



FAQs concerning photoresists from Allresist

1. What are photoresists composed of, and how do they work?
2. For how long are photoresists stable, and what the optimal storage conditions?
3. How may age-related changes influence the quality of a photoresist?
4. What is the optimal pre-treatment of substrates for photoresists?
5. What are the adhesion features of photoresists on different wafers?
6. What are the optimum coating parameters for photoresists in order to achieve good film images?
7. Why do air bubbles develop in photoresist films, and how can they be avoided?
8. What is the function of the softbake of photoresist films after coating?
9. How are photo resists exposed, and how can the optimum exposure dose be determined? For how long can coated and baked substrates be stored prior to irradiation?
10. Which developers are optimal for photoresist, and how do factors like developer concentration and temperature influence the result?
11. How can resist coatings be removed again?
12. What is the application range of protective coatings?
13. How do image reversal resists work?
14. How can undercut patterns (lift-off structures) be produced in one- or two layer systems?
15. How can thick films of $> 10 \mu\text{m}$ be processed in an optimal way?
16. Which resolution and which contrast can be obtained with photoresists?
17. How high is the plasma etch resistance of photoresists?
18. How high is the etch resistance of photoresist in the presence of strong acids?
19. Which photoresists are suitable for hydrofluoric acid (HF) etching?
20. How high is the solvent resistance of photoresist films?



FAQs concerning photoresists

1. What are photoresists composed of, and how do they work?

Photoresists are in particular used in microelectronics and microsystems technologies for the fabrication of μm - and sub- μm structures. Allresist provides a broad range of different resist types which cover a wide range of applications:

Photoresists produced by Allresist like e.g. AR-P 1200 (spray resists), AR-P 3100, 3200, 3500, 3700 are composed of a combination of film-forming agents such as e.g. cresol novolac resins and light-sensitive components such as e.g. naphthoquinone diazide (NCD), which are dissolved in solvents such as e.g. methoxy propyl acetate (equivalent to PGMEA). The addition of a light-sensitive component to the alkali-soluble novolac leads to a reduced alkali-solubility. The NCD-groups block the OH-groups of the cresol novolac resins; the alkali-solubility decreases (inhibitory effect). After exposure at 308 - 450 nm (UV range) using an exposure mask, the light-sensitive component is converted into the respective indene carbonic acid derivative, the blockage is released and the alkali-solubility of positive resists is thus enhanced by a factor of 100. After development, only those areas which were protected by the mask remain, while exposed areas are detached. The refractive index of novolac-based resists is in a range between 1.58 – 1.63. After development, only areas protected by the mask remain while irradiated areas are dissolved. Photoresists provide an excellent protection against liquid etch media with pH values between 0 and 12.

Negative photoresists like AR-N 4200, 4300, 4400 are composed of novolacs and bisazides (4200, no CAR) or novolacs, acid generators and amine components (4300, 4400, CAR) dissolved in safer solvents like e.g. methoxypropyl acetate (PGMEA). (CAR = Chemically Amplified Resist). The chemical amplification is based on the formation of acids during irradiation and a subsequent cross-linking of amine components with the novolacs. Since acids (protons) are continuously formed during the crosslinking reaction, each proton can induce many cross-linking events which results in a high sensitivity.

After exposure and a subsequent tempering step, the composition of CAR leads to a cross-linking of the exposed negative-tone resist film. Irradiated areas are consequently rendered insoluble and remain after development, while unexposed areas are still soluble and dissolved by the developer.

Thick negative films up to 200 μm can be produced with CAR 44 (AR-N 4400). These resists which are highly sensitive in a range between 300 - 440 nm and to synchrotron radiation provide excellent structural quality. Layers and structures up to 100 μm can be realised with photolithography.

Image reversal resists for example resists of the AR-U 4000 series; positive resists with an additional amine component. Depending on the manufacturing process, positive or negative images can be generated. For the positive mode, exposure and development is carried out as usual for positive resists. Negative images are produced if an additional tempering step and flood exposure of the entire surface is performed after image-wise exposure (☞ Question 13).

Resists for lift-off applications are positive resists AR-P 5300 and the two-component resist system AR-BR 5400/AR-P 3510. Lift-off (evaporation and sputtering of metal) is also possible with negative resists AR-N 4200, 4300 and 4450 as well as with the image reversal resists AR-U 4000. In all cases, an undercut resist edge has to be generated, so that the resist is not dissolved by the remover any further than the metallised edge after metal deposition.



Protective coatings like AR-PC 500 and 5000 are offered by Allresist for a large variety of applications, e.g. for the backside protection of processed wafers during KOH and HF etchings, for a mechanical protection during transport, or as insulating layer. A special protective coating is Electra 92 (AR-PC 4010, 5091), which is conductive and used for e-beam lithography. Protective coatings are not light-sensitive and cannot be patterned if used alone. They can however be patterned with photoresists within the context of a two-layer system.

Allresist also produces a wide range of special resists, e.g. electroplating-stable resists like SX AR-P 5900/4 for applications performed at a pH-value of 13.

For **hydrofluoric acid etchings and BOE-processes** (up to 5 % HF), the 5 µm-resist AR-P 5910 (formerly X AR-P 3100/10) offers considerably better adhesion properties than all other photoresists.

For a **patterning of glass/SiO₂ substrates in concentrated HF**, the positive-tone two-component system SX ARPC 5000/40 – AR-P 3540 T or the negative-tone two-component system SX AR-PC 5000/40 –AR-N 4400-10 is recommended. The upper photoresist layer is initially developed under aqueous-alkaline conditions before the lower SX AR-PC 5000/40 film is developed with solvents.

AR products are available both for the deep **UV range of 240 – 300 nm** (AR-N 4200, 4300) as well as for the **long-wavelength exposure range up to 500 nm** (SX AR-P 3500/6).

Thermally stable resists up to 400 °C are the polyimide resists SX AR-PC 5000/80 and SX AR-P 5000/82 and SX AR-P 3500/8 (PHS).

2. For how long are photoresists stable, and what are optimal storage conditions?

Photoresists are light-sensitive, they are affected by light exposure and high temperatures, and also age-related changes occur during storage. Resists are therefore filled in light-protected amber glass bottles, stored in a cool place, and may only be processed under yellow safe light ($\lambda > 500$ nm). Date of expiry and recommended storage temperature are indicated on the product label of each bottle. Following these recommended storage guidelines, resists are stable until expiry date, at least however for 6 month after date of sale. Short-term temperatures deviations have no influence on general product properties.

☞ If resists are to be used later than 6 month after date of sale or are processed within a very small process window, storage at 4 – 8 °C is recommended. Exceptions are only resists with recommended storage temperatures between 18 – 25 °C. These resists should not be stored cooler. Photoresists stored for several years are outdated and may only be used with considerable restrictions (see also Question 3.).

☞ Bottles which were kept in the refrigerator should never be opened immediately, since in this case air moisture may precipitate on the cold resist. Resists should be adapted to room temperature before opening.

3. How may age-related changes influence the quality of a photoresist?

During storage, red azo-dyes develop due to a thermal chemical reaction of the light-sensitive component with the novolac, causing a darkening of the resist. Even small amounts of the dye lead to darkening, which however has no significant effect on general resist properties.



Photoresists which were stored for several years are too old and may only be used with considerable limitations. This also applies to resists stored at high temperatures and to highly diluted resists which age faster than normal. Possible effects are the formation of particles due to a precipitation of the light-sensitive component. Filtration with a pore size of 0.2 μm may be helpful at an early stage. After repeated filtrations however, the steadily declining concentration of the light-sensitive component causes lower development rates, an increased dark field loss, as well as reduced adherence of the resist.

If resists are stored for prolonged times at higher temperatures against all recommendations (e.g. during the summer), nitrogen may be cleaved from the light-sensitive component which is indicated by fizzling and foaming after the bottle is opened. In this case, the lid of the bottle should be opened a bit and the bottle left undisturbed for 1 – 2 days until the resist has settled again. If the resist has not been kept for too long under improper storage conditions, it may still be used.

4. What is the optimal pre-treatment of substrates for photoresists?

The adhesion between substrate and resist is of major importance for the safe processing of resists. Smallest changes in the cleaning procedure or the technology itself can exhibit a significant influence on the adhesive strength. Silicon, silicon nitride and base metals (aluminium, copper) are generally characterised by good resist adhesion properties, while adhesion is reduced on SiO_2 , glass, noble metals such as gold and silver or on gallium arsenide. For these substrates, adhesion promoters are absolutely required to improve the adhesion strength. A too high air humidity (> 60 %) also reduces the adhesion substantially. If new clean substrates (wafers) are used, a bake at approximately 200 °C minutes (3 min, hot plate) is sufficient for drying, but substrates should be processed quickly thereafter. A temporary storage in a desiccator is highly recommended in order to prevent rehydration.

Pre-used wafers or wafers which are contaminated with organic agents require previous cleaning steps, e.g. in easy cases cleaning in acetone, followed by isopropanol or ethanol treatment and subsequent bake (☞ Section I). This procedure improves the adhesion features of the resist. On no account only acetone should be used, since the evaporative heat loss during the bake causes a condensation of air humidity on the wafer. If only acetone is used for cleaning, the substrate must be dried in a drying oven to remove the condensed moisture.

If a technology involves repeated processing of wafers or subjecting these to various conditions, a thorough cleaning is recommended. The cleaning procedure is however highly process- and substrate-dependent (and also on the structures already deposited). The use of removers or acids (e.g. piranha) with subsequent rinse and bake step (☞ Section I) may be required in this case. For very difficult cases, a treatment with ultra- or megasonics is advisable.

To improve the adhesion features, adhesive agents such as e.g. adhesion promoter AR 300-80 may be used, which is applied directly before the resist coating by spin coating as a thin layer of approx. 15 nm thickness. It is also possible to evaporate HMDS onto the substrates. The monomolecular layer on the wafer surface improves adhesion features since this layer is hydrophobic and absorbs the resist better.



5. What about the adhesion features of photoresists on different wafers?

Adhesion between coating and substrates is a very sensitive issue. Smallest changes of the cleaning procedures or the process parameters can have a fatal impact on the adhesive strength. Silica, silicon nitride, and base metals (such as aluminium, copper) generally exhibit good resist adhesion properties, while adhesion is reduced on SiO_2 , glass, noble metals such as gold and silver, as well as on gallium arsenide. For the last-mentioned substrates, adhesion promoters are absolutely required to improve the adhesion strength (☞ Question 4: Optimal pre-treatment of substrates). If the air humidity is too high (> 60 %), adhesion is also substantially reduced.

6. What are the optimum coating parameters for photoresists in order to achieve good film images?

Photoresists (also photo coatings) are primarily used in micro electronics and micro systems technologies for the production of μm - and sub- μm structures. These resists are generally deposited by spin coating. The optimal spin speed is in a range between 2000 – 4000 rpm for thin resists and between 800 – 2000 rpm (rpm = rotations per minute) for thick resists. Generally possible is a spin speed of up to 9000 rpm or as low as 250 rpm. Depending on the type of resist, films of 100 nm to 200 μm can be produced with this technique. Thicker films of up to 1 mm are generated with casting procedures.

As a rule of thumb: A resist with a layer thickness of 1.0 μm at 4000 rpm will be 2.0 μm thick at 1000 rpm. At 250 rpm, this resist will have a thickness of 4.0 μm , but with major edge bead formation. By varying the spin speed (250-9000 rpm), the layer thickness of each resist can in general maximally be quadrupled.

30 seconds are sufficient to obtain the desired film thickness at spin speeds > 1500 rpm. The time should be extended to 60 s if lower spin speeds are used.

Alternative coating techniques are:

- Dip coating (for large and/or uneven substrates)
- Spray coating (in combination with spin coating for economic use, for highly structured topologies, or for otherwise complicated substrates)
- Roller coating (large formats, e.g. printing plates)

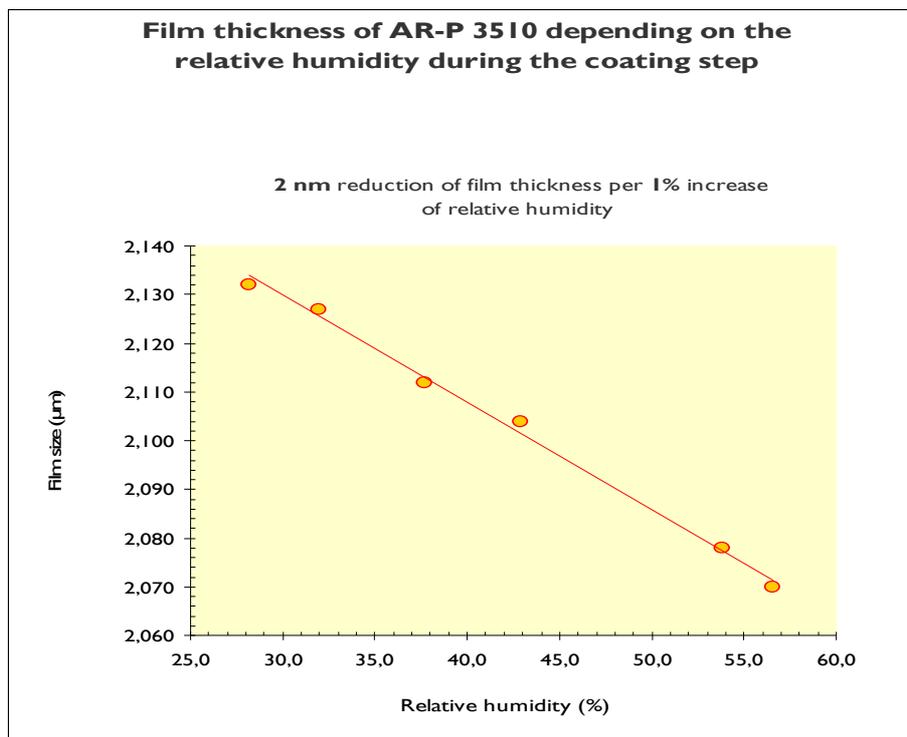
Substrates should have room temperature before coating. Resists have to be adjusted to the temperature of the (preferably air-conditioned) working area. If the resist is too cold, air moisture precipitates on the resist. Bottles removed from the refrigerator should therefore be warmed to room temperature for a few hours prior to opening.

Air bubbles can be avoided if resist bottles are slightly opened a few hours before coating to allow for pressure compensation and are then left undisturbed. Thick resists require several hours for this process, thin resists need less time. Applying the resist with caution and not too fast with a pipette or dispenser will also prevent bubbles and inhomogeneity of the resist films.

A repeated opening of resist bottles causes evaporation of the solvent and an increased viscosity of the resist. For resist films with a thickness of 1.4 μm , a loss of only 1 % of the solvent already increases the film thickness by 4 %, thus requiring considerably higher exposure doses.



Generally used coating conditions are temperatures of 20 to 25 °C with a temperature constancy of + 1 °C (optimum 21 °C) and a relative humidity of 30 to 50 % (optimum 43 %). Above a humidity of 70 %, coating is basically impossible. The air moisture also affects the film thickness which is reduced with increasing humidity. For AR-P 3510, the film thickness decreases by about 2 nm per each percent of humidity. At spin speeds of > 1500 rpm, 30 s are sufficient to obtain the desired film thickness. At lower spin speeds, the time should be extended to 60 s. For an exposure of rectangular masks, usually a Gyrset (closed chuck) system is used which provides a higher film quality and reduces edge bead formation. It has however to be taken into account that the film thickness decreases to approximately 70 % of the film thickness which is obtained with open chucks.



7. Why do air bubbles develop in photoresist films, and how can they be avoided?

Bubbles after spin deposition are in most cases air bubbles, e.g. if the resist bottle was agitated or moved around, or if the resist was diluted prior to the coating step. Coating procedures performed immediately after bottle opening, in particular if the resist temperature was not adjusted to room temperature, may also result in the formation of bubbles. Similarly, an inaccurate application of the resist with pipettes or a dispenser (low pressure caused by pulling too fast) may lead to bubbles and thus cause inhomogeneity of the resist film.

Air bubbles can be avoided if the resist is adjusted to the temperature of the work place before the coating step, if the bottle is opened a bit to facilitate pressure equalisation a few hours before use and not moved around during this time. Thick resists require several hours for this process, thin resists need less time. For thick resists, an ultrasound treatment may be helpful to expel air bubbles. Furthermore, conditions of the working area are of great importance. If the air humidity is too high, may this fact also be responsible for the formation of bubbles.



Air bubbles during the bake step develop mainly in thick films, if these are baked immediately after coating. A certain holding time (depending on the respective film thickness) solves this problem.

Air bubbles during or after exposure of positive resists develop e.g. if the light dose or light intensity was too high. This is due to the nitrogen which is formed from the naphthoquinone diazide during exposure. In this case, the optimum light dose has to be determined by exposure bracketing or with repeated exposure steps in intervals. If the subsequent bake step is too short or performed at too low temperatures, films will dry insufficiently and evaporation of the remaining resist solvent may then cause the formation of bubbles (☞ Question: Softbake 8). Negative resists AR-N 4300 and 4400 will not develop any gas bubbles, since these resists do not contain any potentially gas-forming components.

8. What is the function of the softbake of photoresist films after the coating?

Shortly before the coating step, resist films still contain a substantial amount of residual solvent which depends on the respective film thickness. The subsequent bake step at 90 – 100 °C is performed in order to dry the resist films which would otherwise stick to the mask. Furthermore, the resist layer is hardened during this step, making it more resistant. Besides an improvement of adhesion features, especially the dark field loss during the development step is reduced.

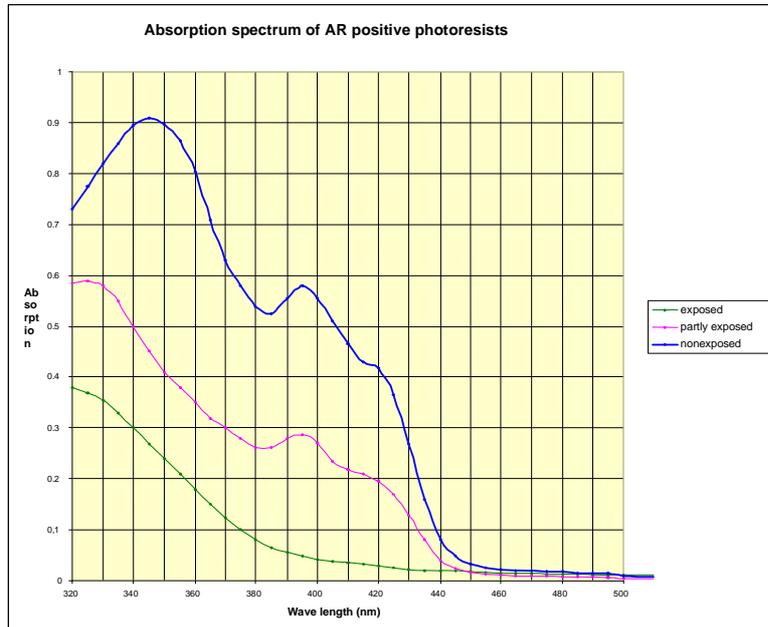
Resist films which are not baked sufficiently (either too short or with too low temperatures) entail a variety of further problems. Successively, air bubbles may develop due to an evaporation of residual solvent (☞ Question 7: Air bubbles). In particular, inaccurate structural images and chamfered resist profiles as well as an unacceptably high dark field loss may be the consequence.

A too rigid bake of resist films (temperature too high, but also baked too long) causes a partial destruction of the light-sensitive component which significantly increases the exposure time and reduces the sensitivity.

9. What about the exposition of photo resists, and how can the optimum exposure dose be determined? For how long can coated and tempered substrates be stored prior to irradiation?

The exposure is performed using masks in suitable exposure systems such as e.g. steppers (i-, g-line), mask aligners or contact exposure systems in the appropriate spectral working range. During laser direct exposure, structures are written directly using a laser beam; a mask is thus not required.

AR photo coatings are sensitive in the broad band UV range (300 - 450 nm) and thus also to the typical emission lines of mercury at 365 nm (i-line), 405 nm (h-line), and 436 nm (g-line) (☞ Spectrum), with maximum sensitivity in the g-line- and the h-line range. The negative resists AR-N 4300 to 4400 are sensitive in a range between 300 and 436 nm. AR-N 4200 is sensitive between 300 and 380 nm.

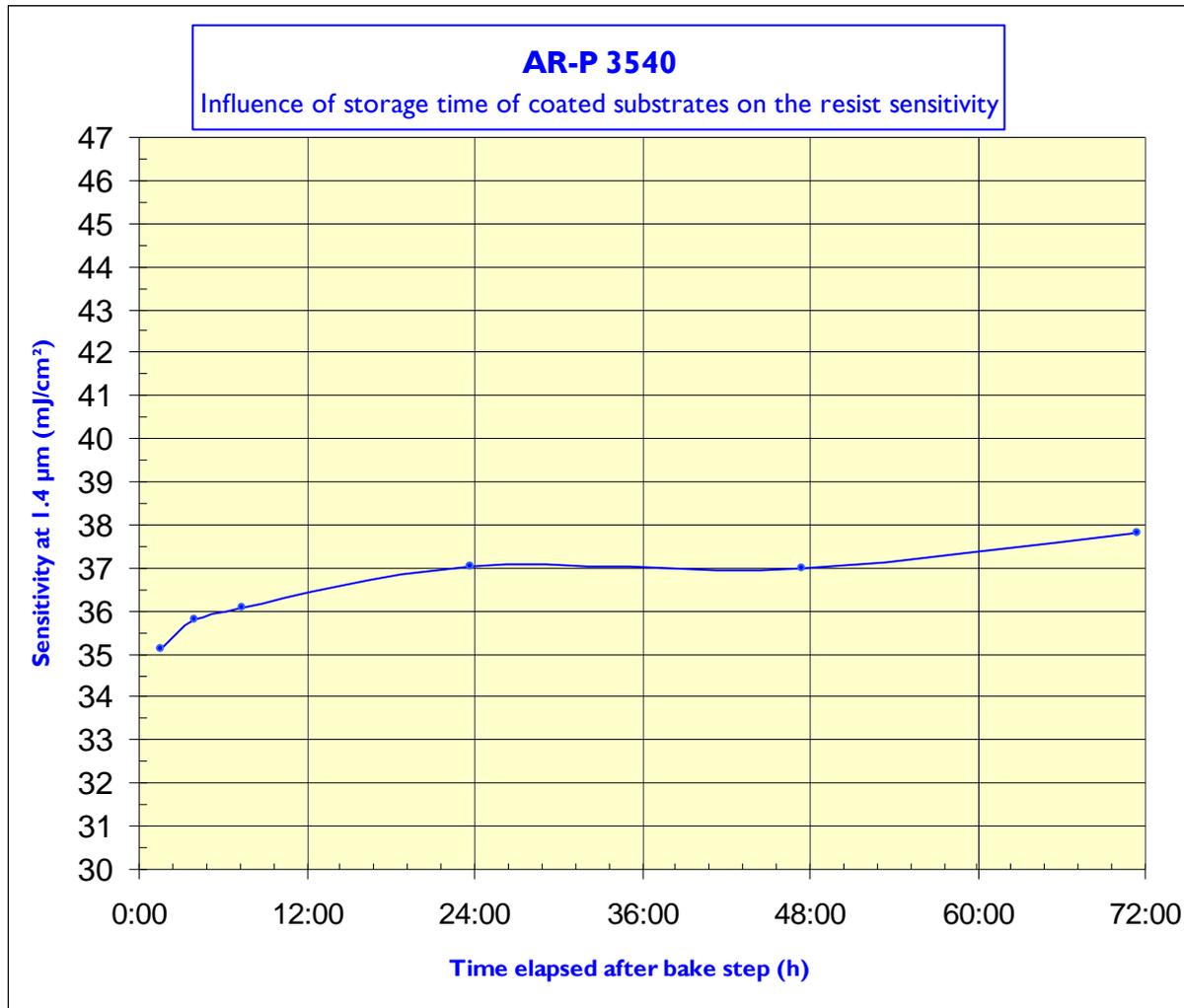


With special resists (e.g. SX AR-P 3500/6), exposure may under certain circumstances also be carried out at 488 nm (argon ion gas laser) or even at 532 nm (Neodym-YAG laser). For the UV range between 248 – 265 nm, resists AR-P 5800 and AR-N 4300 are particularly suited. In principle, also PMMA resists and CSAR 62 can be irradiated with light at this wavelength, have however only a low sensitivity.

Values for the light sensitivity as indicated in our product information are only guideline values which we determined in our standard assays.

The actual sensitivity as given in our product information depends on at least a dozen parameters. The most important factors are: bake conditions (temperature, time, equipment: hotplate or oven), exposure wavelength, exposure device (filter), layer thickness, developers (strength, time, temperature, type (buffered or not)), time after bake and after exposure, rehydration time after the bake, service life of the developer bath. But every user employs different procedures and thus has to determine the optimum exposure dose in own tests. For positive resists, the exposure dose (dose to clear) which is required to develop a large area without structures in a suitable development time (depending on the film thickness, for 1 – 2 μm approximately 30 – 40 s) should be increased by 10 – 20 % for structural imaging. For negative resists, the time for a complete development of unexposed areas of 1 – 2 μm is also about 30 – 40 s. The exposure dose which produces a film of > 90 % of D_0 should similarly be increased by 10 – 20 % for patterning.

Coated and baked resist films can be stored for several weeks prior to exposure without quality loss. The photoresists are more sensitive directly after the coating step as compared to coated films which were stored for several hours or days. The decrease in sensitivity is approximately 3 % after 3 h, approximately 6 % after 72 h, and 8 % after 72 hours (as compared to the initially achieved value).



10. Which developers are optimal for photoresist, and how do factors like developer concentration and temperature influence the result?

During development, a positive tone resist film is structured by a removal of exposed areas, while unexposed areas are removed if negative resists are used. To achieve reproducible results, temperatures between 21 and 23 °C ± 0.5 °C are highly recommended.

Allresist offers two different kinds of developers which are either buffered systems (AR 300-26, AR 300-35) or metal ion free (unbuffered) TMAH developers (AR 300-44 ... 475):

Developer AR 300-26 is a buffered system with high activity which is preferably used for the development of thick resist films > 5 μm, if high contrast, steep edges, and short development times are desired. Provided as developer concentrate, this developer is diluted with deionised water and can also be used for spray developments.

Developer AR 300-35 is a buffer system with broad process range and particularly characterised by a wide variation range with respect to contrast and sensitivity. This highly versatile developer suitable for most photoresists is provided as developer concentrate which can be diluted with deionised water. The undiluted developer solution is primarily designed for the development of 3 - 6 μm resist films. This



developer is suitable for aluminium-containing surfaces, since it does (in contrast to other developers) not attack aluminium.

The developer product line AR 300-40 comprises four metal ion-free developers of various concentrations, which particularly well meet the high demands of micro lithographic applications in semiconductor industry. The use of these developers minimises the possibility of metal ion contamination on the substrate surface. They exhibit excellent netting features and work, as aqueous alkaline solutions, without leaving any residues. The developers are each adjusted to the different resist systems AR-P 3000-5000 and 7000.

☞ Metal ion-free developers are more sensitive to dilution variations than buffer systems. These developers should be diluted very carefully, if possible with scales and immediately prior to use, in order to assure reproducible results.

Higher developer concentrations result in an increased light sensitivity of positive resist developer systems. The required exposure energy is minimised and development time is reduced, allowing a high operational capacity. Possible disadvantages might be a higher dark erosion of unexposed areas and also a low process stability (reaction too fast). Using higher developer concentrations, negative resists require a higher exposure dose for cross-linking.

Lower developer concentrations provide a higher contrast, e.g. of positive resist films, and reduce the resist thickness loss of unexposed or partly exposed border areas even at longer development times. The best contrast values can be obtained with carefully diluted buffered systems (AR 300-26, AR 300-35). In this case, the exposure energy required is mandatorily increased. Negative resists require a lower exposure dose (for cross-linking) at lower developer concentrations. However, the time for complete development is extended. As a rule of thumb for the developer strength: high speed (strong) or high contrast (weak).

The **service life of the developing bath** for immersion development is limited by factors such as process throughput and CO₂ absorption from air. The throughput is dependent on the fraction of exposed areas. CO₂ absorption is also caused by frequent opening of the developer bottle and leads to a reduced development rate.

Different methods exist for the development:

Immersion development: The wafer is completely immersed in a bath and move.

Puddle development: A defined amount of the developer is placed on the wafer, the wafer is then gently turned back and forth.

Spray development: The developer is sprayed through nozzles onto the rotating wafer. This development is significantly faster than other methods.

No interruptions should occur during aqueous alkaline development. If wafers are rinsed with water after development and the development is then continued, development rates will increase significantly.

11. How can resist coatings be removed again?

For the removal of **softbaked coatings**, polar solvents such as e.g. the respective resist thinner AR 300-12 (methoxy propyl acetate = PGMEA) and the remover AR 600-70 (acetone-based) may be used. Remover AR 600-70 is most commonly used.



For the wet-chemical removal of photoresist layers high-baked **up to 180 °C**, Allresist recommends the organic all-round mover **AR 300-76** which can be heated to 80 °C to reduce the dissolution time. Furthermore suitable are the organic removers AR 300-70 and AR 300-72 which however contain NEP as main component which was classified as toxic for reproduction.

For photoresist films baked **up to 170 °C**, also the aqueous-alkaline remover **AR 300-73** is well suited which can be heated up to 50 °C, but this remover attacks aluminium surfaces.

For photoresist films which were tempered **up to 170 °C**, we recommend remover **AR 600-71** which works very efficiently already at room temperature. This remover is especially intended for customers who use removers with low flash point.

Tempered photoresist films	AR 600-70	AR 600-71	AR 300-76 * heated to 80 °C	AR 300-70, -72 * heated to 80 °C	AR 300-73 + heated to 50 °C
120 °C	optimal	optimal	optimal	optimal	optimal
150 °C	optimal	optimal	* optimal	* optimal	* optimal
180 °C	suitable	suitable	* optimal	* optimal	* suitable
200 °C	unsuitable	unsuitable	* limited suitability	* limited suitability	* limited suitability

– details see product information remover

In semiconductor industries, the removal (stripping) is mostly performed by ashing in a plasma asher. The O₂-plasma generated by microwave excitation is used for an isotropic etching of the photoresist. But also oxidizing acid mixtures (piranha, nitrohydrochloric acid, nitric acid and others) may be applied in wet chemical removal procedures.

12. What is the application range of protective coatings?

Protective coatings are available for a large variety of applications, e.g. for the protection of wafer backsides:

- for mechanical protection during transport
- as insulating layer
- for KOH- and HF-etchings (AR-PC 503, AR-PC 504 (both adhesion-enhanced), SX AR-PC 5000/40)
- as temperature-stable intermediate layer for two-layer procedures (SX AR-PC 5000/80).

Protective coatings are generally applied by spin coating. Protective coatings AR-PC 504, X AR-PC 5000/19, and 5000/30 contain polymethacrylate and tend to show the so-called “candy-floss“-effect at suboptimal rotational speeds. This effect can be reduced with a lower rotational speed, local exhaustion, and the removal of the “candy strings” with a glass rod during spin coating. Recommended are coatings at 1000 rpm.

13. How do image-reversal resists work?

With image-reversal resists such as AR-U 4000, positive or negative tone images can be generated of the optical transmitted pattern depending on the manufacturing process. If the resist is processed according to the general protocol for positive resists without any additional steps, it works like a normal positive tone resist.



With the additional process steps “reversal bake” after image-wise exposure and subsequent “flood exposure”, the material provides a negative resist image which is characterised by a particularly high contrast of patterns. As guideline value for the reversal bake, 30 min at 100 °C in a convection oven or 5 min on a hot plate at 115 °C is recommended. The subsequent flood exposure (2- to 3-fold exposure dose of the initial exposure) converts the unexposed areas into a developable form. For optimal patterning, the process steps image-wise exposure, flood exposure, and development have to be coordinated thoroughly.

14. How can undercut patterns (lift-off structures) be produced in one- or two-layer systems?

A variety of one- or two-layer systems are available which generate undercut patterns. For example, AR-P 5350 is a layer system suitable for the production of metallic vapour phase structures. The resist contains components which harden the resist surface during the bake step (which is performed at slightly higher temperatures than usual). During the aqueous-alkaline development, undercut patterns are formed. The optimally adjusted developer for this purpose is AR 300-26.

Lift-off processes can also be employed with the two component system AR-P 5400 – 3510. This system also allows to generate thermally stable structures up to temperatures of 230 °C and optically transparent structures up to the IR range. As first layer, the copolymer mixture AR-P 5400 is deposited by spin coating. After a bake step at 150 °C, the photoresist AR-P 3510 is applied onto the cooled copolymer mixture, followed by a bake at 100 °C. For the aqueous-alkaline development, MIF-developer AR 300-47 is diluted 1 : 1 with deionised water. After exposed areas of the upper photoresist layer are developed, the developer begins to dissolve the copolymer mixture in a random manner (isotropic) in all directions. The longer the development time, the more polymer is dissolved underneath the photoresist layer. An undercut as desired can thus be achieved by adjusting the development time accordingly. For strong lift-off effects, the resist layers should be relatively thin (1.0 µm), while the copolymer layer should be thicker (1.5 µm). For a dimensional stable structure transfer into the copolymer layer, both films should have approximately the same thickness.

15. How can thick films of > 10 µm be processed in an optimal manner?

Coating: As a general rule for the coating with thick positive and negative tone resists, resists should be left undisturbed for several hours up to one day before processing (☞ Question 6: Optimum coating parameters, and 7: Air bubbles). Above a solids content of more than 50 % (AR-P 3220 and AR-N 4400-25 and -50), degassing by ultrasound is recommended. To avoid bubbles, thick coatings should be applied slowly and from a low distance to the substrate. ☞ It is recommended to always apply equal quantities of resist, e.g. approximately 8 - 12 ml for a wafer of 4 inches, depending on the viscosity of the resist.

For layers < 10 µm, coating and bake steps are conducted according to the protocol for standard resists (☞ AR-P 3500). For layers between 10 - 30 µm, spin times of 30-60 s are recommended. For layers above > 30 µm thickness, the coating should be performed in several steps. After a low initial rotational speed of 200 - 400 rpm for 30 s, rotation is continued at the final speed for further 2 - 5 min. A subsequent short spin (250 - 500 rpm) at a higher speed (600 - 800 rpm) reduces the formation of edge beads. ☞ The general



rule is that the film thickness increases with shorter exposure times. For highly viscous resists such as AR-N 4400-50, spin numbers of more 1000 rpm are disadvantageous due to a negative impact on the film quality. With increasing film thickness, the process window generally decreases.

Softbake: Positive resist system AR-P 3200: Films with high thicknesses between **10 – 30 µm** should be dried on a hot plate (95 – 100 °C, 8 – 15 min). For higher thicknesses **> 30 µm**, a bake in two steps is advisable: 1.) 75 °C, 5 min and 2.) 90 °C, 15 - 30 min.

☞ A longer bake step reduces the sensitivity as well as the tendency to form undercut profiles. These profiles are formed when layers still contains a relatively high amount of solvent, in particular in the bottom sections of the layers. A slow cooling step is recommended to avoid possible stress cracks.

Negative resist system AR-N 4400 (CAR 44): The bake step at 85 – 95 °C is highly dependent on the film thickness. For films **of 10 – 30 µm**, bake times on the hot plate are in the range of 8 – 20 min, while **40 – 50 µm** films require already a bake of 30 – 60 min. Films with thicknesses above 50 µm need even more bake time, which has to be determined individually by the respective user. It is absolutely recommended to use temperature ramps, since a fast cooling step (cool plate) may cause stress cracks. Drying times are extended by a factor of three in the convection oven. ☞ Long, rigid bake steps result in a low sensitivity during development.

Drying times are here also film thickness-dependent and in a range between 8 - 30 min on a hot plate and 30 - 60 min in the convection oven.

Below, detailed information is given concerning process steps such as exposure and, for CAR 44, the additional cross-linking bake at 95 - 105 °C which is required for this resist. The time for this additional bake step is again dependent on the film thickness and in a range of 8 - 30 min (hot plate).

Development: Thick resist films are developed in an aqueous-alkaline environment (☞ Question 10: Influence of developer concentration and time).

For the development of AR-P 3220, developer AR 300-26 is optimally suited. Depending on the respective film thickness and type of coating, a development in dilutions of 2 : 1 to in deionised water for 2 – 5 min is recommended.

For AR-N 4400, the MIF developer product line AR 300-40 is best suited. Thinner films of **up to 10 µm** demand developers in low concentrations such as AR 300-47 (in concentrations ranging from 3 : 2 dilution with deionised water up to undiluted use). **50-µm** films require more concentrated developers such as AR 300-44 or 300-46, depending on the intensity of the bake step. The development time is strongly determined by factors such as film thickness and developer concentration. For example, a 30-µm film is developed after approximately 8 min in developer AR 300-47, while thicker films require even longer. By combining a prolonged development with a just about sufficient exposure time, undercut profiles (lift-offs) can be obtained with AR-N 4450-10.

☞ The general rule is that longer development times in lower developer concentrations result in a higher image quality.

After development, resist films have to be rinsed with deionised water. The following removal step can easily performed with remover AR 300-70 (AR-P 3220) or, in the case of AR-N 4400, with remover AR 600-70 or AR 300-72 (☞ Product information).

16. Which resolution and which contrast can be obtained with photoresists?



The resolution of resists is influenced by several parameter such as e.g. the type of mask liner used, most of the respective NA (numerical aperture), film thickness, exposure wavelength, concentration of developer and time of development, substrate (e.g. reflexion properties), and a few other parameters with minor influence on the result.

Typical values for 1.4 µm thick positive resists are resolutions between 0.4 and 0.5 and a contrast of 4.5 to 5.

Respective parameters for each type of photoresist are specified in our Parameter Collection (see “Photoresists”).

17. How high is the plasma etch resistance of photoresists?

Photoresists of the AR-series 3000 to 4000 display a very high etch resistance due to the polymers which are used for their production. This is especially the case for dry etch processes such as e.g. argon sputter, CF₄ and CF₄/O₂-mixtures. A postbake at 110 °C prior to the etch process for re-stabilization increases the etch stability slightly. The etch stability can be further improved by adding aromatic conjugated compounds.

Resist etch rates are highly dependent on the etch conditions. In addition to the equipment used (plasma etcher), the rate is also influenced by etch gas composition, pressure, temperature, and voltage.

The following parameters were determined for our photoresists at 5 Pa and 240 – 250 V bias:

Argon sputter:	3 – 8 nm/min
CF ₄ :	31 – 42 nm/min
80 CF ₄ + 16 O ₂ :	81 – 93 nm/min
O ₂ -plasma:	122 – 174 nm/min

Respective parameters for each type of photoresist are specified in our Parameter Collection (see “Plasma Etching Rates”)

Careful etch procedures (low pressure and voltage) lead to a higher resistance of the resist, but the etch process requires more time. Cooling during the etching improves the resistance accordingly. If resists are etched too rigidly (e.g. too high temperatures), the subsequent removal step will cause major problems.

18. How high is the etch resistance of photoresist in the presence of strong acids?

Concentrated oxidising acids (sulphuric acid, nitric acid, aqua regia ¹), piranha ²) attack resist films already at room temperatures and are often used as removers for persistent resist structures. Already moderate dilution of these acids prevents this reaction with the resist. Non-oxidising acids however (hydrochloric acid, hydrofluoric acid) leave the resist film intact, even if concentrated solutions of these acids are used. Hydrofluoric acid however removes the undamaged resist layer in most cases completely (see Question 19). After a bake of all photoresist films (AR-P 3000 – 5000) at 95 °C for 25 min in a convection oven, the following parameters were determined:



- Sulphuric acid 50 %: no attack after 2 hours (room temperature and heated to 60° C)
- Sulphuric acid 96 %: films peel off after 15 s, only PMMA protective coatings are heavily attacked and gradually removed. Slow stripping of AR-PC 503, 504, X AR-P 3100/10, SX AR-PC 5000/40).
- Hydrochloric acid 20 %: no attack after 2 hours (room temperature and heated to 60° C).
- Hydrochloric acid conc. 37 %: no reaction with films observed, only AR-N 4340 shows adhesion problems after 10 min (film is floating off).
- Hydrofluoric acid 2 %: Films float off immediately for coatings < 5 µm thickness, thicker layers remain stable for 1 – 3 min, but structures begin to peel off already after 30 s. Exceptions: X AR-P 3100/10, AR-PC 503, 504, X AR-P 3100/10, SX AR-PC 5000/40 (☞ Question 12: Protective coating).
- Hydrofluoric acid 5 %: Processing of X AR-P 3100/10 is only possible at short etch times (< 5 min) and with protective coating AR-PC 503, 504, SX AR-PC 5000/40.
- Hydrofluoric acid conc. 50 %: Processing is only possible with protective coating SX AR-PC 5000/40 (☞ Question 19 HF etching).

A postbake of resist films (100 – 130 °C) leads only to a minor improvement with respect to the stability in concentrated sulphuric acid and hydrofluoric acid.

- 1) Aqua regia: Mixture of hydrochloric acid and nitric acid (3 : 1)
- 2) Piranha: Mixture of sulphuric acid and hydrogen peroxide (1 : 1)

19. Which photoresists are suitable for hydrofluoric acid (HF) etching?

The positive tone **photoresist AR-P 5910** is highly adhesion-enhanced and thus suitable for HF etching of up to 5 % HF. In particular on glass or silicon oxide, a pre-treatment of substrates with the adhesion promoter AR 300-80 is strongly recommended. With AR-P 5910, a film thickness of 5 µm can be achieved at 4 000 rpm. This high thickness is advantageous to obtain a high etch resistance since HF is able to diffuse through the layer and to remove it consequently.

After the coating step, the hotbake should be performed on a hot plate at 85 - 90 °C for 2 min. In comparison to standard resists, this resist is less sensitive and consequently requires longer exposure times.

For the development of exposed resist films, undiluted developer AR 300-26 is recommended. The development time should amount to approximately 60 s.

A bake of developed structures at 105 - 115 °C increases stability and adhesion of the resist mask to the substrate substantially. Higher temperature should however be avoided. On well-adhesive surfaces such as e.g. silica, the resist mask is stable for hours in 5 % HF or HF/isopropanol mixtures. In the case of deeper etchings however, the resist begins to peel off at the edges of structures.

The protective coating SX AR-PC 5000/40 is HF and KOH resistant (KOH: caustic potash solution). This coating is used to generate stable protective films which reliably protect the backside of wafers while the etch process is performed on the front (e.g. 40 % KOH or 50 % HF).



In addition, the protective coating can be patterned in a two layer system using photoresist AR-P 3250 which allows a transfer of structures into glass or silicon oxide.

20. How high is the solvent resistance of photoresist films?

With respect to the raw materials used, photoresists fall into two different categories:

- PMMA resists (protective coating AR-PC 5000/4, -19, -30, and SX AR-N 4800)
- SX AR-PC 5000/40
- Novolac resists (AR-P 3000, AR-N/U 4000, a few 5000)

☞ The general rule is that with increasing bake or process temperature, the solubility of the resist films decreases. This is reflected by gradually increasing removal problems.

PMMA resists:

Easily soluble in: acetone, MEK, PMA (PGMEA), chlorobenzene, ethylbenzene, anisole, MIBK

Particular in: NMP, ethyl lactate

Not soluble in: water, isopropanol, ethanol, nonane, and the like.

SX AR-PC 5000/40

Well soluble in: chlorobenzene, ethylbenzene

Not soluble in: anisole, MIBK, ethyl lactate, and the like.

Novolac resists:

Well soluble in: acetone, MEK, PMA (PGMEA), anisole, MIBK, butyl acetate

Particular in: isopropanol, NMP, ethanol, ethyl lactate

Not soluble in: water, chlorobenzene, ethylbenzene, nonane, and the like.

Abbreviations of solvents and raw materials used: MEK: methyl ethyl ketone; PMA (= PGMEA): 1-methoxy-2-propyl acetate, NMP: N-methyl-2-pyrrolidone, MIBK: methyl isobutyl ketone, TMAH: tetra methyl ammonium hydroxide, KOH: caustic potash solution, HF: hydrofluoric acid

Please find more detailed information in the Parameter Collection Table and our Product information on our homepage ☞ www.allresist.de