HARDBAKE, REFLOW AND DUV HARDENING

Depending on the purpose of the resist mask, it may be appropriate to chemically or physically stabilise the developed resist structures by suitable means. This can be done either by means of a baking step for the thermal cross-linking of the entire resist structures, called hardbake. Or via a combination of low-UV radiation and elevated temperatures, which cross-links only the resist surface via deep UV hardening.

In both cases described in the following, thermal softening and rounding of the resist structures can occur, intended or undesired, which is also described in this chapter called "Reflow".

Hardbake

Definition and Purpose

A hardbake is an optional baking step carried out after the development of the resist. The aim is to make the resist structures more stable by subsequent physical or chemical processes in the resist, such as wet or dry etching or electroplating.

This raises the question of the optimum baking temperature for a given process. The following sections describe the desired but also undesirable processes take place in the resist structures at different temperatures.

Thermal Rounding (Reflow)

Non-cross-linked resist structures, i.e. developed positive and image reversal resist masks thermally soften - depending on the photoresist and previous processing - from approx. 100°C - 130°C. The resist upper edges are rounded here, while the contact points of the resist/substrate largely remain (described in detail in section 19.2).

For wet-chemical etching, rounded resist structures can usually be tolerated. For dry etching or electroplating, in which vertical resist sidewalls must also remain vertical, a thermally more stable photoresist, such as the AZ® 701 MiR or the AZ® ECI 3000 series, or cross-linked negative resists such as the AZ® 15 nXT or AZ® 125 nXT optimised for electroplating, are recommended.

Reducing the Concentration of Solvents

The reduction of the residual solvent content is actually the task of the softbake carried out after the coating operation. However, especially in the case of thick resist films, the solvent concentration in the recommended softbake conditions remains comparatively high in the vicinity of the substrate.

After development, a suitable baking step below the softening point of the photoresist used can help to make the resist sidewalls in the vicinity of the substrate more solvent-free and thus more stable for subsequent process steps (Fig. 101).

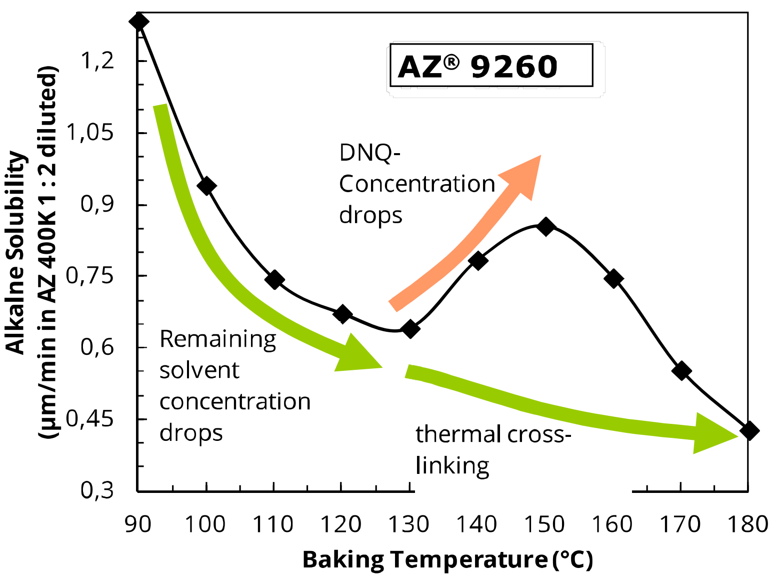


Fig. 101: A hardbake triggers various physical and chemical reactions in the resist film. First at temperatures above 140°C do positive resist film structures cross-link and stabilise which can increase their chemical stability for subsequent process steps.

Thermal Decomposition of the Photoinitiator

In the case of positive resists, a significant fraction of the photoinitiator decomposes within a few minutes from about 120°C. Although this is no longer necessary for the photoreaction after development, in the unexposed state it can be beneficial in the resist mask to increase its alkaline stability for certain subsequent wet-chemical etching steps or electroplating in solutions with a pH value > 7.

As a result of the decay of the photoinitiator, the stability of the resist mask may even decrease (Fig. 101).

Thermal Cross-linking

In the case of positive resists, an increasingly strong thermal cross-linking of the resin takes place from about 130° -140°C, which may, in particular, increase the wet-chemical stability against alkaline media or organic solvents (Fig. 101).

In the case of negative resists, a hardbake may cause an increase in the degree of cross-linking, especially when applied at temperatures above any preceding post-exposure bake which may have taken place during the negative resist processing. If the developed negative resist structures are subjected to a flood exposure (without photo masks) prior to the hardbake, the increase in the degree of cross-linking and, thus, the wet-chemical stability of the resist sidewalls is improved at the resist sidewalls in the vicinity of the substrate where thick resist films have so far received a comparatively low exposure dose and thus have a comparable low degree of cross-linking.

Brittleness of the Resist Film

The further reduction in the residual solvent content during the hardbake reduces the elasticity of the resist structures, which react simultaneously with oxygen and begin to embrittle from about 120 -130°C. The different thermal expansion coefficients of the photoresist and the substrate can then lead, for example, in the case of thick resist films and substrates, to (with the bare eye) invisible stress cracks in the resist film, which makes them unsuitable for subsequent electroplating or wet-chemical process steps.

If neither the hardbake can be missed, nor its temperature lowered, the crack formation can be suppressed by slowly cooling the film, for example, by leaving the substrate on the hotplate switched off or in the furnace until cooled down (never put the hot substrates on a surface at room temperature!). For the same reason, the baked substrates should be handled carefully and any deformation such as bending of the substrates should be avoided.

Removability of the Resist Structures

The higher the degree of cross-linking of a resist film increases by a hardbake, the more difficult it can be removed at the end of the process. In the case of positive resists, conventional strippers like the AZ® 100 remover or organic solvents reach their limits from hardbake temperatures of approx. 150 - 160°C, and their dissolution capacity can already be greatly worsened with the cross-linked negative resists already at 130 - 140°C.

For the removal of cross-linked resist structures, we recommend the correspondingly suitable high performance remover from the TechniStrip® series.

Hardbake necessary?

The high wet-chemical stability of AZ® and TI resists together with an optimal substrate pretreatment in many cases makes a hardbake unnecessary, which simplifies process management and helps to make subsequent wet-chemical processes more reproducible. Whether a hardbake is necessary and if so, at what temperatures, should be critically questioned for each process.

In critical processes (e.g. mesa etching with HNO_3) or the necessity to further minimise the degree of under-etching, a hardbake at temperatures > 130°C is often indispensable.

Reflow

Definition and Fields of Application

While the thermal softening (*Reflow*) of developed photoresist structures above their softening point, for example, during the coating of the resist mask for later lift-off is undesirable, it is sometimes used in the micro-optics: Through the reflow, spherical or cylindrically rounded resist structures are transferred via dry etching into the substrate, where, for example, microlenses can be realised.

Softening Temperatures of Photoresists

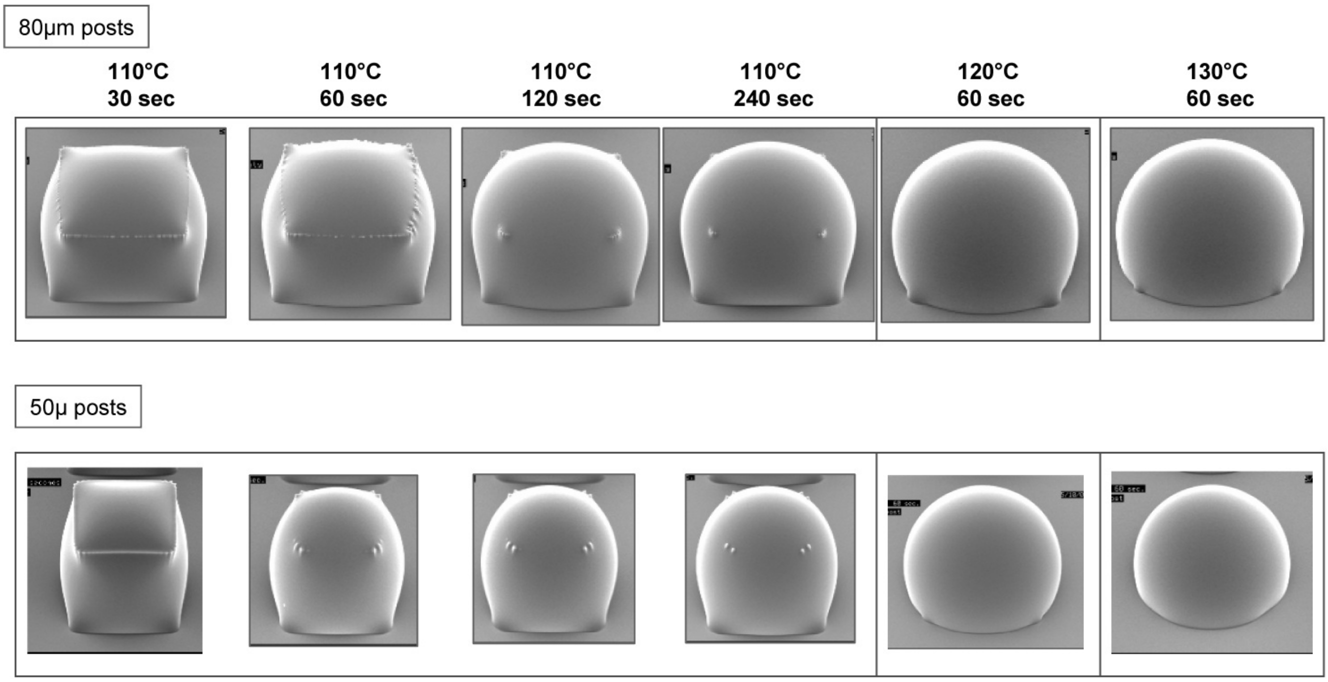


Fig. 102: The thermal softening (reflow) of developed rectangular resist structures from the AZ® 40 XT at different temperatures and times for 80 µm resist film thickness (above) and 50 µm resist film thickness (below). The figures are taken from the data sheet 'AZ® 40XT-11D Thermal Flow' from the manufacturer.

The temperatures required for reflow depend on the resist system. The AZ® 1500 thin-film series (AZ® 1505, 1512HS, 1514H, 1518) as well as the thicker AZ® 4500 series (AZ® 4533 and 4562) and the AZ® 9260 soften from approximately 100 - 110°C on, while the more thermally stable resists of the AZ® ECI 3000 series only from 110 - 120°C, the AZ® 701 MiR and 5214 E only soften beginning at 130 - 135°C. Cross-linked negative resist structures from the AZ® 15 nXT or the AZ® nLOF 2000 series do not thermally reflow at all. In the case of higher temperatures, the AZ® 125 nXT causes the evaporation of volatile resin components to shrink, which can resemble the rounding of resist structures.

The exact softening temperature also depends on the residual solvent content. At least 10 - 20°C below this temperature, the resist begins to deform when the mechanical stresses caused by the softbake (solvent loss) and exposure (gas formation) relaxes.

Attained Form of the Resist Structures

During reflow, as a simple model, the resist structure attempts to minimise its surface area to the air while maximising the interface to the substrate. The influence of both mechanisms depends on the ratio of cohesive forces in the resist to the adhesion forces between resist and substrate. With a very large ratio of the cohesive to adhesive force (corresponding to a very poor resist wetting), resist beads would theoretically form on the substrate, whereas a dominant adhesive force (very strong resist adhesion) would lead to the resist structure attempting to wet the substrate over a large area.

Under real conditions, the formation of a resist lens is only possible with a certain aspect ratio (height:

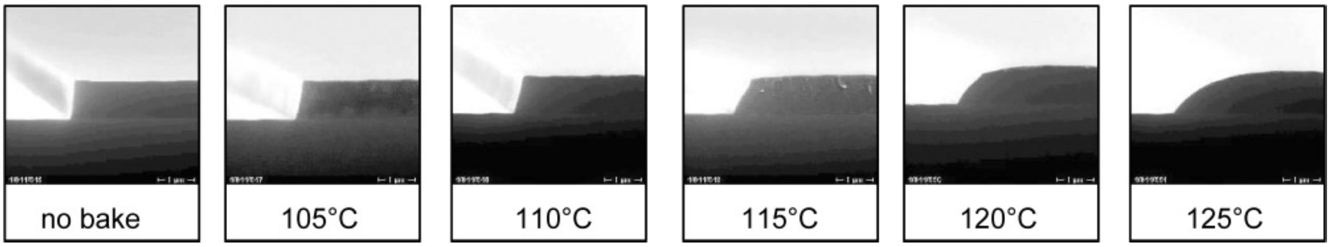


Fig. 103: Cross-sections of thermally softened AZ® ECI 3027 resist structures (increasing temperature from left to right) (Source: AZ® ECI 3000 Product Data Sheet by the manufacturer)

width of the developed resist structure). With small aspect ratios, a "donut-shaped" structure sometimes forms with a bulged edge and a central depression. This is also due to the fact that during the reflow, the mechanical properties of the resist change: The residual solvent loss and possibly an initial thermal cross-linking of the resin of the resist slow down the reflow during the annealing and finally "freeze" the attained form.

Deep UV Hardening

The Purpose and Objectives

If developed photoresist structures are heated over their softening temperature during coating (thermal evaporation, sputtering) or dry etching, the resist structure starts to soften. If the temperature cannot sufficiently be lowered, the softening temperature can be raised by means of deep-UV hardening, from which the resist structures start to soften.

Mechanism and Limits

Radiation around 250 nm wavelength breaks resin molecules of the photoresist, subsequent heating (stepwise or ramp-shaped on a hotplate, starting below the softening point followed by 10°C steps upwards) leads to cross-linking of the resist structures.

Due to the low penetration depth of the short-wave radiation, a few 10 nm thick, cross-linked "crust" is formed on the resist surface which protects the photoresist structure to a certain degree from thermal flow. If there is no special radiation source for deep UV radiation, a standard mask aligner can also be used for g-, h- and i-line exposure. Here, however, the proportion of radiation around 250 nm is so small that a flood exposure (without mask) may be necessary for several hours in order to show a (possibly still small) impact.

It should be noted that the removability of the photoresist film through the cross-linked surface can be significantly worsened.

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® 2026 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® 2026 MIF	
		AZ® PL 177	AZ® PL 177	≈ 3 - 8 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF	
	Spray coating	AZ® 4999		≈ 1 - 15 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF	
	Dip coating	MC Dip Coating Resist		≈ 2 - 15 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 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® 2026 MIF	TechniStrip® NI555 TechniStrip® NF52 TechniStrip® MLO 07
		AZ® nLOF 5500	AZ® nLOF 5510	≈ 0.7 - 1.5 µm		
	Improved adhesion, steep resist side-walls 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® 2026 MIF	
			AZ® 125 nXT	≈ 20 - 100 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF	TechniStrip® P1316 TechniStrip® P1331 TechniStrip® NF52 TechniStrip® MLO 07

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.

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.

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. Not compatible with Au.

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

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

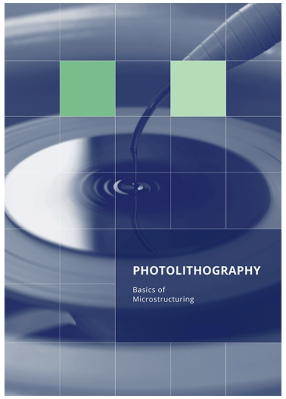
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

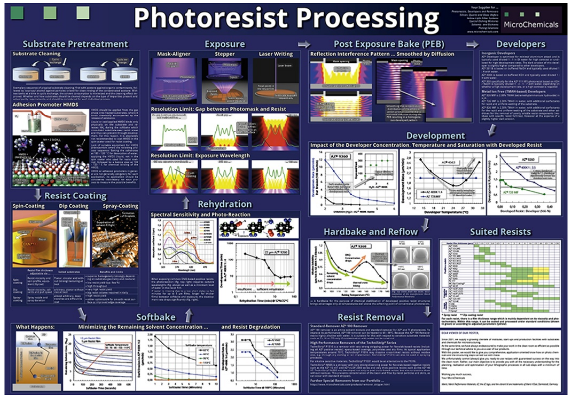
Further Information

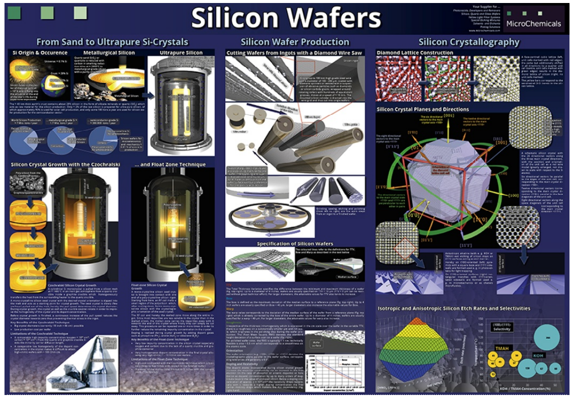
Technical Data Sheets: www.microchemicals.com/downloads/product_data_sheets/photoresists.html

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

Our Photolithography Book and -Posters







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