THE BEST-SUITED PHOTORESIST

The question of the optimal photoresist to use is at the beginning of each new photolithography process. In addition to the requirement for the film thickness and resolution, questions about the chemical and physical properties of the resist masks attained for their use as well as the compatibility of the resist on the equipment used are to be clarified.

This chapter would like to assist you in the selection of the proper photoresist that is most appropriate for your lithography process by explaining all the selection criteria mentioned and refers to the respective chapters of this book to allow you a more in-depth look.

Which Resist Mode?

Positive Resists

In the case of positive resists, exposed areas are soluble in the developer due to the formation of an indene-carboxylic acid taking place during exposure, while unexposed resist areas remain on the substrate. Since positive resists do not cross-link, exceeding their softening temperature (typically 100 - 130 °C) leads to a rounding of the resist profiles, which is sometimes undesired, sometimes intentionally applied for certain applications (Re/flow).

Negative Resists

Negative resists such as the AZ® nLOF 2000 series or AZ® 15 nXT and AZ® 125 nXT are cross-linked at the exposed areas and remain there on the substrate after development, while the non-exposed areas are cleared. The cross-linking prevents a thermal softening of the resist profiles.

Image Reversal Resists

Image reversal resists can either be processed positively or negatively. While in the positive mode, the process sequence is the same as for positive resists, the negative mode requires an image reversal bake step after exposure with subsequent flood exposure. Even in the negative mode, the degree of cross-linking of the resist is rather low, so the resist structures will soften beyond the softening point of typically 130°C.

Which Resist Coating Technique?

Spin-coating

Most AZ® and TI resists are optimised for spin-coating and allow smooth and very homogeneous film thicknesses of only a few hundred nm (AZ® 1505, ECI 3007, or 701 MiR) up to 100 μm with e. g. the posi-

![Fig. 52: The schematic process sequence of the exposure (above) up to the developed resist features (below) in the processing of positive resists (left column), negative resists (centre) and image reversal resists (right); the latter in two possible modes. The special features of the attainable resist profiles are not included in this scheme.](image)
active AZ® 40 XT or negative AZ® 125 nXT, that can be set within limits via the spin profile.

**Spray Coating**
By means of spraying, highly textured substrates can be satisfactorily coated. For a homogeneous resist film thickness, a smooth resist surface and good edge coverage, an individually optimised composition of two or more solvents with varying vapour pressure is required, as they are present in appropriate spray resists such as the AZ® 4999 for optimised edge coverage or the TI spray for smooth resist films.

**Dip Coating**
Due to the high resist yield, the dip coating allows a very cost-effective coating for large, rectangular substrates up to the m² range. For a homogeneous resist film thickness over the entire substrate, a certain solvent composition in the resist is required as realised in the MC Dip Coating Resist.

**Purpose of the Photo Mask?**

**Wet-chemical Etching**
Wet-chemical etching requires optimum adhesion to the substrate to minimise the degree of lateral under-etching. The AZ® 1500 series is suitable for film thicknesses from 500 nm to 3 μm, the AZ® ECI 3000 series for resist films from 1 - 4 μm, or the AZ® 4500 series for film thicknesses up to several 10 μm.

With low demands on the resolution, the PL 177 is a cost-effective alternative. In the case of hydrofluoric acid-containing etching solutions, the diffusion of the fluoride ions through the photoresist mask to the substrate and subsequent removal of the entire resist film is often the main problem. In this case, it is recommended to use a sufficiently thick resist such as the AZ® 4562, the AZ® 9260 or for very large film thicknesses of the AZ® 40 XT.

**Dry Etching**
Dry etching often requires a resist mask with a sufficiently high softening temperature as well as steep sidewalls which can both be realised with the AZ® 701 MiR. For coating thicknesses of 1 - 4 μm, the AZ® ECI 3000 series is recommended; for even thicker resist films, the AZ® 4562 or AZ® 9260.

**Lift-off**
Stable and reproducible lift-off processes can be attained with an undercut resist profile such as the AZ® 5214E (resist film thickness 1 - 2 μm), the TI 35ESX (3 - 5 μm) or the negative resists AZ® nLOF 2000 (2 - 15 μm) in order to obtain reproducibility. In the case of these resists, the thermal stability is also sufficiently high to prevent the resist from flowing during the coating. If the mask design requires a positive resist, the resist sidewalls should be as steep as possible in order to prevent or reduce a coating of these sidewalls.

**Electroplating**
Electroplating usually makes high demands on the adhesion and 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 optimised 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 are used for electroplating, the resists of the AZ® 4500 and 9200 families (or the AZ® 40 XT for very thick films) allow good adhesion as well as steep resist sidewall.

**Resolution and Aspect Ratio**

**Limitations Through the Resist**
The photoresist itself as well as the resist film thickness limit the theoretically attainable resolution. Under optimum conditions, high-resolution thin resists such as the AZ® 701 MiR or AZ® ECI 3007 allow feature sizes of approx. 300 nm using i-line exposure (365 nm wavelength).
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 AZ® 9260 or ultra thick resists such as the AZ® 40 XT allow an aspect ratio over five, and even higher values under optimised process conditions.

**Limitations Through the Equipment Used**
In many cases not the resist, but the equipment and process parameters limit the attainable resolution. In order to maximise 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 have carefully to be optimised.

**Exposure**

**Spectral Sensitivity**
The spectral sensitivity of the resist must match the exposure tool used. Nearly all AZ® and TI resists are sensitive to one or more of the three lines i-line (365 nm), h-line (405 nm) or g-line (435 nm) emitted by typical Hg mask aligners or steppers.

**Mask Aligner, Stepper or Laser Direct Writer?**
While mask aligners or steppers, exposure intensities occur by some 10 to some 100 mW/cm² corresponding to exposure times in the range from seconds to minutes.

Laser exposure can yield several orders of magnitude higher intensities. With such short exposure times, DNQ-based positive resists, the nitrogen formed during the photo reaction is released in such a short time that bubbles or cracks can form in the resist film. In addition to adapted process parameters, such as a sufficient softbake and a very thin resist film, it may be useful to use a resist with a low photoinitiator concentration, such as the AZ® 4500 and 9200 series, or a resist such as the chemically amplified AZ® 40 XT which does not release nitrogen during exposure.

**Film Thicknesses**

**Limitations of the Resist Coating Technique**
During the coating by means of spin-coating, the resist film thickness achieved can be set within limits for a given resist via the spin profile. Since many coatings are offered in several viscosities by manufacturers, this range can be extended via an appropriate dilution. However, because too greatly diluted resists age rapidly, the possible degree of dilution and thus the lower limit of the resist film thickness attainable by spin coating are restricted.

**Limitations during Processing**
The process times for the softbake and the exposure which increase with increasing resist film thickness make it advisable to use photoresists for very thick resist films, whose chemistry is also designed for correspondingly thick films. In the case of DNQ-based positive resists, the formation of bubbles due to nitrogen from the photo reaction is problematic for large resist thicknesses in addition to the topic of rehydration. Here, corresponding photoinitiator-poor photoresists such as the AZ® 4562 or 9260, or chemically amplified resists such as the AZ® 40 XT which do not release any nitrogen during exposure are recommended.
Overview of our AZ® and TI Resists

Table 4 represents the attainable and processable film thickness ranges of our AZ® and TI positive, negative and image reversal resists. Whether and under which conditions or with which restrictions these areas can be expanded downwards or upwards depends on the respective resist, the available equipment and the requirements on the process times and the process result. We will be happy to advise you!

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<thead>
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<th>Resist film thickness (µm):</th>
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* Spray coating
** Dip coating

Table 4: For each resist, there is a film thickness range which is mainly dependent on its viscosity and photochemistry. Within this range, it can be coated and processed under standard conditions (shown in green) or according to adjusted parameters (yellow). Whether it is possible to build up and process thinner or thicker resist films by means of a dilution of the resist or special coating techniques or spin profiles depends, on the one hand, on the resist itself, and on the other hand, on the tolerable complexity of the process control.
## Our Photoresists: Application Areas and Compatibilities

### Positive

<table>
<thead>
<tr>
<th>Resist Family</th>
<th>Photosists</th>
<th>Resist Film Thickness</th>
<th>Recommended Developers 3</th>
<th>Recommended Removers</th>
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<td>AZ® 1500</td>
<td>AZ® 1505</td>
<td>≈ 0.5 µm</td>
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<td>AZ® 100 Remover, TechniStrip® P1316</td>
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<td>AZ® 1518</td>
<td>≈ 1.5 - 2.5 µm</td>
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<td>AZ® 4500</td>
<td>AZ® 4533</td>
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<td>AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
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<td></td>
<td>AZ® 4562</td>
<td>≈ 5 - 10 µm</td>
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### Metal Ion Free (MIF) Developers

- AZ® 326 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water.

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## Our Developers: Application Areas and Compatibilities

### Inorganic Developers

AZ® Developer is based on sodium phosphate and –meta-silicate, 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.

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### Metal Ion Free (TMAH-based) Developers

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 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® P1316 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 dissolveing 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 Si, Cu, Ti, TiN, W and Ni.

TechniStrip™ NFS2 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 SiO₂, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO₂. 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: E www.microchemicals.com/products/wafers/waferslist.html

Further Products from our Portfolio

Plating

Plating solutions for e. g. gold, copper, nickel, tin or palladium: E www.microchemicals.com/products/electroplating.html

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... E www.microchemicals.com/products/solvents.html

Acids and Bases (MOS, VLSI, ULSI)

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, ... E www.microchemicals.com/products/etchants.html

Etching Mixtures

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


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!

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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 cannot 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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