FAQs concerning e-beam resists provided by Allresist

1. What are e-beam resists composed of, and how do they work?
2. For how long are e-beam resists stable, and what are the optimal storage conditions?
3. What is the optimal pre-treatment of substrates for e-beam resist application?
4. How high is the adhesion strength of e-beam resists to different wafers?
5. How are e-beam resists irradiated, and how can the optimum exposure dose be determined?
6. Which developers are optimal for e-beam resists, and how do factors like developer concentration and temperature influence the result?
7. How can e-beam resist films be removed again?
8. Which resolutions do e-beam resists achieve?
9. How high is the plasma etch resistance of e-beam resists?
10. How high is the etch resistance of e-beam resists in the presence of strong acids?
11. How high is the solvent resistance of e-beam resist films?

FAQs concerning e-beam resists

1. What are e-beam resists composed of, and how do they work?

E-beam resists (electron beam resists) are designed for electron beam and deep UV applications for the fabrication of highly integrated circuits, mainly for mask fabrication. These resists generally allow the realisation of 100 to 500 nm structures on masks and wafers with film thickness values between 200 and 500 nm.

E-beam resist are also used in electron beam direct writing and multilayer processes. Thin layers of these resists < 100 nm are excellently suited for nanometre lithography. With an optimised process regime, even structures of less than 10 nm thickness can be realised at a film thickness of 50 nm.

They are characterised by a very good adhesion to silicon, glass and most metals. They are applied by spin coating between 6000 and 1000 rpm, and films with a thickness between 20 nm and 1.75 µm can be achieved. For special e-beam applications, film thickness values of even10 µm are possible (AR-P 6510).

Allresist offers several types of e-beam resists.

1) PMMA resists are composed of poly(meth)acrylates with different molecular masses (50K, 200K, 600K, and 950K) which are dissolved in chlorobenzene (AR-P 631 … 671) or the safer solvent ethyl lactate (AR-P 639 … 679) and 1-methoxy-2-propyl acetate (AR-P 6510). These resists work as positive tone resists. In comparison to polymer 950K, the sensitivity of polymer 50K is enhanced by 20 %. The glass temperature of PMMA layers is in the range of 105 °C, and polymers are thermostable up to a temperature of 230 °C.

2) Copolymer resists are composed of copolymers based on methyl methacrylate and methacrylic acid (PMMA/MA 33 %), which are dissolved in safer solvent 1-methoxy-2-propanole (AR-P 617). Copolymer resists also work as positive tone resists. Due to the chemical properties of methacrylic acid during the bake step at 200 °C in which dehydration leads to ring formation, copolymers possess a 3- to 4-fold higher sensitivity and a considerably higher contrast than PMMA resists. In addition, polymer layers are thermostable up to 240 °C, with a glass temperature of 150 °C.

As special resist for thick films of 5 – 250 µm suitable for LIGA techniques (synchrotron radiation) is AR-P 6510.

PMMA and copolymer layers are optically transparent above a wavelength of 260 nm. Since they resist however also absorbe at 248 nm, and a deep-UV exposure and patterning with these resists is thus possible, even though with lower sensitivity.

3.) CSAR 62 (AR-P 6200) is based on styrene acrylates and dissolved in the safer solvent anisole. Polymer layers are furthermore thermally stable up to 240 °C; the glass transition temperature is 148 °C. They are approximately twice as sensitive as PMMA resists and a bit less sensitive than the copolymer (AR-P 617). These differences may be exploited for two- and three-layer processes (e.g. T-gate manufacturing). CSAR 62 has a very high contrast (> 15) and good plasma etch stability.

4) Novolac-based e-beam resists (AR-P 7400, AR-N 7500…7700) are in general aqueous-alkaline developable. These resists are available as positive or negative tone electron beam resists. Positive-working resists contain naphthoquinone diazide and novolac (AR-P 7400). Negative resists contain in addition to the novolac organic or amine cross-linking agents and/or acid generators. As additional component, AR-N 7500 contains naphthoquinone diazide.

Novolac-based resists are approximately twice as stable in plasma etchings as compared to PMMA- and copolymer resists (AR-P 617); they are used for the fabrication of structures in electron beam lithographic processes and for mask production. A few e-beam resists also allow for mix-&-match processes, combining e-beam- and UV exposure (AR-P 7400, 7520 and 7700/30). The fine structures are written into the resist layer by e-beam lithography, immediately followed by UV exposure (i-line) of larger structures. Subsequently, resists are developed in one step according to the usual protocol.

A maximum resolution of < 10 nm can be realised for very thin films with AR-P 7400 and AR-N 7520. ~~With AR-N 7520, even 6 nm lines could already be achieved, at an aspect ratio of 10.~~

Chemically enhanced e-beam resists are AR-N 7700, 7720 as well as AR-N 7700/30 and ~~/-37~~. The latter resist has a very high sensitivity, is highly process- and storage stable, and allows also exposition in the deep UV and broad range UV spectrum. Resists of the AR-N 7700 series are high-resolution resists and reach a structural resolution of 50 – 100 nm with very good sensitivity. Resist AR-N 7720 is particularly well suited for three-dimensional structures, due to the low contrast which was specifically adjusted for this application.

An important addition to previous e-beam resists is Electra 92 (AR-PC 5090 and 5091). The conductive resist itself is not structurable, is however needed for the dissipation of electrical charges in order to realise accurate structural images on insulating substrates (glass, quartz, polymers).

Refractive indices for PMMAs are 1.48, for copolymers 1.49, for styrene acrylates 1,54 and for novolac-based e-beam resists 1.60 – 1.61.

2. For how long are e-beam resists stable, and what are optimal storage conditions?

PMMA-, copolymer and styrene acrylate resist are not light-sensitive in the visible UV range; they consequently don't react to light exposure (no yellow light required) and are substantially less temperature-sensitive than novolac-based resists. These resists thus age only slowly. Typical age-related changes are a slow thickening of the resist, which however has no negative impact on the quality. In this case, films just tend to be slightly thicker which can easily be corrected during the coating procedure.

In contrast, novolac-based e-beam resists are about as light-sensitive as photoresists. They react to light- and temperature exposure and age much faster during storage. The resists are thus provided in light-protected amber glass bottles which should be stored at low temperatures and only be processed under yellow safe light (λ > 500 nm). Exceptions are experimental samples SX AR-N 7530/1 and SX AR-N 7730/1. Due to their specific acid generators are both resists also not sensitive in the visible UV (> 300 nm) and thus do not require yellow light.

Date of expiry and recommended storage temperature are indicated on the product label of each e-beam resist. Following these recommended storage guidelines, resists are stable until expiry date, at least however for 6 month after date of sale. Repeated opening of resist bottles leads to evaporation of the solvent, causing an increased viscosity of the resist which results in thicker films upon usage. For a resist with a film thickness of 1.4 µm, evaporation of only 1 % of the solvent increases the film thickness by 3 – 5 % and consequently also an increase of the expose dose.

Examples of our customers and own long-term studies demonstrate that PMMA- and copolymer e-beam resists have already safely been used for up to 2 years without quality loss.

☞ Bottles which were stored 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. What is the optimal pre-treatment of substrates for e-beam resist application?

If new and clean substrates (wafers) are used, a bake at approximately 200 °C for a few minutes is sufficient in order to dry the substrates, which however then have to be processed quickly. 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 with acetone and subsequent isopropanol or ethanol treatment, followed by a bake.

If a technology involves repeated processing of wafers or if wafers are subjected 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 1) may be required in this case. For very difficult cases, a treatment with ultra- or mega-sound is advisable.

PMMA-, copolymer and styrene acrylate resist are characterised by excellent adhesion properties to silica, silicon nitride, glass, and most metal surfaces and thus require only in exceptional cases additional adhesion promoters (AR 300-80, HMDS).

Novolac-based e-beam resists however generally require the use of adhesion promoters such as e.g. adhesion promoter AR 300-80 to improve adhesion features. AR 300-80 is deposited immediately before coating (by spin coating) as a thin film of approximately 15 nm. It is also possible to evaporate HMDS onto the substrates. A monomolecular HMDS layer improves the adhesion properties of the wafer surface (which becomes more hydrophobic and thus more organophilic), which then retains the resist much better.

4. How high is the adhesion strength of e-beam resists to different wafers?

Adhesion between substrate and coating is a sensitive feature of a resists, which is also true for e-beam resists.

PMMA-, copolymer and styrene acrylate resist are however significantly less prone for adhesion problems than e-beam resists of the AR 7000 product line, where smallest changes of the cleaning procedure or other parameters may have a fatal impact on the adhesion strength.

Silica, silicon nitride, and base metals (such as aluminium, copper) generally possess good resist adhesion features, while adhesion on SiO_2, glass, noble metals such as gold or silver, and on gallium arsenide is often insufficient. In this case, measures have to be taken to improve adhesion (☞ Question 3: Pre-treatment of substrates).

If the air humidity is too high (> 60 %), adhesion is substantially reduced.

5. How are e-beam resists irradiated, and how can the optimum exposure dose be determined?

Using very short-wavelength electrons for resist irradiation, an excellent resolution of up to 2 nm can be achieved (single spot exposure). The exposure is performed with standard equipments for electron beam lithography and is based on the principle of direct writing or raster scan shaped beam procedures. For mix&match technologies with resists of the AR 7000 product line, additional exposure procedures can be realised with (i-, g-line) steppers or contact developers in the respective spectral UV working range.

Values for the photosensitivity as given in our product information are guideline values which we determined in our product-specific standard tests. Every user however employs different procedures and thus has to determine the optimum exposure dose in own tests. With respect to sensitivity, already considerably high differences exist between e.g. silicon wafers and mask blanks (PMMA mask: 15 µC/cm² - PMMA wafer 80 µC/cm²). Likewise, the influence of the acceleration voltage is substantial.

For positive PMMA resists, the minimum 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 0.5 µm: 30 – 60 s) should be increased by 10 – 20 % for structural imaging. For negative resists, the time for complete development of unexposed areas of 0.5 µm is also about 30 – 40 s. The exposure dose which produces a film of > 90 % of the initial resist thickness should similarly be increased by 10 – 20 % for patterning. If a shorter dose to clear is chosen (stronger developer), the sensitivity will decrease since more cross-linking is required (higher dose).

6. Which developers are optimal for e-beam resists, and how do factors like developer concentration and temperature influence the result?

During development, a positive tone resist film is patterned by a removal of exposed areas, while unexposed areas are removed when negative resists are used. To achieve reproducible results, temperatures between 21 and 23 °C ± 0,5 °C for organic solvent developers (AR 600-50, -50, -56) and ± 0,5 °C for aqueous-alkaline developers (AR 300-26, -35, -40) are highly recommended.

Developer AR 600-50 is a solvent-based developer which was especially designed for copolymer films (AR-P 617). With this developer, the sensitivity of the e-beam resist is further enhanced.

Developer AR 600-55 is, just like the next AR 600-56 resist, also solvent-based. As high speed developer, AR 600-55 is preferably used for PMMA films (AR-P 630-670), if short development times for a high process throughput are desired. Copolymer films (AR-P 617), e.g. also as two-layer system PMMA/copolymer, can likewise be developed with this developer.

Developer AR 600-56 is slower than 600-55 and preferably used for PMMA films (AR-P 630-670), if high resolutions and a high contrast are desired despite prolonged development times. This developer is also suitable for copolymer films.

In contrast to novolac-based resists, the development of PMMA layers may be interrupted at any time and continued later without problems. To achieve a particularly high resolution, isopropanol or isopropanol/water developers may be used. In this case however, a higher dose is required for exposure.

For the development of exposed CSAR resist films, **developers AR 600-546, 600-548, and 600-549** are suitable. As the weakest developer, AR 600-546 provides a broad process window with the highest contrast values > 15. If the stronger developer AR 600-548 is used, the sensitivity can be increased by a factor of 6 to 10 µC/cm² (30 kV). Developer AR 600-549 with intermediate strength renders CSAR 62 twice as sensitive as compared to AR 600-546, shows likewise no dark erosion, and the contrast is about 4. Especially for CSAR 62, the temperature of the developer plays a major role. Lower temperatures reduce the dark field loss, but also the sensitivity. Own tests may be necessary to determine the optimal conditions.

The aqueous-alkaline **developer AR 300-40 product line** comprises metal ion free developers of various concentrations. Usage of these developers minimises the possibility of metal ion contamination on the substrate surface as compared to the metal ion-containing developers (AR 300-46, AR 300-35). They exhibit excellent netting features and work, as aqueous-based solutions, without leaving any residues. Especially developer AR 300-46 and 300-47 are recommended (some also in dilutions) for the novolac-based e-beam resists AR-P 7000. ☞ Metal ion free developers are more sensitive to dilution variations. These developers should thus be diluted very carefully, if possible with scales and immediately prior to use in order to assure reproducible results.

Higher developer concentrations of AR 300-40 formally lead to a higher photosensitivity for positive resist developer systems, resulting in a minimum exposure intensity required, reduced development times, and a high process throughput. Possible disadvantages are however a higher dark field loss and also, in some cases, a low process stability (too fast). Negative coatings demand higher exposure doses for crosslinking at higher developer concentrations.

Low developer concentrations of AR 300-40 result in a higher contrast for positive resist films and reduce the resist removal in unexposed or only partly exposed areas even at longer development times. Mandatorily, however, the exposure intensity has to be increased. Negative resists require a lower exposure dose at lower developer concentrations (for cross-linking). The time needed for complete development is extended.

The **service time of the developing bath** of aqueous-alkaline developers for immersion development is limited by factors such as the process throughput and CO_2 absorption from air. The throughput is dependent on the fraction of exposed areas. CO_2 absorption is also caused by frequent opening of developer containers and results in a reduced development rate. CO_2 does not play a role in the case of solvent developers, but a solvent mixture (e.g. AR 600-55, 600-56 AR) may nevertheless change due to the different evaporation numbers of the respective solvents. It is thus also recommended to rather replace the developer in doubt.

7. How can e-beam resist films be removed again?

For the removal of all e-beam resist coatings baked at lower temperatures (softbake), polar solvents may be used such as e.g. the recommended thinner AR 300-12 or AR 600-01, 600-07 and 600-09, as well as remover AR 600-70 (acetone-based). AR 600-70 is the most commonly used remover for this purpose.

For a wet-chemical stripping of e-beam resist films highly tempered **up to 200 °C**, Allresist recommends the organic all-round remover **AR 300-76** which can be heated to 80 °C in order to reduce the dissolution time. Also available for this purpose are the organic removers AR 300-70 and AR 300-72, but both contain NEP as main component which was classified as toxic for reproduction.

The aqueous-alkaline remover **AR 300-73** can be heated to 50 °C and is particularly suitable for novolac-based e-beam resist films which were tempered **up to 200 °C**. This developer however attacks aluminium surfaces.

For e-beam resist films (except novolac-based layers) that were tempered **up to 200 °C**, we generally recommend remover **AR 600-71** which works already at room temperature highly efficiently. This product is especially intended for customers who are able to use removers with low flash point.

Tempered e-beam resist 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
150 °C PMMA	optimal	optimal	* optimal	* optimal	+ suitable
200 °C PMMA	suitable	suitable	* limited suitability	* limited suitability	+ unsuitable
210 °C copolymer	optimal	optimal	* optimal	* optimal	+ limited suitability
150 °C CSAR 62	unsuitable	optimal	* optimal	* optimal	+ suitable
200 °C CSAR 62	unsuitable	optimal	* suitable	* suitable	+ suitable
120 °C novolac-based	optimal ~	optimal ~	* optimal ~	* optimal ~	+ suitable
150 °C novolac-based	suitable ~	suitable ~	* optimal ~	* optimal ~	+ suitable

~ For 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.

8. Which resolution can e-beam resists achieve?

With respect to the achievable resolution, purely academic resolution values and industrially utilisable values represent two quite different aspects. Theoretically, resolutions of 2 nm are possible (single electron spot).

With CSAR e-beam resists, 6 nm lines can be achieved at a film thickness of 80 nm. Resolutions of up to 10 nm are possible with a film thickness of 180 nm.

With **PMMA resists**, similarly high resolutions are obtained at film thicknesses of max. 50 nm, but these structures can only be used with restrictions for commercial applications due to the process parameters (most of all the required high exposure doses). Resolutions up to 150 nm can be achieved with PMMA for films with 400 nm thickness as mostly utilised in industrial mask production.

Novolac-based negative e-beam resists allow a maximum resolution of 30 nm bars, while in industrial manufacturing processes, only 80 - 100 nm structures can be realised.

9. How high is the plasma etch resistance of e-beam resists?

Electron beam resists of the AR 6000 and AR 7000 series display quite different etch resistance features in dry etch processes such as e.g. argon sputter and CF_4. Novolac-based e-beam resists have a high etch stability, while PMMA resists are significantly more susceptible to etchings. CSAR 62 has a similarly high etch stability like novolac-based e-beam resists. Prior to the etch process, a postbake at 110 °C for re-stabilization increases the etch stability slightly. Resist **etch rates** are highly dependent on the respective conditions. In addition to the device used (plasma etcher), the rate is also influenced by etch gas composition, pressure, temperature, and voltage.

The following **etch rates** (nm/min) were determined for our e-beam resists at 5 Pa and 240 – 250 V bias:

	AR-P 600(0)	AR-P/N 7000
Argon sputter:	10 – 22 nm/min	8 – 9 nm/min
CF_4:	51 – 61 nm/min	33 – 41 nm/min
80 CF_4 + 16 O_2:	116 – 169 nm/min	89 – 90 nm/min
O_2-Plasma:	173 – 350 nm/min	168 – 170 nm/min

Cautious plasma etch procedures (low pressure and voltage) lead to a higher resistance of the resist, but the etch process itself requires more time. Thorough cooling during the etching improves the resistance likewise. If resists are etched too rigidly (e.g. temperatures too high), the subsequent removal step may cause major problems.

10. How high is the etch resistance of e-beam resists 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 remover for persistent resist structures.

In the presence of these agents, **novolac resists** are easily removed, while **PMMA resists** begin to swell and are then removed slowly. Already moderate dilution of oxidising acids with di-water however prevents this attack of acidic solutions. In contrast, non-oxidising acids (hydrochloric acid, hydrofluoric acid) leave resist films intact, even if concentrated solutions of these acids are used.

After a tempering of e-beam resist films (AR-P 600(0), AR-P/N 7000) at 95 °C for 25 min, the following parameters were determined:

- <u>Sulphuric acid 50 %:</u> no attack after 2 hours (room temperature and heated to 60° C)

- Sulphuric acid 96 %: dissolution of films after 15 s, except for PMMA protective coatings are heavily attacked and gradually removed
- 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 7500 shows adhesion problems after 10 min (film is floating off)
- Hydrofluoric acid 2 %: coatings < 2 µm film thickness float off immediately

With respect to the stability in concentrated sulphuric acid and hydrofluoric acid, a postbake of resists films (PMMA 190 °C, novolac 150 °C) only leads to a minor improvement.

1) Aqua regia: Mixture of hydrochloric acid and nitric acid (3 : 1)

2) Piranha: Mixture of sulphuric acid and hydrogen peroxide (1 : 1)

11. How high is the solvent resistance of e-beam resist films?

With respect to the raw material used, e-beam resists fall into four different categories:

- PMMA- resists (AR-P 600(0)
- CSAR 62
- Novolac e-beam resists (AR-N/P 7000)
- Electra 92

The general rule is that with increasing bake- or process temperatures, the solubility of resist films decreases, which consequently results in gradually increasing removal problems. After a bake step above a temperature of 200 °C, resists are inert in the presence of most solvents. Only remover AR 300-70, 300-72 (NMP) and AR 300-73 (TMAH, aqueous-alkaline) still cause film swelling and are in some cases able to remove layers.

PMMA- and styrene acrylate resists:

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

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

CSAR 62

Easily soluble in: chlorobenzene, ethylbenzene, anisole, MEK, hardly soluble in: acetone, MIBK, ethyl lactate

Not soluble in: water, strong alkaline solutions, isopropanol, ethanol, nonane and others.

Novolac resists:

Easily soluble in: acetone, MEK, PMA (PGMEA), NMP, anisole, MIBK, isopropanol, butyl acetate, ethyl lactate, strong acids

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

Electra 92:

Easily soluble in: water

Not soluble in**: acetone, MEK, PMA (PGMEA), NMP, anisole, MIBK, isopropanol, butyl-acetate, 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: tetramethylammonium hydroxide, KOH: caustic potash solution, HF: hydrofluoric acid

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