PROCESSING OF AZ® NEGATIVE RESISTS

With negative resists, in contrast to positive resists, the non-exposed areas are developed away, the exposed areas remain after development. Thus negative resists show a similar behaviour as image reversal resists in the negative mode, but with a significant difference: In contrast to most reversal resists, the exposed negative resists cross-link which impacts their chemical and thermal stability, but also the possibilities of removing the resist structures at the end of the lithography process.

Exposure

Spectral Sensitivity:

The AZ® nLOF 2000 negative resist series as well as the AZ® 15 nXT and 125 nXT are i-line resists with a sensitivity in the wavelength range of approx. 340 - 380 nm. However, the g- and h-line need not be filtered out during the exposure, these wavelengths are largely transmitted by the resist film.

Chemical Amplification

The AZ® 15 and 125 nXT are chemically amplified, i.e. several cross-linking reactions are carried out in the resist per absorbed photon. The absorption coefficient of the resist can thus be kept so low that even very thick resist films of a few 10 µm (in the case of the AZ® 15 nXT) up to several 100 µm (AZ® 125 nXT) can be exposed with moderate light doses.

Light Dose

A too low light dose leads to an incomplete cross-linking or, in the case of optically thick resist films, the cross-linking does not reach the substrate. This increases the erosion of the exposed resist structures in the developer, but this may be desirable in the case of lift-off processes for the resist areas to form a negative resist profile near the substrate.

In the case of over-exposure, resist areas are also exposed and cross-linked by diffraction, scattering or reflection on the substrate, which should remain nominally unexposed. As a result, the developed resist structures are widened to the effect that narrow openings can no longer be cleared during development.

Bleaching

Contrary to DNQ-based resists, AZ® negative resists do not bleach. With the rel. strong absorbing AZ® nLOF 2000 resists with an i-line penetration depth of 1 - 2 µm, this manifests itself in the impossibility of exposing thick resist films of approx. > 10 µm towards to the substrate. As a result, the resist areas in the vicinity of the substrate do not cross-link, remain soluble in the developer, and thus allow an especially advantageous resist profile which is progressively undercut for lift-off processes.

Post Exposure Bake

Processes in the Resist Layer

In the resists of the AZ® nLOF 2000 series or the AZ®15 nXT, the exposure activates a melamine crosslinker, which in a subsequent baking step (Post Exposure Bake, PEB) affects the linking of short phenolic resin molecules to longer chains. Without the PEB, no appreciable cross-linking takes place, that is, in the developer, the exposed resist areas would be dissolved at a similar rate as the unexposed resist.

With the AZ® 125 nXT, the exposure starts a photo polymerisation of acrylic monomers already at room temperature. This resist does not require a post exposure bake.

Bake Parameters

The recommended PEB parameters of temperature and time depend on the photoresist used and are typically 110 - 125°C for 1 - 2 minutes.

The cooler or shorter the baking, the weaker the degree of cross-linking and the greater the erosion of the exposed resist areas later in the developer.

In the case of excessively high temperatures or too long PEB times, a thermal cross-linking of non-exposed resist areas takes place, which thus can be developed much more slowly. In the case of the desire

As in the image reversal baking step of image reversal resists (see previous chapter), the PEB temperature usually should be kept constant at ± 1 - 2°C for stable negative resist processes during defined times. This condition is difficult to maintain when baking in ovens, which is why the use of a hotplate is strongly recommended at least for critical processes.

With the use of a hotplate, the temperature progression attained on the substrate surface (= in the resist film) is sensitive to the nature of the substrate. Therefore, the post exposure baking parameters should be optimised individually when using massive or poorly thermally conductive substrates, or a gap between hotplate and substrate.

Developing, Lift-off and Stripping

Appropriate Developers

For the above mentioned AZ® negative resists, we recommend TMAH-based developers such as AZ® 326, 726 or 826 MIF, as well as the AZ® 303. NaOH - or KOH-based developers such as AZ® 351 B or 400 K while work well enough in some cases, cannot generally be recommended as first choice.

Appropriate Strippers

Organic solvents such as NMP or DMSO, are generally suitable for removing the resist film, but conventional strippers, such as the AZ® 100 Remover can also be used if the degree of cross-linking is not too high. Depending on the thickness of the resist film and the degree of cross-linking, these substances should be heated to 60 - 80°C.

Especially in the case of highly cross-linked films, the TechniStrip® products are much more suitable as stripper or lift-off medium. Additionally, support by a ultrasonic bath may be necessary for residual-free resist removal.

Low-boiling solvents are theoretically also suitable as strippers, but because of the impossibility of their use at higher temperatures, they are restricted in their performance.

Suitable Lift-off Media

For the lift-off, the same recommendations apply, with the exception of the AZ® 100 remover, which is not a well suited media for this process step.

Areas of Application of Negative Resist

AZ® NLOF 2000

The AZ® nLOF 2000 negative resist series is optimised for lift-off applications. In the resist film thickness range of approximately 1 to 15 µm, an undercut which can be adjusted to a limited extent can be attained, which becomes increasingly progressive in the case of larger resist thicknesses (Fig. 108) since hereby the substrate-near resist keeps unexposed, thus non-cross-linked and soluble in the developer.

Due to their cross-linking, the resist structures are not thermally softened even at high temperatures, but the evaporation temperature should not exceed 140 - 150°C. Because the degree of cross-linking rises so

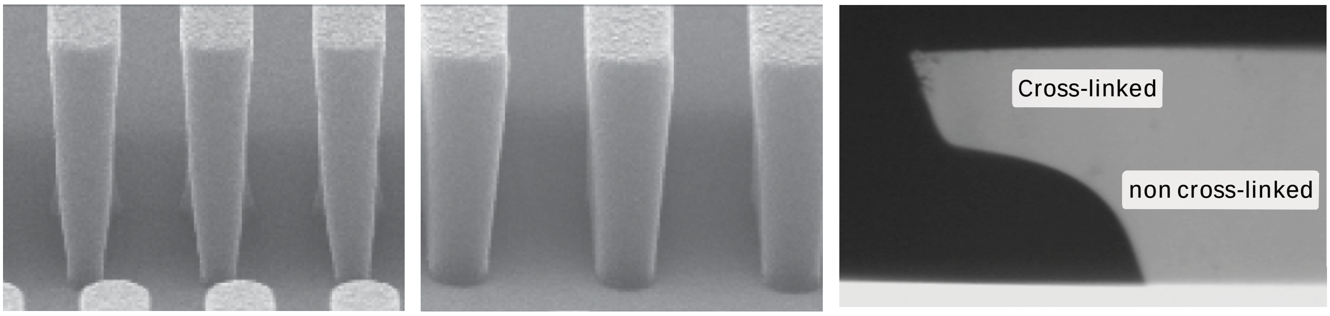


Fig. 108: Left: 700 nm resist bars with a 2.0 µm thick AZ® nLOF 2020. Centre: 900 nm resist lines with a 3.5 µm thick AZ® nLOF 2035. Source: AZ® nLOF™ 2000 product Data Sheet by the manufacturer. Right: If the AZ® nLOF 2070 is applied on large thicknesses (here: 22 µm), a very pronounced undercut results since the substrate-near resist keeps non-cross-linked and thus developable.

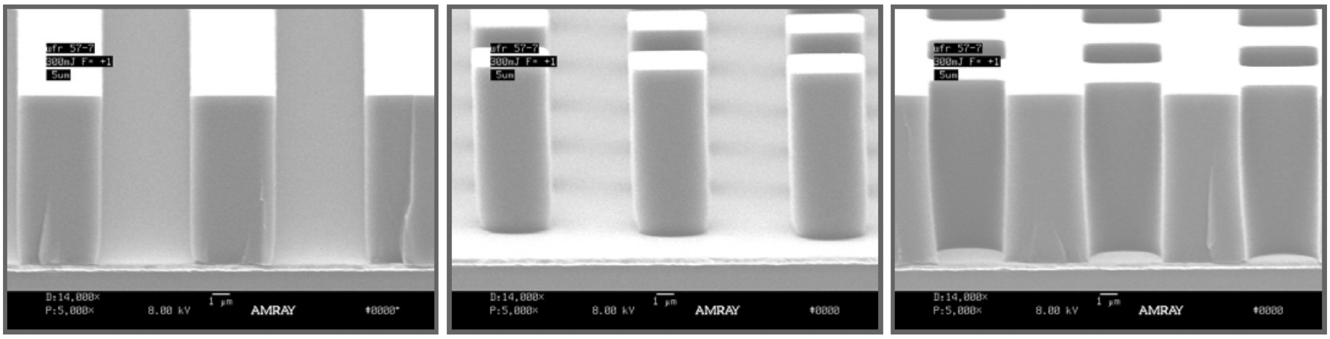


Fig. 109: 5 µm wide bars, rectangular columns and rectangular openings developed from a 10 µm thick AZ® nXT 15 (Source: Technical data sheet from the manufacturer)

much that a lift off is very difficult. The TechniStrip® NI555 is advisable as a lift-off medium or stripper for strongly cross-linked resist film.

AZ® 15 NXT

The AZ® 15 nXT allows vertical resist sidewalls in the range of approx. 5 - 25 µm of resist film thickness. Due to its high chemical stability and good adhesion to conventional substrate materials, it is particularly suitable for electroplating. For highly cross-linked resist films, the TechniStrip® NI555 is recommended as a stripper.

AZ® 125 NXT

The AZ® 125 nXT extends the application range of the AZ® 15 nXT to resist film thicknesses of approx. 30 - 150 µm. Film thicknesses of several 100 µm can also be attained via adapted processes. For high resist film thicknesses and/or highly cross-linked resist films, the TechniStrip® P1316 or 1331 is recommended as a stripper.

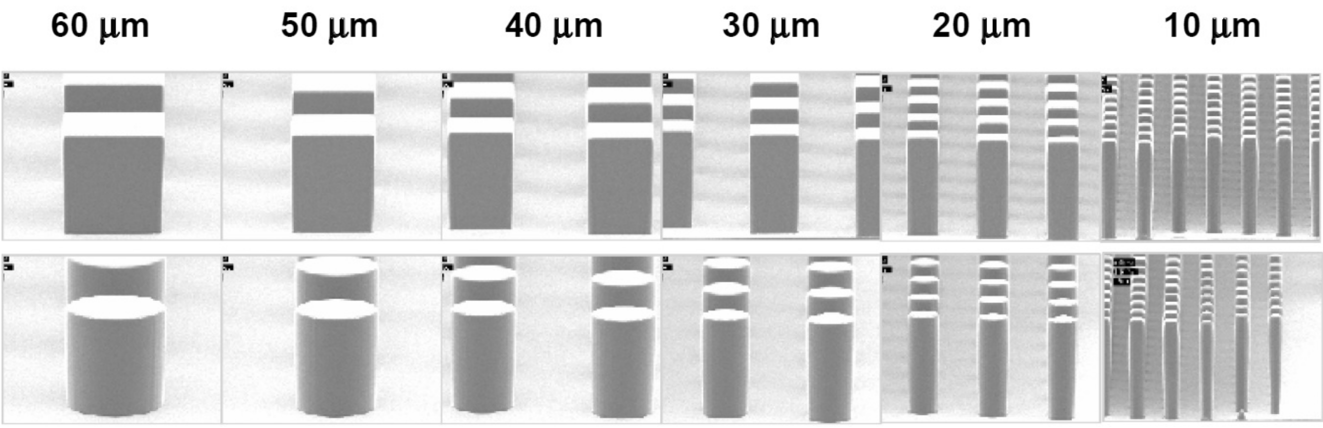


Fig. 110: From the left to the right increasingly finer structures developed from a 60 µm thick AZ® 125 nXT show their potential with regard to a high aspect ratio (Source: Technical data sheet from the manufacturer)

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 Re-versal	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

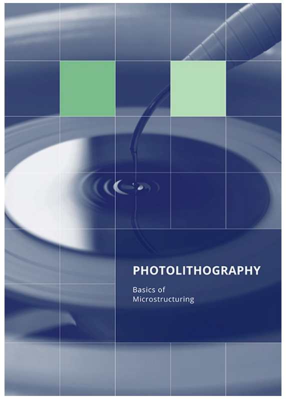
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

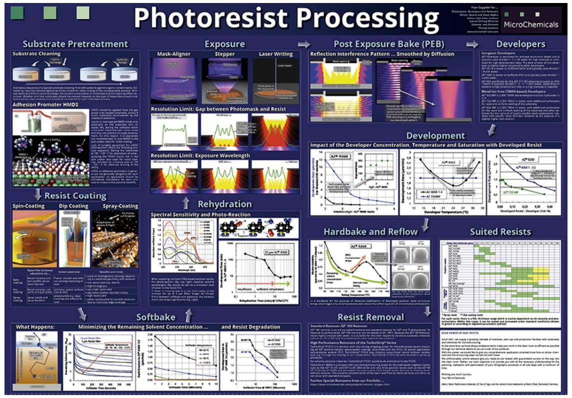
Further Information

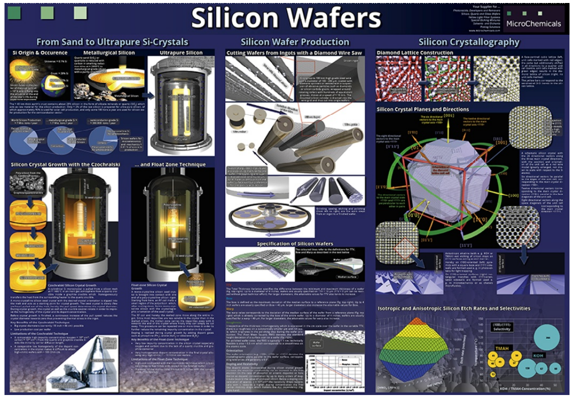
Technical Data Sheets: www.microchemicals.com/downloads/product_data_sheets/photoresists.html

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

Our Photolithography Book and -Posters







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):

www.microchemicals.com/downloads/brochures.html

www.microchemicals.com/downloads/posters.html

Thank you for your interest!

Disclaimer of Warranty & Trademarks

All information, process descriptions, recipes, etc. contained in this document are compiled to the best of our knowledge. Nevertheless, we can not guarantee the correctness of the information. Particularly with regard to the formulations for chemical (etching) processes we assume no guarantee for the correct specification of the components, the mixing conditions, the preparation of the batches and their application.

The safe sequence of mixing components of a recipe usually does not correspond to the order of their listing. We do not warrant the full disclosure of any indications (among other things, health, work safety) of the risks associated with the preparation and use of the recipes and processes. The information in this book is based on our current knowledge and experience. Due to the abundance of possible influences in the processing and application of our products, they do not exempt the user from their own tests and trials. A guarantee of certain properties or suitability for a specific application can not be derived from our data. As a matter of principle, each employee is required to provide sufficient information in advance in the appropriate cases in order to prevent damage to persons and equipment. All descriptions, illustrations, data, conditions, weights, etc. can be changed without prior notice and do not constitute a contractually agreed product characteristics. The user of our products is responsible for any proprietary rights and existing laws.

Merck, Merck Performance Materials, AZ, the AZ logo, and the vibrant M are trademarks of Merck KGaA, Darmstadt, Germany

MicroChemicals GmbH
Nicolaus-Otto-Str. 39
89079, Ulm
Germany

Fon: +49 (0)731 977 343 0
Fax: +49 (0)731 977 343 29
e-Mail: info@microchemicals.net
Internet: www.microchemicals.net