Exposure of Photoresists

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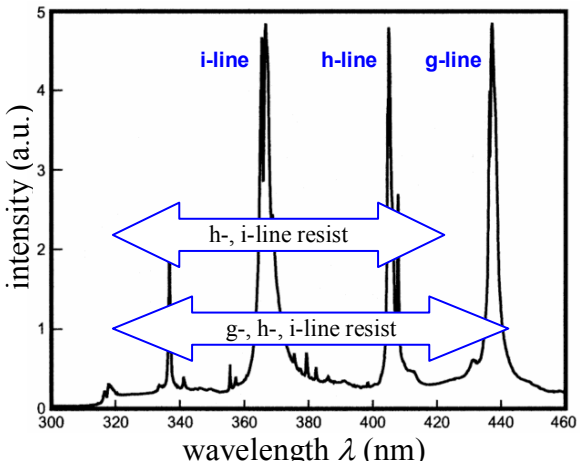
Mask-Aligner, Stepper, an Laser as Light Source

Mask-Aligner and Stepper

The typical emission spectrum of a mask aligner or stepper with Hg light source and without optical selective mirrors/filters contains g- (wavelength 436 nm), h- (405 nm) and i-line (365 nm) (fig. right-hand), with an i-line intensity approx. 40 % of the total emission between 440 and 340 nm.



The absorption spectrum (spectral sensitivity see next section) of AZ® and TI photoresists is matched to this Hg emission spectrum.

Especially for exposure dose sensitive processes (image reversal-, thick resist processing, high resolution) a calibration of the illumination intensity (changing with bulb operating time) is strongly recommended. A measurement of the lateral intensity distribution should reveal less then 10 % deviation over the substrate size in order to allow a proper exposure dose for central *and* edge-near regions of the resist film.

Laser Exposure of Photoresists

When using a laser beam as light source for photoresist exposure in stead of the usually used Hg bulbs, one has to consider two main points:

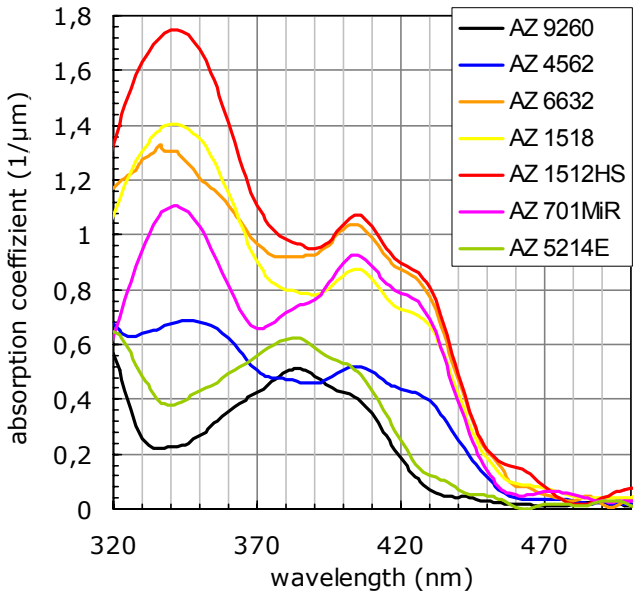
The light intensity is quite different: While in laser interference lithography, the light intensity is rather low, laser scribing causes intensities many orders of magnitude beyond the intensity of a mask aligner or stepper. The exposure wavelengths of the laser often differs from the 365, 405, or 435 nm Hg lines which are matched to the spectral sensitivity of photoresists.

The spectral sensitivity of photoresists does not abruptly end at a certain wavelength, but smoothly drops to zero over few 10 nm. Therefore, using an adjusted exposure dose (e. g. laser scribing), exposure with wavelengths outside the sensitivity range given in the technical data sheet is also possible to a certain extent.

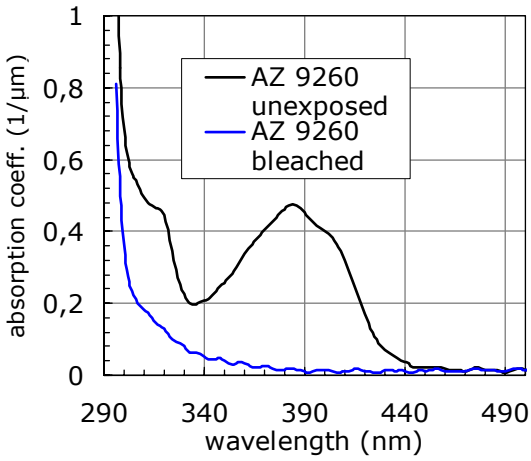
The document Laser Exposure of Photoresists gives further details on this topic.

Optical Absorption and Spectral Sensitivity

The optical absorption of most unexposed photoresist ranges from the approx. 440 nm in the VIS to near UV. This spectral sensitivity is matched to the emission spectrum of Hg lamps (i-line = 365 nm, h-line = 405 nm, g-line = 435 nm) in mask aligners (fig. bottom, left-hand) and causes the typical reddish-brownish colour of many photoresists. Some modern resists such as the AZ® 9260 or 5214E miss the g-line absorption, and modern negative resists such as the AZ® nLOF 2000 series or the AZ® 15 nXT / 125 nXT are i-line resists with an absorption only below approx. 380 nm.



During exposure, positive photoresists almost completely bleach down to approx. 300 nm (fig. bottom):

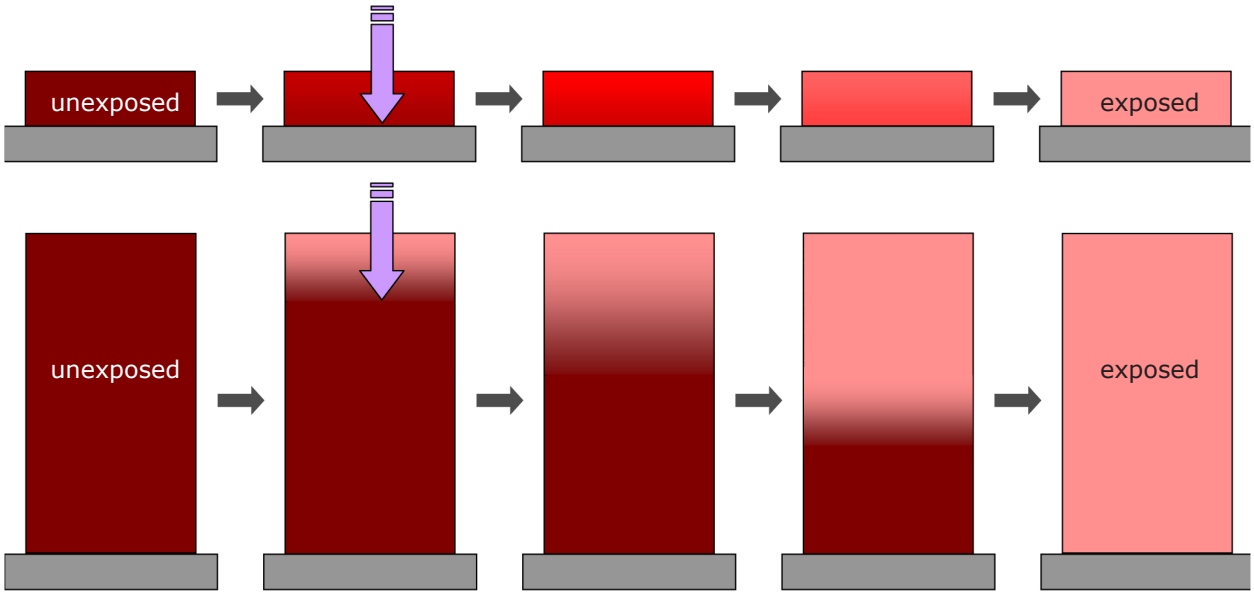


Exposure of "Thick" and "Thin" Resists

In this context, "thick" resist means a film thickness much higher than the penetration depth of the exposure light. For standard positive resists and standard exposure wavelengths (g-, h-, i-line), this means a thickness of > 5 µm, while "thin" resists hold for film thicknesses < 1 µm which is below the penetration depth of typical exposure wavelengths.

One would assume that a very thick resist film cannot be completely exposed towards the substrate. However, the "trick" is the bleaching of the resist: As the plot right-hand shows, DNQ-based photoresists (= almost all AZ® positive resists) become UV-transparent during exposure.

Therefore, in the beginning of the exposure, light only penetrates the upper 1-2 µm of the resist film. This part of the resist film bleaches, so with the exposure going on, light will be able to penetrate the first 2-3 µm of the film, and so on (see schema below). As a consequence, the exposed (and developable) resist film thickness goes approx. linear with the exposure dose. The transition exposed/unexposed is sufficiently sharp for reproducible grey-



While "thin" resist films show a rather homogeneous illumination depth profile (top), 'thick' resist films bleach towards the substrate during exposure (bottom).

scale lithography applications (for further information of greyscale lithography please consult the document Greyscale Lithography with Photoresists).

On the other hand, a thin resist film is homogeneously exposed from the very beginning of exposure. Hereby, the later development rate increases with the exposure dose to a certain extent.

Exposure Dose and Exposure Time: Good to Know ...

Concerning the Exposure Tool and the Resist Data Sheets

When calculating the correct exposure *time* from the exposure *doses* given in the technical data sheet for each resist, the following has to be considered:

- Is the light source spectrum broadband (g-, h-, and i-line) or monochromatic?
- Measuring the light intensity: Does the sensor only respond to g-, h-, or i-line, or to broadband intensity? For which spectral range is the illumination intensity given in the mask aligner manual?
- On which spectral range does the photoresist technical data sheet refer with respect to the necessary exposure dose, either

  a) a certain spectral range (g-, h-, *or* i-line) when using broadband exposure, or
  b) i-line using monochromatic exposure, or
  c) the integrated g-, h-, *and* i-line intensity?
- What is the spectral sensitivity of the photoresist?

Light Intensities of Typical Mask-Aligners

The commonly used mask-aligners with 350 W Hg bulb typically achieve a light intensity of approx. 20-30 mW/cm^2 over g-, h-, and i-line, with an i-line fraction of 6-12 mW/cm^2. If a 1000 W bulb is used instead, these values can be tripled.

Determining the Optimum Exposure Dose

For most positive resist applications, the optimum exposure dose is the one where the development rate starts to saturate. If the exposure dose is too low, the development time and thus the dark erosion increase. Too high exposure dose values cause light scattering and diffraction in the resist film which deteriorates the resolution. In case of negative resists, the optimum exposure dose depends on the required degree of cross-linking as well as the desired resist sidewall profile.

If the light intensity of a mask-aligner is unknown and no tools to measure this value are available, a value of approx. 20-25 mW/cm2 is a good approximation for a 350 W mask-aligner, and three times more for 1000 W Hg bulbs. If an i-line filter or i-line resists (such as the AZ® nLOF 2000 series, or the AZ® 15 nXT or 125 nXT, details here) are used, the effective intensities can be divided by a factor of three.

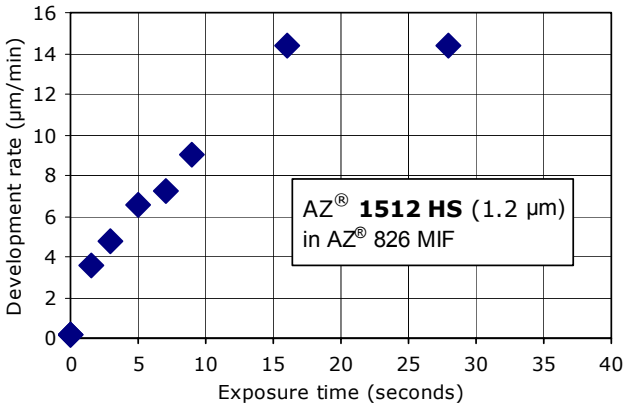
Generally, each new process and each process optimization requires an exposure series where the exposure dose varies between approx. 50% and 200% of the estimated optimum value. In case of positive resists, the development rate as a function of the exposure dose shows a saturation from a certain dose on which is a recommended dose most applications. In case of negative resists, the degree of cross-linking, and the resist sidewall profile determine the optimum exposure dose.

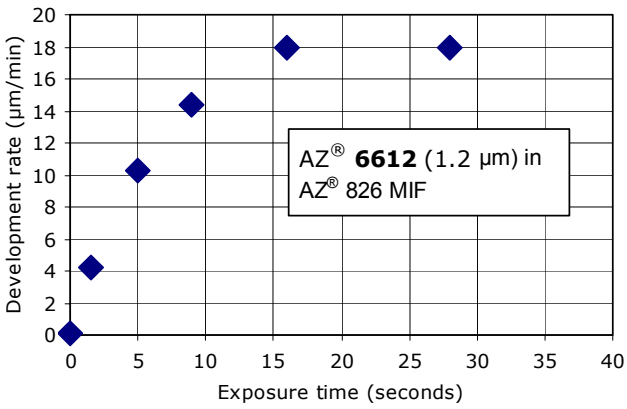
Exposure Series of Typical Photoresists

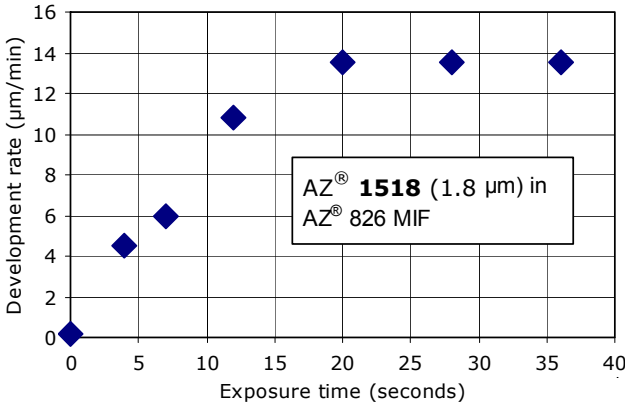
In order to give you a clue for your own (very recommended!) exposure series, the following plots show the dependency of the exposure time on the development rate for certain positive resists processed as follows:

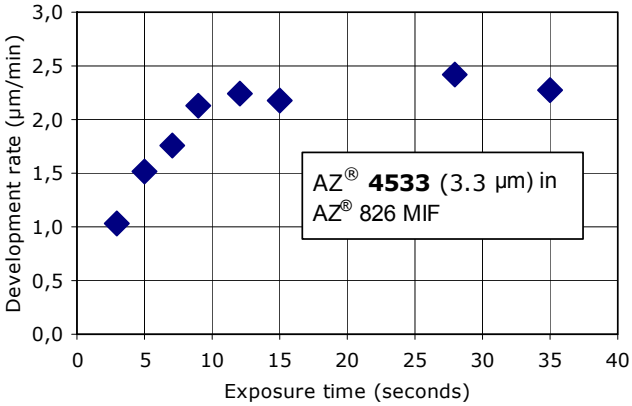
Spin coating at 4.000 U/min, softbake at 100°C contact hotplate for 1 minute for each µm resist film thickness, development in AZ® 826 MIF. In all plots, the saturation of the development rate from a certain exposure time is clearly visible.

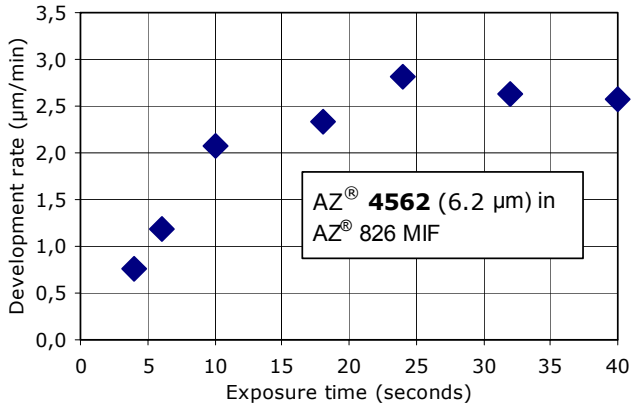
The exposure tool was a mask aligner with 350 W Hg light source, an i-line intensity of 8.5 mW/cm^2, and an integrated g-, h-, and i-line intensity of 20 mW/cm^2.









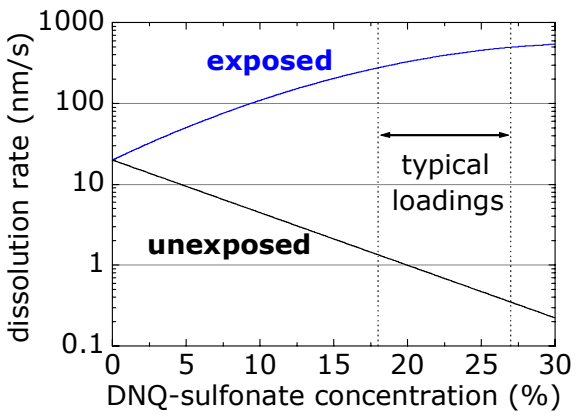


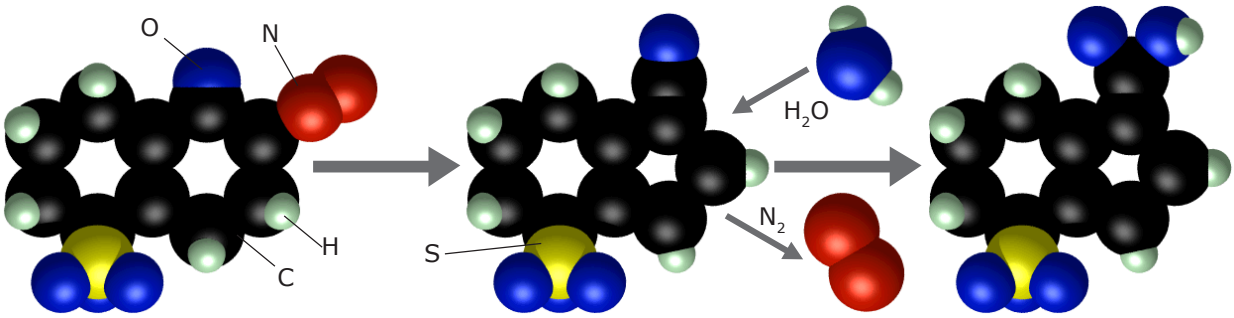
The Photo Reaction

Positive and Image Reversal Resists

The photo active compound of AZ® and TI photoresists belongs to the group of diazonaphtho-quinone-sulphonates (DNQ). Their presence in photoresists reduces the alkaline solubility by more than one order of magnitude (Meyerhofer-plot right-hand).

During exposure, the DNQ transforms into a carboxylic acid, accompanied by the release of nitrogen and the absorption of water (schema overleaf). Thus, the alkaline solubility increases by several orders of magnitude and is finally more than one order of magnitude higher as compared to pure Novolak.





In order to improve the DNQ solubility in the resist and to increase the inhibitor property (dark erosion reduction), generally several DNQ-sulfonate molecules are bonded to a so-called *backbone*-molecule.

The photoreaction quantum efficiency defines the number of above-mentioned reactions in relation to the photons absorbed in the resist film. Using a sufficiently transparent resin, a suited photon energy (g-, h-, i-line with respect to the specific DNQ) and a sufficient H_2O-concentration in the resist, the quantum efficiency in DNQ-based positive-tone photoresists achieves values of typically 20-30 %.

If the resist lacks a minimum concentration of water, the ketone (scheme above, center) may perform various side reactions (e. g. esterify with the resin or polymerize accompanied by CO_2-separation). In both cases, the development rate solely increases by the reduction of the inhibitor (DNQ-sulfonate) concentration. As a consequence, the total dark erosion increases due to the longer development time required. Thus, steep resist sidewalls as well as very high resolutions or aspect ratios can not be realized. For details on this topic, please consult the document Rehydration of Photoresists.

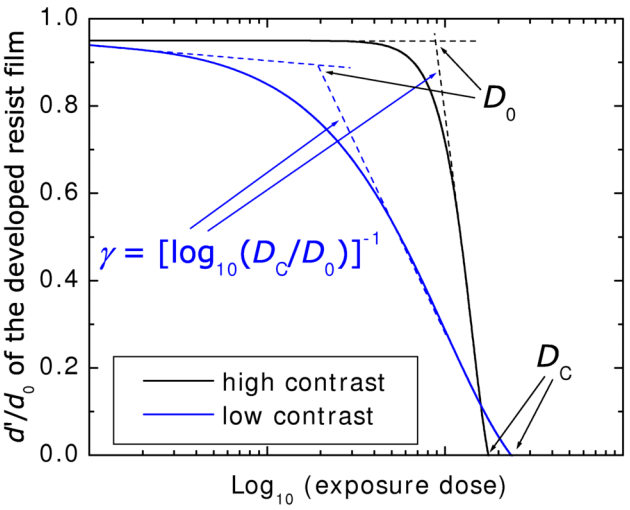
Negative (Cross-Linking) Resists

Negative resists such as the AZ® nLOF 2000 series, or the AZ® 15 nXT and 125 nXT (details here) contain a crosslinker which is activated during exposure and thermally activated crosslinks the resin during a subsequent baking step. Higher exposure doses increase the degree of cross-linking, which improves the thermal and chemical stability, and makes an impact on the attained resist profile after development.

The Contrast of Photoresists

The contrast of a photoresist defines the development rate as a function of the absorbed light dose. Photoresists with a high contrast show minor dark erosion and develop from a certain dose D_0 on at a constant rate, while resist parts exposed with $D < D_0$ (e. g. diffraction patterns) remain on the substrate.

The contrast curve of a photoresist (plot below) plots the remaining resist film thickness after development (in relation to the thickness before development) d'/d_0 as a function of the (logarithmically plotted) exposure dose. The transfer of information from a given contrast curve to an individual lithographic process requires information of all process parameters which impact on the development rate, such as resist thickness, soft-bake, rehydration, air temperature and -humidity, developer etc.



The contrast curve of an ideal positive resist is a step function (contrast = infinity). Realistic contrast curves show a $d'/d_0 < 1$ for an exposure dose = 0 (dark erosion) and a non-infinitesimal logarithmic decay in $d'/d_0 \rightarrow 0$ over a nonzero range of the dose towards D_C ('dose to clear'). The slope of this decay defines the contrast.

Exposure-Related Resolution Limits

The Photomask

At low exposure doses, the contrast of photoresists reduces the impact of defects in the mask (holes in the Cr film) to a certain extent. Towards higher exposure doses, however, the contrast curve enhances irregularities in the mask as well as interference patterns in the resist. As a consequence, positive resists reveal regions of high dark erosion (mouse-bites, holes, thinning). The contrast enhancement in image reversal resist processing furthermore promotes a resist pattern strongly revealing spatial exposure intensity irregularities.

The exposure wavelength

The exposure wavelength limits the theoretical resolution limit: Small transparent features in the photomask act as slits causing an interference pattern on/in the resist film, which later transfers into the resist features after development.

As the figure right-hand shows, such a distribution of the light intensity differs from an ideal, sharply bounded rectangular distribution. Since the dimensions of the diffraction pattern increases with the exposure wavelength, smaller wavelengths improve the (theoretical) attainable resolution.

Cross-section of the modelled i-line (365 nm) exposure intensity distribution in a 1 µm thick resist film and a 1 µm slit in the photomask.

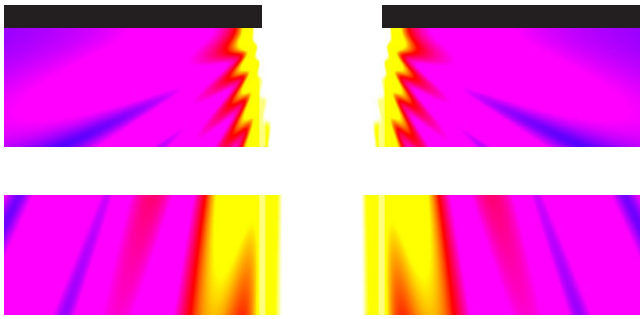
However, two points have to be considered in this context: The theoretical resolution limits only goes with the square root of the wavelengths, so the difference between g-line (435 nm), and i-line (365 nm), is less than 10 % resolution gain. Using smaller wavelength than i-line for g-/h-/i-line resists is not recommended, since the absorption of these resists is not matched to wavelengths < 340 nm where the resist absorption strongly increases. Therefore, comparable high exposure doses are required to through-expose a given resist film which also increases the intensity of scattered and diffracted light thus deteriorating the resolution.

A Gap between Photomask and Resist

A Gap between Photomask and resist surface extends the diffraction pattern and therefore deteriorates the resolution.

Possible (unintended) reasons for a gap > 0 are:

- Particles in the resist caused by either insufficient cleanroom conditions, contaminated substrates, or expired photoresist,
- bubbles in the resist film caused during dispensing, or an insufficient delay time after refilling/diluting/moving the resist,
- mask contamination by particles, or resist from previous exposure steps,
- rough, textured, or curved (strained) substrates,
- an edge bead, or a mask attached upside-down ☺.



Cross-section of the modelled i-line (365 nm) exposure intensity distribution in a 2 µm thick resist film and a 2 µm slit in the photomask with no (top) and 10 µm (bottom) proximity gap.

The Exposure Dose

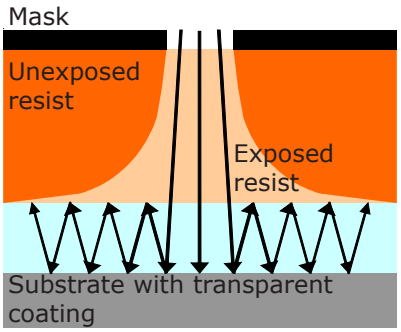
An optimized exposure dose is another requirement for attaining the maximum resolution of a given resist: If the exposure dose is too low, the development time of positive resists increases which increases the total dark erosion, while negative resists show an increased erosion of the exposed areas due too a weak cross-linking.

Too high exposure doses cause an undesired exposure by scattering, diffraction and reflection of the part of the resist which should not be exposed. As a consequence, too much (in case of positive resists) or too less (in case of negative resists) of the resist is cleared dur-

ing development.

The section "Determining the Optimum Exposure Dose" in this document explains how the find the optimum value for the exposure dose.

Optical Substrate Properties



Highly UV-reflecting (e. g. metallized) substrates increase the absorbed light dose in the resist near the substrate, and thereby reduce the exposure time necessary for through-development. UV-transmissive substrates (e. g. quartz, glass, thick SiO_2 on Si, transparent polymers) laterally guide light along the substrate (fig. left-hand), cause reflections from the chuck and reduce the lateral resolution (in the latter case, UV-absorbing films or foils between resist/substrate and substrate/chuck, respectively, will help).

In both cases (UV-reflecting or/and -transparent substrates), the usage of image reversal resists in image reversal mode will help, since hereby the first exposure does not penetrate the entire resist film, therefore the sensitivity to the optical behavior of the substrate is minimized.

Further Resolution Limits

The document High Resolution Photoresist Processing gives details on further resolution limits of photoresists.

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