Wet Chemical Etching

MicroChemicals

Version: 2007-02-29
Source: www.microchemicals.eu/technical-information

Etching and Dissolving

While solving describes the overcoming of intermolecular interactions between two solids or liquids, etching breaks intramolecular/-atomar bonds of a solid. The following chapters aim for an understanding how the chemical properties of etchants can be explained, and which etchant is suited for your individual purpose.

Acids and Bases: Oxidation and Reduction

At room temperature, pure water contains approx. 10^{-7} mol H_3O^+ and OH^- ions per litre formed by the autoprotolysis $H_2O + H_2O$ à $H_3O^+ + OH^-$, corresponding to a (neutral) pH-value of 7 due to the equation

$$pH = -\log_{10}\left[H_3O^+\right]$$

Due to the thermally activated autoprotolysis, the pH-value of 100°C DI-H_2O, drops to approx. 6, since the H_3O^+ and OH^- concentrations both increase. The following table lists the pH-value of some common acids and bases:

Substance	HCl (20%)	Gastric juice	Vinegar	DI-H_2O	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 H_3O^+-ion concentration in aqueous solutions via the release of protons (e. g. hydrochloric acid: $HCl + H_2O$ à $H_3O^+ + Cl^-$) hereby decreasing the pH-value. The pK_S-value defines the strength (= degree of dissociation) of an acid as aqueous solution as follows:

$$pK_S = -\log_{10}\left(\frac{\left[H_3O^+\right]\cdot\left[dissociated\ acid^-\right]}{\left[undissociated\ acid\right]}\right)$$

Very strong acids such as $HClO_4$, HI, HCL, or H_2SO_4 are almost completely dissociated in aqueous solutions. The following table lists the pK_S-value of some acids at room temperature:

The strong trend of H_3O^+ to release a proton accompanied by the assimilation of an electron explains the oxidative characteristics of acids.

Bases as proton acceptors increase the OH^--ion concentration in aqueous solutions. Due to the law of mass action, at given temperature and pressure, the product $[H_3O^+]\cdot[OH^-]$ always keeps constant. Therefore, with $[OH^-]$ increasing, the H_3O^+-concentration drops thus increasing the pH-value. Corresponding to acids, the strength of a base as aqueous solution can be defined as follows:

Substance	HNO_3	H_3PO_4	$H_2SO_4^-$	HF	HNO_2	CH_3COOH	H_2CO_3
pK_S-value	-1.32	2.13	1.92	3.14	3.35	4.75	6.52

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

Substance	NaOH	KOH	S^{2-}	PO_4^{3-}	NH_3	HS^-	F^-
pK_B-value	0.2	0.5	1.0	1.67	4.75	7.08	10.86

The strong trend of OH^--ions to release an electron explains the reductive characteristics of bases.

Chemical Buffers

Chemical buffers are substances keeping the pH-value of an aqueous solution at a fixed level almost constant, despite the addition or consumption of H_3O^+- or OH^- ion (e. g. by their consumption during wet etching). This characteristics of chemical buffers bases on their ability to bind H_3O^+- as well as OH^--ions (or, respectively, neutralize them by releasing their conjugated acid/base), if the H_3O^+- or OH^--ion concentration increases, and release H_3O^+- as well as OH^--ions if their concentration drops. Chemical buffer solutions generally are weak (= only partially dissociated) acids/bases, and their conjugated bases/acids.

Complex Formation

In order to suppress the reassembly of already etched atoms 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 valence electron 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.

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 some 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 evolution 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 spatio-temporal homogeneous etching.

Base and noble Metal Etching: Energy, Entropy and Enthalpy

Etching of metals can be described as the oxidation of the metal via protons donated by the H_3O^+ hereby reduced to hydrogen as follows:

$$\text{metal} + H^+ \text{ à } \text{metal}^+ + H$$

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 H^+ ionizes the metal atom.

Oxidizing noble metals with H^+, however, requires energy (endothermic reaction, $\Delta U > 0$). The reason why noble metals with $E_0 > 0$ (e. g. $E_{0,copper} = +0.34$) can be etched despite a required increase in the intrinsic energy 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 ΔU 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 (à oxidation), noble metals have a comparably high first ionization energy (à 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 a completely occupied d-orbital with the quantum number n-1 (e. g. electron configuration of gold: $[Xe]4f^{14}5d^{10}6s^{1}$). 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 an electron duplet (Iridium), both further increasing the first ionization energy and the chemical stability. As a consequence, the only way to etch Iridium is hot (approx. 100°C) aqua regia.

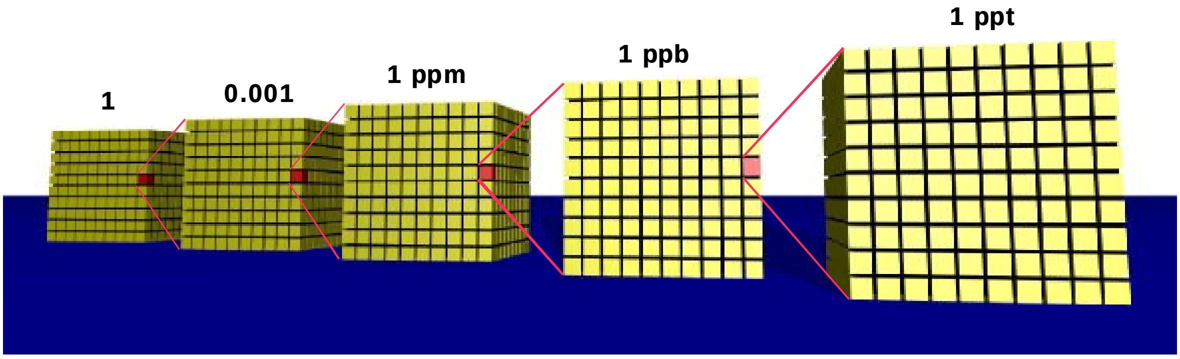
Purification Grades

MOS (metal oxide semiconductor): Impurity metal ion concentration (per element) approx. 100 ppb, particle concentration < 1.000/ml

VLSI (very large scale integration): Impurity metal ion concentration (per element) approx. 10-50 ppb, particle concentration < 250/ml

ULSI (ultra large scale integration): Impurity metal ion concentration (per element) approx. 10 ppb, particle concentration < 30 ... 100/ml

SLSI (super large scale integration): Impurity metal ion concentration (per element) approx. 1 ppb, particle concentration < 30 ... 100/ml



1 ppm (parts per million, 10^{-6}) approximately corresponds to a drop (approx. 30 µl) in a rather big bucket.

1 ppb (parts per billion, 10^{-9}) corresponds to a drop in a comparable small swimming-pool.

1 ppt (parts per trillion, 10^{-12}) would be a drop in a small lake, or a 5 µm particle solved in a cup of coffee, or anyhow approx. 100.000 atoms in a drop!

The reasonable purity degree of process chemicals depends – among many other parameters – on the minimum feature size to be realized, the required yield, the cleanroom class, and subsequent process steps.

It is almost impossible to definitely correlate suboptimum process results with a purity degree of the chemicals applied being too low. Therefore, one cannot give a certain statement on the required purity grade.

With VLSI and ULSI quality, we fulfil almost all requirements in research and development as well as in production.

Our Acids, Bases and HMDS

Ammonia Solution (28-30 %)	Available in 2.5 L sales volumes in VLSI quality
Acetic Acid (99.8 %)	Available in 2.5 L sales volumes in VLSI quality
Hydrofluoric Acid (Various Conc.)	Available in 2.5 L sales volumes in VLSI quality
BOE 7:1 (Buffered HF)	Available in 2.5 L sales volumes in VLSI quality.
HMDS (99.5 %)	Available in 1 L sales volumes in VLSI quality
KOH Solution (50 %)	Available in 5.0 L sales volumes in VLSI quality
Phosphoric Acid (86 %)	Available in 2.5 L sales volumes in VLSI quality
Nitric Acid (70 %)	Available in 2.5 L sales volumes in VLSI quality
Hydrochloric Acid (37 %)	Available in 2.5 L sales volumes in VLSI quality, and in 2.5L sales units in ULSI quality
Sulphuric Acid (96 %)	Available in 2.5 L sales volumes in VLSI quality
Hydrogen Peroxide (31 %)	Available in 2.5 L sales volumes in VLSI quality

Our Ready-to-Use Etching Mixtures

Aluminium Etchant	H_3PO_4 / HNO_3 / CH_3COOH Available in 2.5 L sales units in MOS quality
Chromium Etchant	$(NH_4)_2[Ce(NO_3)_6]$ / $HClO_4$ Available in 2.5 L sales units in VLSI quality
Gold Etchant	HNO_3 / HF Available in 2.5 L sales units in VLSI quality
Silicon Etchant	HF / HNO_3 Available in 2.5 L sales units in VLSI quality

Specifications and Shipping

The specifications of the products mentioned above are available on request.

Beside single bottles, we also offer cardboxes of 6 x 1.0 L, 6 x 2.5 L or 4 x 5.0 L.

Our typical lead time is 3-5 working days within Germany, lead times to other countries on request. On demand, in urgent cases our etchants can be shipped within 24 hours within Germany.

Contact us!

Interested? Please send your request to:

e-mail: sales@microchemicals.eu
phone: +49 (0)731 36080 409
fax: +49 (0)731 36080 908

Thank you very much for your interest!