IMAGE REVERSAL RESISTS AND THEIR PROCESSING

Image reversal resists can be processed both positively and negatively and are therefore also suitable for users who want to process one resist in both modes. This chapter focuses on the special features of the processing of image reverse resists.

Basics on Image Reversal Resists

Application Areas

In image reversal mode, undercut resist sidewalls can be attained with suitable process parameters. The main application area for this is lift-off processes in which the undercut reduces or prevents the covering of the resist edges with the deposited material, which allows a clean lifting of the resist structures.

In the image reversal baking step, a small improvement of the thermal as well as chemical resistance of the photoresist can be attained. As a result, moderate advantages in processing can be seen in wet or dry etching as well as in electroplating. However, these advantages are usually compensated by the disadvantages of the more time-consuming image reversal resist processing, such as additional process steps and the difficulty or impossibility of obtaining perpendicular resist sidewalls. Therefore, it makes sense to instead optimise the appropriate positive resist process for most of the processes which do not require any undercut resist sidewalls.

Process Sequence

Compared to positive resists, the image reversal baking step and flood exposure process steps are additionally required, which render the first exposed areas insoluble in the developer and then make the areas that have not yet been exposed able to be developed.

Without these two steps, the image reversal resist behaves like an ordinary positive resist with correspondingly positive resist sidewalls; undercut resist sidewalls can only be attained in the image reversal mode.

The first Exposure

The first, structure-defining exposure is done with a photo mask exposing the resist areas remaining on the substrate after development. The photo mask is therefore inverted compared to masks for positive resists. The exposure dose strongly impacts the attained resist profile:

Low Light Doses

The larger the resist film thickness compared to the penetration depth of the light (e. g. 1 - 2 µm for the AZ® 5214E and TI 35ESX), the more pronounced is the depth profile of the received light dose in the resist film. In the case of low light doses, resist areas near the substrate receive substantially less light than the resist surface and later remain largely soluble in the developer, resulting in a more pronounced undercut of the resist profile.

If the exposure dose is too low, the image reversal bake step cannot convert even the surface-near resist which increases its erosion rate in the developer. As a result the resist film can strongly thin out when developing, which in turn, reduces the undercut.

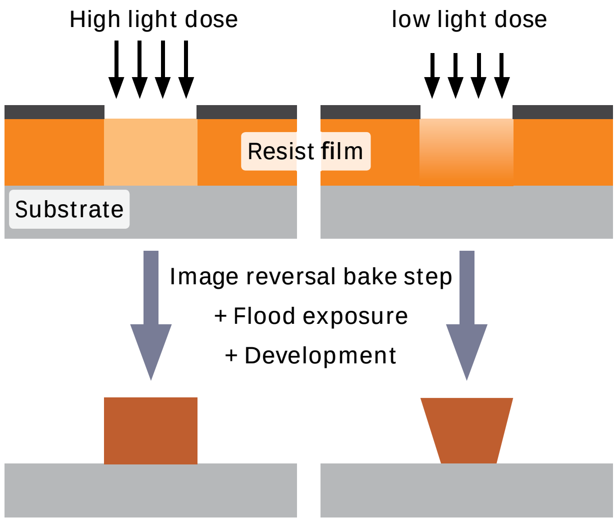

Fig. 104: The lower the dose of the first exposure in the image reversal resist processing, the more pronounced (tendency) the undercut attained after development.

High Light Doses

High exposure doses homogeneously expose the resist film towards the substrate, the resist profile shows almost no undercut.

An exposure dose too high also illuminates nominal

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dark resist areas via scattering, diffraction, or reflection. As a consequence, the resist structures remaining after development are much larger than desired. In extreme cases, the development of narrow spaces will become more and more difficult or impossible.

The Image Reversal Bake Step

What Happens in the Resist

During the image reversal bake step, the substrate is heated after exposure. Hereby, the exposed areas of the resist lose their ability to develop, while the unexposed areas remain photoactive. The optimal baking parameters depend on the resist and the desired profile of the resist profile and are typically 110 - 130°C for a few minutes, details can be found in the respective technical data sheet.

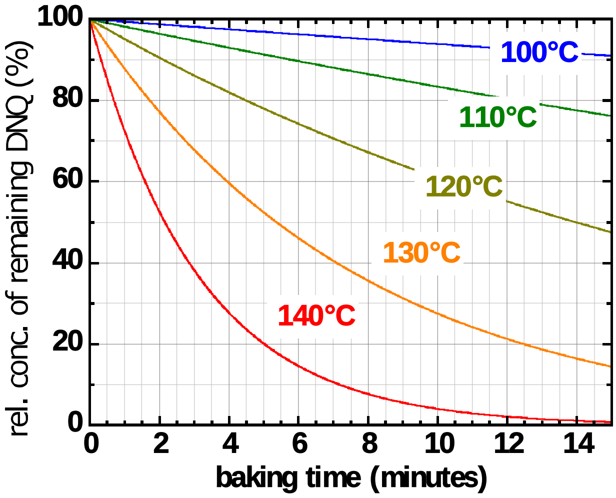


Fig. 105: With the image reversal bake step, a baking temperature and time-dependent part of the photoinitiator is destroyed.

Influence of Baking Parameters

Low bake temperatures (or/and short baking times) mainly convert the strongly exposed resist surface, thus resulting in a rather pronounced and progressive undercut. Too low bake temperatures (-times) cannot convert even the highly-exposed surface-near part of the resist film, causing a strong erosion of also the exposed resist in the developer which thins out the resist film, lowers the dimensional accuracy and possibly develops an undercut.

High bake temperatures (-times) also convert the weakly exposed (substrate-near) resist area, which is why the resist profile attained during development shows a less pronounced undercut.

Too high bake temperatures (- times) thermally decompose a significant part of the photoinitiator in the resist not yet developed (Fig. 105), which means that after the flood exposure the resist can only be developed with a slower rate.

Formation of Bubbles in the Resist Film

The photochemistry of the AZ® 5214E and TI image reversal resists is DNQ-based which is why nitrogen is released during the exposure. If the latter did not have time to diffuse out of the resist film after exposure, the bubble formation may occur during the image reversal baking step promoted by the softening of the resist. These may become visible only after development over crater-like structures in the resist profiles.

It is therefore important to allow the nitrogen formed during exposure to be outgassed before the reversal baking step. The required delay for this depends on the resist and very much on its film thickness, and lies within the range of minutes (for approximately 1 to 2 µm thick resist films) to hours (> 10 µm film thickness). This makes it especially advisable in the case of large resist films to consider an alternative use of negative resists such as the AZ®nLOF 2000 series, optimised for lift-off processes, which do not release gases during exposure.

Influence of Substrate and Equipment

For stable image reversal resist processes, the reverse baking temperature should be kept constant at ± 1 - 2°C during defined times. This condition is difficult to comply with when baking in convection ovens, which is why the use of a hotplate is strongly recommended for critical processes.

When a hotplate is used, the temperature profile obtained on the substrate surface (= in the resist film) is sensitive to the nature of the substrate. Therefore, the image reversal baking parameters should be optimised individually when using massive or poorly thermally conductive substrates, or a gap between substrate and hotplate.

The Flood Exposure

Purpose of the Flood Exposure and Recommended Minimum Dose

During the flood exposure following the image reversal back step without mask, the resist areas which have not yet been exposed are also exposed and can thereby later be developed. In order to attain an undercut of the resist profile extending as far as the substrate, the (substrate-near) resist areas should also be given a sufficient light dose. An overexposure does not damage the process since the already exposed areas of the resist are no longer photosensitive due to the reversal baking step. Therefore we recommend a flood exposure dose at least twice to three times as high as would be required to expose the same resist film in positive mode.

Good to Know ...

Especially in the case of thick resist films (approx. > 3 µm), the same things have to be taken into account in the flood exposure, which are also relevant for the exposure of thick positive resists:

Since the resist is anhydrous after the reversal baking step, the exposure of DNQ-based resists requires a minimum dose of water, the need for a prior rehydration also applies to the flood exposure.

Due to the relatively high dose of the flood exposure, bubble or crack formation can result from the released nitrogen during exposure.

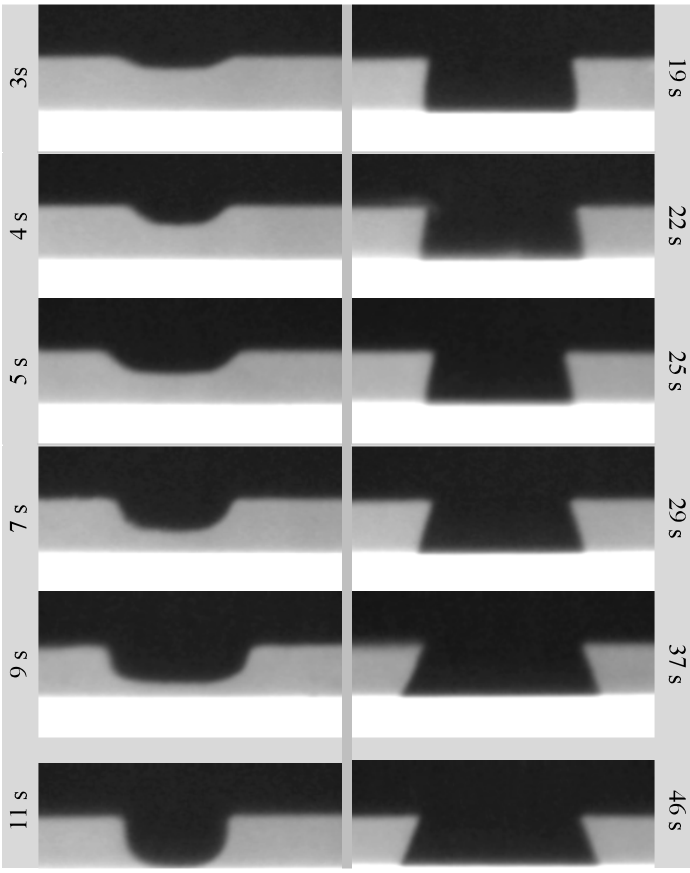


Fig. 106: This series of cross-section images in different stages of development shows how the undercut develops mainly after the development. The time specification given refers to the development start.

Development

Development Rate

The development rate mainly depends on the resist used and the parameters time and temperature of the image reversal bake step.

The hotter and longer this took place, the greater the fraction of the photoinitiator decomposed thermally. A development rate > 1 µm/minute is desirable in conventional developer compositions, but not a necessity.

Formation of the Undercut

The degree of over-development (the development time after the substrate is free-developed in relation to the entire development time) significantly impacts the undercut: Fig. 106 shows on the basis of a chronological development series how the undercut becomes more and more pronounced after the resist film is already freely developed.

An over-development of 30 % is a good starting point for your own optimisations. In case of high aspect ratios, one has to take care that the undercut does not ‘short-circuit’ small/narrow resist structures and thereby lift them from the substrate.

Sufficient Resist Film Thickness

In the case of directed evaporation, the thickness of the applied material may even exceed the thickness of the resist film. The reason for this is the fact that the evaporated material slowly grows together over the free areas thus forming a tapering shadow mask for the following material (Fig. 107). However, in order to make the lift-off simple and clean, it is advisable to keep the resist film thickness much greater than that of the applied material. This applies even more to undirected sputtered layers, in which the resist sidewalls are always also coated.

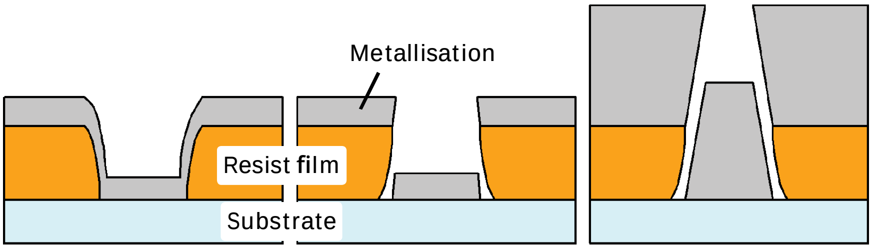


Fig. 107: With undercut resist profiles of an image reversal resist and directed evaporation, the applied thickness can be at least theoretically greater than the thickness of the resist film (right).

The upper limit of the resist film thickness is defined by the required resolution as well as the greater complexity of the processing of thick resist films.

Image Reversal Resists or Negative Resists?

In contrast to image reversal resists, negative resists can only be processed negatively. They do not require flood exposure, which simplifies the process sequence. In addition, for example, the AZ® nLOF 2000 negative resist series as well as the also negative AZ® 15 and AZ® 125 nXT do not have DNQ as a photoinitiator, eliminating the need to wait for nitrogen to outgas or rehydration.

The strong cross-linking of negative resists also makes the resist structures thermally and chemically more stable than the resist profiles of image reversal resists, which are inert in the developer and, are, at most moderately cross-linked, which prevents a rounding during the metallisation. Due to the cross-linking, negative resists are also more difficult to strip or lift, in particular when process temperatures occurring prior exceed 130-140°C.

Please contact us if you are unsure as to whether an image reversal or negative resist is more suitable for your process!

Suitable Reversal Resists

AZ® 5214E

AZ® 5214E is a thin, high-resolution image reversal resist with 1 - 2 µm resist thickness. Even thinner film thicknesses can be attained and processed by means of a dilution of the resist, but it becomes increasingly difficult with an decreasing resist film thickness to attain an undercut: If the penetration depth of light significantly exceeds the resist layer thickness, the resist is exposed almost homogeneously to the substrate without gradient of the absorbed dose.

TI 35E and TI 35ESX

TI 35ESX follows the AZ® 5214E with a thickness of 3 - 5 µm. The processing of even thicker films is increasingly critical because of the formation of nitrogen during exposure which can cause bubbles in the subsequent image reversal bake.

TI XLiftX

TI xLift allows resist thicknesses also over 10 µm. However, as the resist thickness increases, the process becomes ever more time-consuming for rehydration or for the outgassing of the nitrogen formed during exposure. Thus a reasonable alternative for most applications would be the AZ®® nLOF 2070 negative resist.

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 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® 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

[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. 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

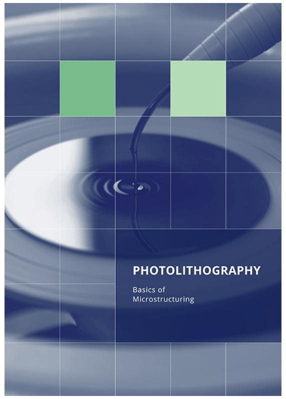
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

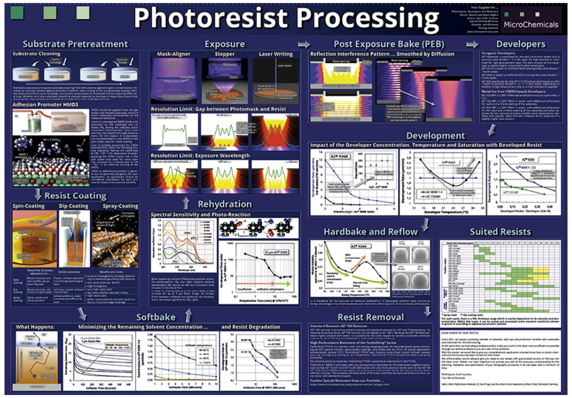
Further Information

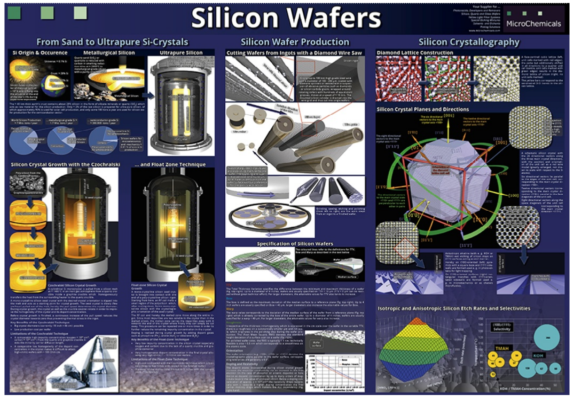
Technical Data Sheets: www.microchemicals.com/downloads/product_data_sheets/photoresists.html

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

Our Photolithography Book and -Posters







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