SOLVENTS AND SOLUBILITIES

With microstructuring, the solubilities of materials often play a crucial role in addition to etching processes. This concerns not only the structuring of materials soluble in organic solvents such as organic films, but all wet-chemical etching processes: In addition to the actual etching process, it is important to bring and to keep the etched substances in solution.

Interactive Forces Involved in the Solution Process

Etching and Dissolving

With both the wet-chemical etching and dissolution of solids, the bonds between atoms or molecules must be broken. While this is done during etching in the context of a chemical redox reaction with a charge transfer between the ions of the etching medium and the particles (atoms or molecules) of the solid to be etched, the dissolution can be regarded as a purely physical process without charge exchange and breaking of chemical bonds.

Therefore, when a solid is dissolved, only the interaction forces which do not act on the chemical valence bonds within a molecule but between the molecules of the solid and the solvent play a role, as explained in the following sections and shown comparatively in Fig. 114 in their distance-dependent magnitude.

Ionic Interactions

Ions, i.e., electrically charged atoms and molecules, are not only found in salts or electrolytes. In pure water at room temperature, one of approx. 1,000,000,000 H_2O molecules is dissociated in OH^- or H_3O^+. In aqueous mixtures of organic solvents with acidic (e.g. ethyl lactate) or alkaline character (e.g. NMP), the concentration of oxonium or hydroxide ions can be orders of magnitude greater.

The electrostatic force between two ions coincides with the square of their distance between each other. The corresponding interaction energy between adjacent ions, i.e. their bonding energy, is typically a few eV and thus lies in of the order of magnitude of intra-molecular chemical bonds.

Interaction between Permanent Electric Dipoles

The different electro negativity of the atoms in polar molecules causes a spatial shift between the centre of the valence electron distribution and the centre of the positive nuclear charges. As a result, the molecule has an electric dipole moment (Fig. 111).

In liquids, adjacent dipoles can align anti-parallel to each other so that an attractive force acts between the positive pole of one dipole and the negative pole of the other, decreasing with the fourth power of the distance. The corresponding interaction energy between molecules is a few 100 meV, in the case of hydrogen bonds up to approx. 0.5 eV which explains the high boiling point of water.

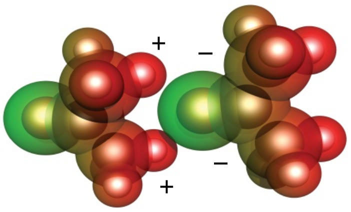

Fig. 111: The polar acetone molecules interact with each other as stationary electric dipoles (green and red marked regions of negative and positive charge density)).

Interaction between Induced Electric Dipoles

In all polar and non-polar atoms and molecules, the valence electron charge distribution permanently fluctuates due to interactions between the molecules with each other as well as electromagnetic radiation. As a consequence, temporary electric dipoles are steadily formed. These temporary dipoles interact with the valence electron orbitals of neighboured atoms/molecules and hereby induce temporary anti-parallelly orientated electric dipoles resulting in a weak interaction (Fig. 112). This process is the more pronounced the higher its polarizability, i.e. the relocatability of the valence electron cloud is.

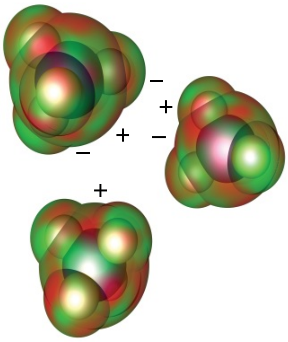

Fig. 112: The non-polar CCl_4 molecules interact among themselves in the form of indexed electric dipoles (green and red areas mark local negatives and fluctuations of the charge density).

The resulting energy of the interaction is comparatively weak even for nearby particles with < 100 meV, the attractive force derived from it drops with the 7th power of the distance between two molecules and is thus very short range.

The Pauli Repulsion

The interactions mentioned in the above sections result at least in an approximate force acting with different reciprocal powers *N* of the distance ($1/R^N$) of two particles, which increases with increasing approximation. As solids and liquids have a finite density and their particles thus a certain average distance, there must be an interaction which counteracts a further approximation below a certain distance between the two particles.

This is the so-called *Lennard-Jones Potential* which is derived from the *Pauli exclusion principle*: If two particles approach each other so far that their electron shells overlap, the electrons must evade energetically higher orbitals in order not to pairwise occupy the same quantum state. This evasion requires all the more energy, the more the two particles approximate, the corresponding repulsive force increases accordingly.

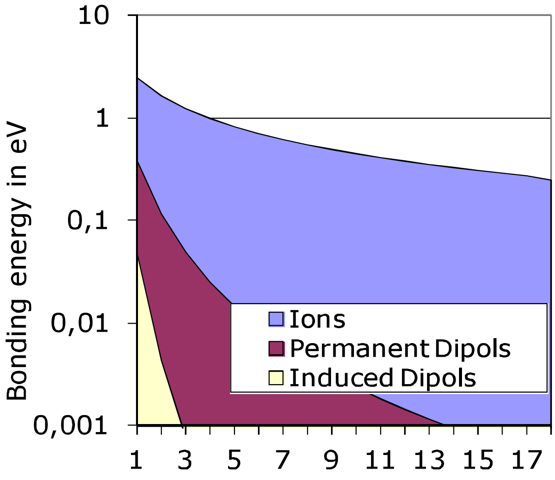

Fig. 114: The various interaction forces between particles have different strengths and decrease at different speeds with distance.

Mixed Interactions

Mixed interactions are those between e. g. ions and dipoles (which play a role in the dissolution of salts in polar solvents such as water) or between permanent and induced dipoles in solvent mixtures.

Solubilities: Energy and Entropy

Some Thermodynamics

The molecules, atoms or ions of liquids or solids possess a negative bonding energy. This is precisely why they are not gaseous at a given temperature and pressure. In order to dissolve these substances, therefore, this bonding energy must first be overcome.

However, since the interactions described in the last section also occur between the substance and the solvent, the sum of the bonding energies can be further reduced during the dissolving process (exothermic mixing heat). An example of this is the heating during the dissolution or dilution of KOH or sulphuric acid in water.

However, when dissolving, for example, sodium chloride (NaCl) in water, the mixture cools below the temperature of the starting materials, the mixture is endothermic, i.e. energy must be supplied: During the hydrogenation of Na^+ and Cl^- -ions by water molecules, less energy is released than is required during the dissolution of the NaCl crystal (Fig. 113).

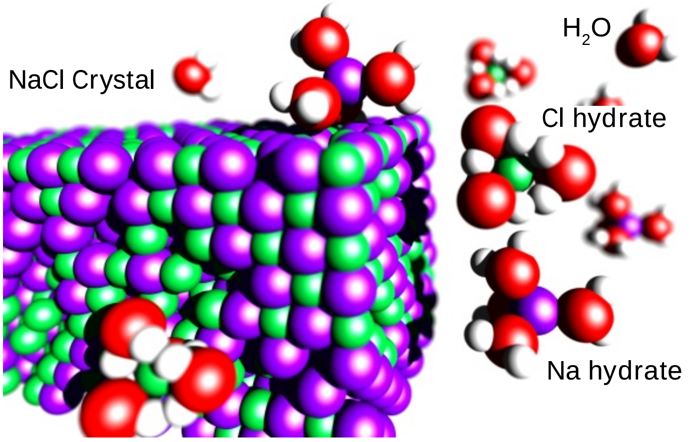

Fig. 113: The dissolving of common salt requires energy. That this still takes place by itself, is due to the entropy gain of the dissolved ions.

The reason why - in this example NaCl - is water-soluble despite the necessary internal energy increase ΔU lies in the simultaneous entropy increase ΔS of the total system: Dissolved ions have more degrees of freedom with respect to location and velocity, and thus entropy (disorder) than ions bound in the crystal.

At constant volume and pressure, a closed system of temperature *T*, tends to minimise the free (mixing) enthalpy $F = U - T\cdot S$, i.e. a solubility is only given if: $\Delta U - T\cdot\Delta S < 0$.

The Hansen Diagram

The condition $\Delta U - T\cdot\Delta S < 0$ mentioned in the last section as a prerequisite for a sufficient solubility of two substances (e.g. a photoresist and solvent or two solvents with each other) can be derived from *Hansen* model by the appearance and size of the different intermolecular interactions.

The solubility of two media A and B with each other is all the greater the better the different interaction energies between A and B are coincident.

If, as shown in Fig. 115, the medium A to be dissolved and various solvents B are shown in a diagram over their respective molar interaction energies of permanent (σ_P) and indicated dipole moments (σ_D) as well as the hydrogen bonding energies (σ_H), suited solvents are shown (green points within the green sphere) near A and unsuitable solvents (red points) farther away from it.

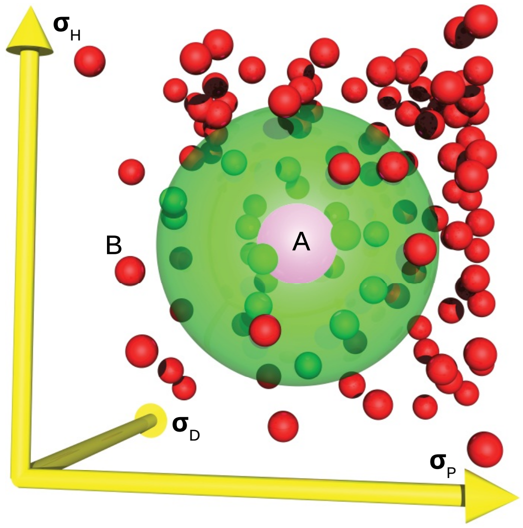

Fig. 115: The Hansen diagram represents substances in the parameter space set by the different interactive forces of the molecules. These substances which are readily soluble with each other are located close together; difficult to dissolve ones far away from each other.

Important Characteristics of Organic Solvents

Vapour Pressure, Evaporation and Boiling Point

In order to pass from the liquid into the gaseous phase, an atom or molecule has to overcome its bonding energy E_B to neighboured molecules with its kinetic energy E_{kin}. In order to fulfil this condition for all molecules in water or many typical organic solvents at the same time, a temperature of several 1000°C would be required. At lower temperatures (also at the boiling point!), only a very small fraction of the molecules fulfils the condition $E_{kin} > E_B$ via the Maxwell-Boltzmann energy distribution (Fig. 116) even considering the comparable small energy gain caused by the interactions between the evaporated molecules.

Without external energy supply, the molecules remaining in the liquid after the high-energy molecules passed to the gaseous phase have a lowered average E_{kin} corresponding to a lower temperature (→ evaporative cooling).

The evaporated atoms or molecules in the gaseous phase also have a Maxwell-Boltzmann energy distribution, so that molecules with $E_{kin} < E_B$ return to the liquid (condensation).

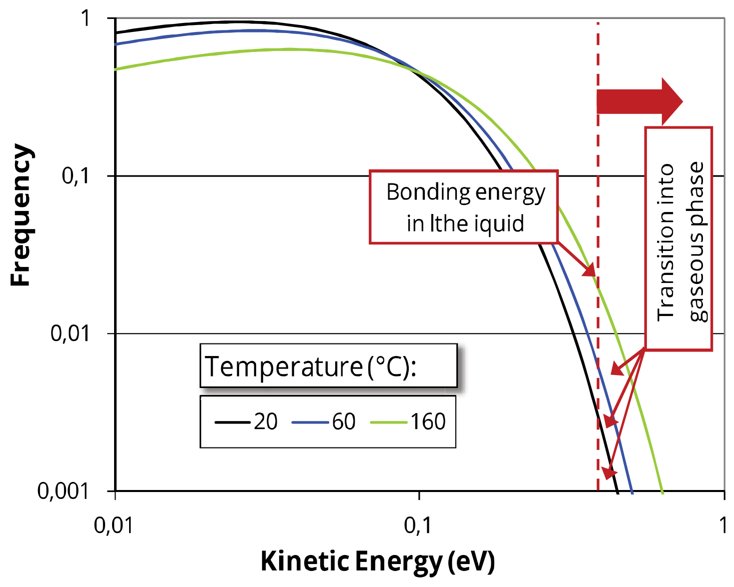

Fig. 116: With increasing temperature, an increasing (but still small) fraction of the molecules of a fictitious solvent has enough kinetic energy to convert from the liquid into the gas phase.

The equilibrium condition between the two transitions defines the temperature dependant vapour pressure of the liquid. If the vapour pressure exceeds the atmospheric pressure at the so defined boiling point, the liquid starts boiling. At lower temperatures, the liquid evaporates.

Since polarisability and (in case of polar molecules) dipole strength roughly increase with the molecular size, liquids with 'large' polar molecules such as NMP bear a low vapour pressure and high boiling point, while liquids with 'small' molecules such as acetone have a high vapour pressure and, respectively, low boiling point.

TLV Value

The TLV value (threshold limit value) is the maximum concentration of a gas, vapour or particulate matter in the air at the workplace to which it is believed a worker can be exposed day after day for a working lifetime without adverse effects. Usually, the TLV value is averaged over periods of time up to one working day or work shift.

Also to comply with TLV values, you should be generally seek to minimise the level of the chemicals in the air at the workplace as far as possible.

Flash Point

The flash-point is the lowest temperature at which a liquid will yield vapours, under the conditions defined in the test method, in such an amount that a flammable vapour/air mixture is produced in the test vessel. The flash point of many organic solvents such as methanol, ethanol, isopropyl alcohol and acetone is < 20°C, and therefore form flammable or explosive vapour at room temperature and even below.

Explosive Range

The explosive range is the range of concentration between the lower and the upper explosion limits. The lower and upper explosive limits denote the two limit values of the fuel gas content in the fuel gas/air mixture in which an independent flame propagation from the ignition source no longer occurs. The lower explosive limit can be below 1 %; the upper explosive limit of many organic solvents is typically some 10 %.

Ignition Temperature

The ignition temperature represents a measure of the auto-flammability, as the inflammation without an external ignition source. The auto-ignition temperature is the lowest temperature at which the test substance will ignite when mixed with air under the conditions defined in the test method. The ignition temperature of most organic solvents is located above 200°C.

Characteristics of Selected Organic Solvents in Comparison

	ρ (g/cm^3)	T_S (°C)	P_S (hPa)	T_F (°C)	T_Z (°C)	D_E (10^{-30} C·m)	α (10^{-40} m^{2}As/V)	LEL (%$_{Vol}$)	UEL (% $_{Vol}$)
Acetone	0.79	56	246	-18	527	9.6	6.4	2.2	14.3
Isopropanol	0.78	82	43	12	425	5.5	7.9	1.9	13.4
MEK	0.81	80	105	-7.5	475	9.2	9.1	1.5	12.6
Methanol	0.79	65	129	9	440	5.7	3.6	6	50
Ethanol	0.79	78	58	12	400	5.8	5.7	3.1	27.7
PGMEA	0.97	149	3.1	45	315		14.6	1.5	7
Ethyl lactate	1.03	154	1.6	46	400		12.6	1.5	11.4
Ethyl acetate	0.89	77	98	-4	470	6.3	9.9	2	12.8
Butyl acetate	0.88	127	10.7	27	390		13.9	1.2	7.5
MIBK	0.80	116	18.8	14	475		13.2	1.2	8
NMP	1.03	203	0.32	86	265	4.1	11.8	1.5	9.5
DMSO	1.1	189	0.06	88	270	13	8.9	1.8	n.d.

Table 5: The characteristics of density (ρ), boiling point (T_S), vapour pressure at 20°C (P_S), flash point (T_F), ignition temperature (T_Z), molecular electric dipole moment (D_E), static polarizing capability (α), lower (LEL) and upper explosion limit (UEL) of selected organic solvents from our portfolio.

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 AZ® 1512 HS AZ® 1514 H AZ® 1518	≈ 0.5 µm ≈ 1.0 - 1.5 µm ≈ 1.2 - 2.0 µm ≈ 1.5 - 2.5 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
		AZ® 4500	AZ® 4533 AZ® 4562	≈ 3 - 5 µm ≈ 5 - 10 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
		AZ® P4000	AZ® P4110 AZ® P4330 AZ® P4620 AZ® P4903	≈ 1 - 2 µm ≈ 3 - 5 µm ≈ 6 - 20 µm ≈ 10 - 30 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
		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 AZ® ECI 3012 AZ® ECI 3027	≈ 0.7 µm ≈ 1.0 - 1.5 µm ≈ 2 - 4 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
		AZ® 9200	AZ® 9245 AZ® 9260	≈ 3 - 6 µm ≈ 5 - 20 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	
	Elevated thermal softening point and high resolution for e. g. dry etching	AZ® 701 MiR	AZ® 701 MiR (14 cPs) AZ® 701 MiR (29 cPs)	≈ 0.8 µm ≈ 2 - 3 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
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 AZ® 12 XT-20PL-10 AZ® 12 XT-20PL-20 AZ® 40 XT	≈ 3 - 5 µm ≈ 6 - 10 µm ≈ 10 - 30 µm ≈ 15 - 50 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
		AZ® IPS 6050		≈ 20 - 100 µm		
Image Reversal	Elevated thermal softening point and undercut for lift-off applications	AZ® 5200	AZ® 5209 AZ® 5214	≈ 1 µm ≈ 1 - 2 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF	TechniStrip® Micro D2 TechniStrip® P1316 TechniStrip® P1331
		TI	TI 35ESX TI xLift-X	≈ 3 - 4 µm ≈ 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 AZ® nLOF 2035 AZ® nLOF 2070	≈ 1.5 - 3 µm ≈ 3 - 5 µm ≈ 6 - 15 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® NI555 TechniStrip® NF52 TechniStrip® MLO 07
		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) AZ® 15 nXT (450 cPs)	≈ 2 - 3 µm ≈ 5 - 20 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
			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- (TetraMethylAmmoniumHydroxide) in water.

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[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

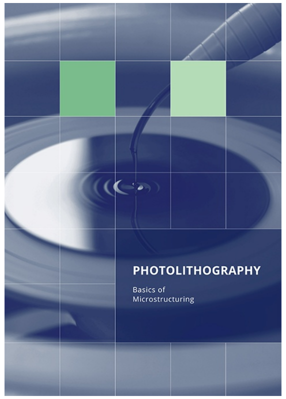
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

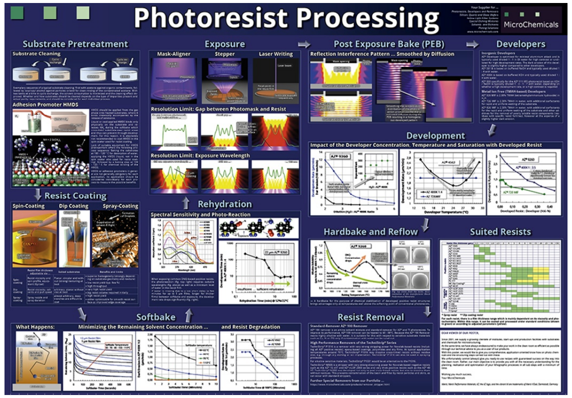
Further Information

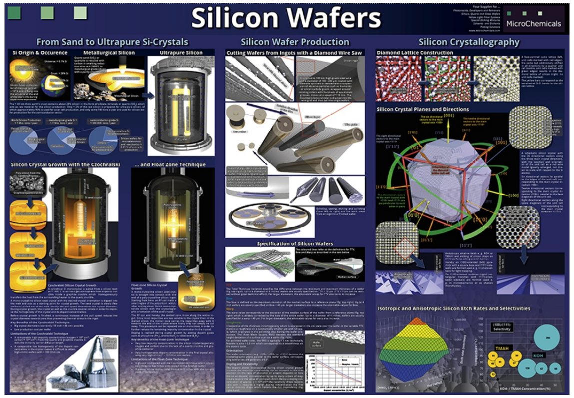
Technical Data Sheets: www.microchemicals.com/downloads/product_data_sheets/photoresists.html

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

Our Photolithography Book and -Posters







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):

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