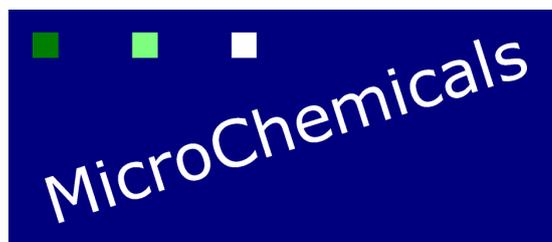


Resists and Developers

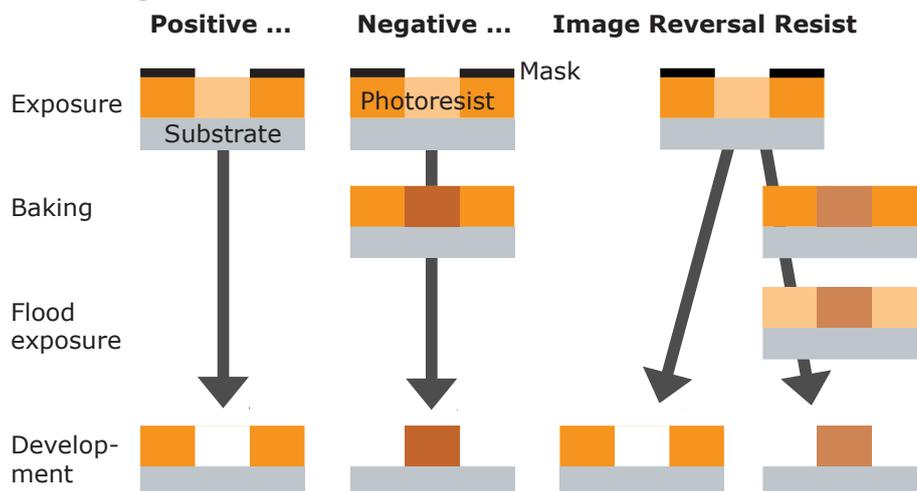


Revised: 2013-11-07 Source:

www.microchemicals.com/downloads/application_notes.html

Positive, Negative or 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 cross-link 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 them thermally stable, so even elevated temperatures will not deteriorate the resist profile. However, towards higher and higher process temperatures, 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 is rather low, so the resist structures will rounden beyond the softening point of typically 110-130°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 maximum spin speed and thus adjustable in a certain range for each resist. However, since the edge bead becomes more pronounced towards low spin speeds, 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, 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 of different solvents with low and high boiling points is required. The spray coating resists AZ[®] 4999 and *TI Spray* meet these requirements for most 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*.

Photoresists, wafers, plating solutions, etchants and solvents ...

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Application of the Resist Mask

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. 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 oder AZ[®] 9260.

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.

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.

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

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, stripped in common removers, and are copatible with all common substrate materials and electrolytes for Cu-, Au-, and NiFe plating.

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

Lateral Resolution and Aspect Ratio

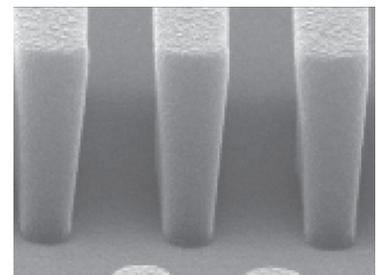
The photoresist itself as well as the resist film thickness limit the theoretical resolution limit. Under optimum conditions, high-resolution thin resists such as the AZ[®] 701MiR allow feature sizes of approx. 300 nm under i-line exposure.

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.

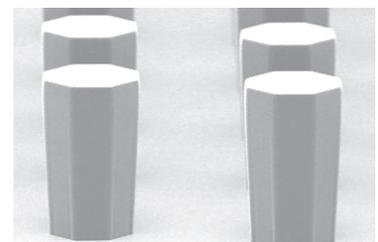
In many cases not the resist, but the equipment and process parameters limit the attainable resolution. In order to maximize the resolution of a given resist, be-



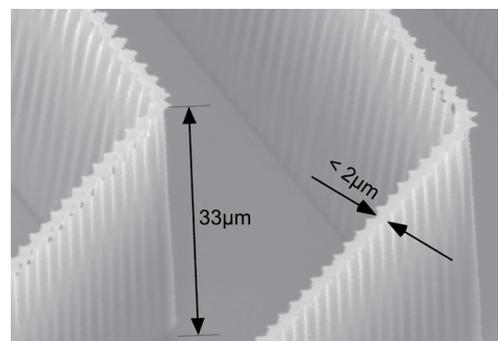
1 μm AZ[®] 701 MiR line after 130°C hardbake



700 nm lines with the AZ[®] nLOF 2020



120 μm plated Cu-coloums (via AZ[®] 125 nXT)



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

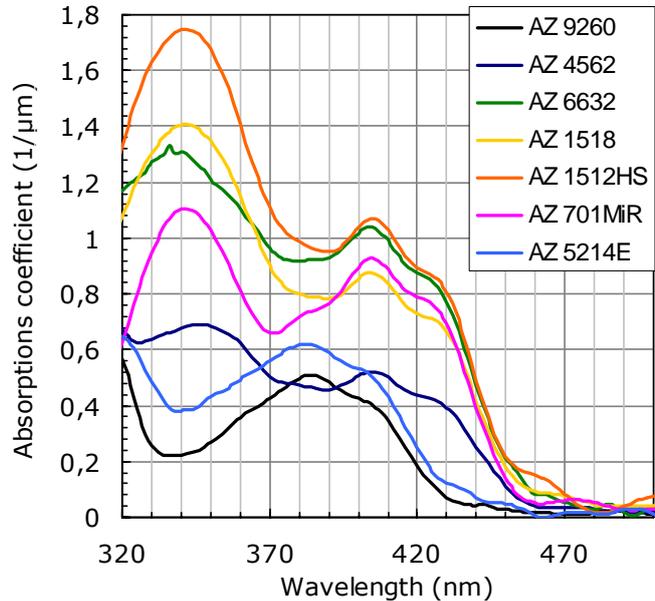
sides the exposure conditions (no gap between mask and resist caused by particles, bubbles, or an edge bead), also the softbake parameters, the exposure dose, and the development (developer and its concentration, development time) have carefully to be optimized.

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 intensities (e. g. laser scribing) or -times allow an exposure also some 10 nm towards the visible part of the spectrum.



Resist Film Thickness

Generally, the last two digits of the resist name (e. g. AZ[®] 6632) indicate the film thickness d attained by spin coating (without gyrset) at $v = 4000$ rpm in 100 nm units. The thickness approximately decreases with the (increasing) square-root of the spin speed (in rpm), 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 consult the following sections or 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) 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 N₂-bubbles formed during exposure.

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.

| 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 | Green | | | | | | | | | | | | | | | |
| | AZ® 1512 HS | Yellow | Green | Green | Green | | | | | | | | | | | | |
| | AZ® 1514 H | | | Green | Green | | | | | | | | | | | | |
| | AZ® 1518 | | | Green | Green | Green | | | | | | | | | | | |
| | TI 35E | | | | | | Green | Green | Green | | | | | | | | |
| Thick resists | AZ® 4533 | | | | | Green | Green | Green | | | | | | | | | |
| | AZ® 4562 | | | | | | Yellow | Yellow | Yellow | Green | Green | Green | Green | Green | Yellow | Yellow | Yellow |
| | AZ® 9260 | | | Yellow | Yellow | Yellow | Yellow | Yellow | Yellow | Green | Green | Green | Green | Green | Yellow | Yellow | Yellow |
| Dry etching | AZ® MiR 701 | Yellow | Green | Green | | | | | | | | | | | | | |
| | AZ® 6612 | | | Green | Green | | | | | | | | | | | | |
| | AZ® 6624 | | | | Green | Green | Green | Green | | | | | | | | | |
| | AZ® 6632 | | | | | Green | Green | Green | | | | | | | | | |
| | TI 35ES | | | | | | Green | Green | Green | | | | | | | | |
| High resolution | AZ® MiR 701 | Yellow | Green | Green | | | | | | | | | | | | | |
| | AZ® ECI 3000 | Yellow | Green | Green | Green | Green | Green | Green | | | | | | | | | |
| | AZ® 9260 | | | Yellow | Yellow | Yellow | Yellow | Yellow | Green | Green | Green | Green | Green | Green | Yellow | Yellow | Yellow |
| Image reversal/ Lift-off | AZ® 5214 E | | Green | Green | Green | | | | | | | | | | | | |
| | TI 35ES | | | | | | Green | Green | | | | | | | | | |
| | TI Spray | | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | | | |
| | TI Plating | | | | | | | | Green | Green | Green | Green | Yellow | Yellow | | | |
| | TI xLift | | | | | | | | Green | Green | Green | Green | Yellow | Yellow | | | |
| Negative/ Lift-off | AZ® nLOF 2000 | | | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | | | |
| Electroplating | AZ® 15 nXT | | | | | | | | Green | Green | Green | Green | Green | Green | | | |
| | AZ® 125 nXT | | | | | | | | | | | | | | Green | Green | Green |
| Spray coating | AZ® 4999 | | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | | | |
| | TI Spray | | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | | | |
| Dip coating | MC Dip Coating | | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | Green | | | |

Standard resist film thickness
Resist film thickness attainable via dilution or multiple coating

Compatibilities of Developers

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

| | | 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 | Green | Orange | Green | Green | Green | Green | Green | Orange |
| | AZ® 726 MIF | Green | Orange | Green | Green | Green | Green | Green | Orange |
| | AZ® 826 MIF | Yellow | Green | Yellow | Yellow | Orange | Yellow | Green | Orange |
| MIC | AZ® Devel. | Yellow | Orange | Yellow | Yellow | Yellow | Yellow | Orange | Orange |
| | AZ® 351B | Green | Orange | Yellow | Yellow | Yellow | Green | Orange | Orange |
| | AZ® 400K | Yellow | Green | Yellow | Green | Yellow | Green | Orange | Orange |
| | AZ® 303 | Orange | Orange | Orange | Orange | Orange | Orange | Yellow | Green |
| | | Recommended | | Possible | | NOT recommended | | | |

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 H₂O.

AZ® 726 MIF is 2.38 % TMAH in H₂O with surfactants added for fast and homogeneous substrate wetting.

AZ® 826 MIF is 2.38 % TMAH in H₂O 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 DI-H₂O 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 overleaf, bottom).

Photoresist Removal

Non cross-linked AZ® and TI photoresists can be removed easily and residual-free from the substrate in many 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.

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.

O₂-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 (solvent 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.

Generally, and especially for the wet chemical etching recipes we do not guarantee the correctness of the specification of the composition, the mixing ratio, the mixing and application of the etches and solutions. The recommended sequence of the mixing of the components of each recipe does not generally correspond to the order of the components listed. Generally, it is recommended to i) add the acid to the dilutor, ii) add stronger acids to weaker acids, and iii) add the oxidizer last.

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.