AZ® Photoresists

Introduction to our Product Range

Clariant

HISTORY

The chemistry of positive photoresists, based on a **novolak resin** and **naphthoquinone diazide**, was first discovered by **O. Süss at KALLE in 1944**. In 1962 Hoechst manufactured the first positive working **AZ® PHOTORESIST**, named AZ 15. Until 1970 there were only two different photoresist types available, namely **AZ 111S** and **AZ 1350H**. In the seventies however, with the rapidly growing semiconductor industry, also the demand on photoresists for specific applications increased.

At that time an enormous evolution began and 0.35 µm design rules are nowadays reality in mass production. But still today all novolak based commercial positive photoresists are based on the same chemistry invented by O. Süss. In the following some milestones in the history of **AZ® PHOTORESISTS** are given:

1944 Photochemistry of diazoquinones discovered by **O. Süss at KALLE**
1962 First **AZ® PHOTORESIST** manufactured, AZ 15
1965 AZ 1350H launched to complement AZ 111S for contact/proximity printing
1971 AZ 1350J, a high sensitivity resist for use on projection printers
1979 AZ 1400-series, striation-free-coating versions of AZ 1300-series
First **chemically amplified resist** - the basis for today's e-beam and Deep UV-resists
1980 AZ 4000-series with low absorption for thick coatings
1985 AZ 1300-SFD-series, the first dyed photoresists on the market
1986 **AZ 5200-series** for image-reversal, all previous AZ-resists available in **safer solvent PGMEA**
1988 **AZ 8100-series**, a "fast" version of **AZ 111XFS** for projection printing
1989 **AZ 6200-series**, for sub-micron g-line lithography, new series of dyed resists (suffix **-xDG**)
1990 AZ 7100-series, first generation of 0.5 µm resolution i-line resists
AZ 1500HS-series, improved adhesion for wet-etch and high photospeed
1992 **AZ 6600-series**, a completely new generation of general purpose photoresists
1993 AZ 7500-series, second generation of sub 0.5 µm i-line resists
1994 **AZ 7200-series**, very fast i-line resists for high throughput at 0.5 µm design rules
1995 **AZ 7800-series**, third generation i-line resist for 0.35 µm lithography
1996 **AZ DX 1000-series** of chemical amplified Deep-UV photoresists for 0.25 µm design rules
1997 **AZ DX 2000-series** of 2nd generation DUV-resists for sub-quarter micron applications
AZ 3300-series of mid-range/cross-over resist for g- and i-line

SAFER SOLVENT (PGMEA)

In 1985 there were indications that the principal solvent of positive photoresists, the "cellosolve acetate" might cause birth defects. Already in 1986 **Hoechst** introduced a carefully selected and proven substitute, the **PGMEA** (methoxy-propyl acetate) as a **"safer solvent"**. This solvent is covered by patents, licences have been granted. From that time on all new developments were exclusively based on **PGMEA**, additionally all existing products were reformulated in the new solvent as well to provide a plug-in replacement for the cellosolve acetate based types. Recently also other „safer solvents" like ethyl lactate and mixtures become popular for utmost coating quality.

A few years ago studies (IBM) were published and European Health Authorities considered cellosolve acetate as poisonous, products containing it had to be marked with "crossed bones" from May 1994 on. The following file of **AZ® DATA SHEETS** does contain only AZ products based on safer solvent **PGMEA**. Some elder product families have been replaced by new developments with improved performance and therefore will be excluded as well.

NOMENCLATURE

In general our AZ® Photoresists are divided in two major groups:

STANDARD PHOTORESISTS comprise of already well known products, mainly safer solvent equivalents for elder cellosolve acetate resist types.

ADVANCED PHOTORESISTS in fact cover almost all applications. They have been developed recently to meet nowadays requirements and are matched to modern exposure equipment.

The product designation of AZ PHOTORESISTS contains different information: the **first two digits** indicate the **resist-series**, for instance **AZ 66**00-**series** (general purpose broadband and g-line resists).

The **last two digits** indicate the **coating thickness at 4000 rpm**, for instance **AZ** 66**12** means that this type will give a thickness of **1.2 µm** at 4000 rpm. We feel that such information is more related to practical application than dealing with viscosity or solids content. (AZ 111XFS is the only exemption for historical reasons)

Some resist types contain a suffix, for instance **-2DG**. Here the **D** indicates a **dyed resist**, **G** means the dye is optimised for **g-line** (including h-line), the digit **2** indicates **dye loading**. We have chosen a relative measure for that, the unit 1DG corresponds to about 0.15 μm^{-1} for B-parameter at 436 nm.

COATING PROPERTIES

All available **AZ® PHOTORESISTS** contain an additive to obtain a striation-free coating quality. Coating uniformity on modern equipment is excellent. With exception of some high-viscosity products (>2 µm film thickness) all resists are filtered through an absolute filter of ≤ 0.1 µm pore size assuring a low coating defect level. This low defect level is maintained over the whole life span of the product. This has been proven by monitoring the filtration constant n/n_0 over long periods of time also at elevated temperatures. Recently we introduced „optical particle counting“ in liquid photoresist and counts (cumulative) per ml for ≥0.5 resp. ≥0.3 µm particles are specified.

Nominal coating thickness, as mentioned above, is indicated by two digits in the product designation. However this value refers to our standard conditions (4000 rpm; 40 s; 21°C; 45%RH; etc.) and not necessarily will be obtained under specific customers conditions. In most cases coating thickness will have to be fine tuned to hit target thickness by readjusting spin speed.

There is a quite simple method to calculate coating thickness from one measured pair of (spin speed/thickness). Between both following relationship exists:

$$\text{thickness} = \text{const.} * (\text{spin speed})^{-1/2}$$

This means that in a plot with [thickness] as vertical scale and horizontal scale [1/square root (rpm)] a straight line is obtained which also hits the origin (thickness=0 / infinite spin speed). So, if one pair of (thickness/rpm) is plotted in this graph and a straight line drawn through this point and the origin, for any desired thickness the corresponding spin speed can be read. Of course this can also be done by calculation. Assume:

d(t) = target thickness — rpm(t) = target spin speed
d(1) = measured thickness — rpm(1) = measured spin speed

Then: $rpm(t) = rpm(1) * [d(1)/d(t)]^2$ will give the target spin speed for target thickness.

This procedure is quite accurate, and deviations in thickness are less than 10 nm over a spin speed range from 3000 to 6000 rpm. In case that both thicknesses are not too far away from each other, following approximation may be used: If thickness is to be increased by x%, then decrease spin speed by 2x%, or vice versa. For convenience a small table is given below for most common resist types:

spin speed [rpm]	2000	3000	**4000**	5000	6000
AZ xx12	1.70	1.39	**1.20**	1.07	0.98
AZ xx15	2.12	1.73	**1.50**	1.34	1.22
AZ xx18	2.55	2.08	**1.80**	1.61	1.47

FILM THICKNESS [µm] as FUNCTION of SPIN SPEED

This table however should be used only for rough selection of the proper resist type and give an indication on the thickness range which can be covered.

PREBAKE

Intention of the prebake is to evaporate most of the solvent and thus dry the resist film. Because of the relatively high boiling point of the solvent (>134°C) there always will remain a small amount in the order of a few percent solvent left in the dried resist. This residual solvent influences dissolution rate of exposed resist and thus photospeed. Therefore prebake conditions also have to be controlled well if a consistent process is desired.

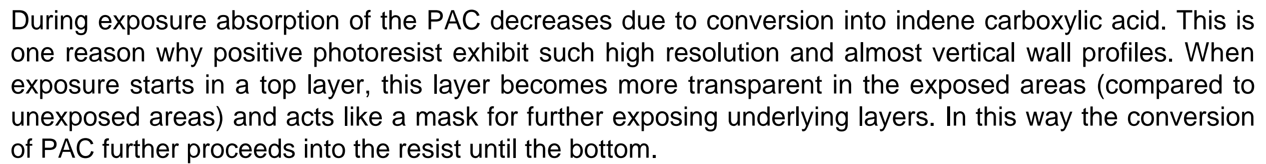
If photoresist is subjected for longer periods to temperatures above 100°C, the light sensitive naphthoquinone diazide (PAC) is thermally decomposed and lithographic performance is degraded. This has to be considered when the prebake is performed in an **convection oven** where bake times are usually around **30 minutes**. Here a temperature of **90°C** is a good choice.

The situation is different when prebake is performed on a **hotplate**. Here the bake time is relatively short, commonly 40-50 seconds. As silicon is a good conductor for heat, temperature equilibrium is reached already after about 10 s. For this reasons the bake temperatures on a hotplate are generally 10 to 20°C higher than in an oven, **110°C for 45 seconds** is a good choice (if no PEB is used).

EXPOSURE

All positive working **AZ® PHOTORESISTS** are sensitive to UV-light, as a light source a mercury lamp is generally used. For proper operation the light energy must be absorbed by the photoactive compound (PAC) which, by exposure is converted into indene carboxylic acid. This acid later on is dissolved in the alkaline developer. The spectrum of light to which the resist responds is determined by two factors: below 310 nm the common novolak resin shows high absorption preventing sufficient penetration of the light (Deep-UV resists use special resins with a window at 248 nm), above 440 nm the naphthoquinone diazide (PAC) shows steep roll-off in absorption and thus photosensitivity. At 475 nm and above the resists are completely transparent and no longer sensitive, therefore they are generally handled and processed under yellow light.

In the above mentioned range of wavelengths there are three major single emissions of the mercury lamp at: 365 nm (i-line), 405 nm (h-line) and 436 nm (g-line). Modern exposure equipment (projection printers) either use a single wavelength like reduction steppers with lenses (mainly g- or i-line), or two or all three wavelengths what is called broadband exposure. For every type of exposure equipment there are optimised resist series available: **AZ 6200B-series for g-line**, **AZ 7200- and AZ 7800-series for i-line** and **AZ 6600-series for broadband** (and also g- or h-line). It should be pointed out that there are three resist series which due to a different PAC (absorption rolls off at 420 nm) do **not respond to g-line: AZ 111XFS, AZ 8100-series, AZ 5200E-series**. All other standard resists may be used with UV-light in the range from 310-440 nm.



During exposure absorption of the PAC decreases due to conversion into indene carboxylic acid. This is one reason why positive photoresist exhibit such high resolution and almost vertical wall profiles. When exposure starts in a top layer, this layer becomes more transparent in the exposed areas (compared to unexposed areas) and acts like a mask for further exposing underlying layers. In this way the conversion of PAC further proceeds into the resist until the bottom.

Exposure of positive photoresist should be carried out under controlled environment, especially relative humidity (RH) and temperature. Background for this is that conversion of the PAC into (developer soluble) carboxylic acid requires 1 molecule of water per molecule of naphthoquinone diazide. If water is missing the PAC will crosslink to an insoluble compound, exposed areas will not dissolve in developer. The necessary water is not contained in the resist film and has to be absorbed as moisture from the atmosphere. For this reason photospeed will drastically fall off if humidity is below 30% RH.

The upper limit for humidity is not determined by the photoresist itself, however if it goes above 60% RH substrate surfaces will absorb too much water resulting finally in adhesion failure of the photoresist. For above reasons a **relative humidity of 45% is recommended**. Additionally it is a good practice to apply HMDS as a primer after a dehydration bake (at 200°C or higher) on surfaces which readily absorb water, before coating photoresist.

POST EXPOSURE BAKE (PEB)

A post exposure bake in most cases is not necessary. The exposed photoresist may be developed immediately after exposure. However in some cases lithographic performance can be improved by applying a PEB after exposure before development. Especially with monochromatic exposure (g- or i-line stepper) the deposited energy varies over the layer thickness of the resist. This variation is caused by interference of incident light and reflected light from the interface substrate/resist. The interference changes from destructive to constructive with distance from the interface. The result of this phenomenon are the so called **standing waves** visible along the wall profile with a SEM. Also as most surfaces cause a phase shift of 180° for the reflected light, there will be a minimum of effective light intensity at the interface substrate resist, if surface layer is (transparent) silicon oxide, also oxide thickness is of importance. As a result of this residues at the bottom of the resist profile may remain after development unless sufficient overexposure is used. This effect is sometimes called **scumming**. Standing waves are the visible part of the interference effect, in practical lithograpy it results in significant variation of exposure dose when film thickness of resist is varied by small amounts. A thickness change of 65 nm (a quarter wavelength at g-line) may result in 20% change in exposure dose. At i-line and DUV this effect is even more pronounced. Such changes in film thickness occur on any surface with topography.

These effects can be minimised by applying a **PEB**. The temperature for this bake should be about **20°C higher than prebake** temperature, time is generally around **45 seconds** to maintain a cycle time for the track of 60 s. During this bake diffusion of exposed and unexposed PAC takes place and results in levelling out the differences in dissolution rate and thus a smooth and clean resist profile. The higher the temperature difference between prebake and PEB, the faster diffusion takes place. PEB temperature should not exceed 130°C to avoid significant thermal destruction of PAC, **110°C for 50 seconds** is a good choice, at the same time the prebake temperature has to be lowered to 90°C for optimum performance. Inserting a **PEB** also **improves adhesion** and **thermal stability** of the resist profile.

DEVELOPMENT

Exposed areas of resist are dissolved during development. Developers are aqueous alkaline solutions either based on sodium hydroxide (inorganic developers) or **t**etra **m**ethyl **a**mmonium **h**ydroxide **TMAH** (organic developers). TMAH is used where mobile ions like Na^+ are of concern, mainly when making MOS-devices. Our **AZ 326 MIF, AZ 726 MIF and AZ 826 m**etal **i**on **f**ree developers are based on 2.38% TMAH and manufactured to highest standards (low ppb trace metal level, better than 1% controlled activity). AZ 326 MIF is pure TMAH, AZ 726 MIF contains a selected surfactant for fast and uniform wetting of the wafer, AZ 826 contains different surfactants for higher dissolution rates and residue-free development. All are normally used in **puddle development**, tank development is applicable also.

AZ 351B is based on sodium hydroxide and buffered by borate. It comes as a concentrate, is normally diluted 1 : 4 with water and used for tank or spray development (not suitable for puddle). Alternatively also 0.5% NaOH solution can be used, but it is difficult to control activity in tight tolerances. **Attention: AZ 111XFS and AZ 8112 do require a special developer AZ 303**, which also is diluted 1 : 4.

Development conditions are mainly determined by the photoresist type. Each resist series gives optimum results with certain development times, details are given in the resist data sheets. In most cases development times fall within the range of **20 - 50 seconds**, only extreme thick resist layers (>3 µm) need longer times. Temperature itself is not critical and room temperature (20 - 25°C) is fine, however it should be kept constant (±1°C) for best process consistency. More details about specific developers are given in the corresponding data sheets.

POSTBAKE

Intention of the postbake is to further stabilise the photoresist for subsequent etch processes. The maximum temperature depends on resist series and their thermal stability (see specific data sheets). Typical values are 110°C to 130°C, either 50 seconds hotplate or 30 minutes in an oven. In some cases the postbake can be omitted. Generally a postbake improves adhesion in wet-etch and should be considered as part of the etch process. This means it should be carried out immediately (max. 2 hours) before etching. If postbake is performed already on the development track and there is a longer delay before etch, the bake should be **repeated prior to etch**. Therefore it is often named **pre-etch bake**.

For dry-etch the necessary stabilisation for harsh conditions may require a **D**eep-**UV** curing (**DUV**). In special available equipment the resist is completely crosslinked. Under high energy DUV illumination the temperature is ramped up to 250°C, DUV preventing degradation of the resist profile.

Auxiliary AZ®-Products

Clariant not only manufactures photoresists, but also auxiliary products which are needed to process them. They include Developers, Removers, solvents for edge-bead removal and dilution of resists, anti-reflective coating materials (top- and bottom-types). These coatings are used to suppress multiple reflections at the interface resist/air (AZ AQUATAR®) and at the interface resist/substrate (AZ BARLi®). Using AZ AQUATAR® coating, the amplitude of the swing curve can be significantly reduced and thus line width variation over topography. AZ BARLi®, a bottom coat can reduce reflection at the substate interface to a few percent at i-line, resulting in almost no standing waves and wider process latitude.

AZ®-Products for Deep UV Lithography

It is worldwide accepted in the lithographic community, that the most mature and cost effective technology to print quarter micron and sub-quarter micron patterns is deep UV (DUV) lithography. Since 1988, Clariant offers an increasingly large material range of chemically amplified resist materials with a strong focus on **DUV photoresists**. Due to the large experience and customer base, there are a genuine know-how base and sophisticated production experience available. Besides their well accepted first generation DUV photoresists **AZ DX 1000-series** designed for quarter micron imaging, Clariant's AZ® Electronic Materials unit offers a range of advanced photoresist products providing practical imaging capabilities for **0.18 µm design rules**, such as **AZ DX 2058P**, a high speed resist material for sub 0.20 µm lines and spaces applications, **AZ DX 2034P** for logic devices featuring excellent iso/dense bias and compatibility with metal level substrates, and **AZ DX 3200P** for advanced contact level imaging.

All Clariant DUV resists are polyhydroxystyrene based chemically amplified photoresist systems taking advantage of the low activation energy acetal chemistry thus providing high resolution capability, large process windows, and outstanding process and delay time stability. Prebake, post-exposure bake and development conditions are 100% compatible with standard i-line processing facilitating their implementation into existing production lines. All photoresists of the AZ® DX series offer excellent etch resistance. In addition to the commercially available materials, a series of pre-commercial advanced DUV photoresists are available upon request.

More recently, Clariant has started to sample photoresists for **ArF-lithography** using radiation of a wavelength of **193 nm** with good customer feedback.

Special **Bottom Anti Reflective Coatings** optimised for DUV and compatibility with various surfaces are available as well.

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