

## REHYDRATION

*The photochemistry of certain resists requires water in the resist film during exposure as an indispensable precursor, but this is not available in sufficient quantities immediately after the softbake. This chapter describes the required water resumption known as rehydration of the resist film by its purpose, implementation and the possible consequences of inadequate rehydration.*

### Chemical and Physical Processes in the Resist Film

#### The Role of Water in the Photoreaction

Photoresists with a photoinitiator based on DNQ-sulphonates such as almost all AZ<sup>®</sup> and TI positive and image reversal resists, except for certain chemically amplified resists such as the AZ<sup>®</sup> 40 XT, require a certain minimum concentration of water of a few per thousand during exposure for the photoreaction.

However, after the softbake water is not present in sufficient quantity in the resist film and must be fed back to it via the *rehydration* in order to give the subsequently exposed areas a sufficiently high development rate.

#### Process of Rehydration

The source of the water for rehydration is the atmosphere in the clean room, which at room temperature contains some 10 g of water per m<sup>3</sup> depending on the relative humidity.

The diffusion of the water molecules adsorbed onto the resist surface into the resist film ultimately leads to a uniform water concentration between the resist surface and the substrate.

As a diffusion-limiting process, the time required for this quadratically increases with the resist film thickness. The homogeneous water concentration attained after the theoretically arbitrary length of time depends on the air humidity above the resist film.

#### Effects of Insufficient Rehydration

Fig. 74 shows how strong the entire development time increases in the case of insufficient rehydration based on a 22 µm AZ<sup>®</sup> 9260 film:

If the delay between the softbake and exposure is too short, the entire development requires more than two hours. A wait time of 10 minutes in contrast, is adequate for the entire water absorption over the entire resist film thickness for a sufficiently short development time.

Fig. 73 confirms, based on the time-resolved determined development rate of the same 22 µm AZ<sup>®</sup> 9260 resist film, that the rehydration is in fact a diffusion process of water molecules starting from the resist surface: After only five minutes of rehydration, only the upper resist films can be developed

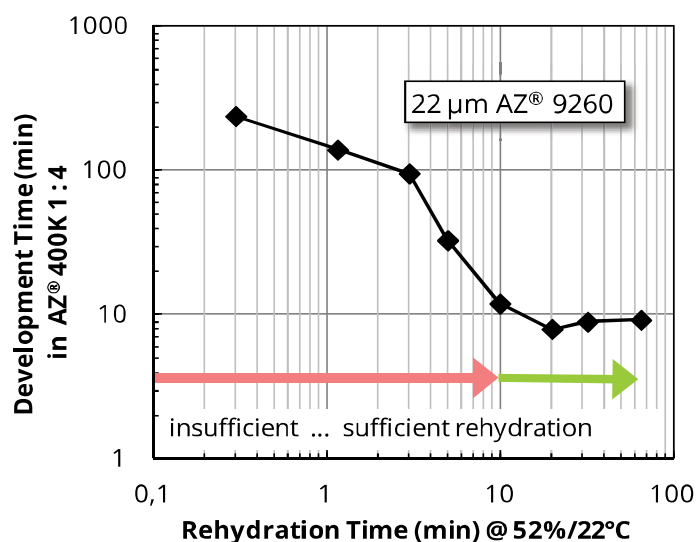


Fig. 74: A too short rehydration leaves virtually water-free substrate near resist areas and increases the necessary time for the development by many orders of magnitude.

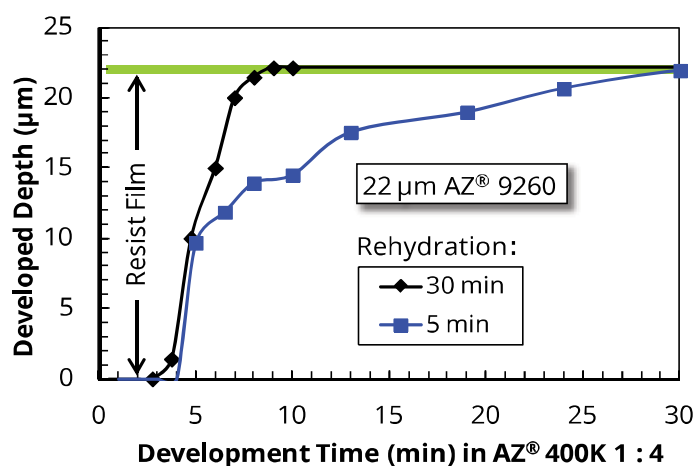


Fig. 73: The time-resolved developed depth of two differently long rehydrated photoresist films

rapidly, after which the development rate in the areas near the substrate which are still free of H<sub>2</sub>O decreases strongly (blue graph). With a sufficient waiting time between softbake and exposure, the film develops uniformly at a sufficiently high rate (black graph).

### Conditions for Sufficient Rehydration

#### The Time

The time it takes until a sufficient amount of water molecules is diffused through the resist film to the substrate mainly depends on the resist film thickness at a given temperature.

Fig. 75 represents the results of a numerical simulation of the diffusion process on differently thick resist films in a time-resolved manner, whereby the still water-free resist is shown in red and after complete rehydration, in blue. While a 1 µm thick resist film is sufficiently rehydrated after only a few seconds, a 7 µm thick film requires one minute, and several 10 µm thick resist films require several hours.

#### The Humidity

The air humidity at the location of the resist-coated substrates determines the level at which the water concentration adjusts in the resist film after an arbitrary waiting time. Even after several hours in air, also thin resist films do not rehydrate when it is too dry in the clean room, since the balance between water absorption and evaporation is at a too low level.

We recommend a relative humidity of 40 - 50% for a sufficient rehydration. Lower values lead to a significant drop in the development rate, while higher values can hardly further improve the rehydration, but can lead to a worsening of the resist adhesion by accelerated adsorption of water to the substrate surface before resist coating takes place.

The rehydration should never take place in a saturated water vapour atmosphere or directly in water. Here, the resist film is so saturated with water that it can lead to severe bubbling during subsequent exposure through the nitrogen thereby formed.

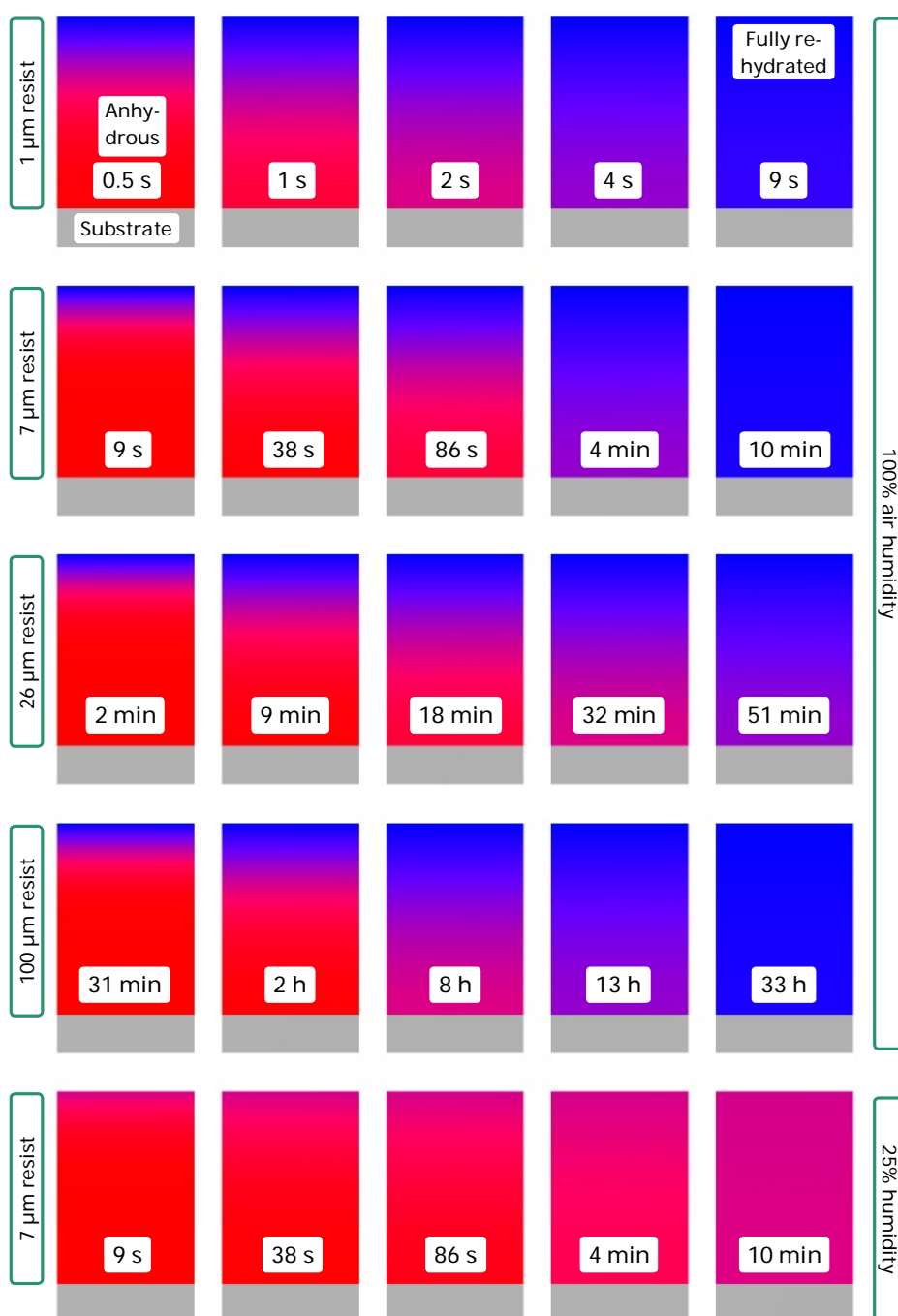


Fig. 75: The rehydration time to attain an equilibrium water concentration in the resist is diffusion-limited and increases quadratically with the film thickness.

If the rehydration is carried out in a different (moister) room than the following exposure, it must be noted that the resist film loses water as quickly as it has absorbed during the rehydration on the way to the exposure tool. Especially in the case of thin resist films, the air humidity at the site of the exposure tool determines the extent of the rehydration and the later development result.

### The Temperature

Higher temperatures accelerate the process of thermally activated diffusion and thus shorten the time within which the water molecules diffuse through the resist film to the substrate. On the other hand, higher temperatures promote the evaporation rate of water from the resist film which reduces the final water concentration.

## Rehydration of Thick Photoresist Films

### Thin and Thick Photoresist Films

The basic necessity of rehydration does not depend on the resist film thickness; but with thin resist films of only a few  $\mu\text{m}$ , a mechanism that is hardly dominant in the process sequence for various reasons:

On the one hand, the necessary time for the rehydration of thin resist films with less than one minute is a time which is usually applied between the softbake and exposure. On the other hand, thin resists usually have a significantly higher concentration of photoinitiator than thick resist and therefore develop notably more rapidly, additionally faster due to the lower resist film thickness.

### Consequences of Insufficient Rehydration in the Case of Thick Resists on the Resist Profile

Fig. 76 shows the effect of missing or too short rehydration on the developed resist profile. While the development rate between the resist surface and the substrate depends on the depth profile of the water concentration before the exposure, the dark erosion which is independent of it, contributes both laterally and vertically to the unexposed resist.

The higher the development rate up to the substrate, that is, the more complete the rehydration, the more steep resist sidewalls are possible. If, due to a too short waiting time between the softbake and exposure, only the upper resist areas are adequately rehydrated, the resist film will develop slower and slower in depth, that is, the upper resist areas are exposed to the dark erosion for a disproportionate time.

### Measures for the Rehydration of Thick Photoresist Films

As represented in Fig. 75, thick resist films of several  $10\ \mu\text{m}$  require rehydration times of several hours which are hardly practical.

A higher humidity does not change the duration of the diffusion of the water molecules from the resist

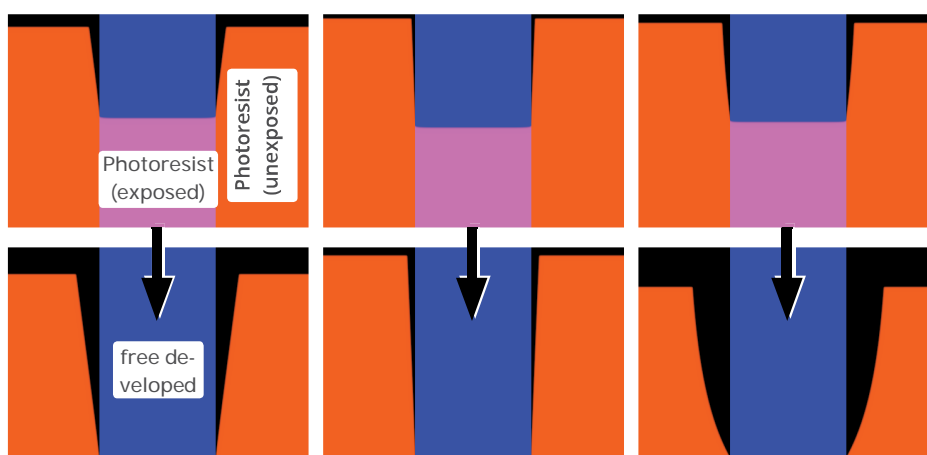


Fig. 76: A numerical simulation of the chronological sequence of the development of positive resist films which are differently rehydrated.

Left: Inclined resist sidewalls from a constantly low development rate due to air which is too dry or missing rehydration.

Centre: Steep resist sidewalls from a constantly high development rate due to sufficiently long rehydration with sufficient humidity.

Right: A tub-shaped profile from an initially high development rate which continues to diminish due to a too short rehydration with sufficient humidity.

surface to the substrate. A higher exposure dose is useless if the photoreaction lacks sufficient water. A sharper developer concentration shortens the duration of the development of insufficiently rehydrated photoresist films, but increases the dark erosion (see Fig. 97 on page 91) disproportionately strongly and thus further deteriorates the resist profile attained.

For photoresist films of several 10 µm resist thickness or more, resists with a photochemistry independent of a rehydration such as the AZ<sup>®</sup> 40 XT are recommended for films between about 15 and 100 µm.

## Our Photoresists: Application Areas and Compatibilities

Recommended Applications <sup>1</sup>		Resist Family	Photoresists	Resist Film Thickness <sup>2</sup>	Recommended Developers <sup>3</sup>	Recommended Re-movers <sup>4</sup>
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls	AZ <sup>®</sup> 1500	AZ <sup>®</sup> 1505 AZ <sup>®</sup> 1512 HS AZ <sup>®</sup> 1514 H AZ <sup>®</sup> 1518	≈ 0.5 µm ≈ 1.0 - 1.5 µm ≈ 1.2 - 2.0 µm ≈ 1.5 - 2.5 µm	AZ <sup>®</sup> 351B, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> Developer	AZ <sup>®</sup> 100 Remover, TechniStrip <sup>®</sup> P1316 TechniStrip <sup>®</sup> P1331
			AZ <sup>®</sup> 4533 AZ <sup>®</sup> 4562	≈ 3 - 5 µm ≈ 5 - 10 µm	AZ <sup>®</sup> 400K, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> 2026 MIF	
			AZ <sup>®</sup> P4110 AZ <sup>®</sup> P4330 AZ <sup>®</sup> P4620 AZ <sup>®</sup> P4903	≈ 1 - 2 µm ≈ 3 - 5 µm ≈ 6 - 20 µm ≈ 10 - 30 µm	AZ <sup>®</sup> 400K, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> 2026 MIF	
			AZ <sup>®</sup> PL 177	AZ <sup>®</sup> PL 177	≈ 3 - 8 µm	
	Spray coating	AZ <sup>®</sup> 4999		≈ 1 - 15 µm	AZ <sup>®</sup> 400K, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> 2026 MIF	
	Dip coating	MC Dip Coating Resist		≈ 2 - 15 µm	AZ <sup>®</sup> 351B, AZ <sup>®</sup> 400K, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> 2026 MIF	
	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ <sup>®</sup> ECI 3000	AZ <sup>®</sup> ECI 3007 AZ <sup>®</sup> ECI 3012 AZ <sup>®</sup> ECI 3027	≈ 0.7 µm ≈ 1.0 - 1.5 µm ≈ 2 - 4 µm	AZ <sup>®</sup> 351B, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> Developer	
			AZ <sup>®</sup> 9245 AZ <sup>®</sup> 9260	≈ 3 - 6 µm ≈ 5 - 20 µm	AZ <sup>®</sup> 400K, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF	
Positive (chem. amplified)	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ <sup>®</sup> XT	AZ <sup>®</sup> 701 MiR (14 cPs) AZ <sup>®</sup> 701 MiR (29 cPs)	≈ 0.8 µm ≈ 2 - 3 µm	AZ <sup>®</sup> 351B, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> Developer	AZ <sup>®</sup> 100 Remover, TechniStrip <sup>®</sup> P1316 TechniStrip <sup>®</sup> P1331
			AZ <sup>®</sup> 12 XT-20PL-05 AZ <sup>®</sup> 12 XT-20PL-10 AZ <sup>®</sup> 12 XT-20PL-20 AZ <sup>®</sup> 40 XT	≈ 3 - 5 µm ≈ 6 - 10 µm ≈ 10 - 30 µm ≈ 15 - 50 µm	AZ <sup>®</sup> 400K, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF	
Image Re-verseal	Elevated thermal softening point and undercut for lift-off applications	AZ <sup>®</sup> 5200	AZ <sup>®</sup> 5209 AZ <sup>®</sup> 5214	≈ 1 µm ≈ 1 - 2 µm	AZ <sup>®</sup> 351B, AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF	TechniStrip <sup>®</sup> Micro D2 TechniStrip <sup>®</sup> P1316 TechniStrip <sup>®</sup> 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 <sup>®</sup> nLOF 2000	AZ <sup>®</sup> nLOF 2020 AZ <sup>®</sup> nLOF 2035 AZ <sup>®</sup> nLOF 2070	≈ 1.5 - 3 µm ≈ 3 - 5 µm ≈ 6 - 15 µm	AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> 2026 MIF	TechniStrip <sup>®</sup> NI555 TechniStrip <sup>®</sup> NF52 TechniStrip <sup>®</sup> MLO 07
		AZ <sup>®</sup> nLOF 5500	AZ <sup>®</sup> nLOF 5510	≈ 0.7 - 1.5 µm		
	Improved adhesion, steep resist sidewalls and high aspect ratios for e. g. dry etching or plating	AZ <sup>®</sup> nXT	AZ <sup>®</sup> 15 nXT (115 cPs) AZ <sup>®</sup> 15 nXT (450 cPs)	≈ 2 - 3 µm ≈ 5 - 20 µm	AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> 2026 MIF	TechniStrip <sup>®</sup> P1316 TechniStrip <sup>®</sup> P1331 TechniStrip <sup>®</sup> NF52 TechniStrip <sup>®</sup> MLO 07
			AZ <sup>®</sup> 125 nXT	≈ 20 - 100 µm	AZ <sup>®</sup> 326 MIF, AZ <sup>®</sup> 726 MIF, AZ <sup>®</sup> 2026 MIF	

<sup>1</sup> 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.

<sup>2</sup> 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.

<sup>3</sup> 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<sup>®</sup> 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<sup>®</sup> 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<sup>®</sup> 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<sup>®</sup> 303** specifically for the AZ<sup>®</sup> 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<sup>®</sup> 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 T1 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<sub>2</sub>, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO<sub>2</sub>. 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: [⇒ www.microchemicals.com/products/wafers/waferlist.html](http://www.microchemicals.com/products/wafers/waferlist.html)

## Further Products from our Portfolio

### Plating

Plating solutions for e. g. gold, copper, nickel, tin or palladium: [⇒ www.microchemicals.com/products/electroplating.html](http://www.microchemicals.com/products/electroplating.html)

### Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... [⇒ www.microchemicals.com/products/solvents.html](http://www.microchemicals.com/products/solvents.html)

### Acids and Bases (MOS, VLSI, ULSI)

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, ... [⇒ www.microchemicals.com/products/etchants.html](http://www.microchemicals.com/products/etchants.html)

### Etching Mixtures

for e. g. chromium, gold, silicon, copper, titanium, ... [⇒ www.microchemicals.com/products/etching\\_mixtures.html](http://www.microchemicals.com/products/etching_mixtures.html)



## Further Information

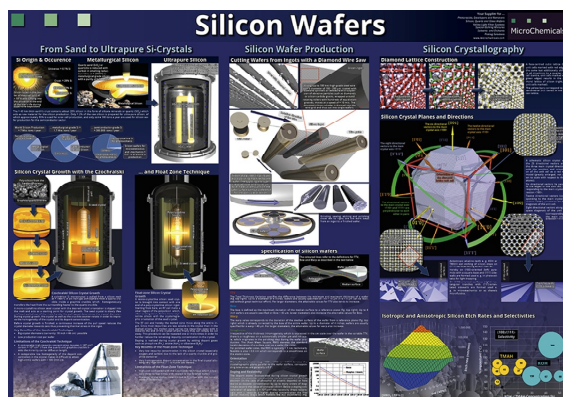
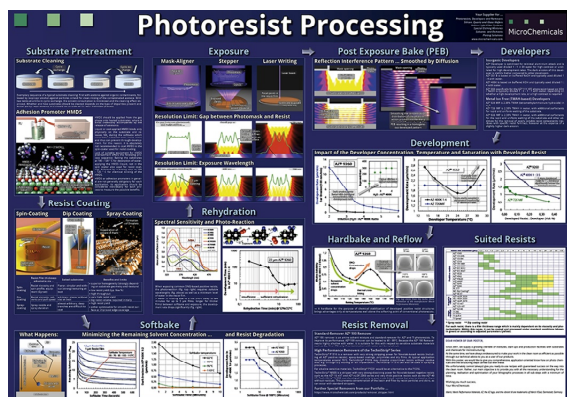
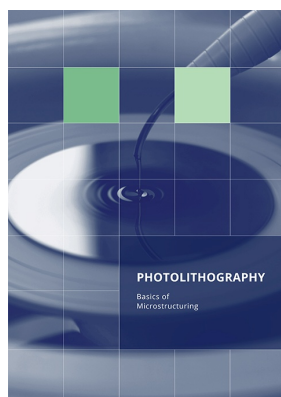
Technical Data Sheets:

[www.microchemicals.com/downloads/product\\_data\\_sheets/photoresists.html](http://www.microchemicals.com/downloads/product_data_sheets/photoresists.html)

Material Safety Data Sheets (MSDS):

[www.microchemicals.com/downloads/safety\\_data\\_sheets/msds\\_links.html](http://www.microchemicals.com/downloads/safety_data_sheets/msds_links.html)

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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.

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