DEVELOPMENT

After exposure, the future resist mask exists as a latent image in the photo-resist: The exposed areas differ chemically from the non-exposed sites. The purpose of the development is to dissolve either the exposed (in the case of positive resists) or the unexposed (in the case of negative resists) resist areas, resulting in the final desired resist structures.

This chapter discusses the basic chemical and physical processes during development and explains the impact of different process parameters on the development rate and selectivity of the development process.

Basic Chemistry of Developers

Aqueous Alkaline Developers

The positive and negative resists we market are usually developed aqueous-alkaline. The corresponding developers are based either on a diluted sodium hydroxide or potassium hydroxide solution or on an aqueous solution of the metal ion free organic TMAH (TetraMethylAmmoniumHydroxide).

Many developers use chemical buffers against neutralisation by CO$_2$ to extend the shelf life, surface wetting agents for puddle development, and additives for removing tenacious resist residues. Opened developer containers should be stored well closed and not left open for an unnecessary length of time in order to prevent the ingress of CO$_2$ from the ambient air. CO$_2$ reduces the activity of the developer after exhaustion of a possible chemical buffer and reduces its rate of development by decreasing the pH value and thus its activity.

Open containers filled with developers also absorb CO$_2$ from the ambient air, where the ratio of surface to volume is decisive: Beakers should be changed at least daily, while larger tanks can remain stable for days and weeks. When the developer is protected by a nitrogen curtain in the process pauses, which is placed on the developer surface like a carpet, thus suppressing the CO$_2$ input, the shelf life is significantly increased.

Organic Solvents

Cross-linked negative resists can generally also be developed with organic solvents in which the cross-linked resist areas are insoluble. However, caution is advised in the usually aqueous alkaline developable AZ® negative resists which we market, as follows: If the resist is exposed to organic solvents too long, there is a risk that the cross-linked resist areas swell and subsequently separate from the substrate, de-

Fig. 96: The schematic process of development of DNQ-based photoresists at the molecular level: In the unexposed state, the photoinitiator is located on the hydrophobic side of the phenolic resin chains, the indene carboxylic acid formed during exposure expands to the hydrophilic side.

There, it separates a proton from the resin, which is thereby negatively charged and now soluble in aqueous alkaline developers.

Carbon atoms are shown here in black, hydrogen atoms light grey, oxygen atoms blue, nitrogen atoms red, and sulphur atoms yellow.
pending on the degree of cross-linking of the resist film and its adhesion.

Selection Criteria of Developers

Compatibility with Photoresists

Not every photoresist can be developed without residue with every developer. For example, the NaOH-based AZ® 351 is less suitable for the AZ® 4500 series than the KOH or TMAH-based developers are, while AZ® 111 XFS requires the AZ® 303 as a developer.

If in the processing of negative resists via scattering, diffraction or reflections, an unintended partial exposure of nominally dark resist areas is to be feared, the TMAH-based AZ® 826 MIF can be beneficial. This developer contains an additive for the removal of slightly cross-linked resist areas.

Metal Ion Containing or Metal Ion Free?

Metal ion-containing developers such as the NaOH-based AZ® 351B or the KOH-based AZ® 400K are generally much cheaper than metal ion-free TMAH-based developers, without a fundamental difference in their performance or capacity.

An important selection criterion for the optimal developer is therefore the question of whether the developer has to be metal ion-free (MIF), or alternatively metal ion-containing (MIC) developers can be used. Metal-ion-freeness is, for example, a condition when it is absolutely necessary to exclude, that residues of sodium or potassium ions of the developer on the substrate diffuse during subsequent high-temperature processes into the semiconductor substrate and affect its electronic properties there as impurities.

Concentrate or ready-to-use?

Metal ion-containing developers such as AZ® 351B, AZ® 400K or AZ® Developer are usually supplied as concentrate and diluted with DI water before application.

The 2.38% TMAH-based AZ® 326 MIF, 726 MIF or 826 MIF are pre-diluted (ready-to-use) and slightly further diluted only when the application requires it.

Compatibility with Substrates

The compatibility of the developer with the substrate material used must also be considered: Most developers attack alkaline sensitive metals such as aluminium and copper as well as various compound semiconductors due to their high pH value of approximately 13, which also entails the risk of the etched material being carried over to other sites on the substrate.

Our "AZ® Developer" (metal ion-containing, based on sodium metasilicate and phosphate) is optimised for minimal aluminium erosion and also attacks many other alkaline-sensitive materials far less than other aqueous alkaline developers.

Compatibility with Equipment or Development Process

For the dip development (in beaker or tank) basically all developers are suitable. However, if a strong
mechanical recirculation of the developer is implemented, a foaming of, for example, surfactants added in the AZ® 726 MIF or 826 MIF may be problematic.

Also in the course of spray development, the foam formation of surfactant-containing developers can lead to an inhomogeneous developmental pattern.

However, these surfactants acting as wetting agents are a prerequisite for rapid and even wetting of the substrate in the puddle development resulting in a development result which is homogeneous over the entire substrate.

Incompatibilities between MIc and MIF Developers

Even small traces of TMAH-based metal ion-free developers such as the AZ® 326 MIF, 726 MIF or 826 MIF) can significantly reduce the development rate of metal ion-containing developers (such as the AZ® 400K or 351B).

If both types of developers are used, extremely clean work is to be ensured to prevent mutual contamination even in the ppm range, such as in the dispensing system or developer containers.

Development: Operations in the Photoresist on a Molecular Level

Positive Resists and Image Reversal Resists

The exposure of our positive resists, our image reversal resists in the positive mode and the flood exposure of image reversal resists in the negative mode is based on the conversion of the DNQ-based photoinitiator in an indene carboxylic acid. The photoinitiator switches from the hydrophobic to the hydrophilic side of the phenol resin chain where the OH bindings are located. Of this group the indene carboxylic acid splits a hydrogen ion, causing the resin molecule to be electrically charged ultimately causing the increased solubility in developers.

Negative Resists

In the case of negative resists, the unexposed resin has a sufficiently high physical solubility in developers, whereas exposed and sufficiently cross-linked resist areas show only negligible erosion.

Definition of Selectivity

As the selectivity of a developer, we refer here to the ratio of the dissolution rate of the resist to be developed to the dissolution rate of the resist structures, which should remain on the substrate.

In the development of positive resists, the development rate (= the rate of erosion of the exposed resist) increases more intensely than dark erosion rate (= the eroded resist film thickness of unexposed photoresist per time) with the developer dilution, as shown in Fig. 97 based on a differently
applied AZ® 400K: A doubling of the degree of dilution of AZ® 400 K: H₂O = 1 : 2 to 1 : 4 increases the selectivity by a factor of five, but at the expense of a much lower development rate.

**Optimum Degree of Dilution**

Therefore, a dilution must be performed when using developer concentrates which is adjusted to the process requirements.

The recommended dilutions for the AZ® 400 K or AZ® 351 B for most of the processes are developer concentrate : Water = 1: 4. For very thick resist films, up to a 1 : 3 ratio can be applied, with a very fine (sub-µm) structures, a 1 : 5 or 1 : 6 ratio can support a high resolution using thin resist films. With AZ® developer, the corresponding dilution window is between 1 : 0 (undiluted concentrate) and 1 : 1.

The 2.38% TMAH-based developers AZ® 326/726/826 MIF are actually "ready-to-use", but can be diluted for very high resolution requirements of thin resist films (for example, 4 : 1 ... 2 : 1).

**Temperature Dependence of the Development Rate**

The temperature dependence of the development rate depends on the used developer and photoresist, as well as its processing, and has its origins in the thermal activation energy of all partial reactions involved in the development process such as dissolution, material transport, solution, complex formation.

Non-constant developer temperatures can have different causes:

- fluctuating clean room temperatures,
- a different temperature of the clean room and where the developer has been stored,
- the heat of mixing during the diluting of developer concentrates,
- a non-constant temperature of the DI-water for the dilution of the developer, or
- evaporative cooling through the flow or the exhaust.

An at least random-sampling measurement of the developer temperature helps to avoid an under or over-development. If the developer concentration cannot be kept constant, their impact on the development rate should be determined and if necessary, the development duration adjusted especially in the case of critical processes.

Fig. 98 shows an example of the KOH-based AZ® 400K and TMAH-based AZ® 726 MIF, different temperature dependencies of the development rate of the AZ® 4562: While the MIF developer has a constant temperature response between 13°C and 32°C, the AZ® 400 K shows a minimum near 25°C. The increase in the development rate with the temperature is explained by an increased reaction rate of the development process. The initially surprising increase in the rate to lower temperatures is due to the fact that at lower temperatures, the formed complex of the already developed resist is more stable and thus its reassembly into the resist film is suppressed.

**Exhaustion of the Developer Through Resist Enrichment**

With a corresponding throughput of substrates, the neutralisation of the developer in the tank development through CO₂ from the air is not necessarily the main cause of a decreasing development rate, but
the exhaustion through the already developed photoresist. Since different photoinitiators absorb quite differently in the visible, the dyeing of the developer bath is not a sufficiently accurate criterion for a necessary change of the developer batch.

In the puddle or spray development, there is often the question of the optimum developer volume per substrate.

A rule of thumb: If one per mill (volume or weight) of developed photoresist is already dissolved in the developer solution, the development rate drops noticeably, so a change of the developer at this time is therefore sensible. From a ratio of 1 : 100, a large fraction of the OH ions are consumed in the developer, and the development rate drops towards zero.

With increasing resist concentration in the developer, a rapid and sufficient rinsing after development becomes more and more important in order to avoid resist residues on the freely developed surfaces of the substrate. For the optimisation (minimisation) of the developer consumption by tank development, a two-stage development can be useful, after the exhaustion of the first developer bath, this is disposed of, replaced by the developer of the second tank and the latter is filled with fresh developer. In the puddle development of thick photoresist films, two or more successive puddle steps are recommended, between which the exhausted developer is briefly spun off without (!) drying between the puddle steps.

**Exposure Dose and Development Rate**

**Positive Resists**

With exposure of DNQ-based positive resists, the following mechanisms impact the course of the later development rate:

- The concentration of already converted photoinitiators decreases exponentially towards zero
- As a result of the bleaching of the resist, the exposure is carried out from the resist surface to the substrate especially with optically thick resist films
- The development rate depends not on a linear function, but comparable to a step function of the photoinitiator converted by the concentration

Fig. 100 shows the effect of increasing light doses on the average development rate of an optically thin (penetration depth of the light > resist film thickness) and optically thick (penetration depth < resist film thickness): From a specific light dose, the photoinitiator is completely converted, the development rate is saturated. In the case of thick resist films, exposure accompanied by bleaching proceeds from the resist surface towards the substrate so that the resist film can be developed.

**Negative Resists and Image Reversal Resists**

The development rate of negative resists and image reversal resists in the negative mode depends only indirectly on the structure-defining exposure dose, since the unexposed (negative resists) or, respectively, flood exposed (image reversal resists) areas are developed. However, these resist areas also receive a certain dose via diffraction and diffuse light, as a result of which especially very fine structures are more difficult to develop with increasing exposure dose. In the case of image reversal resists, care must generally be taken that the dose of the flood exposure is sufficient to completely convert the photoinitiator. The erosion of the resist areas exposed through the photomask increases markedly below a certain light dose when the cross-linking or reversing reaction no longer takes place completely.

**Surface Inhibition Layer**

**Impact**

Developed positive resist structures sometimes show an overhang (“T-Topping”), which results from a suppressed development rate on the resist surface.

Possible explanatory approaches for such a surface inhibition layer (not to be confused with the undercut desired in the case of negative or image reversal resists but attained by means of the reverse reaction) are controversially discussed in the literature. This effect is to be summarised here in the following without any claim to completeness, together with possible explanatory approaches:
Surface Cross-linking
The deep-UV radiation around 250 nm wavelength which, with very low intensity, is also emitted during exposure with Hg lamps, as well as oxygen from air, break chemical bonds in the phenolic resin chains. In the case of subsequent baking steps (e.g. post exposure bake), resist areas near the surface can be cross-linked thermally activated and are thereby difficult to dissolve in the developer.
In the case of non-extremely high exposure doses (as required, for example, in the processing of very thick resist films), the proportionate low UV dose does not, however, result in a significant cracking of phenolic resin chains; and the high diffusion constant of O$_2$ in photoresist cannot explained thermally induced oxidation exclusively near the resist surface.

Spatial Segregation of Resist Components
The different boundary conditions (polar/non-polar) of the photoresist/air and the photoresist/substrate interfaces support spatial segregation of resin molecules - selected according to their molecular size - and theoretically permit the accumulation of resin components which are difficult to dissolve in the developer on the surface of the resist.
Also the formation of spatial gradients of other resist components which impact on the development rate (especially the indene carboxylic acid or residual solvent formed during the exposure) are discussed in conjunction with the surface inhibition layer.

Delayed Start of Development
The - sometimes milky appearance observable with the bare eye - roughening of the resist surface to be developed during the development start increases the effective surface of the developer and explains the initially low development rate, but not the overhangs in the resist profile mentioned at the beginning of this section.
## Our Photoresists: Application Areas and Compatibilities

### Recommended Applications

<table>
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<tr>
<th>Resist Family</th>
<th>Photosists</th>
<th>Resist Film Thickness</th>
<th>Recommended Developers</th>
<th>Recommended Removers</th>
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</thead>
<tbody>
<tr>
<td>AZ® 1500</td>
<td>AZ® 1505, AZ® 1512 HS, AZ® 1514 H, AZ® 1518</td>
<td>≈ 0.3 - 1.0 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® 400K</td>
<td>AZ® 4533, AZ® 4562</td>
<td>≈ 1.0 - 1.5 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® 400K</td>
<td>AZ® 4533, AZ® 4562</td>
<td>≈ 3.0 - 5.0 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® P4000</td>
<td>AZ® P4110, AZ® P4330, AZ® P4620, AZ® P4930</td>
<td>≈ 1.0 - 1.5 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® PL 177</td>
<td>AZ® PL 177</td>
<td>≈ 1.0 - 1.5 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® 4999</td>
<td>AZ® 4999</td>
<td>≈ 1.0 - 1.5 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
</tbody>
</table>

### Positive (chem. amplified)

<table>
<thead>
<tr>
<th>Resist Family</th>
<th>Photosists</th>
<th>Resist Film Thickness</th>
<th>Recommended Developers</th>
<th>Recommended Removers</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ® ECI 3000</td>
<td>AZ® ECI 3007, AZ® ECI 3012, AZ® ECI 3027</td>
<td>≈ 0.7 - 1.0 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® 9200</td>
<td>AZ® 9245, AZ® 9260</td>
<td>≈ 0.7 - 1.5 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® 701 MR</td>
<td>AZ® 701 MR (14 cPs), AZ® 701 MR (29 cPs)</td>
<td>≈ 0.8 - 3.0 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® XT</td>
<td>AZ® 12 XT-20PL-05, AZ® 12 XT-20PL-10, AZ® 12 XT-20PL-20, AZ® 40 XT</td>
<td>≈ 3.0 - 6.0 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® IPS 6050</td>
<td>AZ® IPS 6050</td>
<td>≈ 20 - 100 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
</tbody>
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### Negative (Cross-linking)

<table>
<thead>
<tr>
<th>Resist Family</th>
<th>Photosists</th>
<th>Resist Film Thickness</th>
<th>Recommended Developers</th>
<th>Recommended Removers</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ® nLOF 2000</td>
<td>AZ® nLOF 2020, AZ® nLOF 2035, AZ® nLOF 2070</td>
<td>≈ 1.5 - 3.5 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® nLOF 5500</td>
<td>AZ® nLOF 5510</td>
<td>≈ 0.7 - 1.5 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® nXT</td>
<td>AZ® nXT (115 cPs)</td>
<td>≈ 2.0 - 3.0 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
<tr>
<td>AZ® 125 nXT</td>
<td>AZ® 125 nXT (450 cPs)</td>
<td>≈ 2.0 - 3.0 µm</td>
<td>AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF</td>
<td>TechniStrip® P1316, TechniStrip® P1318</td>
</tr>
</tbody>
</table>

### 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 photo resist based on KOH / NaOH is typically used diluted 1 : 3 - 1 : 7 with water, depending on whether a high development rate, or a high contrast is required.

**Metal Ion Free (TMAB-based) Developers**

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

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.

Resist film thickness achievable and processable with standard equipment under standard conditions. Some resists can also be developed with additional equipment or mixed with other resists.

Also depends on the resist processing and substrate materials used, further details see section 'removers' next page.
Our Removers: Application Areas and Compatibilities

AZ® 100 Remover is an amine solvent mixture and standard remover for AZ® and TI photoreists. 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...

Our 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, besides the crystal orientation (e.g. <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.

Further Products from our Portfolio

Plating

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

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, … 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

Etching Mixtures

for e.g. chromium, gold, silicon, copper, titanium, … 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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