EXPOSURE

The previous chapters have described the steps and which are necessary to provide a substrate with an exposable resist coating. As the name photolithography already clearly expresses, the following exposure of photoresists represents the main key process in microstructuring.

The chemical processes occurring here in the resist film result in an increased (positive resists) or reduced (negative resists) solubility in the developer, whereby a structured resist mask can be produced.

This chapter enters into detail on all aspects of exposure: From the chemical and physical processes in the resist film, the spectral sensitivities of photoresists and the spectral emissions and properties of common exposure methods through application-oriented explanations with focus on an optimally exposed resist film.

The Photoreaction

DNQ-based Positive and Image Reversal Resists

The schema in Fig. 82 shows the essential steps of the photoreaction, i.e. the desired chemical reaction during the exposure of the photoinitiator in the photoresist: Under nitrogen release and the binding of water molecules, the photoinitiator molecule is converted into an indene carboxylic acid.

The binding site of the SO_2-R group determines whether a photoresist is h- and i-line sensitive (binding site on the "right" carbon ring) or g-line (binding site on the "left" carbon ring). In order to increase their thermal stability and solubility in the resist as well as to strengthen the properties as an "inhibitor" (reduced dark erosion), several DNQ sulphonate molecules can be bound to a so-called *backbone* molecule.

The quantum efficiency of the photoreaction defines the number of photoreactions per photons absorbed in the resist film. Sufficiently rehydrated DNQ-based photoresists with transparent resin, exposed at suitable wavelengths (g, h, i-line depending on DNQ), achieve a quantum efficiency of approx. 20 - 30%.

If a minimum amount of water is missing in the resist film (insufficient rehydration, see Chapter 14), the ketone (Fig. 82 centre) may undergo various undesired secondary reactions (e.g. esterification with the resin or polymerisation with CO_2 splitting). In both cases, no indene carboxylic acid is formed, the rate of development increases exclusively through the decrease in the concentration of the inhibitor DNQ.

Non-DNQ-based Positive Resists

In the case of special chemically amplified resists such as the AZ® 40 XT, no indene carboxylic acid but rather sulphonic acid is formed during exposure. Neither water is chemically bound nor N_2 released, which makes the processing of this resist much easier and faster even with very large resist film thicknesses than would be possible with DNQ-based resists.

Cross-linked Negative Resists

In some negative resists such as the AZ® nLOF 2000 series or the AZ® 15 nXT, the exposure activates a melamine cross-linker which in the subsequent baking step (post-exposure bake) causes the linking of short phenolic resin units to longer chains.

With the AZ® 125 nXT, the exposure starts a photo polymerisation of acrylic monomers already at room temperature. This resist does not require a post exposure bake.

Spectral Sensitivity of Photoresists

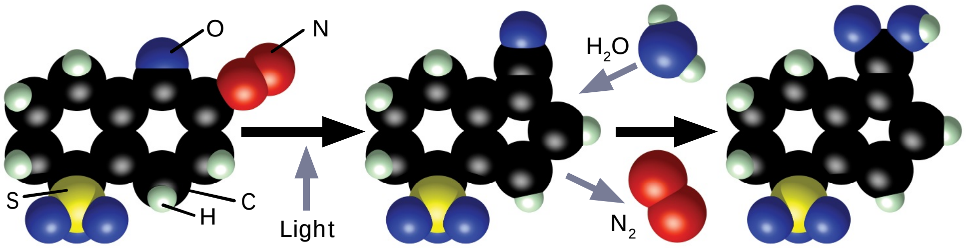


Fig. 82: The photoinitiator, a diazo-naphthoquinone (DNQ) sulphonate (left) is converted into an indene carboxylic acid (right) under N_2 release (centre) and H_2O absorption by exposure to suitable wavelengths.

G-, H- and I-line Sensitive Photoresists

The spectral sensitivity of the AZ® and TI photoresists we sell is in the near-UV range, and with most resists, also in the visible short-wavelength (blue) spectral range.

Resists which are only sensitive in the range of the i-line (365 nm) are called *i-line resists*. These include, among others, chemically-amplified positive resists such as the AZ® 40 XT or negative resists such as the AZ® 15 nXT, AZ® 125 nXT or the AZ® nLOF 2000 series. Broadband resists also absorb the g- (435 nm) and h- (405 nm) lines, but can also be exposed monochromatically within their spectral sensitivity.

Deep-UV Resists

Deep-UV resists have a spectral sensitivity below 280 nm wavelength. Through exposure wavelengths of, for example, 247 or 193 nm, the resolution of attained resist structures can be improved significantly compared with i-line or broadband resists. Combined with the so-called immersion lithography, structure sizes under 50 nm are attained.

Next Generation Photoresists

To meet the requirement of smaller and smaller structure sizes, photoresists which can be exposed at even shorter wavelengths are required. However, the transition to the so-called *extreme UV* (EUV) radiation (< 120 nm wavelength) and X-ray lithography (< 10 nm) requires completely different optical systems and materials than the currently mainly used photolithography methods.

Exposure Techniques

Mask Aligners

With exposure using a mask aligner, parallel light passes through the transparent areas of a photo mask onto the resist film (Fig. 83 left). The photo mask usually consists of a glass or quartz plate as carrier on which a thin lithographically patterned chromium coating forms the non-transparent pattern.

The dimensions of the structures on the photo mask correspond to 1 : 1 the dimensions of the exposed areas of the resist film, the image is thus *congruent*.

For an optimisation of the attained resolution, the photo mask and the surface of the resist film are in direct contact, whereas, for example, textured substrates may require a gap between the mask and the resist film.

Stepper

Using a stepper, exposure is also performed as a projection through a photo mask (Fig. 83 centre). By reduction optics, the dimensions of the exposed resist areas are, however, smaller than the structures of the photo mask on which lower requirements can be placed.

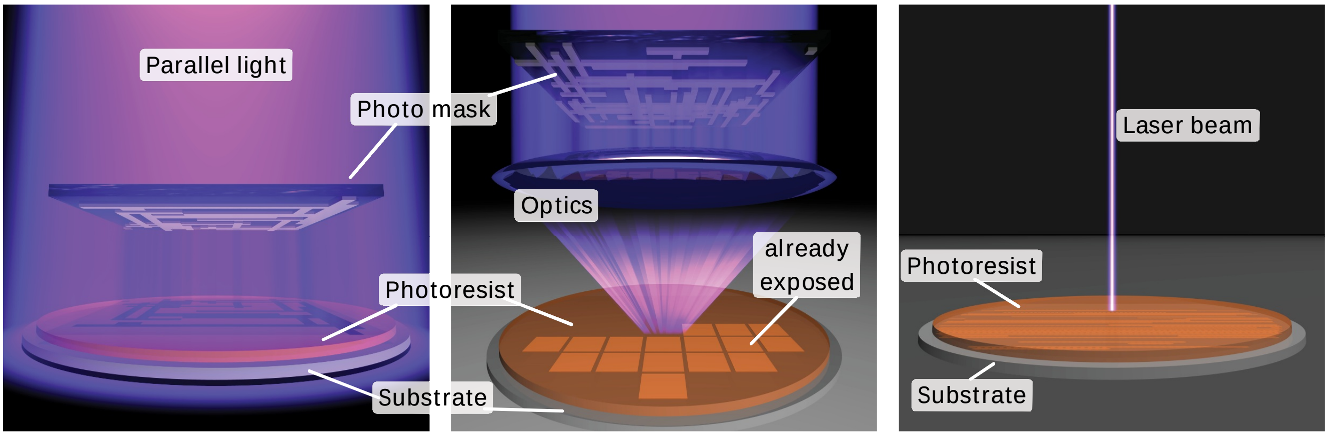


Fig. 83: The most common methods for exposure of photoresist layers are the direct projection onto the whole substrate with a *mask aligner* (left, usually the photomask and resist are in close contact), the stepwise exposure of rectangular partial surfaces by a reduction optics (*stepper*, centre) or the direct writing of the structures with a laser (right).

Since only a part of the resist film is exposed by the reduced image during each exposure step, the exposure of the entire wafer takes place step by step in sequence always having the same image, whereby, for example, a large number of identical circuits or components are realised on one wafer.

Laser Direct Writing

In this case, a laser sequentially exposes the photoresist film on a direct path (Fig. 83 right), i.e. pixel by pixel. This eliminates the need for the production of expensive photo masks. Layouts can be implemented immediately if they are available in a suitable electronic form to the laser exposure tool. One drawback of the laser exposure is the long writing times per substrate, which is why this exposure technology then lends itself if a layout is only to be written on a few substrates as is the case in the production of photo masks.

Section 16.10 treats the laser exposure from the perspective of photoresist processing in detail.

Other Exposure Techniques

In order to implement high resolution requirements, reproducible structure and defined resist sidewalls, exposure wavelengths adapted to the absorption of the resist, as well as perfect optics, such as offered with mask aligners, steppers or laser exposures, are indispensable.

If neither corresponding equipment is available, nor high demands by means of resolution made on the attained resist mask, an exposure can also be done via, for example, printed foil masks over any other light sources with a suitable spectrum. For example, the emission spectrum of white fluorescent tubes with the blue g-line (435 nm wavelength) strongly represented, allows the exposure of standard broadband resist in a rather simple way.

Spectral Emission of Typical Exposure Tools

Mercury Vapour Lamps

The typical emission spectrum of a mask aligner or stepper with mercury vapour lamp without further optically selective elements contains the g- (wavelength 435 nm), h- (405 nm) and i-line (365 nm). A 6” mask aligner with a 350 W Hg lamp usually attains a light output of approx. 15 - 30 mW/cm^2, whereby the i-line intensity usually accounts for approx. 40% of the total emission of all three emission lines. The absorption spectrum of the photoinitiator of corresponding photoresists is adapted to these lines.

Particularly for dose-sensitive applications such as image reversal resist, thick-resist processing or for high resolution requirements, a periodic calibration of the light intensity is recommended, which changes with the operating time of the lamp. As a rule of thumb for non-critical litho-processes, a measurement of the lateral intensity distribution over the illuminated area should yield less than 10% relative deviation to allow the adjustment of an optimal exposure time for central and peripheral regions.

Laser Exposure

In addition to Hg lamps, lasers with a suitable wavelength are also a suitable light source for the exposure of photoresists. Because the spectral absorption bands of the photoinitiator do not abruptly terminate at a particular wavelength, a correspondingly adapted dose can also be exposed at wavelengths of some 10 nm above the ranges indicated in the data sheets, which, however, significantly extends the writing times.

Determination of Optimum Exposure Dose and Exposure Duration

Conversion Factors between Exposure Dose and Exposure Duration

For the correct determination of the exposure time from the recommended exposure doses given in the technical data sheets, the following must be known:

- What is the spectrum of the exposure tool (monochromatic at i-, h- or g-line or broadband across all lines)? Without optically selective elements such as i-line filters, all three lines are usually present in Hg vapour lamps.
- At which wavelength was the light intensity determined? Many detectors measure only i-line, which typical 350 W Hg lamps emit with approx. 6 - 12 mW / cm^2, with 1000 W Hg lamps about three times higher.
- At which wavelengths is the photoresist sensitive (i-, h- or / and g-line), and how sensitive?

- To which wavelength corresponds the light dose in the technical data sheets of the photoresists? Usually, the exposure series shown there are performed with monochromatic i-line exposure.

Interchangeability of Exposure Intensity and Exposure Time

The photoreaction with positive and image reversal resists usually is a one-photon process. For this reason, it does not matter in principle how much time (from femtoseconds in pulsed lasers, to seconds in contact lithography to hours in laser interference lithography) the required dose is applied onto the resist film as a product of intensity and time.

However, it must be taken into account that the delayed discharge of the heat or gases formed during exposure (N_2 in the case of positive and image reversal resists) from the resist film can lead to thermal or mechanical damage to the resist with increasing light intensity and resist film thickness.

Further Influencing Factors on the Optimal Exposure Dose

The reflectivity of the substrate has an effect on the exposure intensity actually absorbed by the resist film, particularly in the case of optically thin resist films. Glass wafers reflect about 10% of the shortwave radiation, silicon wafers about 30%, and metal films can have a reflection coefficient of over 90%.

Which exposure dose is "optimal" also depends on the requirements for the lithography process. A certain under exposure may reduce exposure artefacts attained on textured or diffuse reflective substrates. In the case of thick-resist processing, a sufficiently dimensioned light dose maintains the later development duration at justifiably short values.

Exposure Series for Positive Resists

In principle, a series of exposures is recommended for the optimisation of the process, for each new process and for changes to equipment or photoresist to determine the optimal light dose. This depends not only on the photoresist, but also on the optical substrate properties and various process requirements.

For positive resists, the "optimal" light dose for most lithographic processes is close to the value at which the development rate begins to saturate, i.e. does not increase further towards larger light doses.

The graphs in Fig. 84 show the development rates of various positive photoresists as a function of the exposure duration or dose. All resists were spin-coated at 4000 rpm, baked at 100°C on the hotplate for 1 minute per µm resist film thickness, and developed (immersion) after exposure in the TMAH-based AZ® 826 MIF. The image was flood-exposed (without photomask) using a mask-aligner with a 350 W Hg lamp at an i-line intensity of 8.5 mW/cm^2 and approx. 22 mW / cm^2 integrated over g-, h- and i-line.

In all examples, it is clearly shown how, with the positive resists used, the development rate starts to saturate from a certain dose, which corresponds to the conversion of the total photoinitiator in the resist.

Exposure Series for Image Reversal Resist and Negative Resists

For image reversal resists processed in the negative mode, a high dose in the first (structure defining) exposure increases the degree of the image reversal reaction as described in Chapter 20 on page 110 in detail.

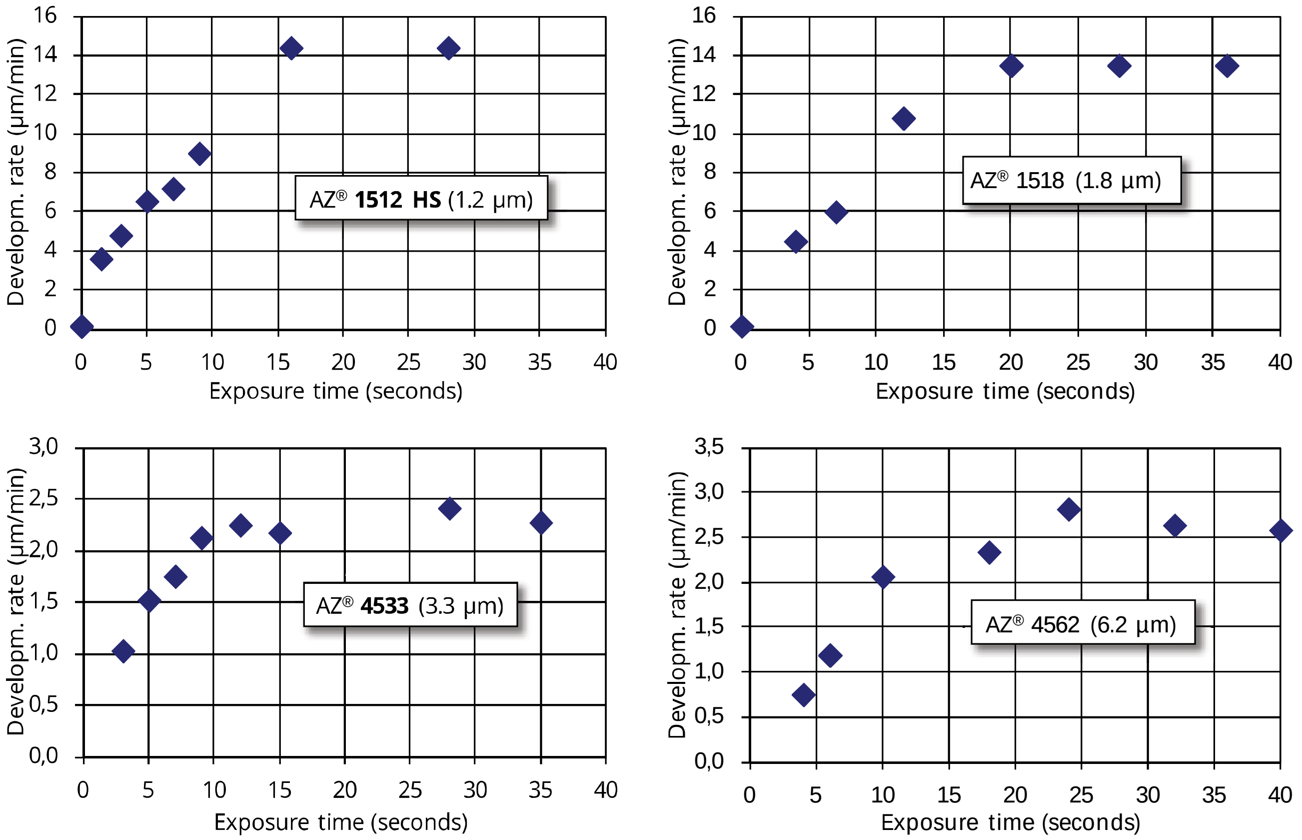
In the case of the negative resist processing, the degree of cross-linking of the resin and therefore the resist insolubility in the developer increases with the light dose, as shown in Fig. 85 based on the AZ® nLOF 2070. Excessive light doses can lead to unintentional exposure of adjacent, "dark" resist areas. This increases the dimensions of the developed resist structures, which makes the through-development of small holes or narrow trenches difficult or impossible.

If image reversal or negative resists are used for lift-off processes, the effect of the exposure dose on the resist profile must be considered: Since the received light dose decreases from the resist surface to the substrate due to the limited penetration depth of the wavelengths used, the optimum exposure dose is defined by the desired resist profile for the respective process.

The Bleaching of DNQ-based Positive Resists

The Absorption Coefficient of Unexposed and Exposed Photoresists

The photoinitiator content of typical photoresists results in an absorption coefficient in the range of the



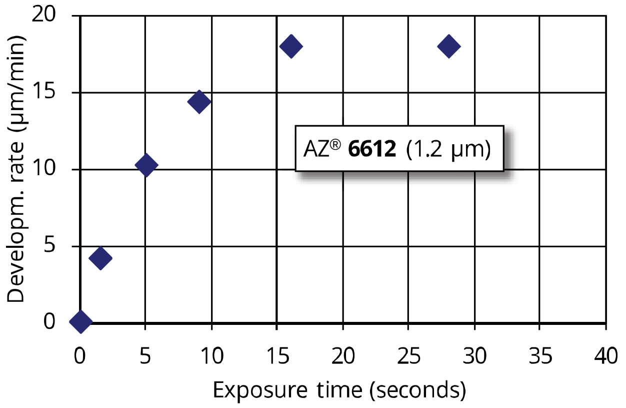


Fig. 84: (Five graphs left and above) The development rate of different photoresists increases initially with an increasing flood exposure dose (without photomask), then saturates to a value which depends on the photoresist, the developer and the preceding process parameters such as softbake and rehydration.

The light intensity of this series was about 22 mW/cm² (summed over the g-, h- and i-line), so that each second exposure time corresponds to approximately 22 mJ/cm². The resist was developed in the AZ® 826 MIF (2.38% TMAH) by means of immersion development, the substrates used were polished silicon wafers.

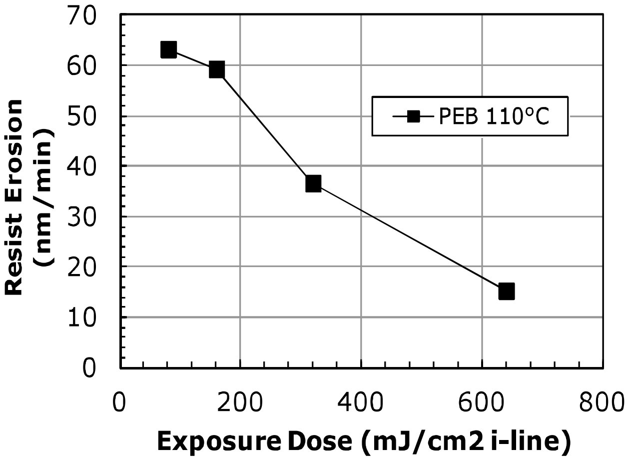


Fig. 85: (Left) With cross-linked negative resists (here: AZ® nLOF 2070), the degree of cross-linking of the resin increases with the exposure dose. The rate of erosion of the exposed resist in the developer shown in this graph decreases with an increasing degree of cross-linking and is zero in the ideal case.

The light intensity of this series was about 8 mW/cm² (i-line). It was developed in the AZ® 826 MIF (2.38% TMAH) by means of immersion development, the substrates used were polished silicon wafers.

sensitivity maximum of approximately 1 - 2 µm^{-1}, which would theoretically make it impossible to expose thick photoresist films.

However, during the exposure by the conversion of the photoinitiator, the absorption coefficient decreases by orders of magnitudes: Photoresists bleach when exposed (*Bleaching*) and become largely transparent below approx. 440 nm wavelength (Fig. 86).

As a result, the penetration depth of the incident light increases in the already exposed resist areas which corresponds to a self-amplified light channelisation in the resist film. This effect allows to achieve a complete exposure of thick resist films as well as achieving high aspect ratios.

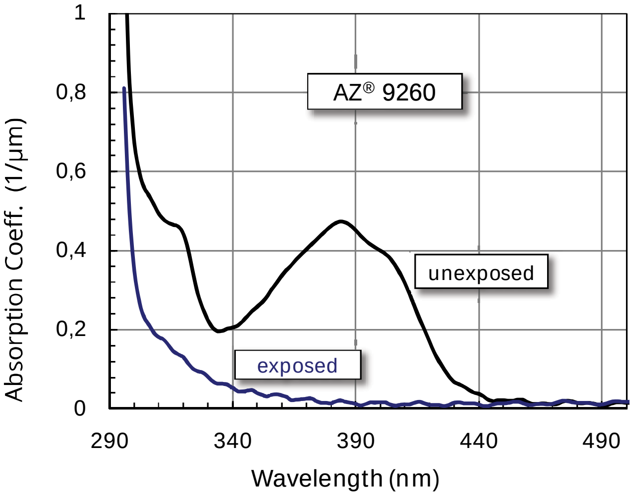


Fig. 86: The absorption spectrum of the AZ® 9260 before (black) and after (blue) the exposure.

Exposure of Thin and Thick Photoresist Films

The resist film thickness related to the penetration depth of the light determines how the depth profile of the already received light dose changes with the exposure time:

In the case of *optically thin* resist films (with a film thickness less than the penetration depth of the exposure wavelength), an almost homogeneous exposure occurs from the exposure start. An increase in the light dose up to the complete conversion of the photoinitiator thus results in a larger, but largely homogeneous, development rate down to the substrate.

Optically thick resist films (with a film thickness much larger than the penetration depth of the light) absorbs only in the uppermost µm at the beginning of the exposure, which thereby bleach and guide the light increasingly deeper toward the substrate during further exposure. In this case, the developable resist thickness increases nearly linearly with the exposure dose, which allows certain applications in the grey-lithography: The resist film can only be completely developed after a certain minimum dose.

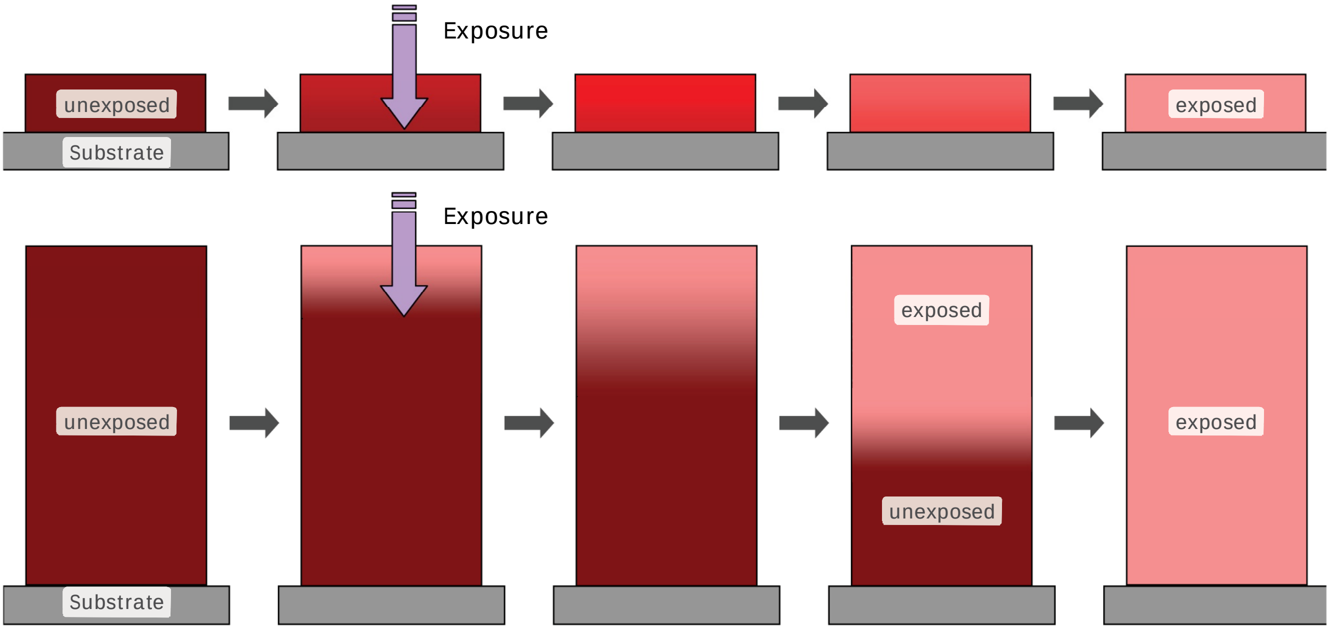


Fig. 87: While optically thin photoresist films (upper row) are almost homogeneously exposed, resist films with a thickness of several penetration depths of the exposure wavelength (lower row) bleach with increasing light dose (from left to right) in the direction of the substrate. A dependency between the exposure dose and the development rate or the duration of the development, which is different for thin and thick resists, results in the later development.

The Contrast of Photoresists

Contrast

The light diffraction prevents a perfect binary mapping of the mask layout in the resist film during the exposure. There will therefore always be "grey areas" in the photoresist, which receive a dose between zero and the maximum dose of larger exposed areas.

If the development rate of a photoresist increases only linearly with the exposure dose, then neither vertical resist sidewalls, nor high resolutions would be possible in the sub-µm range. However, that both can be attained is due to the *contrast* of a photoresist. High-contrast photoresists have very low erosion of weakly exposed areas and develop at a constant and high rate from a specific light dose.

Contrast Curve

The contrast curve of a photoresist reveals the ratio of the remaining resist film thickness to the original film thickness d'/d_0 after the development as a function of the logarithmically scaled exposure dose (Fig. 88).

The contrast curve of a "perfect" positive resist would be a step function (infinitely high contrast). Realistic contrast curves show a $d'/d_0 < 1$ for an exposure dose = 0 (dark erosion) and an infinitely logarithmic drop in $d'/d_0 \rightarrow 0$ over an area of the exposure dose up to D_C (*dose to clear*). The slope of this drop defines the contrast.

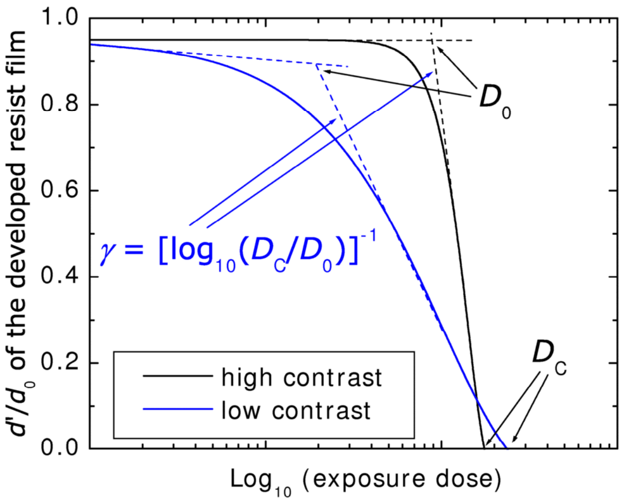


Fig. 88: The contrast of photoresists defined as the increase of the dependency of the remaining resist film thickness after the development to the original resist film thickness d'/d_0 from the logarithmically scaled exposure dose.

The possible or attained contrast does not only depend on the photoresist itself: When comparing a given contrast curve and its corresponding process, all parameters affecting the development rate and time, such as resist film thickness, softbake, rehydration, air temperature, developer etc., are to be considered.

Contrast Enhancement for Maximum Resolution and Aspect Ratio

Suitable methods for contrasts increase (= steep resist profile and high aspect ratio) are ...

- the use a high contrast photoresist such as the thin resist AZ® 1512HS or the AZ® ECI 3000 series with comparatively high photoinitiator content, allowing a high rate of development with minimal dark erosion,
- the use of a negative resist such as the AZ® nLOF 2000 series or AZ® 15 nXT or AZ® 125 nXT) which demonstrates a very low erosion in the developer on the exposed sites through their cross-linking.
- with DNQ-based resists, a sufficient rehydration, which allows a short development time hereby lowering the total dark erosion.
- the minimising of the dark erosion and maintenance of a high development rate of positive resists via optimised softbake parameters, and
- the use of a highly selective, optimally diluted developer such as the TMAH-based developers AZ® 326 MIF and AZ® 726 MIF or the AZ® 400K or 351B in a 1 : 4 or in the case of very thin resist films, also higher dilution if required.

The advantage of a high contrast can only be used with positive resists if the optimal exposure dose is determined for this and evaluated over an exposure series. Only in this way can an unnecessarily long development for weakly exposed resists, as well as an erosion of nominally unexposed resist areas be prevented.

Contrast Reduction in Grey Lithography with Positive Resists

On the contrary, with the grey lithography as well as with several applications of laser interference lithography (*LIL*), a low contrast is desired, that is, a relationship as linear as possible between the light dose and development rate.

Wavelength and Mask Distance as the Lower Resolution Limit

Physical Principles of Diffraction

The dimensions of the transparent areas in photo masks are often of the order of magnitude of some to a few 10 exposure wavelengths. Therefore, the image through such an opening on the resist surface is not a perfect parallel image but needs to be calculated as diffraction pattern behind a slit.

If this case is treated as *diffraction on the single slit*, the attainable lateral resolution d of the incident image on the surface of the resist is represented by the formula $d = (\lambda\ g)^{1/2}$ with the exposure wavelength λ and the gap (= distance of the masking underside to the resist surface) g.

Such a defined gap can be intended to prevent damage to the photo mask in the case of textured substrates or, on smooth substrates, sticking of the photo mask with the resist film. Reasons for an unintentional gap, however, can be:

- particles in the resist film from clean room air, contaminated substrates or expired photoresist,
- air bubbles in the resist film from the manual dispensing of the resist or a too short waiting time after moving of resist containers,
- a mask contamination by particles or resist residues,
- rough, textured or curved (strained) substrates, or
- a resist edge bead, or a mask attached upside-down

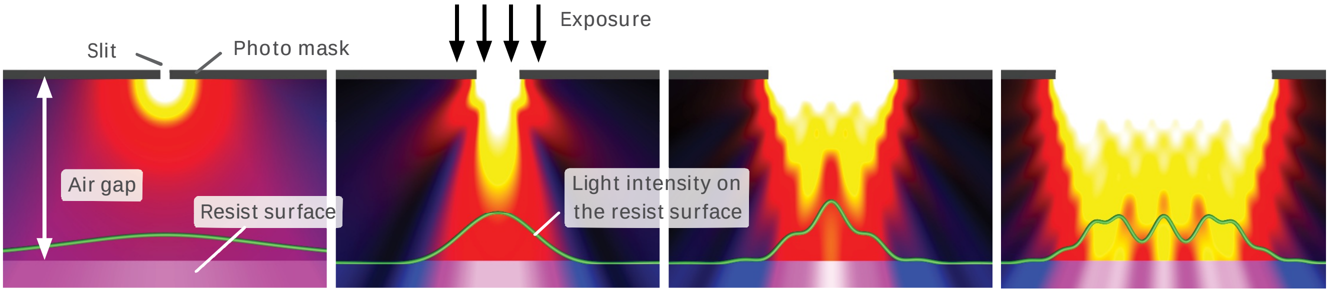
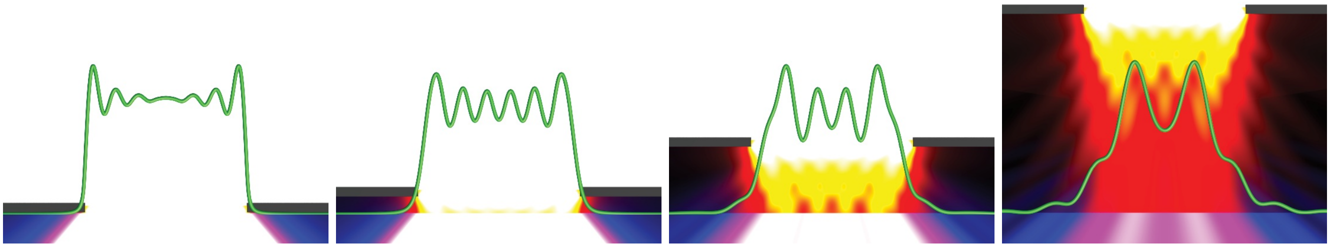


Fig. 89: (Upper row) The intensity distribution of the light in the air gap between the photo mask and the resist surface (from black to red to yellow and white) corresponds to the single slit diffraction pattern when a resist film is exposed through differently sized openings of a photo mask. The light intensity distribution on the surface of the resist (from black to blue and increasingly purple to white, also represented as green plot) in case of a narrow slit (far left) relative to the exposure wavelength and gap represents a point or line source, and for a wide slit (far right) to an increasingly parallel figure through the opening of the photo mask on the resist surface.

Fig. 90: (Lower row) In the same colour scheme as in Fig. 89, the distance between the photo mask and the resist surface is varied from zero (contact exposure, left) to a value of several exposure wavelengths (right) at a constant slit width of the photomask. From left to right, an increasingly distinctive diffraction pattern with corresponding inhomogeneous intensity distribution arises from a nearly rectangular figure of the light intensity.



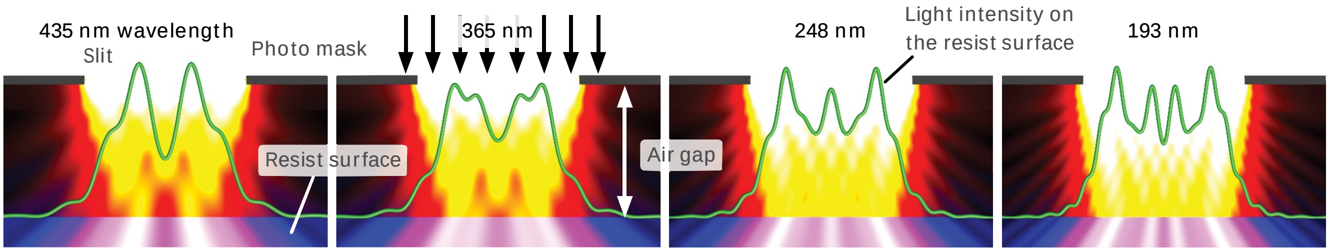


Fig. 91: The light intensity distribution of different exposure wavelengths (from left to right: 435 nm, 365 nm, 248 nm and 193 nm) in the air gap under a 1 µm wide opening (slit) in the photo mask shows how larger wavelengths cause a more pronounced diffraction pattern (same colour schema as in Fig. 89).

Fig. 89 illustrates the diffraction pattern in the air gap between the photo mask and resist surface and the resulting intensity distribution on the resist surface for different opening widths of the photo mask at constant values for wavelength and gap.

In Fig. 90 the gap is varied at constant values for wavelength and slit width in the same scheme. As you can see, even with a perfect contact ($G = 0$), the lateral intensity distribution on the resist surface is inhomogeneous, since the finite gap width forms a diffraction pattern immediately behind the slit.

In addition, the resist film itself has a certain thickness; the resist areas near the substrate having a corresponding higher distance from the photo mask and thus show a more pronounced diffraction pattern. Also, due to the inevitable Rayleigh scattering in the resist film, the light laterally enters the resist film a few penetration depths under the chrome-plated areas of the photo mask.

Fig. 91 illustrates the diffraction pattern in the air gap between the photo mask and resist surface as well as the resulting intensity distribution on the resist surface for different wavelengths at constant values for the opening width in the photo mask and the gap.

Disruptive Influences of Photo Masks and Substrates

Photomask Defects with the Exposure of Positive Resists

Point defects (holes with dimensions in the range of the wavelength of the light or smaller) in the chromium layer of the photo mask are without great impact if the exposure dose at these points remains below the threshold at which the resist becomes nevertheless developable. At higher doses, "craters" develop from these defects, which do not, however, generally render the resist film unusable for subsequent processes, as long as they do not reach the substrate.

Particles on the free areas of the photo mask lead to a local shading of the resist film during exposure. The smaller the particle and the greater the resist film thickness and light dose, the more likely it is that these sites are cleared during development.

Photomask Defects with the Exposure of Negative Resists or Image Reversal Resists in Negative Mode

During the exposure of image reversal and negative resists, defects in the chromium layer of the photo mask have in principle the same effect as particles on the free areas of the photo mask during the exposure of positive resists, and vice versa.

However, the image reversal bake or post-exposure bake of negative resists results in a strong contrast increase. As a result, a thin resist film may, above all, cross-link under very small defects in the chromium layer and withstand the development.

Impact of the Optical Substrate Properties

Highly UV-reflective (e.g. metallised) substrates increase the effective light dose absorbed by the photoresist, that is, the exposure time required for development is reduced. On the other hand, the interference of the incidental light with the reflected light causes a reduction of the light intensity immediately above the substrate.

UV-transmitting substrates (e.g. quartz, glass, thick SiO_2 on Si, polymers such as PET, PC ...) conduct light laterally in the substrate, allow reflections from the substrate holder and thus reduce the lateral resolution and edge steepness of the developed resist structures.

In this case,

- an optimal, especially not very large exposure dose,
- an anti-reflective coating such as AZ® Barli II, or
- the use of image reversal or negative resists in which an exposure down to the substrate is not required, and where its optical properties do not play a dominant role help.

Laser Exposure

Suitable Wavelengths

In principle, in laser exposure an exposure wavelength in the range of the sensitivity maxima of the photoresist to be exposed is recommended. However, since the spectral sensitivity of photoresists to large wavelengths does not drop abruptly to zero, due to the very high light intensities of laser beams, an exposure with laser direct writing is also possible some 10 nm away from the absorption bands. Hereby, due to the low absorption there, the writing times are extended significantly.

Direct Writing

The writing of lines in the photoresist film using lasers as the light source differs from conventional methods of exposure due to the very high light intensity of the laser beam (approx.10^{10} - 10^{11} mW/cm^2 in laser diodes!). Thus the resist film can heat up so much, that the photoinitiator thermally decomposes, which decreases the subsequent rate of development. At higher temperatures, the resist film starts to be cross-linked in exposed places which can hamper their removal at the end of the process. With image reversal - or negative resists, the reversal reaction or the cross-linking of the warming can occur already during laser exposure itself.

In the case of DNQ-based positive resists, bubble formation in the resist is possible up to the popping off of the resist film by the nitrogen formed during exposure, which may not be able to outgas the resist film quickly enough.

In all these cases, the only way out can be to expose each point for a longer time, either at a lower dose, or to write the entire structure in multiple passes with each time a lower exposure dose.

Laser Interference Lithography: Suitable Photoresists

With the laser interference lithography, the requirements on resolution of the resist are usually very high. In addition, very thin resist films of a few hundred nm are required, which must be realised by diluting existing resists. For both reasons, laser interference lithography, e.g. the AZ® 701 MiR (suitable for subsequent dry etching or lift-off) or the AZ® ECI 3000 series (optimised for wet-chemical processes such as etching) are recommended.

Grey-tone Lithography

Basics of Grey-tone Lithography

Normally one is striving in lithography to achieve a binary behaviour of the photoresist used: Certain areas on the substrate should be developed completely freely, but the remaining resist structures should have a cross-section as rectangular as possible.

The aim of the grey-tone lithography is to develop a specific topography from the resist film by means of the lateral variation of the exposure dose. The following describes the mechanisms and process parameters that can be achieved. The selection of suitable resists depends essentially on the function of the resist mask.

Grey-tone Lithography with "thin" Photoresists

The term "thin resist films" refers to optically thin resists, whose film thickness is thus smaller than the penetration depth of the exposure wavelength used (cf. upper row in Fig. 87). In typical g- / h- / i-line resists which are exposed with these lines, this condition usually applies to film thicknesses < 1 - 2 µm.

Because during the exposure of thin resist films, this is substantially uniformly exposed to the substrate, the development rate of the resist surface to the substrate is also constant. The development rate, however, depends on the laterally varying exposure dose, which thus transfers to the desired resist topology during the development.

The key parameter is thus the form of the dependency of the development rate on the exposure dose. As Fig. 92 shows, a real resist (green) has a dependency similar to a step function: Below a certain exposure dose, the resist is only dissolved via the dark erosion in the developer. Slightly above this dose, the development rate begins to saturate at a high level. To operate with such resist grey-tone lithography, the light dose needs to be varied within a very narrow range over the substrate, which is difficult to reproduce. The development rate of a photoresist ideal for the grey-tone lithography would be a linear function of the light dose (blue).

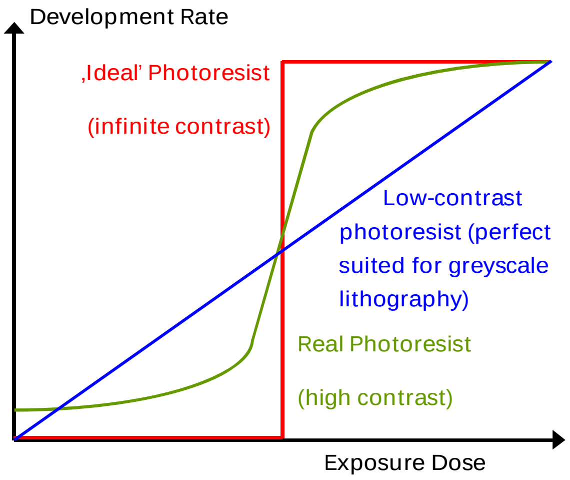


Fig. 92: The diagram of the importance of a low (blue curve), high (green curve) and in an ideal case, the infinite (red curve) contrast in the photoresists with regard to dependence between exposure dose and achievable development rate.

Within limits, the contrast of a real photoresist can be reduced by its process parameters that it becomes suitable for grey-tone lithography, i.e. the development rate is controlled over a wider range of the exposure dose:

A short or/and cool softbake (e.g. 60 - 70°C for one minute per µm of resist film thickness) increases the dark erosion over the high residual solvent content more than the development rate of exposed photoresists.

Alternatively, a very hot or/and long softbake (e.g. 120°C for 5 - 10 minutes) reduces the contrast over i) reducing the rate of development by a thermally decomposed photoinitiator, and ii) increasing the dark erosion due to decomposed photoinitiator which, in the unexposed state, is no longer available as an inhibitor.

In addition, a short flood exposure can cause an "offset" of the development rate.

An unusually highly concentrated developer (e.g., AZ® 400K or 351B 1: 2.5 ... 1 : 3 in H_2O) has a much lower selectivity (ratio of the development rate of the dark erosion) as compared to a highly diluted developer.

Grey-tone Lithography with "thick" Photoresists

By "thick resist films", resists are meant in this connection, the film thickness of which is a multiple of the penetration depth of the exposure wavelength used (see lower row in Fig. 87). In conventional g-/h-/i-line resists exposed with these lines, this condition applies to film thicknesses > 5 µm.

As can be seen in Fig. 87, in the case of correspondingly thick resist films, the bleaching of the photoresist during exposure can be carried out in the grey-tone lithography: Due to the effect of the bleaching, thick resist films only absorb in the uppermost µm at the beginning of the exposure, which thereby becomes UV-transparent and hereby directs the light increasingly deeper towards the substrate during further exposure. Thus the film thickness that can be developed increases almost linearly with the exposure dose.

In contrast to the requirements listed in the previous subsection for thin resist films, thick resist films should be processed in grey-tone lithography as high-contrast as possible. The measures listed in the section 16.7 help to develop the resist film down to a defined distance from the substrate.

Nitrogen Formation during Exposure

Photoreaction and Nitrogen Formation

Most DNQ-based positive resists release nitrogen during exposure in amounts which can be a multiple of the resist volume.

In the ideal case, the nitrogen formed already during the exposure diffuses rapidly enough from the resist film without damaging it. However, as the resist film thickness and exposure intensity increase as well as the subsequent baking steps during exposure, there is a risk that the N_2 pressure in the resist film increases so much that bubbles or stress cracks can form therein.

Blister Formation during Exposure

If N_2 bubbles are formed in the resist during the exposure or immediately thereafter, the resist films foam veritably (milky or styrofoam-like appearance under the microscope, see Fig. 93), this can have the following effect:

- N_2 bubbles formed already during exposure scatter the light, which on the one hand, reduces the possible resolution and, on the other hand, a greatly reduced light intensity close to the substrate is obtained. Especially with thick resist films, this can make a through-development difficult or impossible.
- Mechanical stress in the resist film due to the N_2 partial pressure can reduce the resist adhesion and lead to underetching in subsequent wet-chemical etching processes or under-growth of the resist structures during electroplating.
- After the development, the resist sidewalls exhibit crater-like structures and cracks, which map the bubbles and stress cracks formed at the boundary from the exposed to the unexposed resist region (Fig. 94).

Possible Causes and Remedies

Poor resist adhesion, enhanced by the higher residual solvent content in the vicinity of the substrate, promotes the formation of N_2 bubbles at the interface to the substrate. Chapters 8 and 13 and give hints for maximising resist adhesion via a correct substrate pretreatment and optimum softbake parameters.

High exposure intensities (e.g. in the case of laser exposure or use of 1000 W mask aligners) mean a high N_2 generation rate, as a result of which the N_2 cannot outgas in time from thick resist films. Possible remedies are either a reduction in the exposure power, or, if technically feasible, a division into several exposure steps with each lower dose and with delays in-between.

Photoinitiator-rich thin resists, such as the AZ®1500 or AZ® 6600 series, are not suitable for large resist film thicknesses above about 5 µm because of their correspondingly stronger tendency to form N_2 during exposure. For thicknesses of approx. 5 - 20 µm, we recommend thick resists such as AZ® 4562 or 9260.

For even thicker resist films, the use of a photoresist is recommended, which does not release any nitrogen during exposure when a different photo chemistry is used. The chemically enhanced ultra-thick resist AZ® 40 XT allows film thicknesses of 20 µm to well over 100 µm.

Nitrogen Formation in Thermal Processes after Exposure

Causes and Appearance

Sometimes nitrogen bubbles are formed first in thermal process steps after exposure in a former bubble-free resist film. Due to the elevated temperature, the nitrogen dissolved in the resist film is, on the one hand, more mobile and can thus more rapidly converge into bubbles. The bubble formation itself is promot-

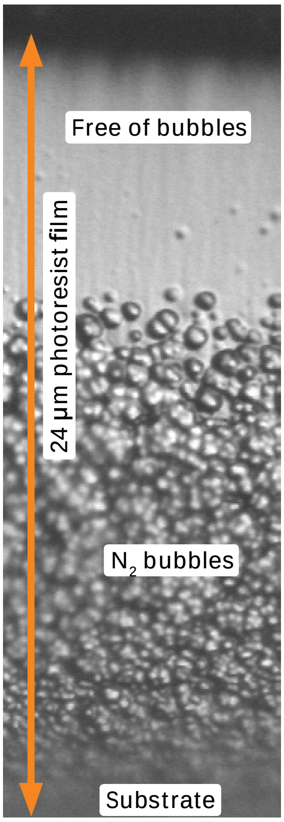


Fig. 93: The cross-section of an exposed, thick positive resist film (here the AZ® 9260) clearly shows how the nitrogen formed during exposure is predominantly manifested in the form of bubbles in the resist area in the vicinity of the substrate.

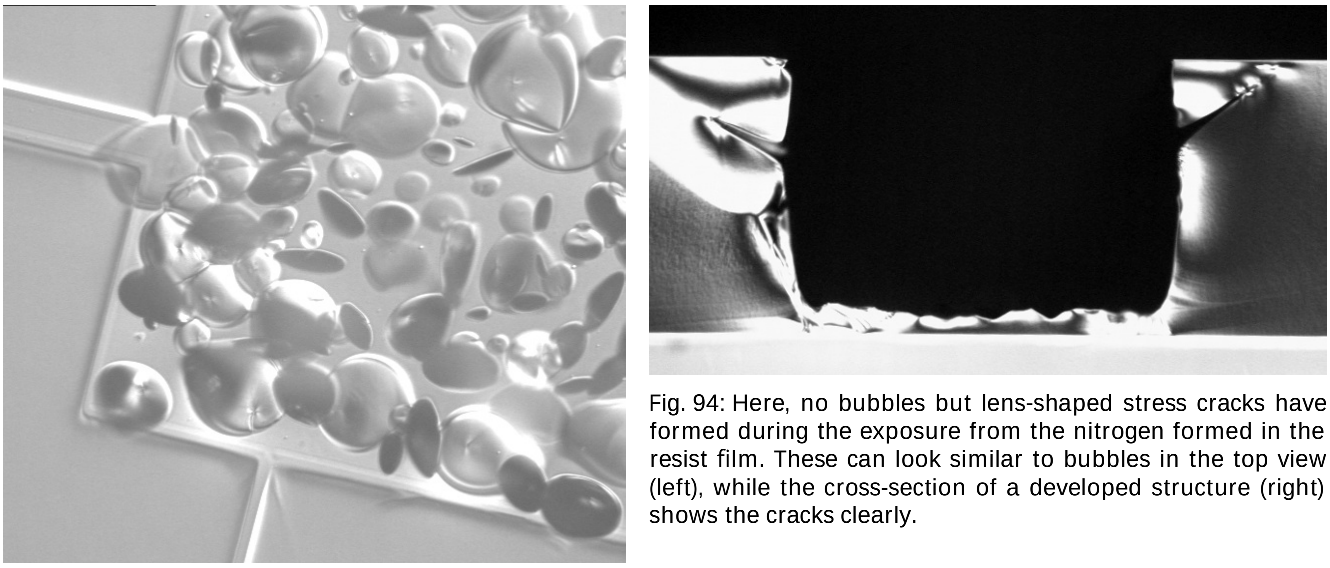


Fig. 94: Here, no bubbles but lens-shaped stress cracks have formed during the exposure from the nitrogen formed in the resist film. These can look similar to bubbles in the top view (left), while the cross-section of a developed structure (right) shows the cracks clearly.

ed by the decrease in the viscosity (hardness) of the heated resist.

Critical baking steps in this respect are, for example, a post-exposure bake or image reversal baking step, in which the nitrogen already formed during the exposure but still present in the resist film forms bubbles during baking of the softening photoresist.

Bubble formation is also possible in previously unexposed, developed resist structures if in the case of a subsequent process step, an unintentional exposure is accompanied by higher temperatures: Such an undesired exposure can appear during coating processes (e.g. via evaporation, sputtering or CVD) or dry etching, where short-wave thermal radiation or UV radiation from the plasma occurs in combination with heating (and hereby softening) of the resist film.

Corrective Measures

If nitrogen bubbles appear after exposure in the exposed resist structures during baking steps, a waiting time at room temperature helps prior to the baking step in order to allow the nitrogen to be outgassed as completely as possible. The duration required for this is increased for a given resist with the square of the resist film thickness, and may be several minutes for resist films which are several µm thick and several hours for resists of several 10 µm.

A cautious, gradual or stepwise elevation of the temperature during this delay, for example, from room temperature to 40°C and 60°C, can significantly shorten the waiting time since the thermally activated diffusion of the nitrogen is accelerated. However, care must be taken that N_2 bubbles do not form in this case. If they nevertheless appear, the previous waiting time should be extended at room temperature, and/or the temperature increase should be decelerated.

Our Photoresists: Application Areas and Compatibilities

	Recommended Applications [1]	Resist Family	Photoresists	Resist Film Thickness [2]	Recommended Developers [3]	Recommended Removers [4]
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls	AZ® 1500	AZ® 1505 AZ® 1512 HS AZ® 1514 H AZ® 1518	≈ 0.5 µm ≈ 1.0 - 1.5 µm ≈ 1.2 - 2.0 µm ≈ 1.5 - 2.5 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
		AZ® 4500	AZ® 4533 AZ® 4562	≈ 3 - 5 µm ≈ 5 - 10 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
		AZ® P4000	AZ® P4110 AZ® P4330 AZ® P4620 AZ® P4903	≈ 1 - 2 µm ≈ 3 - 5 µm ≈ 6 - 20 µm ≈ 10 - 30 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
		AZ® PL 177	AZ® PL 177	≈ 3 - 8 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Spray coating	AZ® 4999		≈ 1 - 15 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Dip coating	MC Dip Coating Resist		≈ 2 - 15 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® ECI 3000	AZ® ECI 3007 AZ® ECI 3012 AZ® ECI 3027	≈ 0.7 µm ≈ 1.0 - 1.5 µm ≈ 2 - 4 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
		AZ® 9200	AZ® 9245 AZ® 9260	≈ 3 - 6 µm ≈ 5 - 20 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	
	Elevated thermal softening point and high resolution for e. g. dry etching	AZ® 701 MiR	AZ® 701 MiR (14 cPs) AZ® 701 MiR (29 cPs)	≈ 0.8 µm ≈ 2 - 3 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
Positive (chem. amplified)	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® XT	AZ® 12 XT-20PL-05 AZ® 12 XT-20PL-10 AZ® 12 XT-20PL-20 AZ® 40 XT	≈ 3 - 5 µm ≈ 6 - 10 µm ≈ 10 - 30 µm ≈ 15 - 50 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
		AZ® IPS 6050		≈ 20 - 100 µm		
Image Reversal	Elevated thermal softening point and undercut for lift-off applications	AZ® 5200	AZ® 5209 AZ® 5214	≈ 1 µm ≈ 1 - 2 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF	TechniStrip® Micro D2 TechniStrip® P1316 TechniStrip® P1331
		TI	TI 35ESX TI xLift-X	≈ 3 - 4 µm ≈ 4 - 8 µm		
Negative (Cross-linking)	Negative resist sidewalls in combination with no thermal softening for lift-off application	AZ® nLOF 2000	AZ® nLOF 2020 AZ® nLOF 2035 AZ® nLOF 2070	≈ 1.5 - 3 µm ≈ 3 - 5 µm ≈ 6 - 15 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® NI555 TechniStrip® NF52 TechniStrip® MLO 07
		AZ® nLOF 5500	AZ® nLOF 5510	≈ 0.7 - 1.5 µm		
	Improved adhesion, steep resist sidewalls and high aspect ratios for e. g. dry etching or plating	AZ® nXT	AZ® 15 nXT (115 cPs) AZ® 15 nXT (450 cPs)	≈ 2 - 3 µm ≈ 5 - 20 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
			AZ® 125 nXT	≈ 20 - 100 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® P1316 TechniStrip® P1331 TechniStrip® NF52 TechniStrip® MLO 07

Our Developers: Application Areas and Compatibilities

Inorganic Developers

(typical demand under standard conditions approx. 20 L developer per L photoresist)

AZ® Developer is based on sodium phosphate and –metasilicate, 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

Metal Ion Free (TMAH-based) Developers

(typical demand under standard conditions approx. 5 - 10 L developer concentrate per L photoresist)

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

---

[1] 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.

[2] Resist film thickness achievable and processable with standard equipment under standard conditions. Some resists can be diluted for lower film thicknesses; with additional effort also thicker resist films can be achieved and processed.

[3] Metal ion free (MIF) developers are significantly more expensive, and reasonable if metal ion free development is required.

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 resists (including all AZ® 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® P1331 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 dissolving 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 Au or 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 Al, Cu, Ti, TiN, W and Ni.

TechniStrip™ NF52 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 SiO_2, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO_2. 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: è www.microchemicals.com/products/wafers/waferlist.html

Further Products from our Portfolio

Plating

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

Solvents (MOS, VLSI, ULSI)

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

Acids and Bases (MOS, VLSI, ULSI)

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

Etching Mixtures

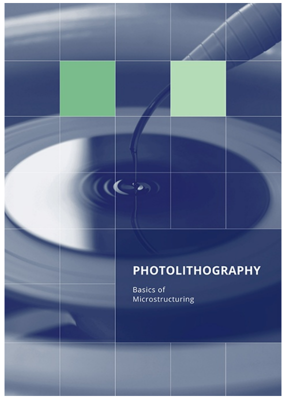
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

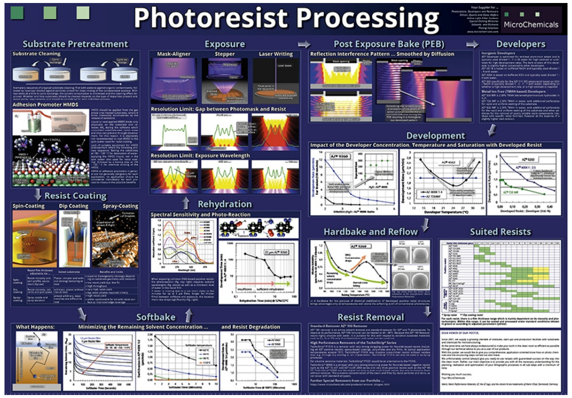
Further Information

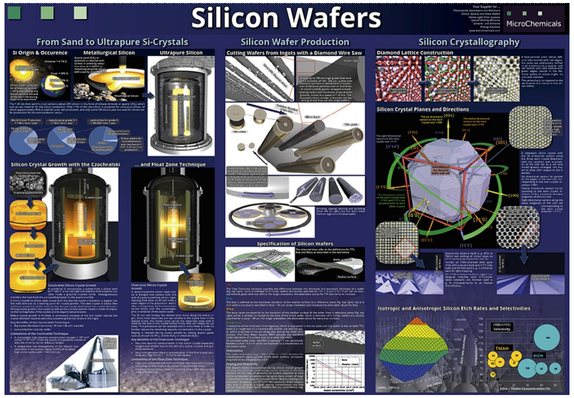
Technical Data Sheets: www.microchemicals.com/downloads/product_data_sheets/photoresists.html

Material Safety Data Sheets (MSDS): www.microchemicals.com/downloads/safety_data_sheets/msds_links.html

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!

Disclaimer of Warranty & Trademarks

All information, process descriptions, recipes, etc. contained in this document are compiled to the best of our knowledge. Nevertheless, we can not guarantee the correctness of the information. Particularly with regard to the formulations for chemical (etching) processes we assume no guarantee for the correct specification of the components, the mixing conditions, the preparation of the batches and their application.

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 can not 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.

Merck, Merck Performance Materials, AZ, the AZ logo, and the vibrant M are trademarks of Merck KGaA, Darmstadt, Germany