Resists, Developers and Removers

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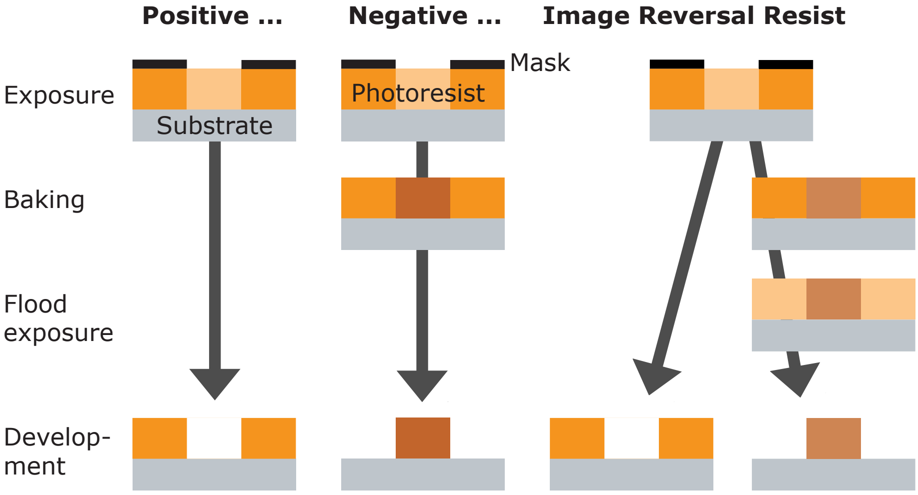
Positive, Negative, and Image Reversal Resists



Positive resists form an indene carboxylic acid during exposure making them soluble in aqueous alkaline solutions. Therefore, positive resists develop where they have been exposed, while the unexposed areas remain on the substrate. Since positive resists do not cross-link, the resist structures rounden beyond their softening point of typically 100-130°C.

Negative resists such as the AZ® nLOF 2000 series or the AZ® 15 nXT or 125 nXT crosslink after exposure and (not required for the AZ® 125 nXT) a subsequent baking step, while the unexposed part of the resist is dissolved in the developer. The crosslinking makes the resist thermally stable, so even elevated temperatures will not deteriorate the resist profile. However, towards higher and higher process temperatures, the degree of crosslinking increases and it becomes hard or even impossible to wet-chemically remove the resist.

Image reversal resists can either be processed in positive or negative mode. In the positive mode, the process sequence is the same as for positive resists. In the image reversal mode, an image reversal bake after the exposure followed by a flood exposure without mask is required. Even in the negative mode, the degree of crosslinking of the resist is rather low, so the resist structures will rounden beyond the softening point of typically 130°C.

Resist Coating Techniques

Spin-coating is the most common coating technique for resists. Almost all AZ® and TI resists are optimized for spin-coating and allow very smooth and homogeneous resist films. The attained resist film thickness goes with the reciprocal square root of the spin speed and thus is adjustable in a certain range for each resist. However, since the edge bead becomes more pronounced towards low spin speeds, for attaining thick films we recommend to use highly viscous resists such as the AZ® 4562 or AZ® 9260, as well as suited spin profiles.

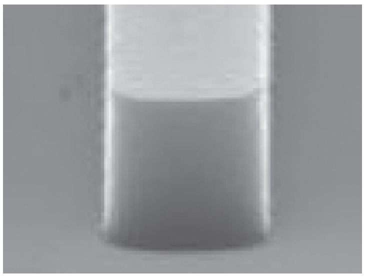
Spray coating allows the coating of almost arbitrary shaped and textured substrates. In order to attain a smooth and homogeneous resist film thickness as well as a good edge coverage of textures (if existing), an optimized resist composition with different solvents with low and high boiling points is required. The spray coating resists AZ® 4999 and *TI Spray* meet these requirements for almost all spray coating applications.

Dip coating is a suited coating technique for large, rectangular shaped substrates and the demand for a minimum resist consumption per coated area. For a homogeneous resist film thickness over the entire substrate, a certain solvent composition in the resist is required as realized in the *MC Dip Coating Resist*.

Fields of Application of the Resist Mask

All photoresists are optimized for one or more fields of application:

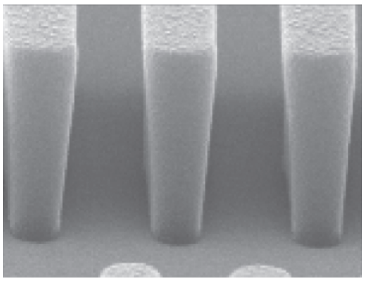
Wet chemical etching requires an optimized adhesion to the substrate. For this purpose, we recommend the AZ® 1500 series for resist film thicknesses of 500 nm to 3 µm, the AZ® ECI 3000 series for 1-4 µm resist film thickness, or the AZ® 4500 series for films of several 10 µm thickness. In case of low resolution requirements, the PL 177 is a economically priced alternative. HF-containing etchants sometimes cause large-scale resist peeling as a consequence of HF-diffusion through the resist towards the substrate underneath. In this case, it's generally beneficial to increase the resist film thickness using resists such as the AZ® 4562 or the AZ® 9260.



1 µm AZ® 701 MiR line after 130°C hardbake

Dry etching requires an elevated softening point of the resist as well as steep sidewalls. The AZ® 6600 series for resist film thicknesses of 1-4 µm, or the high-resolution AZ® 701 MiR, are optimized for both requirements and reveal a softening point of 130°C.

If resist film thicknesses exceeding 5 µm are required, the thick positive resists AZ® 4562 or AZ® 9260, or the negative AZ® 15 nXT or AZ® 125 nXT are recommended. The two nXT resists cross-link and therefore reveal an excellent thermal stability during dry etching.

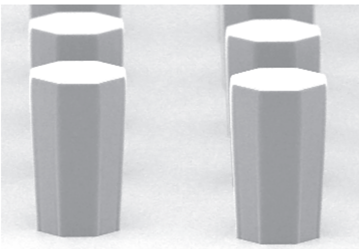


700 nm lines with the AZ® nLOF 2020

Lift-off processes recommend an undercut resist profile which can be attained with image reversal resists such as the AZ® 5214E (resist film thickness 1-2 µm), the TI 35ES (3-5 µm), or the AZ® nLOF 2000 (2-20 µm) negative resists.

Additionally, these resists are thermally stable and therefore help to prevent a rounding of the resist structures during coating.

If the mask design requires positive resists for lift-off application, the resist sidewalls should be as steep as possible in order to prevent a coating of these sidewalls. For this purpose, we recommend the thermally stable AZ® 6600 resists, or the high-resolution AZ® 701 MiR.

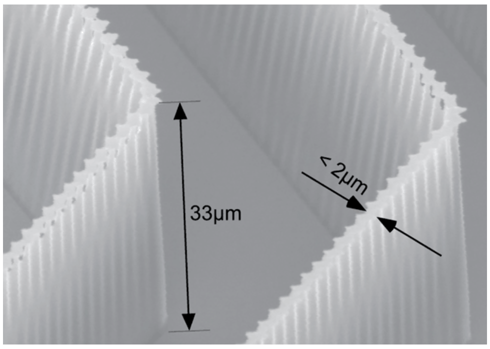


120 µm plated Cu-coloums (with the AZ® 125 nXT)

Electroplating requires an improved adhesion of the resist to the substrate as well as an enhanced stability of the resist in the electrolyte.

The negative resists AZ® 15 nXT (resist film thickness 5-30 µm) and AZ® 125 nXT (up to approx. 150 µm) are optimized for these requirements. Both resists can be developed in TMAH-based developers, wet-chemically stripped in common removers, and are compatible with all common substrate materials and electrolytes for Cu-, Au-, and NiFe plating.

If positive resists have to be used for electroplating, the AZ® 4500 series and the AZ® 9260 allow steep sidewalls and a good adhesion.



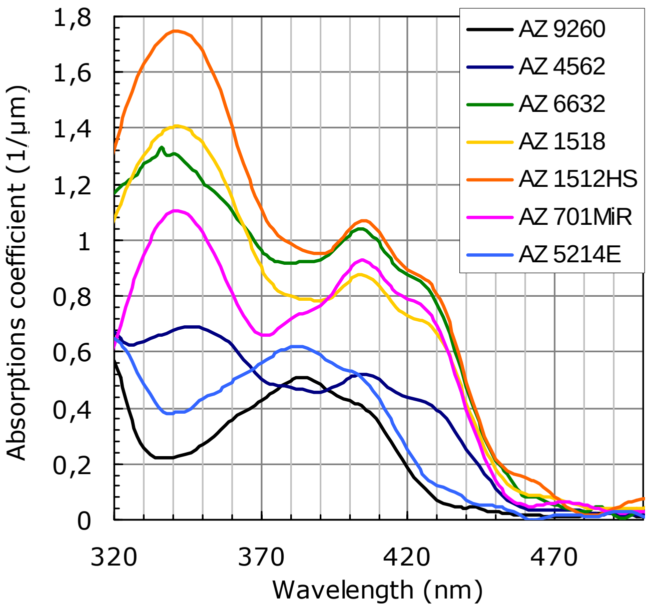
AZ® 9260 lines with an aspect ratio > 16 (prozess and picture by Mr. Roger Bischofberger, applied microSWISS GmbH)

Lateral Resolution and Aspect Ratio

The photoresist itself as well as the resist film thickness limit the theoretical resolution. Under optimum conditions, high-resolution thin resists such as the AZ® 701 MiR allow feature sizes of approx. 300 nm using i-line exposure.

Beside a high absolute resolution, some processes require a high aspect ratio (ratio of the feature height to their width). Modern thick resists such as the AZ® 9260 allow an aspect ratio of 6-10, and even higher values under optimized process conditions.

In many cases not the resist, but the equipment and process parameters limit the attainable resolution. In order to maximize the resolution of a given resist, besides the exposure conditions (no gap between mask and resist caused by particles, bubbles, or an edge bead), also the softbake parameters, the exposure dose, and the development (developer and its concentration, development time) have carefully to be optimized.



Spectral Sensitivity

The optical absorption (fig. right-hand) of unexposed positive photoresists ranges from approx. 460 nm in the VIS to near UV, which is matched to the emission spectrum of Hg lamps in mask aligners. This absorption spectrum causes the typical reddish-brownish colour of many photoresists. During exposure, photoresists almost completely bleach down to approx. 310 nm.

Some modern positive resists such as the AZ® 5214E or AZ® 9260 are not sensitive at g-line, while most negative resists such as the AZ® nLOF 2000 series, or the AZ® 15 nXT and 125 nXT are only sensitive near i-line and therefore appear almost uncoloured to the human eye.

The optical absorption range does not end abruptly towards higher wavelengths. Therefore, high illumination intensity (e. g. laser scribing) or -times allow an exposure also some 10 nm towards the visible part of the spectrum.

Some resists such as the PL 177 or AZ® 520D are dyed which makes it more easy to inspect the coating result.

Please find here detailed information on optical properties of photoresists.

Attainable Resist Film Thicknesses

Generally, the last two digits of the resist name (e. g. AZ® 6632) indicate the film thickness attained by spin coating (without gyrset) at 4000 rpm in 100 nm units. The thickness approximately decreases with the (increasing) square-root of the spin speed, so a given resist allows a certain range in the attainable resist film thickness. If the desired resist film thickness can/should not be realized by varying the spin speed, the usage of a different available viscosity of the given resist is recommended. Otherwise, the following has to be considered:

Dilution of high-viscosity resists with PGMEA (= AZ® EBR Solvent) allows to perform several applications with different film thicknesses using only one resist. However, diluted resists are sensitive to particle formation with a reduced expiry date depending on the resist, the dilution ratio and the storage temperature and -time for the diluted resist. Since the particles partially consist of the photo active compound, a particle filtration before usage increases the dark erosion and decreases the development rate of the resist. For information on specific dilution recipes please contact us.

Realizing **thick films with low-viscosity resists** is problematic for two main reasons: i) The required low spin speeds increase the edge bead, and ii) in case of positive or image reversal resists, the rather high concentration of the photo active compound (low optical transparency) in typical 'thin resists' requires high exposure doses for a sufficient exposure, which makes steep resist profiles hard to realize and may cause popping and foaming by N_2-bubbles formed during exposure.

	Attainable **resist film thickness** (µm)	0.5	1.0	1.5	2.0	2.5	3	4	5	6	8	10	15	20	25	50	150
Standard/ wet etching	AZ® 1505	standard															
	AZ® 1512 HS	dilution	standard	standard	standard												
	AZ® 1514 H			standard	standard												
	AZ® 1518			standard	standard	standard											
	TI 35E						standard	standard	standard								
Thick resists	AZ® 4533					standard	standard	standard	standard								
	AZ® 4562						dilution	dilution	dilution	standard	standard	standard	standard	dilution	dilution	dilution	dilution
	AZ® 9260			dilution	dilution	dilution	dilution	dilution	dilution	standard	standard	standard	standard	standard	dilution	dilution	dilution
Dry etching	AZ® MiR 701	dilution	standard	standard													
	AZ® 6612			standard	standard												
	AZ® 6624				standard	standard	standard	standard									
	AZ® 6632					standard	standard	standard	standard								
	TI 35ES						standard	standard	standard								
High resolution	AZ® MiR 701	dilution	standard	standard													
	AZ® ECI 3000	dilution	standard	standard	standard	standard	standard	standard	standard								
	AZ® 9260			dilution	dilution	dilution	dilution	standard	standard	standard	standard	standard	standard	standard	dilution	dilution	dilution
Image reversal/ Lift-off	AZ® 5214 E		standard	standard	standard												
	TI 35ES						standard	standard	standard								
	TI Spray		standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard			
	TI Plating								standard	standard	standard	standard	dilution	dilution			
	TI xLift								standard	standard	standard	standard	dilution	dilution			
Negative/ Lift-off	AZ® nLOF 2000			standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard			
Electroplating	AZ® 15 nXT								standard	standard	standard	standard	standard	standard			
	AZ® 125 nXT														standard	standard	standard
Spray coating	AZ® 4999		standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard			
	TI Spray		standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard			
Dip coating	MC Dip Coating		standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard	standard			

Standard resist film thickness

Resist film thickness attainable via dilution or multiple coating

Our Resists and their Fields of Application

The following table gives an overview on our resists, their main field of application, and the attainable thickness range.

		AZ® 1500 AZ® 5214 E	AZ® 4500 AZ® 4999 TI 35E TI Spray	AZ® 6600 AZ® ECI 3000	AZ® 9200	AZ® MiR 701	PL 177 TI 35ES TI xLift	AZ® nLOF 2000, AZ® 15/125 nXT	AZ® 111 XFS
MIF	AZ® 326 MIF	Recommended	NOT recommended	Recommended	Recommended	Recommended	Recommended	Recommended	NOT recommended
	AZ® 726 MIF	Recommended	NOT recommended	Recommended	Recommended	Recommended	Recommended	Recommended	NOT recommended
	AZ® 826 MIF	Possible	Recommended	Possible	Possible	NOT recommended	Possible	Recommended	NOT recommended
MIC	AZ® Devel.	Possible	NOT recommended	Possible	Possible	Possible	Possible	NOT recommended	NOT recommended
	AZ® 351B	Recommended	Possible	Possible	Possible	Possible	Recommended	NOT recommended	NOT recommended
	AZ® 400K	Possible	Recommended	Possible	Recommended	Possible	Recommended	NOT recommended	NOT recommended
	AZ® 303	NOT recommended	NOT recommended	NOT recommended	NOT recommended	NOT recommended	NOT recommended	Possible	Recommended

Recommended Possible NOT recommended

Compatibilities of Developers

The following table gives an overview on the compatibilities between developers and photoresists

Which Developer for which Application?

First of all, it has to be checked whether the developer has to be metal ion free (MIF) or if alternatively metal ion containing (MIC) developers can be used. Most MIF developers are ready-to-use solutions, while typical MIC developers are supplied as a concentrate which has to be diluted before use.

AZ® 326 MIF is 2.38 % TMAH (*TetraMethylAmmoniumHydroxide*) in H_2O.

AZ® 726 MIF is 2.38 % TMAH in H_2O with surfactants added for fast and homogeneous substrate wetting for the puddle- or spray development.

AZ® 826 MIF is 2.38 % TMAH in H_2O with surfactants added for fast and homogeneous substrate wetting, and further additives for removal of resist residuals occasionally remaining after development. These additives, however, slightly increase the dark erosion.

AZ® Developer (MIC) is optimized for minimum Al attack. It is typically applied 1 : 1 diluted in H_2O for high contrast, or undiluted for a high development rate. The dark erosion of AZ® Developer is slightly higher as compared to other developers.

AZ® 351B (MIC) is based on buffered NaOH and typically used in 1 : 4 dilution.

AZ® 400K (MIC) is based on buffered KOH and typically used in 1 : 4 dilution.

AZ® 303 (MIC) is based on KOH and NaOH and designed for the resist AZ® 111 XFS.

The next selection characteristics is the **compatibility** of the developer to a certain **photoresist** or/and a certain **substrate material** (table previous page, bottom).

Photoresist Removal

Non cross-linked AZ® and TI photoresists can be removed easily and residual-free from the substrate in all common strippers. If not, one or more of the following reasons decreasing the removableness of resist films have to be considered:

- From temperatures of approx. 150°C on, all Novolak based resists start to thermally crosslink. Such temperatures can - on purpose or not - be applied during a hardbake, evaporation or sputtering of coatings, or dry-etching through the resist mask.
- Crosslinking is also activated under DUV radiation (wavelengths < 250 nm), which also occurs during evaporation or sputtering of coatings, or dry-etching.
- Desired crosslinking of negative tone resists - in case of high process temperatures, the degree of crosslinking becomes very high.
- Material re-deposited on the resist structures during dry-etching

Acetone is not well-suited as a stripper for photoresists: The high vapour pressure of acetone causes a fast drying and thus re-deposition of stripped photoresist onto the substrate forming striations. If nevertheless acetone is used for this purpose, a subsequent rinse with isopropyl alcohol - immediately after the acetone step - allows a residual free removal process.

NMP (1-Methyl-2-pyrrolidon) is a powerful stripper due to its physical properties: NMP yields a low vapour pressure (no striation formation), strongly dissolves organic impurities as well as resists, keeps the removed resist in solution, and can be heated to 80°C due to its high boiling point thus improving the performance as remover.

3-5 % **KOH** or **NaOH** can be used as stripper if the alkaline stability of the substrate is high enough. For highly cross-linked resists, higher concentrations or/and elevated temperatures might be required. One has to consider that many metals such as aluminium or copper are not sufficiently alkaline stable, and crystalline silicon is also attacked at high pH-values and temperatures.

AZ® 100 Remover is an amine-solvent mixture, and a ready-to-use standard remover for AZ® and TI photoresists. In order to improve its performance, AZ® 100 Remover can be heated up to 80°C. Since AZ® 100 Remover becomes strongly alkaline after contact with water, Al containing substrates might be attacked as well as copper- or GaAs alloys/compounds. In this case, AZ® 100 Remover should be used as a concentrate, any dilution or contamination (even in small traces!) of AZ® 100 Remover with water should be avoided.

O_2-Combustion will act as suited removal for even highly cross-linked resists if a photoresist film cannot be removed wet-chemically.

Sales Units of our Photoresists

Available sales volumes: 250 ml, 500 ml, 1000 ml, 2.5/5 L or gallons.

Sales Units of our Developers

Available sales volumes: 5 L PE cans

Sales Units of our Removers

Available sales volumes: 5 L PE cans (AZ® 100 Remover) or 2.5 L bottles (solvents such as acetone or NMP)

Disclaimer of Warranty

All information, process guides, recipes etc. given in this brochure have been added to the best of our knowledge. However, we cannot issue any guarantee concerning the accuracy of the information.

We assume no liability for any hazard for staff and equipment which might stem from the information given in this brochure.

Generally speaking, it is in the responsibility of every staff member to inform herself/himself about the processes to be performed in the appropriate (technical) literature, in order to minimize any risk to man or machine.