the chemical stability. As a consequence, the only way to etch Iridium is hot (approx. 100°C) aqua regia.

## n Aluminium Etching

Typical Al-etchants contain mixtures of 1-5%  $\text{HNO}_3^*$  (for Al oxidation), 65-75%  $\text{H}_3\text{PO}_4^*$  (to dissolve the Al-oxide), 5-10%  $\text{CH}_3\text{COOH}^*$  (for wetting) and  $\text{H}_2\text{O}$  dilution to define the etch rate at given temperature.

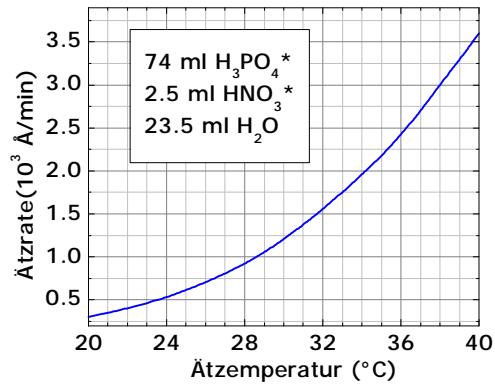
Al etching is highly exothermic, an (inevitable, since isotropic etching) underetching of the resist mask causes local heating (increased etch rate) and super-proportional under etching of the mask as a consequence, if no agitation is performed.

Positive Resists Thinner	Negative Resists Solvents	Image Reversal Resists Etching Solutions	Developers Process Chemicals
MicroChemicals GmbH	<a href="http://www.microchemicals.com">www.microchemicals.com</a>	<a href="mailto:tech@microchemicals.com">tech@microchemicals.com</a>	p. 2



Strong H<sub>2</sub>-bubbling reduces etch **homogeneity**. Generally, etching starts after the dissolution (by H<sub>3</sub>PO<sub>4</sub>) of few nm Al-oxide film present on each Al surface.

For this reason, the photo resist processing impacts on the Al etching: The alkaline developers preferentially dissolve the Al-oxide (at regions with lower resist film thickness, near the edges of cleared structures, or below cleared structures with larger features). Dependant on the extent of (desired or undesired) over-developing as well as delay between development and Al-etching, the process parameters may lead to a spatial inhomogeneous Al etching start.

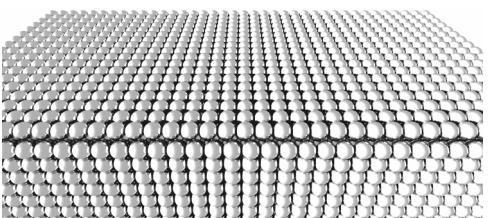


HNO<sub>3</sub>\* = 70% HNO<sub>3</sub> in H<sub>2</sub>O

H<sub>3</sub>PO<sub>4</sub>\* = 85% H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O

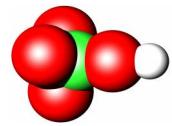
CH<sub>3</sub>COOH\* = 99% CH<sub>3</sub>COOH in H<sub>2</sub>O

## n Chromium Etching

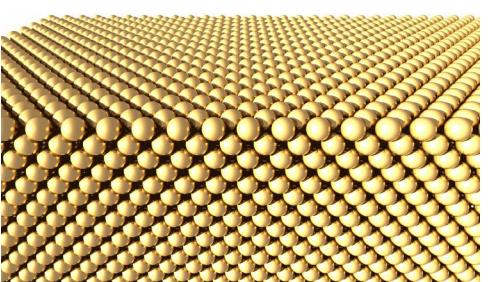


Chromium etchants typically are mixtures of perchloric acid (HClO<sub>4</sub>, structure of the undissociated molecule right-hand), and ceric ammonium nitrate (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>].

Perchloric acid is a very strong acid and therefore almost completely dissociated in aqueous solutions (pK<sub>s</sub> < -8), ammonium nitrate a very strong oxidizer.



## n Gold Etching



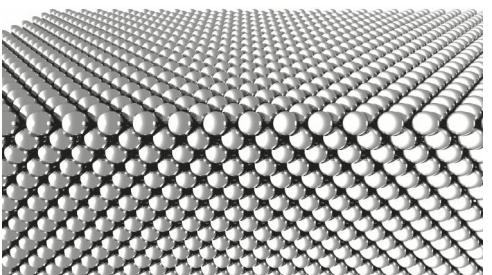
Gold etchants often are mixtures of **nitric acid** and **hydrochloric acid** (in the mixing ratio of 1:3 also called **aqua regia**). The very strong oxidative effect of this mixture stems from the formation of **nitrosyl chloride** (NOCl) via



while free Cl radicals formed in the solution keep the noble metal solved as a Cl-complex thus allowing etch rates of some 10 µm/minute.

Alternatively to aqua regia, an aqueous KI/I<sub>2</sub> solution (KI:I<sub>2</sub>:H<sub>2</sub>O = 4:1:40) reveals an etch rate of approx. 1 µm/minute.

## n Silver Etching



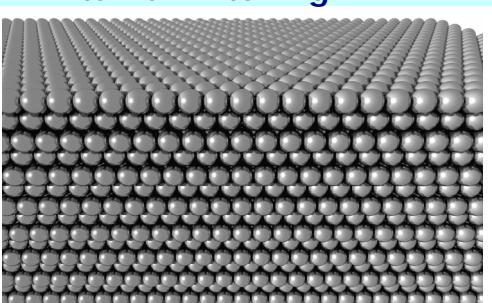
(with HNO<sub>3</sub> = 70% HNO<sub>3</sub> in H<sub>2</sub>O, HCl

Silver crystallises in the face-centred cubic structure. Silver etching solutions require a component for oxidising the Ag, and a second substance for dissolving the silver oxide:

Beside the KI/I<sub>2</sub>/H<sub>2</sub>O etching mixture described in the previous section, silver can also be etched with a NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub>:methanol = 1:1:4 mixture (where 'NH<sub>4</sub>OH' and 'H<sub>2</sub>O<sub>2</sub>' hold for a 30% concentration in water). The toxic methanol is not obligatory and can be substituted with water.

A further etching solution for silver is a HNO<sub>3</sub>:HCl:H<sub>2</sub>O = 1:1:1 mixture = 37% HCl in H<sub>2</sub>O).

## n Titanium Etching

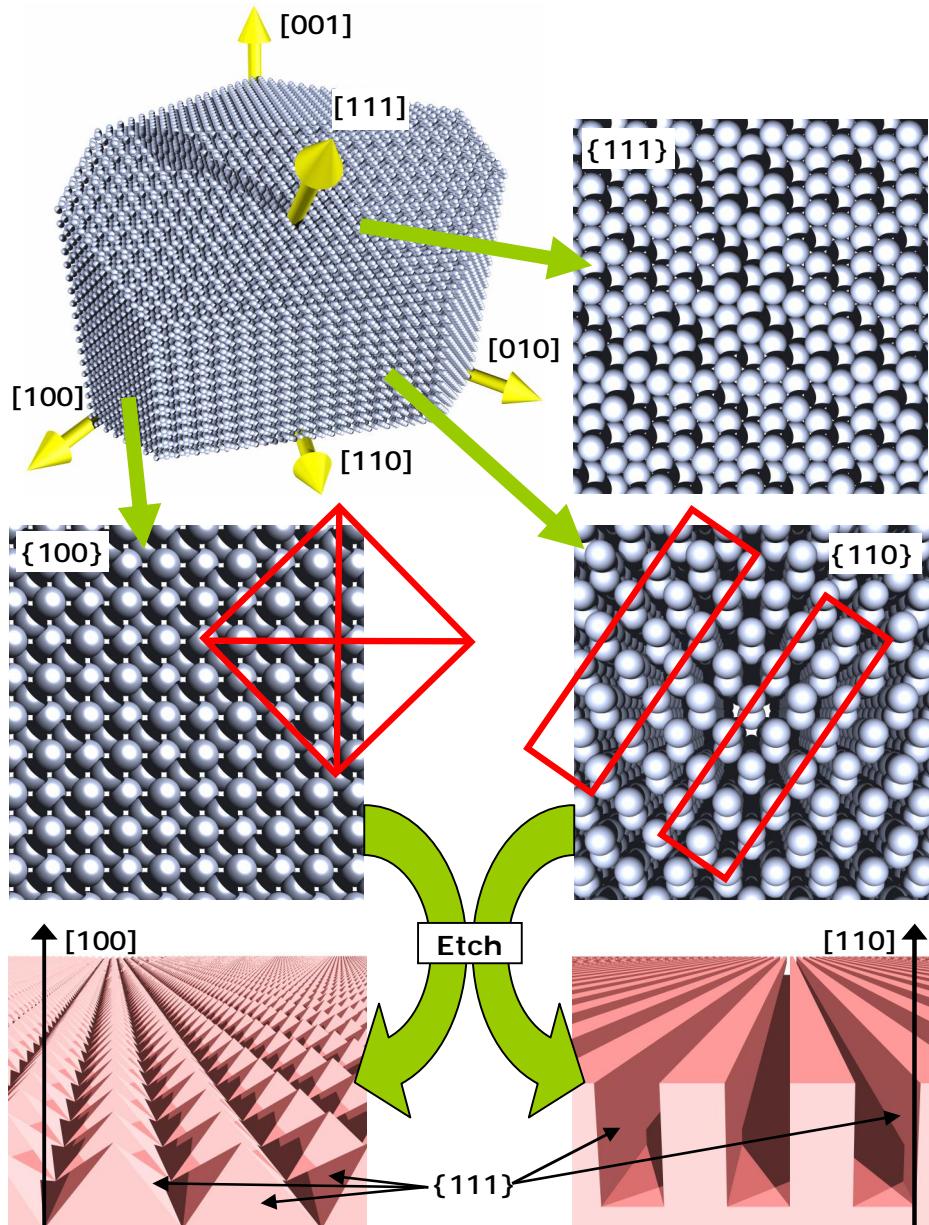


In the field of microstructuring, Titanium is often used as adhesion promoter between substrates and other metals. Titanium crystallizes in the diamond lattice and forms a very stable TiO<sub>2</sub> film on air. The only applicable way to dissolve TiO<sub>2</sub> is HF, which therefore is a typical component in Ti etching mixtures. Oxidizers such as H<sub>2</sub>O<sub>2</sub> are required to again oxidize the Ti below.

Using a etching mixture of HF (50%) : H<sub>2</sub>O<sub>2</sub> (30%) : H<sub>2</sub>O = 1:1:20 allows an etch rate of approx. 1 µm/minute at room temperature.

Positive Resists	Negative Resists	Image Reversal Resists	Developers
Thinner	Solvents	Etching Solutions	Process Chemicals
MicroChemicals GmbH	<a href="http://www.microchemicals.com">www.microchemicals.com</a>		<a href="mailto:tech@microchemicals.com">tech@microchemicals.com</a>

## Anisotropic Silicon Etching



silicon forms borosilicate glass on the surface which acts as etch stop if the boron doping concentration exceeds  $10^{19} \text{ cm}^{-3}$ .

The following table lists etch rates of Si and typical hard masks such as  $\text{Si}_3\text{N}_4$  und  $\text{SiO}_2$ , and etch selectivity between different crystal planes as a function of the etchant:

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

Strong alkaline ( $\text{pH} > 12$ ) solutions such as aqueous KOH- or TMAH solutions etch silicon via



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, the 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-wafer are almost not attacked by the etch.

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

§ (110)-orientated wafer form perpendicular trenches with {111}-planes forming the sidewalls. Such trenches are used as e.g. microchannels in the field of micromechanics and microfluidics.

The degree of anisotropy (= the selectivity in the etch rate between different crystal planes), the absolute 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.

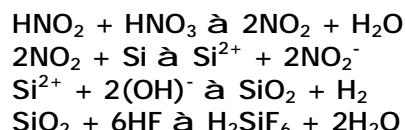
The doping concentration of the Si to be etched also strongly impacts on the etching: During etching, Boron doped silicon forms borosilicate glass on the surface which acts as etch stop if the boron doping concentration exceeds  $10^{19} \text{ cm}^{-3}$ .

## n Isotropic Etching of Silicon and SiO<sub>2</sub> with HF/HNO<sub>3</sub>

### Etch Mechanism, Etch Rates, and Selectivity

The following chemical reactions summarize the basic etch mechanism for isotropic etching of silicon (steps 1-4), and SiO<sub>2</sub> (only step 4) using a HF/HNO<sub>3</sub> etching mixture:

- (1) NO<sub>2</sub> formation (HNO<sub>2</sub> traces always present in HNO<sub>3</sub>):
- (2) Oxidation of Silicon by NO<sub>2</sub>:
- (3) SiO<sub>2</sub> formation:
- (4) SiO<sub>2</sub> etching:



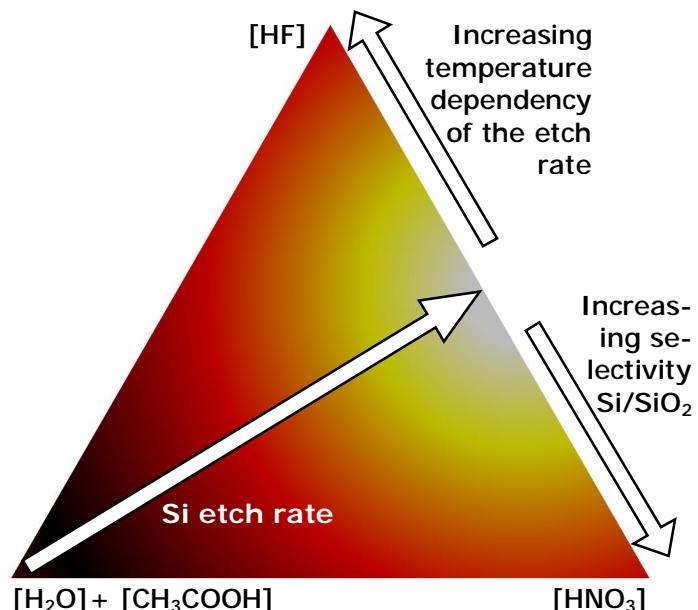
In conclusion, HNO<sub>3</sub> oxidises Si, and HF etches the SiO<sub>2</sub> hereby formed.

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

The SiO<sub>2</sub> 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<sub>2</sub> 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  $\pm 0.5^\circ\text{C}$  (fig. left-hand). 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<sub>2</sub> etches faster than undoped Si or SiO<sub>2</sub>.



### HF and BHF: Unbuffered and buffered Hydrofluoric Acid

Etching of Si and SiO<sub>2</sub> with HF-containing mixtures consumes F<sup>-</sup>-ions via the reaction  $\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$ . HF buffered with ammonia fluoride ( $\text{NH}_4\text{F} + \text{H}_2\text{O} + \text{HF} = \text{BHF}$ ) causes:

- § The maintenance of the free F<sup>-</sup>-ion concentration via  $\text{NH}_4\text{F} \rightarrow \text{HF} + \text{NH}_3$ , 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<sub>2</sub><sup>-</sup>-ions
- § An **increase of the pH-value** ( $\rightarrow$  minor resist underetching and resist lifting)

! Despite an increased reactivity, strongly buffered hydrofluoric acid has a pH-value of up to 7 and therefore may not be detected by chemical indicators !

## n Glass Etching

Unlike SiO<sub>2</sub>, glasses with various compositions show a strong dependency between their etch rate and additives in the etch. Such additives (e.g. HCl, HNO<sub>3</sub>) 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:H<sub>2</sub>O. Therefore, such additives allow a continued etching at a constant and high rate. This allows to increase the etch rate at a reduced HF-concentration (= increased resist stability).

	Etchant	Etch rate / comments
Borosilicate glass	HF*: HNO <sub>3</sub> *: H <sub>2</sub> O = 1:100:100	300 Å/min (9 mol% B <sub>2</sub> O <sub>3</sub> ), 50 Å/min (SiO <sub>2</sub> )
	HF*: HNO <sub>3</sub> *: H <sub>2</sub> O = 4.4:100:100	750 Å/min (9 mol% B <sub>2</sub> O <sub>3</sub> ), 135 Å/min (SiO <sub>2</sub> )
Phosphosilicate glass	28ml HF* + 113g NH <sub>4</sub> F + 170ml H <sub>2</sub> O	5500 Å/min für 8 mol% P <sub>2</sub> O <sub>5</sub>
	HF*: HNO <sub>3</sub> *: H <sub>2</sub> O = 15:10:300	34000 Å/min (16 mol% P <sub>2</sub> O <sub>5</sub> ), 110 Å/min (SiO <sub>2</sub> )
Pb glass	HF*: HCl*: H <sub>2</sub> O = 18:46:75	ca. 70000 Å/min
	HF*: HCl*: CH <sub>3</sub> COOH* = 25:46:75	ca. 70000 Å/min

HF\* =  
37% HCl in H<sub>2</sub>O

HNO<sub>3</sub>\* =  
70% HNO<sub>3</sub> in H<sub>2</sub>O

HF\* =  
49% HF in H<sub>2</sub>O

CH<sub>3</sub>COOH\* =  
99% CH<sub>3</sub>COOH in H<sub>2</sub>O

Positive Resists  
Thinner

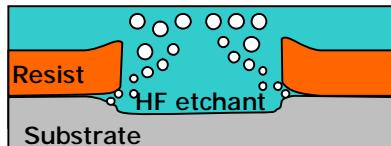
Negative Resists  
Solvents

Image Reversal Resists  
Etching Solutions

Developers  
Process Chemicals

## n Lifting of small/narrow Structures during wet chemical (etching) Steps

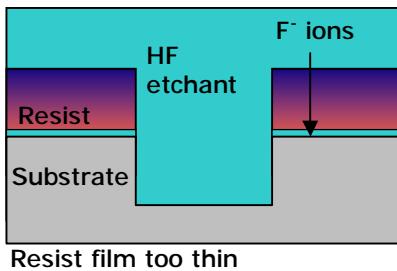
A peeling of primarily small/narrow resist structures during wet chemical etching processes points towards under-etching of the resist with a decrease of the contact area between resist and substrate as a consequence. Sometimes accompanied by elevated temperatures or/and gas formation, small resist structures lift from the substrate during etching.



In case of isotropic etchants, the grade of under-etching cannot be minimized under a certain minimum. However, the recommendations for adhesion improvement given in this document will help to reduce the consequences.

## n (Large-scale) Resist Peeling during wet chemical (etching) Steps

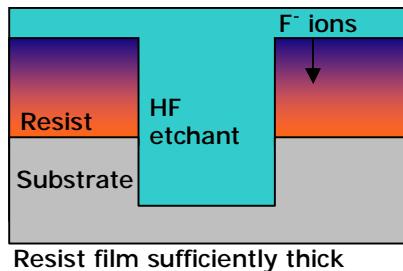
Wet chemical etchants (especially HF) diffuse into the resist film and may lead to a large scale resist peeling either during the etching, or after the subsequent rinsing by one or both of the two following reasons:



§ Resist swelling caused by the etchant diffusing into the resist film

§ Large-scale etching of the resist covered substrate after the etchant has diffused through the resist film towards the substrate (schema left-hand in case of HF etching of glass or SiO<sub>2</sub>).

Beside an adjusted etchant, both mechanisms can be reduced by a **thicker resist film**.



Resist film sufficiently thick

Double-sided metalized substrates (e.g. Ag & Al) for a galvanic cell in aqueous solutions, sometimes accompanied by H<sub>2</sub> formation lifting the resist film beyond. In this case, coat the opposite side of the substrate with protective coating (such as AZ® 520D) or any other resist.

## n Etching of Metals (Overview)

	Etching mixture	Etch rate / comments
Cr	HCl*: glycerol = 1:1	800 Å/min after depassivation
	HCl*: CeSO <sub>4</sub> (saturated) = 1:9	800 Å/min, after depassivation
	Ce(NH <sub>4</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> + CH <sub>3</sub> COOH in 1L H <sub>2</sub> O	1000 Å/min (first dissolve CH <sub>3</sub> COOH in 1L H <sub>2</sub> O!)
Mo	H <sub>3</sub> PO <sub>4</sub> *: HNO <sub>3</sub> *: CH <sub>3</sub> COOH* : H <sub>2</sub> O = 5:2:4:150	5000 Å/min
	11g K <sub>3</sub> Fe(CN) <sub>6</sub> + 10g KOH in 150ml H <sub>2</sub> O	10000 Å/min
	HCl*: H <sub>2</sub> O <sub>2</sub> *: H <sub>2</sub> O = 1:1:1	
W	34g KH <sub>2</sub> PO <sub>4</sub> * + 13.4g KOH + 33g K <sub>3</sub> Fe(CN) <sub>6</sub> in 1L H <sub>2</sub> O	1600 Å/min
Ag	NH <sub>4</sub> OH*: H <sub>2</sub> O <sub>2</sub> * : CH <sub>3</sub> OH = 1:1:4	3600 Å/min, immediately rinse with water after etching!
	HCl*: H <sub>2</sub> O <sub>2</sub> *: H <sub>2</sub> O = 1:1:1	
	KI : I <sub>2</sub> : H <sub>2</sub> O = 4:1:40	
Au	HCl*: HNO <sub>3</sub> * = 3:1	'aqua regia', 25-50 µm/min
	KI : I <sub>2</sub> : H <sub>2</sub> O = 4:1:40	0.5-1 µm/min
Pt	HCl*: HNO <sub>3</sub> * = 3:1	'aqua regia', 20 µm/min
	HCl*: HNO <sub>3</sub> *: H <sub>2</sub> O = 7:1:8	400-500 Å/min at 85°C
Pd	HCl*: HNO <sub>3</sub> *: CH <sub>3</sub> COOH* = 1:10:10	1000 Å/min
	HCl*: HNO <sub>3</sub> * = 3:1	'aqua regia'
	KI : I <sub>2</sub> : H <sub>2</sub> O = 4:1:40	1 µm/min
Cu	150g Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> in 1L H <sub>2</sub> O	1 µm/min at 45°C, selective to Ni if Fe-free
Ni	H <sub>3</sub> PO <sub>4</sub> *:HNO <sub>3</sub> *:CH <sub>3</sub> COOH*:H <sub>2</sub> O = 3:3:1:1	65 nm/min at 20°C, contact with O <sub>2</sub> (air) each 15 seconds
	H <sub>2</sub> O <sub>2</sub> *: HF*: H <sub>2</sub> O = 1:1:20	
Ti	H <sub>2</sub> O <sub>2</sub> *: HF*: H <sub>2</sub> O = 1:1:20	8800 Å/min at 20°C
Sb	H <sub>3</sub> PO <sub>4</sub> *: HNO <sub>3</sub> *: CH <sub>3</sub> COOH*: H <sub>2</sub> O = 3:3:1:1	contact with O <sub>2</sub> (air) each 15 seconds

HCl\* = 37% HCl in H<sub>2</sub>O

HNO<sub>3</sub>\* = 70% HNO<sub>3</sub> in H<sub>2</sub>O

H<sub>2</sub>SO<sub>4</sub>\* = 98% H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O

HF\* = 49% HF in H<sub>2</sub>O

HClO<sub>4</sub>\* = 70% HClO<sub>4</sub> in H<sub>2</sub>O

H<sub>3</sub>PO<sub>4</sub>\* = 85% H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O

NH<sub>4</sub>OH\* = 29% NH<sub>3</sub> in H<sub>2</sub>O

H<sub>2</sub>O<sub>2</sub>\* = 30% H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>O

CH<sub>3</sub>COOH\* = 99% CH<sub>3</sub>COOH in H<sub>2</sub>O

## n Etching of III/V-Semiconductors (Overview)

Material Etchant	GaAs	InP	InGaAs	InGaAsP	GaInP	GaAsP	AlGaP	AlGaAs	AlInP	InAlAs	InGaAlAs
HCl* : H <sub>3</sub> PO <sub>4</sub> * : H <sub>2</sub> O	orange	green	orange	orange	green				green		
H <sub>3</sub> PO <sub>4</sub> * : H <sub>2</sub> O <sub>2</sub> * : H <sub>2</sub> O	green	orange	green		orange						
H <sub>2</sub> SO <sub>4</sub> * : H <sub>2</sub> O <sub>2</sub> * : H <sub>2</sub> O	green	orange	green	green							
C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> : H <sub>2</sub> O <sub>2</sub> * : H <sub>2</sub> O	yellow	orange	yellow					yellow		yellow	
HCl* : HNO <sub>3</sub> * : H <sub>2</sub> O	green	green					green		green		
HNO <sub>3</sub> * : H <sub>2</sub> SO <sub>4</sub> * : H <sub>2</sub> O	green					green					
HCl* : *H <sub>2</sub> O <sub>2</sub> : H <sub>2</sub> O	green	green				green					
HCl* : H <sub>2</sub> O	orange	green	orange						green	yellow	
BHF : H <sub>2</sub> O								yellow			

etches      depends on composition      selective against (etch stop)

*HCl\* = 37% HCl in H<sub>2</sub>O*

*HNO<sub>3</sub>\* = 70% HNO<sub>3</sub> in H<sub>2</sub>O*

*H<sub>2</sub>SO<sub>4</sub>\* = 98% H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O*

*HF\* = 49% HF in H<sub>2</sub>O*

*HClO<sub>4</sub>\* = 70% HClO<sub>4</sub> in H<sub>2</sub>O*

*H<sub>3</sub>PO<sub>4</sub>\* = 85% H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O*

*NH<sub>4</sub>OH\* = 29% NH<sub>3</sub> in H<sub>2</sub>O*

*H<sub>2</sub>O<sub>2</sub>\* = 30% H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>O*

*CH<sub>3</sub>COOH\* = 99% CH<sub>3</sub>COOH in H<sub>2</sub>O*

## n Resist Stability against various Etchants

The following specifications refer to Novolak based positive, image reversal, and negative tone resists (such as the crosslinking AZ® nLOF 2000 series).

§ Almost all organic solvents dissolve positive tone and image reversal resist films within few seconds. Only strongly (at high temperatures) crosslinked AZ® nLOF 2000 resist films are able to terminally withstand organic solvents.

§ HCl only barely attacks resists.

§ HF can cause problems due to the high HF permeability of resists which causes large-scale substrate etching beneath the resist film. In this case, a thicker or crosslinked (less permeable) resist will help for most etching applications.

§ Strongly oxidizing substances such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or H<sub>2</sub>O<sub>2</sub> attack and damage resist. However, if correctly processed (sufficient resist adhesion and softbake/hardbake), resists are capable for many etching processes requiring the mentioned substances.

## n Selected Etchants: Risks and Precaution

HCl/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixtures react strongly exothermic during/after preparing the mixture, which may lead to an explosive decomposition of the H<sub>2</sub>O<sub>2</sub> if its concentration is too high.

H<sub>2</sub>SO<sub>4</sub> reacts strongly exothermic with when diluted with H<sub>2</sub>O. General, always give the acid to the dilutor (water, weaker acids), never vice versa.

HF is not only strongly corrosive, but also highly toxic: Local effects include tissue destruction and necrosis. Burns may involve underlying bone. Systemic fluoride ion poisoning from severe burns is associated with hypocalcemia (low Ca levels), hyperkalemia (low Potassium levels), hypomagnesemia (low Mg levels), and sudden death. Deaths have been reported from concentrated acid burns to as little as 2.5% body surface area.

## n Disclaimer of Warranty

All information, process guides, recipes etc. given in this brochure have been added to the best of our knowledge. However, we cannot issue any guarantee concerning the accuracy of the information.

Generally, and especially for the wet chemical etching recipes we do not guarantee the correctness of the specification of the composition, the mixing ratio, the mixing and application of the etches and solutions. The recommended sequence of the mixing of the components of each recipe does generally not correspond to the order the components are listed. Generally, it is recommended to i) add the acid to the diluent, ii) add stronger acids to weaker acids, and iii) add the oxidizer last.

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

In general, it is in the responsibility of each staff member to inform about the processes to be performed in the suited (technical) literature, in order to minimize any risk for man and machine.

Positive Resists Thinner	Negative Resists Solvents	Image Reversal Resists Etching Solutions	Developers Process Chemicals
MicroChemicals GmbH	www.microchemicals.com		tech@microchemicals.com