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Product information

E-BEAM RESISTS

THE ALLRESIST GMBH

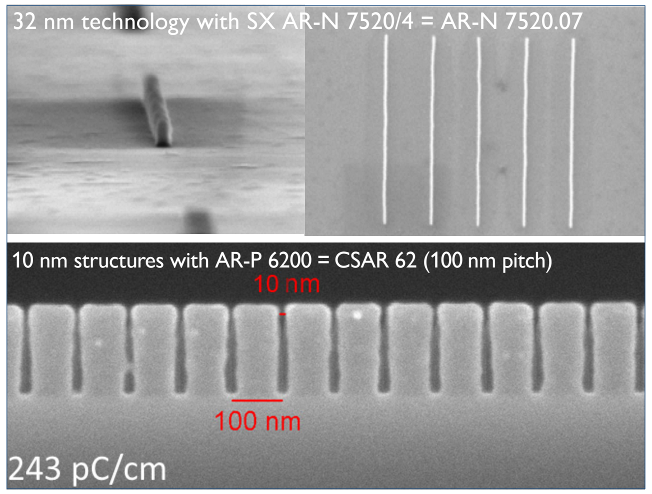
Company for chemical Products

The executive board Brigitte und Matthias Schirmer with daugther and successor Ulrike Schirmer

The company is represented worldwide with an extensive product range. In addition to our standard products, we also manufacture customer-specific products on request.

Allresist furthermore develops innovative products for future-oriented technologies like e.g. microsystems technologies and electron beam lithography. In these constantly growing markets, top-performance resists with high sensitivity and a high resolution are in strong demand.

Our newly developed e-beam resists CSAR 62 and Medusa 82 meet these demands, pushing forward innovative technologies with their excellent properties. With Electra 92 as top layer, e-beam resists can be processed also on insulating substrates like glass, quartz, or GaAs.



The Allresist GmbH offers a wide range of resists and process chemicals for all standard applications of photo and e-beam lithography which are required for the fabrication of electronic components.

As independent resist manufacturer, we develop, produce and distribute our products worldwide. On the market since 1992, Allresist benefits from a comprehensive know-how gained in 30 years of resist research, and fabricates products with highest quality (ISO 9001).

As chemical company, we are particularly aware of our obligation to a healthy environment. A responsible and protective resource management and voluntary replacement of environmentally hazardous products is living politics for us. Allresist is environmentally certified (ISO 14001) and environmental partner of the Federal State of Brandenburg.

Our flexible approach to customer's demands, together with effective production technologies, allows us to provide fast availability which results in very short delivery times, small packaging sizes from ¼ l onwards, 30 ml test samples as well as an individually tailored advisory service.

Allresist received a number of awards for scientific and economic top performance (technology transfer prize, innovation award, customer's champion, quality award and Ludwig-Erhard-prize).

Interesting news and further information for you are compiled on our web page where you will find answers to many questions in our resist-WIKI and the FAQ.

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OUR NEWS

for Microstructuring

2017 - 2020

Three further important new developments in principle allow new resist applications: very stable negative resist **Atlas 46** (AR-N 4600, comparable to SU-8), thermally structurable **Phoenix 81** (AR-P 8100, nanofrazor), and high-resolution **Medusa 82** (SX AR-N 8200, comparable to HSQ). Medusa 82 has higher storage stability than HSQ. The sensitivity can be increased by up to 20 times by a post exposure bake or an addition of acid generators. Currently under development is a variant that can also be processed with broadband UV.

The ready-to-use spray resists AR-P 1200, AR-N 2200 are used to evenly cover vertical trenches, for etched 54 ° slopes, and for spin coating.

2016

AR-PC 5090 and 5091 were specifically developed for the efficient dissipation of electrical charges during e-beam lithography on insulating substrates. The new, highly conductive protective coatings can be applied on PMMA, CSAR 62, and HSQ as well as on novolac-based e-beam resists and are removed easily and completely after the process. **Electra 92** can furthermore be used as a replacement for metal vapour deposition in SEM images.

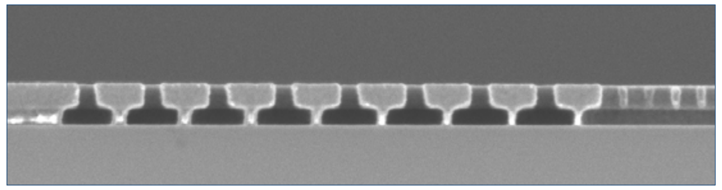
2014, 2015

Due to the classification of the raw material NEP which is contained in removers AR 300-70 and 300-72 as toxic for reproduction, Allresist now introduced the less harmful new remover **AR 300-76** with respect to dissolving power.

Additional eight PMMA solids complement the PMMA product portfolio which now comprises 43 solids contents.

2013

The new 5 µm-resist **AR 4400-05** completes the CAR series 44 and represents an efficient alternative to SU-8. The possible film thickness values now range from 2.5 µm to 100 µm.



Structures with extreme undercuts is possible: 22 nm structures with two-layer system AR-P 6200 / AR-P 679.03

The new remover **AR 600-71** is already at room temperature particularly efficient for the removal of e-beam- and photoresist films baked at higher temperatures.

The new electron beam resist **CSAR 62** is a further development of the well-known ZEP resists. This copolymer on the basis of methyl styrene-co-α-chloromethacrylate with addition of halogenated acid generators ensures a high sensitivity and excellent resolution, a steep contrast as well as excellent plasma etching stability.

With different developers, a resolution of up to 10 nm and sensitivities of about 10 µC/cm² can be realised. If used in a two-layer system with PMMA, the fabrication of smallest.

2012

With the new e-beam resist **AR-N 7520/4** (replacing resist AR-N 7520 new), Allresist introduces a high-resolution and at the same time sensitive new resist onto the market. In contrast to currently available e-beam resists, this resist is characterised by a 7-fold higher sensitivity. The dose to clear a 100-nm layer reduces the writing times at 30 KV to 35 µC/cm².

18 new anisole-PMMA resists AR-P 632…672 of types 50K, 200K, 600K and 950K complement the current anisole PMMA resist palette which also, just like the chlorobenzene PMMAs, meet the high demands of e-beam lithography.

2011

Other new products are polyimide resists which are temperature-stable up to 400 °C: protective coating **SX AR-PC 5000/80** and the positive resist **AR-P 5000/82**.

Currently still in development

We work with high pressure to develop a positive, highly sensitive CAR E-beam resist **EOS 72 (alternative to FEP 171).**

With **our new fluorescent and coloured resists,** new applications in microbiology and optics arise. Dyes or quantum dots illuminate the structures.

The bottom resists of the AR-BR 5400 series have been optimised for the technological requirements of some large customers. They are used as a lower layer in a two-layer system (photoresist on top), especially for lift-off applications.

Contents & Product Overview E-Beam Resists

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Product Portfolio E-Beam Resists

Resist system	Product	Do/ µm 4000 rpm	Type	Characteristic Properties	Application	Resolution [nm] *	Contrast	Exposure	Thinner	Developer	Remover
AR-P 617	**copolymer PMMA/MA 33%**	0.09-1.75 methoxy propanole		highest resolution, 2x more sensitiver than PMMA, lift off	ICs, masks	10 / 100	6.0		600-07	600-50 600-55	600-71 300-76
AR-P 641-671	**PMMA 200K, 600K, 950K**	0.02-1.70 chlorobenzene		highest resolution, process stable, universally, simple processing	ICs, masks	6 / 100	7.0		600-01	600-55 600-56	600-71 300-76
AR-P 632-672	**PMMA 50K, 200K, 600K, 950K**	0.01-1.87 anisole	positive	highest resolution, process stable, universally, simple processing	ICs, masks	6 / 100	7.0	e-beam, deep UV	600-02	600-55 600-56	600-71 300-76
AR-P 639-679	**PMMA 50K, 200K, 600K, 950K**	0.02-0.74 ethyl lactate		highest resolution, process stable, universally, simple processing	ICs, masks	6 / 100	7.0		600-09	300-55 300-56	600-71 300-76
AR-P 6200 CSAR 62	**6200.04, .09, 6200.13** **styrene acryl.**	0.08 ; 0.4 ; 0.2		highest resolution, high sensitivity, plasma etching-resistant	ICs, sensors, masks	6	15		600-02	600-546 600-548 600-549	600-71 300-76
AR-P 6500	**6510.15, .17 PMMA**	350 rpm: 28, 56		thick PMMA films up to 100 µm for MST	micro components	1 µm	10	e-beam	300-12	600-56	600-71 300-76
AR-PC 5000 Electra 92	**polyaniline 5090.02 5091.02**	0,04 ; 0,03	PC	conductive protective coating for the dissipation of charges. PMMA e-beam resists (PMMA, CSAR 62, HSQ) Novolac e-beam resists (e.g. AR-N 7500, 7700)					-	-	DI water
AR-N 7500	**7500.08, 7500.18 novolac**	0.1 ; 0.4		mix&match, high resolution, plasma etching-resistant, pos./neg.	ICs, masks	40 / 100	5.0	e-beam, deep UV, g-line, i-line	300-12	300-47	300-76 300-73
AR-N 7520 new	**7520.07, .11, 7520.17 novolac**	0.1 ; 0.2; 0.4		mix&match, highly sensitive, highest resolution	ICs, masks	30	8.0	e-beam, deep UV, i-line	300-12	300-46 300-47	300-73 300-76
AR-N 7520	**7520.073, 7520.18 novolac**	0,1 ; 0,4	negative	mix&match, highest resolution, high-precision edges	ICs, masks	28	10.0	e-beam, deep UV, i-line	300-12	300-47	300-76 300-73
AR-N 7700	**7700.08, 7700.18 novolac**	0.1 ; 0.4		CAR, high resolution, high sensitivity, steep gradation	ICs, masks	80 / 100	5.0	e-beam, deep UV	300-12	300-46 300-47	300-73 300-76
AR-N 7720	**7720.13, 7720.30 novolac**	0.25 ; 1.4		CAR, high resolution, flat gradation for 3-dimens. struct.	diffract. optics	80 / 200	< 1.0		300-12	300-46 300-47	300-76 300-72
PPA-Polymer Phoenix 81	**8100.03, 8100.06**	0,03 ; 0,08	pos.	thermostructurable resist, highest resolution with NanoFrazor		10	1-10	tSPL	600-02	-	600-02
SX AR-N 8200 Medusa 82	**8200.03, 8200.06, 8200.18**	0,05 ; 0,10 ; 0,40	negative	high-resolution and etch-stable e-beam resists, comparable to HSQ, but considerably more process-stable		10 10 20	5 5 5	e-beam	600-07	300-47	2 n NaOH, BOE
SX AR-N 8250 Medusa 82	**8250.03, 8250.06, 8250.18**	0,05 ; 0,10 ; 0,40		high-resolution and etch-stable e-beam resists, comparable to HSQ, but considerably more sensitive, more process-stable		15 15 20	8 8 8		600-07	300-47	2 n NaOH, BOE

All resist systems show optimal adhesion features with adhesion promoter AR 300-80 new which is applied prior to the resist.

Resists AR-P 617, 631-679, 6200 require brief stopping in stopper AR 600-60 after development.

General Product Information on Allresist E-Beam Resists

This general part explains and completes our individual photoresist product information and provides a first overview as well as profound background knowledge. At www.allresist.de, you will find further information in our FAQ as well as our resist-WIKI and a detailed collection of product parameters.

Overview of composition, mode of action and specific properties of e-beam resists

E-beam resists (electron beam resists) are in particular designed for electron beam, ion beam and deep UV applications for the manufacture of highly integrated structures. They are used for mask production and for maskless lithographic procedures to structure layers or wafers in prototype or small batch production.

E-beam resists are utilised in direct writing procedures or in mask-based technologies (e.g. stencil mask) and can also be used for multi-layer processes (e.g. the fabrication of T-gates). In thin layers (< 100 nm), e-beam resists are perfectly suited for nanometer lithography. In optimised processing regimes it is possible to realise structures of < 10 nm at a film thickness of 50 nm.

E-beam resists are applied by spin coating and are characterised by a very good adhesion to silicon, glass and most metals. For thin resists, the optimum rotational speed ranges from 2000 to 3000 rpm, for thick resists between 500 and 2000 rpm. For novolac-based resists, spin speeds of up to 9000 rpm may be used. If the high-molecular PMMA resists (600K, 950K) are processed, spin speeds above of 6000 rpm should however be avoided since these resists tend to show the so-called “cotton candy” effect. Depending on the type of resist, e-beam resist films of 10 nm to 4 µm can be realised.

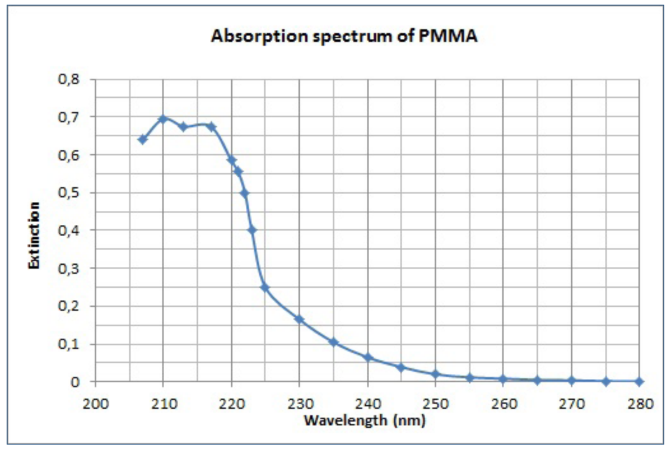
Allresist offers a large variety of different types of resists which cover a wide range of possible applications:

PMMA resists are composed of polymethacrylates with different molecular weight (50K, 200K, 600K, and 950K) dissolved in chlorobenzene (AR-P 641…671) or the safer solvents anisole (AR-P 632…672), ethyl lactate (AR-P 639 … 679) or 1-methoxy-2-propyl acetate (AR-P 6510). All resists work in a positive manner. The polymer 50K is characterised by a 20 % higher sensitivity as compared to the 950K polymer. The glass transition temperature of PMMA films is about 105 °C, and polymers are temperature-stable up to 230 °C.

PMMAs are characterised by an excellent resolution. For example, 6 nm lines with an aspect ratio of 10 can be obtained for AR-P 679.02.

Special resists are the resists of the AR-P 6510 PMMA series which allow to generate very thick films (to 100 µm) for LIGA technologies.

Copolymer resists like AR-P 617 are composed of copolymers on the basis of methylmethacrylate and methacrylic acid (PMMA/MA 33 %), dissolved in the safer solvent 1-methoxy-2-propanol. The CSAR 62 (AR-P 6200) is based on styrene acrylates which are dissolved in the safer solvent anisole. Copolymer resists are positive-working and exhibit a 3-4 fold higher sensitivity as compared to PMMA resists. Copolymer layers are furthermore temperature-stable up to 240 °C; the glass transition temperature for AR-P 617 is around 150 °C and approximately 148 °C for CSAR 62. Above a wavelength of 260 nm, PMMA and copolymer layers are optically transparent. Since these resists also absorb at 248 nm, irradiation with deep UV and structuring is possible, even though with a lower sensitivity.



Novolac-based e-beam resists like AR-N 7500, 7520, 7700 and 7720 can generally be developed under alkaline-aqueous conditions and are distinguished into positive and negative-tone e-beam resists. In addition to novolac, they contain organic or amine-based crosslinking agents and/or acid generators. AR-N 7500 furthermore contains positive-working naphthoquinone diazides. Novolac-based e-beam resists are about twice as resistant during plasma etching as PMMA resists and are used for the generation of structures with e-beam lithography or for mask production. A few e-beam resists can also be patterned with mix & match procedures which combine e-beam and UV exposure (7520, 7700).

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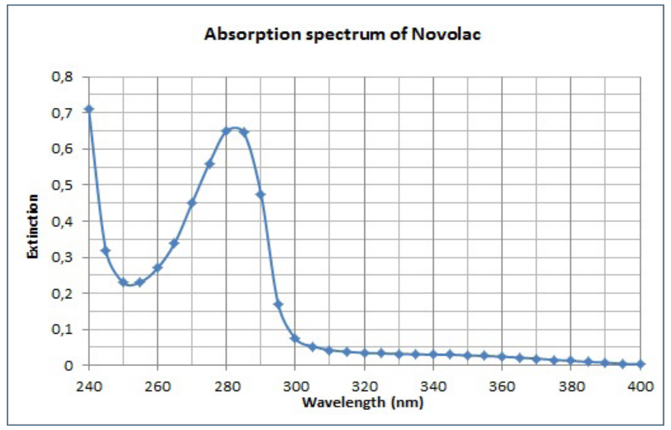
General Product Information on Allresist E-Beam Resists

E-Beam Resists

The fine structures are written in the resist layer using an electron beam, followed by exposed to UV light (i-line) of the larger structures and a development step as usual. For very thin films of AR-N 7520, a maximum resolution of < 30 nm can be obtained.



Chemically enhanced e-beam resists are AR-N 7700 and 7720. These resists which contain radiation-sensitive acid generators and always require a crosslinking bake after exposure provide a high resolution and allow for structural resolutions of 50 -100 nm, with very high sensitivity. Due to its specifically adjusted low contrast, AR-N 7720 is particularly well suited for three-dimensional structures like diffractive optics or holograms.

Refractive indices are 1.48 for PMMAs, 1.49 for copolymers AR-P 617 and 1.54 for CSAR, while refractive indices are in a range of 1.60 - 1.61 for novolac-based e-beam resists.

Customer-specific e-beam resists

The broad range of Allresist e-beam resists covers almost all applications of e-beam lithography. For industry customers, Allresist develops tailor-made resists or modifies standard resists according to the respective technology requirements.

Stability and optimum storage conditions

PMMA and copolymer e-beam resists are not light-sensitive in the visible wavelength range (no yellow light required) and react considerably less sensitive than novolac-based resists to temperature changes. They age only slowly; observed age-related changes mainly concern a gradual thickening of the resist which however does not compromise product quality. In this case, only the film thickness will increase which can easily be corrected during coating.

Novolac-based e-beam resists in contrast are light-sensitive like photoresists, they react to light exposure or temperature changes and age faster during storage. These resists are therefore filled in light-protected amber bottles, stored in a cool place and may only be processed under yellow light (λ > 500 nm).

The shelf life of 6 months from the date of sale is guaranteed if the product is handled and stored as specified in the product information. Beyond that, products can be used without guarantee up to the date indicated on the label if stored according to the instructions.

Our recommended storage temperatures are listed in the product information under the respective product in the table “Properties“.

Any use after the minimum shelf life is possible without guarantee until the date indicated on the label, but please check beforehand if this is sufficient for your specific technological needs. This additional information is our contribution to customer service and environmental protection.

Novolac-based e-beam resists stored for several years are outdated and may only be used with considerable restrictions. This also applies to resists stored at too high temperatures and to highly diluted resists which age faster than normal.

Wastewater treatment

Up to 90 % of the organic material can be removed from developer wastes if the pH of used aqueous-alkaline developer and remover solutions is adjusted to pH 9 to 10 by addition of acids, followed by subsequent separation of the precipitate. Prior to waste disposal, filtered solutions have to be adjusted to pH 6.5 – 8.0. Solid wastes may be disposed of at sanitary landfills or by incineration in officially authorized plants. Collected resist and solvent wastes have to be disposed of in approved incinerators.

Safety instructions

Resists, thinner and remover contain organic solvents. Adequate ventilation in the working area is thus mandatory.

Development solutions are caustic alkaline liquids which may irritate the skin. Avoid direct contact with products and their vapours (wear safety goggles and gloves).

EG-safety data sheets of our products may be downloaded from www.allresist.de/products or be requested at info@allresist.de.

Detailed Instructions for Optimum Processing of E-Beam Resists

0. Adhesion – substrate pre-treatment

The adhesion between substrate and resist is of major importance for a safe processing of resists. Smallest changes of the cleaning procedure or the technology 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. High air humidity (> 60 %) also reduces 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 a previous cleaning in acetone, followed by isopropanol or ethanol treatment and subsequent drying. This procedure will improve adhesion of the resist. If only acetone is used for cleaning, the substrate must be dried in a drying oven to remove the condensed moisture which is due to the cooling effect caused by acetone evaporation.

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 depends also on the structures already deposited). The use of removers or acids (e.g. piranha) for removal, followed by rinsing and tempering, may be required. In very difficult cases, an ultra- or megasonic cleaning may be helpful.

To improve the adhesion features, adhesion-enhancing agents such as e.g. adhesion promoter AR 300-80 new may be used which is applied immediately before resist coating in a very simple procedure by spin coating as thin layer of approx. 15 nm thickness and tempered. It is also possible to evaporate HMDS onto the substrates. The monomolecular layer on the wafer surface has an adhesion-promoting effect due to its hydrophobic properties which facilitate adsorption of the resist.

1. Coating

Substratees should be cooled down prior to coating, and 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 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 inhomogeneities in 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 %). A higher air humidity significantly reduces the adhesion features. Above a humidity of 70 %, coating is basically impossible. The air moisture also affects the film thickness which is reduced with increasing 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. The tendency to develop edge beads is increased above a film thickness of 5 µm. In this case, an edge bead removal with resist solvent AR 300-12 or isopropanol after spin coating is helpful (acetone is not recommended). A Gyrset (closed chuck) system also 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.

2. Tempering / Softbake

Newly coated resists films still contain, depending on the film thickness, a certain amount of residual solvent. A subsequent tempering at 85 – 210 °C is performed to dry and to harden the resist films. In addition to improved resist adhesion properties, also the dark erosion during development is reduced.

If temperature-sensitive substrates are processed it is also possible to work at considerably lower softbake temperatures (< 60 °C). The development regime has to be adjusted accordingly.

Detailed Instructions for Optimum Processing of E-Beam Resists

After the softbake, substrates are cooled to room temperature prior to further use.

3. 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. Due to the use of electrons with very short wavelength for resist exposure, an excellent resolution of up to 2 nm can be obtained (point beam).

For mix&match procedures with resists of the AR 7000 series, in addition exposures with i- and g-line steppers or with contact exposure systems in the respective spectral UV working range can be realised.

All values for the exposure sensitivity specified in our product information are only guideline values determined for our standard processes and have to be confirmed accordingly in own experiments.

Alone the difference of sensitivity between silicon wafers and mask blanks is considerable - (PMMA mask: 15 µC/cm² – PMMA wafer 80 µC/cm²), and also the acceleration voltage influences the sensitivity to a large degree. The higher the voltage, the more insensitive will the resist react.

The exposure dose (dose to clear) which is required to develop a large area of an e-beam resist without structures in a suitable development time (film thickness dependent, 0.5 µm: 30 – 60 s) should be increased by 10 – 20 % for normal structural patterns. To obtain maximum resolution however, even higher exposure doses are required. The time required for complete development of unexposed areas (TCD) of 0.5 µm negative resist films should be in a range of 30 – 40 s. The exposure dose which produces a layer buildup of > 90 % should accordingly also be increased by 10 – 20 % for patterning purposes. If a shorter TCD is chosen (use of a stronger developer), the sensitivity is reduced since the crosslinking rate is increased at a higher exposure dose.

Coated and tempered e-beam resist films can be stored for several weeks prior to exposure without quality loss. PMMA layers are even more stable and can be stored more or less indefinitely.

4. Development

During development, positive resist films are structured by dissolution of exposed areas, while unexposed areas are removed if negative resists are developed. For reproducible results, temperatures between 21 and 23 °C with a temperature constancy of Δ 1 °C should be maintained for solvent-based developers (AR 600-50, -55, -56), and Δ 0.5 °C for aqueous-alkaline developers (AR 300-26, -35, -40).

One exception is the CSAR 62, since this resist can also be developed with specific developers at lower temperatures < 0 °C.

The solvent-based developer AR 600-50 was specifically designed for copolymer films (AR-P 617) and enhances the sensitivity of this e-beam resist even further. The developer AR 600-55 is, just like AR 600-56, also solvent-based and is preferred as fast developer for PMMA films (e.g. AR-P 630 - 670 series), if short development times are required to achieve e.g. a fast production throughput. Copolymer films (AR-P 617) can also be developed either alone or in a two component system PMMA/copolymer with this developer.

Development AR 600-56 develops more slowly than AR 600-55 and is preferably used if a good resolution and high contrast (with at the same time prolonged development times) is desired for PMMA films (AR-P 630 - 670 series). This developer can also be used for AR-P 617 copolymer films.

The development of PMMA films may, in contrast to novolac-based resists, be interrupted any time and continued later as often as desired. To obtain a particularly high resolution, developers with isopropanol or isopropanol/water should be used. In this case however considerably higher exposure doses are required.

For the development of exposed CSAR resist films, developers AR 600-546, 600-548, and 600-549 are well suited. As 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. 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.

The aqueous-alkaline developer series AR 300-40 include metal ion-free developers with different concentrations. The use of these developers reduces the danger of metal-contamination on the substrate surface. All developers have excellent wetting properties and work without leaving any residues. Developments AR 300-46 and 300-47 are specifically recommended for the novolac-based e-beam resists AR-N 7500 … 7700 (in dilutions, if required).

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Detailed Instructions for Optimum Processing of E-Beam Resists

Development concentrations as listed in our product information were determined for specific film thickness values or process parameters and can only serve as guideline values under other conditions. The exact developer concentration has always to be adjusted to specific demands (film thickness, development time, tempering).
The two parameters contrast and sensitivity are adjusted via the developer concentration by defined dilution of the developer with DI water.

Note: Metal ion-free developers of the 300-40 series are more sensitive to dilution differences than buffered systems. These developers should be diluted immediately prior to use and extremely thoroughly, if possible with scales, in order to assure reproducible results.

Higher developer concentrations formally result in an increased light sensitivity of positive resist developer systems. The required exposure energy is minimised and the development time is reduced, which allows for a high process throughput. Possible disadvantages are an increased dark erosion and (in some cases) a too low process stability (too fast). Negative resists require a higher exposure dose for crosslinking at higher developer concentrations.

Lower developer concentrations provide a higher contrast for positive resist films and reduce resist erosion in unexposed regions or only partly exposed interface areas even at longer development times. This particularly selective working method ensures a high degree of detail rendition at higher exposure intensities.

The effectiveness of the developing bath for immersion development is limited by factors such as process throughput and CO_2 absorption from air. The throughput depends on the fraction of exposed areas. CO_2 absorption is also caused by frequent opening of the developer bottle and leads to a reduced development rate. This effect is avoided by if the surface of the developer bath is kept under nitrogen.

5. Rinse

After development, substrates with PMMA, copolymer and styrene acrylates e-beam resists have to be stopped immediately with stopper AR 600-60, substrates with novolac-based resists are rinsed with deionised water until all residual developer is completely removed and subsequently dried.

6. Postbake/Hardbake

For specific process steps, a postbake at approximately 115 °C (novolac-based) or at 180 °C (PMMA-based) leads to a higher etch stability during wet-chemical and plasma-chemical etching procedures. Higher temperatures are possible for stronger etch conditions, may however result in a rounding of resist profiles.

7. Customer-specific technologies

The generation of semiconductor properties: the produced resist mask is utilised for technological processes according to the user's requirements. Semiconductor properties are generated in a user-specific manner, e.g. by boron or phosphorous doping, by etch processes or by formation of conductor paths. Thereafter, the resist is in most cases no longer needed and removed. In a few cases, the resist structures are utilised as actual function on the component and thus remain on the substrate.

8. Removal

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 600-07, and 600-09, as well as remover AR 600-70 (acetone-based). MOS grade acetone can also be used.

For a wet-chemical stripping of highly tempered e-beam resist films 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 use removers with a low flash point.

Positive E-Beam Resists AR-P 610 series

AR-P 617 e-beam resists for nanometer lithography

Copolymer resist series for the production of integrated circuits and masks

Characterisation

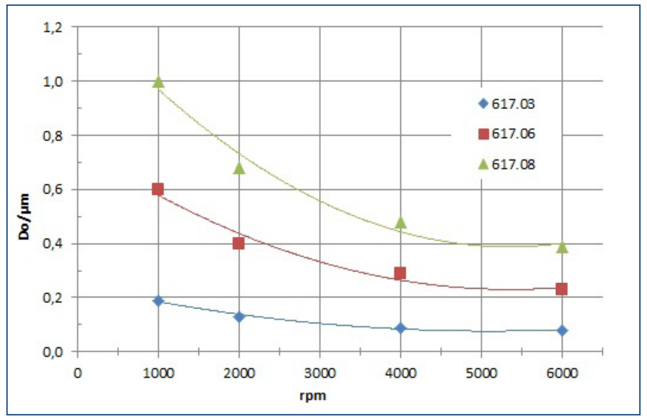
- e-beam, deep UV (248 nm)
- highest resolution, high contrast
- strong adhesion to glass, silicon and metals
- 3-4 times more sensitive than PMMA
- sensitivity can be adjusted via the softbake
- for planarization and multi-layer processes
- temperature-stable up to 240 °C
- copolymer on the basis of methyl methacrylate and methacrylic acid, safer solvent 1-methoxy-2-propanol

Properties I

Parameter / AR-P	617.03	617.06	617.08
Solids content (%)	3.0	6.0	8.0
Viscosity 25 °C (mPas)	7	20	36
Film thickness/4000 rpm (nm)	90	290	480
Resolution best value (nm)	10		
Contrast	6		
Flash point (°C)	38		
Storage temperature (°C) *	10 - 22		

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

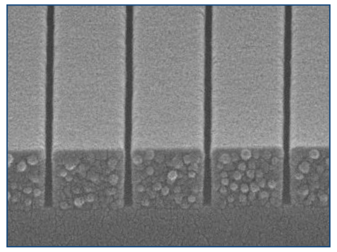
Spin curve



Properties II

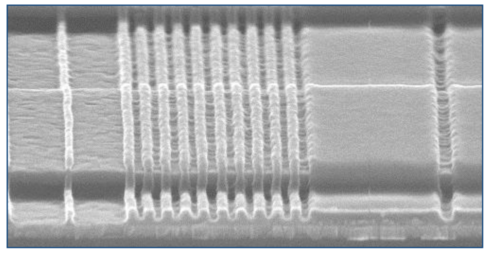
Glass trans. temperature (°C)	150	
Dielectric constant	2.6	
Cauchy coefficients	N_0	1.488
	N_1	44.0
	N_2	1.1
Plasma etching rates (nm/min)	Ar-sputtering:	16
(5 Pa, 240-250 V Bias)	O_2	291
	CF_4	56
	80 CF_4 + 16 O_2	151

Structure resolution



AR-P 617.03
30 nm trenches at film thickness of 120 nm

Resist structures



AR-P 617.03
150 nm lines across 200 nm oxide steps

Process parameters

Substrate	Si 4" waver
Soft bake	200 °C, 2 min, hot plate
Exposure	ZBA 21, 20 kV
Development	AR 600-50, 2 min, 21°C

Process chemicals

Adhesion promoter	AR 300-80 new
Developer	AR 600-50, AR 600-55
Thinner	AR 600-07
Stopper	AR 600-60
Remover	AR 600-71, AR 300-76

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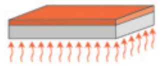
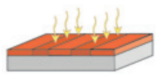
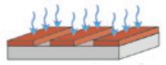
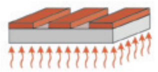
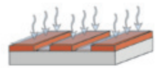
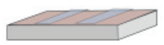
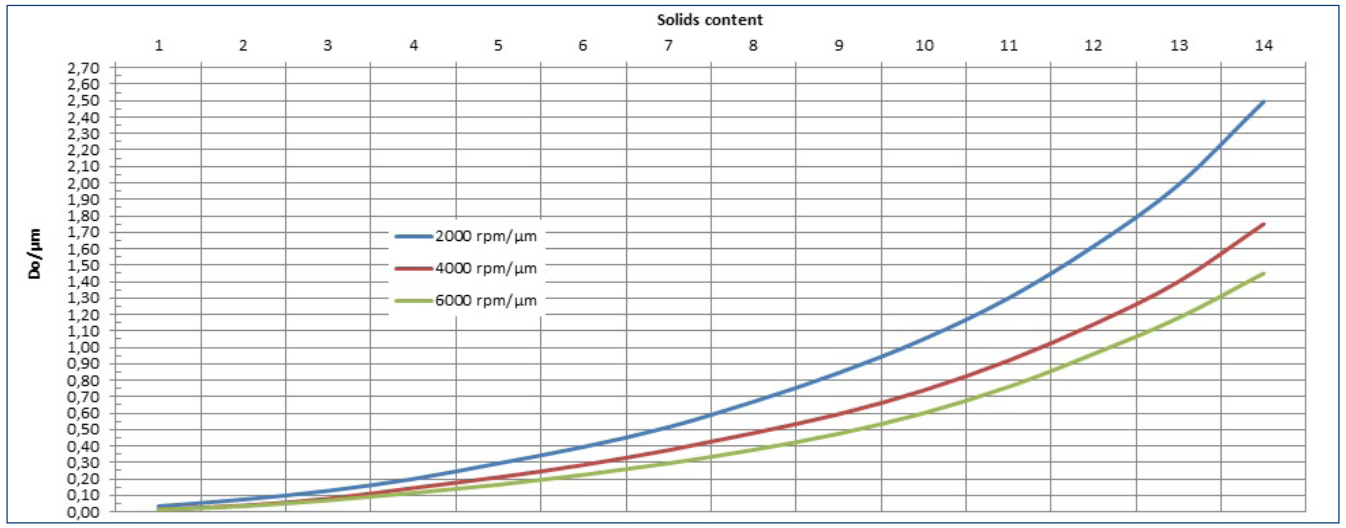
Positive E-Beam Resists AR-P 610 series

Process conditions

This diagram shows exemplary process steps for resists of the AR-P 610 series. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

Coating		AR-P 617.06 4000 rpm, 60 s, 290 nm
Soft bake (± 1 °C)		200 °C, 25 min hot plate or 200 °C, 60 min convection oven
E-beam exposure		ZBA 21, 20 kV Exposure dose (E_0): 30 µC/cm², 500 nm space & lines
Development (21-23 °C ± 1 °C) puddle		AR 600-50, 60 s
Stopping		AR 600-60, 30 s
Post-bake (optional)		130 °C, 1 min hot plate or 130 °C, 25 min convection oven for slightly enhanced plasma etching resistance
Customer-specific technologies		Generation of semiconductor properties
Removal		AR 300-76 or O_2 plasma ashing

Film thickness of AR-P 617 vs. solids content and spin number



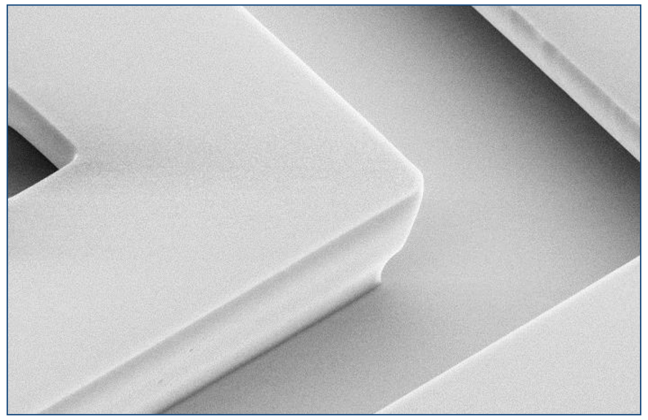
Positive E-Beam Resists AR-P 610 series

Processing instructions

The sensitivity of the resist increases with increasing softbake temperature due to the more intense formation of anhydrides of the methacrylic acid under separation of water (☞ diagram dose vs. softbake temperature). AR-P 617 tempered at 200 °C is therefore about 20 % more sensitive as compared to a tempering at 180 °C. The dose can be adjusted accordingly, which is of major importance for two-layer systems with two layers of AR-P 617. In this case, at first the bottom layer is dried at 200 °C and then tempered at 180 °C together with the upper film.

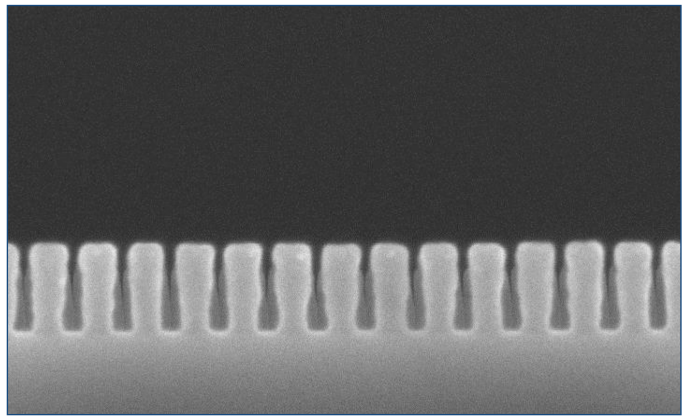
Due to differentiation processes, the lower layer is attacked faster by the developer and pronounced undercut structures are formed (lift-off). These lift-off structures can also be produced with the two-layer system PMMA/ copolymer. At first AR-P 617 is coated and tempered at 190 °C, then the PMMA resist AR-P 679.03 is applied by spin-coating and dried at 150 °C. After exposure, both layers are developed in one step e.g. with AR 600-56, treated with stopper AR 600-60 and rinsed.

Lift-off structure with two layers of AR-P 617



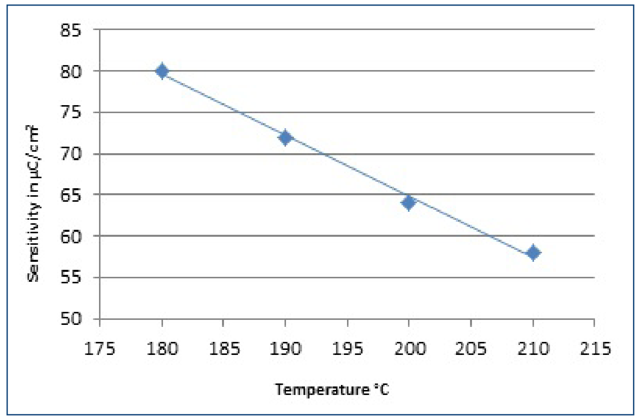
After development with AR 600-50
Bottom: AR-P 617.06, 400 nm thick, tempered at 200 °C
Top: AR-P 617.06, 500 nm thick, tempered at 180 °C

Undercut structure with PMMA/Copolymer



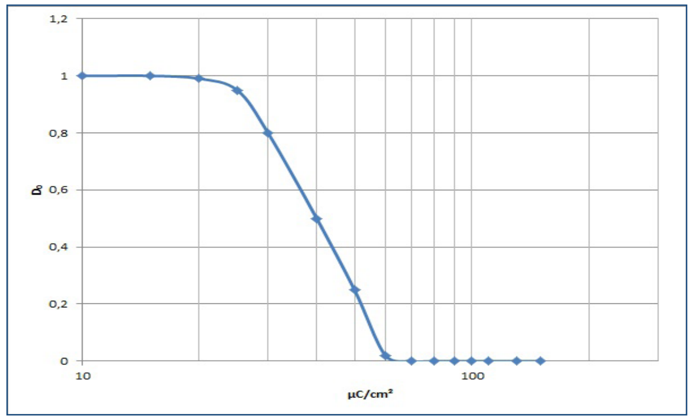
Two-layer system PMMA/copolymer after development
Bottom: AR-P 617.06, 400 nm thick, tempered at 190 °C
Top: AR-P 679.06, 180 nm thick, tempered at 150 °C

Dose vs. softbake temperature for AR-P 617



With increasing temperature, the sensitivity of AR-P 617.08 (film thickness 680 nm) increases linearly.

Gradation curve of AR-P 617



At a film thickness of 350 nm, a contrast of 5.0 was determined (30 kV, developer AR 600-50)

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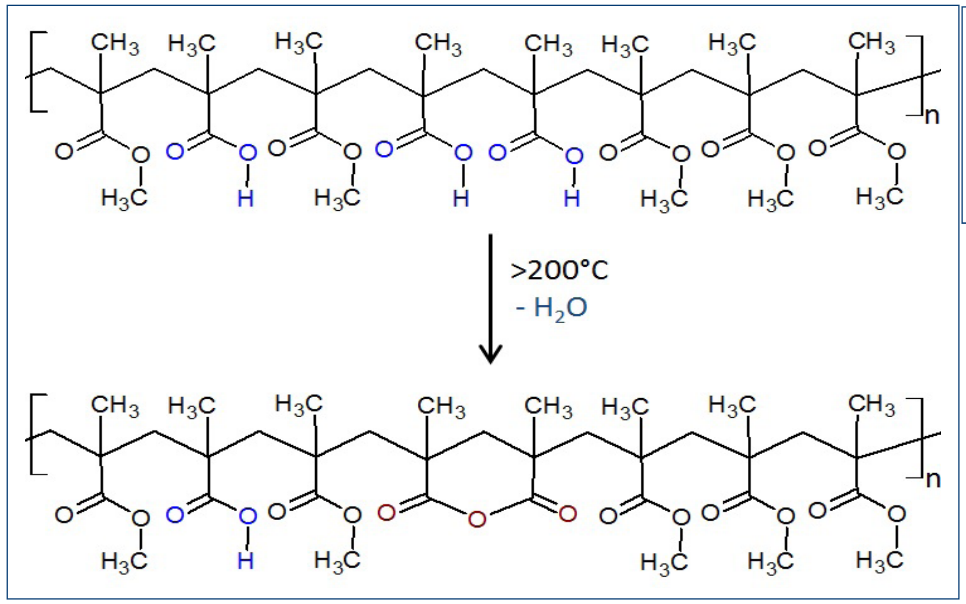
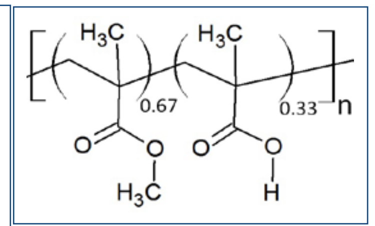
Positive E-Beam Resists AR-P 610 series

Sensitivity-enhancing reaction during tempering

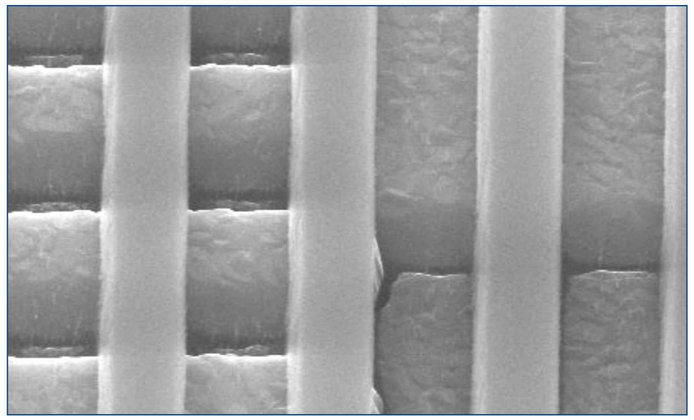




The copolymer composed of methyl methacrylate and methacrylic acid is, in contrast to pure PMMA products, able to form a 6-ring during thermal loading. In this case, 2 methacrylic acid groups have to be arranged adjacent to each other in the polymer chain (see large structural formula left), which statistically occurs with sufficiently high frequency at a mixing ratio of 2 : 1 (see molecular formula top right).
The reaction is possible at this temperature, since the water which is produced during the reaction is a very good leaving group.

The 6-ring which is formed breaks apart more easily during irradiation with electrons than the aliphatic chain remainder which causes the higher sensitivity of the copolymer. Once adjusted, the sensitivity will remain unchanged. The reverse ring-opening reaction is impossible.

Planarization with AR-P 617



AR-P 617.12 Structures across topologies

Due to the excellent coating properties is it possible to level out topologies which are present on the wafer before development. In this example, 200 nm high oxide structures were coated with AR-P 617.08. The film thickness was 780 nm. After exposure (20 kV) and development (AR 600-50, 2 min), the structured wafer is covered with entirely planar resist lines.

Positive PMMA E-Beam Resists AR-P 630 – 670 series

AR-P 631-679 e-beam resists for nanometer lithography

PMMA resist series 50K – 950K for the production of integrated circuits and masks

Characterisation

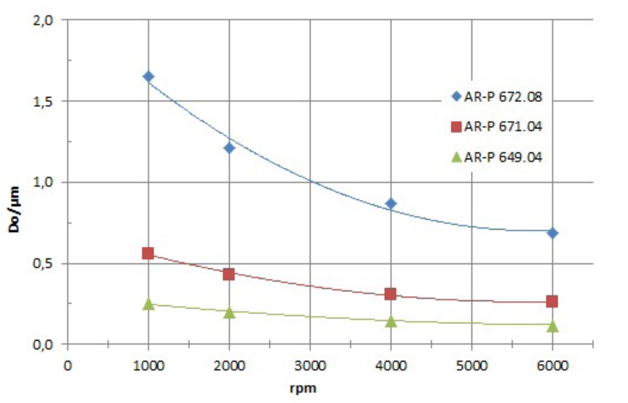
- e-beam, deep UV (248 nm)
- very good adhesion to glass, silicon and metals
- 50K 20 % more sensitive than 950K
- for planarization and multi-layer processes
- highest resolution, high contrast
- poly(methyl methacrylate) with diff. molecular weights
- AR-P 641-671 solvent chlorobenzene, flash p. 28 °C
- AR-P 632-672 safer solvent anisole, flash p. 44 °C
- AR-P 639-679 safer solvent ethyl lactate, flash p. 36 °C

Properties I

Parameter / AR-P	632-639	641-649	661-669	671-679
PMMA type	50 K	200 K	600 K	950 K
Film thickness/ 4000 rpm (nm) according to solids content	0.02-0.31	0.02-0.78	0.02-1.04	0.03-1.87
Solids content (%)	1-12	1-12	1-11	1-11
Resolution best value (nm)	6			
Contrast	7			
Storage temperature (°C)*	10 - 22			

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

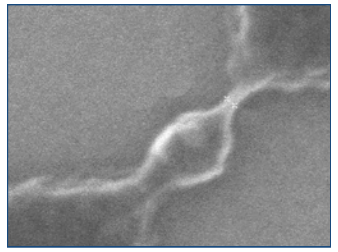
Spin curve



Properties II

Glass trans. temperature (°C)	105	
Dielectric constant	2.6	
Cauchy coefficients	N_0	1.478
	N_1	47.3
	N_2	0
Plasma etching rates (nm/min)	Ar-sputtering:	21
(5 Pa, 240-250 V Bias)	O_2	344
	CF_4	59
	80 CF_4 + 16 O_2	164

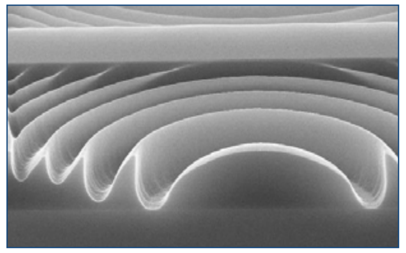
Structure resolution



AR-P 679.02

Structural resolution: 6.2 nm gap, 65 nm high

Resist structures



AR-P 671.09 diffractive optics, thickness of 4.4 µm

Process parameters

Substrate	Si 4" waver
Soft bake	150 °C, 3 min. hot plate
Exposure	Raith Pioneer, 30 kV
Development	AR 600-56, 60 s, 21 °C
Stopper	AR 600-60, 30 s, 21 °C

Process chemicals

Adhesion promoter	AR 300-80 new
Developer	AR 600-55, AR 600-56
Thinner	Chlorobenzene or AR 600-02, 600-09
Stopper	AR 600-60
Remover	AR 600-71, AR 300-76

Positive PMMA E-Beam Resists AR-P 630 – 670 series

Process conditions

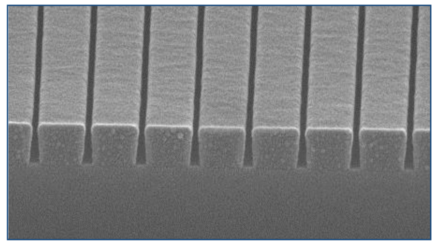
This diagram shows exemplary process steps for resists of the series AR-P 630 - 670. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

Coating	AR-P 632.06 4000 rpm, 60 s, 110 nm	AR-P 671.05 2000 rpm, 60 s, 690 nm
Soft bake (± 1 °C)	150 °C, 3 min hot plate or 150 °C, 60 min convection oven	
E-beam exposure	ZBA 21, 20 kV Exposure dose (E_0): 95 µC/cm²	Raith Pioneer, 30 kV 770 µC/cm²
Development (21-23 °C ± 1 °C) puddle	AR 600-55 1 min	AR 600-56 3 min
Stopping	AR 600-60, 30 s	
Post-bake (optional)	130 °C, 1 min hot plate or 130 °C, 25 min convection oven for slightly enhanced plasma etching resistance	
Customer-specific technologies	Generation of semiconductor properties	
Removal	AR 300-71 or O_2 plasma ashing	

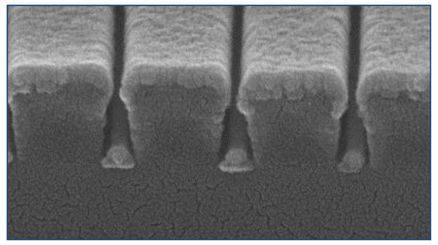
Processing instructions for coating

Large undercut structures (lift-off) are obtained if PMMA resists with different molecular weight are chosen for a two component system. As upper layer, an ethyl lactate PMMA is recommended since ethyl lactate does not, in contrast to other solvents, attack the second layer. For the lower layer, a chlorobenzene, anisole or ethyl lactate PMMA is suitable. Both tempering steps are performed at 150 °C.

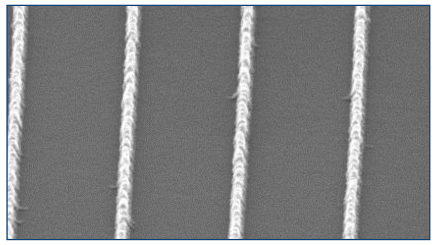
Recommendation: large undercut (low resolution): bottom layer 50K, upper layer 200K, 600K or 950K. High resolution (smaller undercut): bottom layer 600K, upper layer 950K.



After development (AR 600-56)



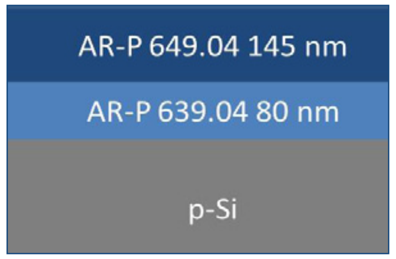
Structures coated with metal films



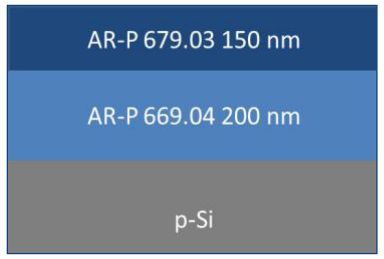
Lifted 30 nm metal lines

Positive PMMA E-Beam Resists AR-P 630 – 670 series

Investigations of 2-layer PMMA lift-off structures



Layer structure of the two-layer system 50K/200K



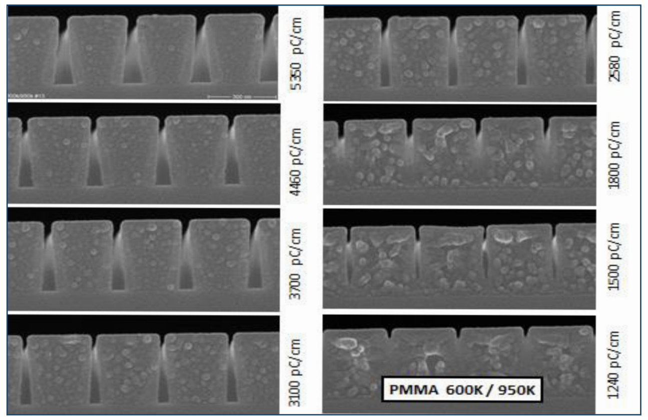
Layer structure of the two-layer system 600K/950K

For these tests, the 2-layer systems were coated as shown to the left and tempered at 180 °C, 60 s, followed by irradiation with different doses (30 kV) and development (AR 600-60, IPA).

The system 50K/200K is more sensitive, the double layer is completely developed at 1500 pC/cm². The variant 600K/950K in contrast requires the higher dose of 2200 pC/cm². With increasing dose, also a larger undercut is generated if the 50K/200K system is used, which is thus predestined for complicated lift-off procedures. Variant 600K/950K may be utilised for higher total film thicknesses (> 500 nm) and is a reliable lift-off system for simple applications. For these investigations, always AR 600-60 (IPA) was used as developer which explains both the comparably high doses and the good process stability.

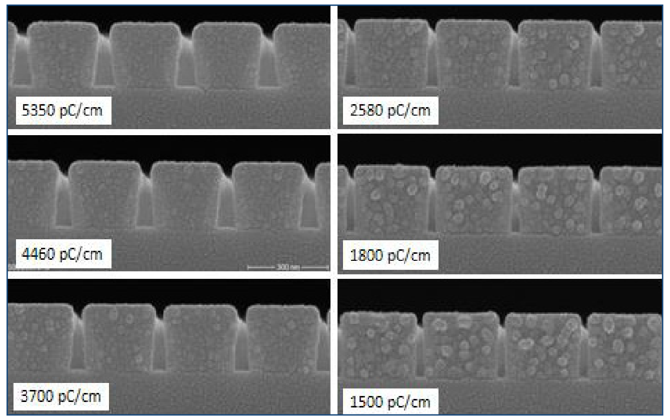
Dose sequence of the 600K/950K system

Definition: The sensitivity is expressed in pC/cm for lines, while the unit for areas is µC/cm².



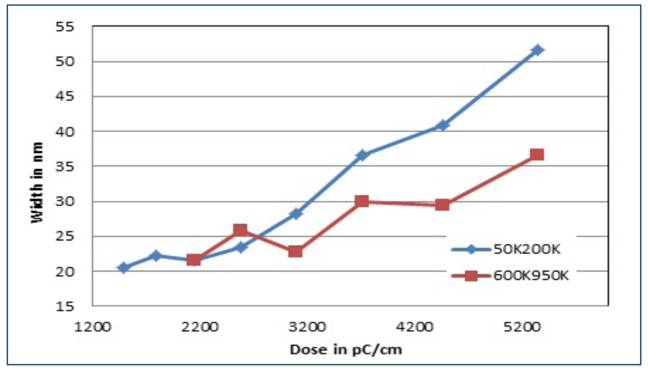
Not yet completely developed at 1800 pC/cm

Dose-scale of 50K/ 200K systems



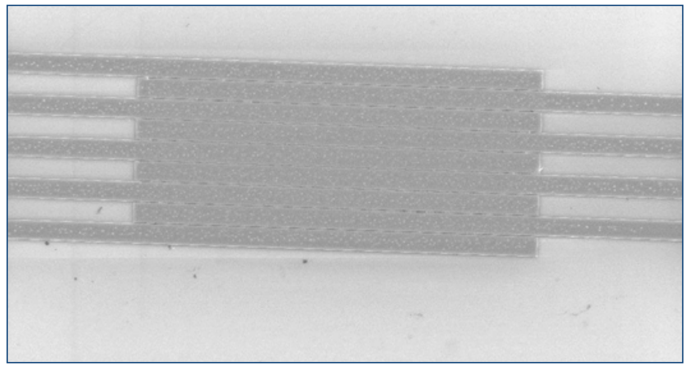
Constantly increasing undercut

Formation of undercut vs. exposure dose



Trench width top: 20 nm, measured values in the diagram: width of trenches at the bottom

Application example



"Finger structures" produced with the special system PMMA 90k/200K, trench width 30 nm

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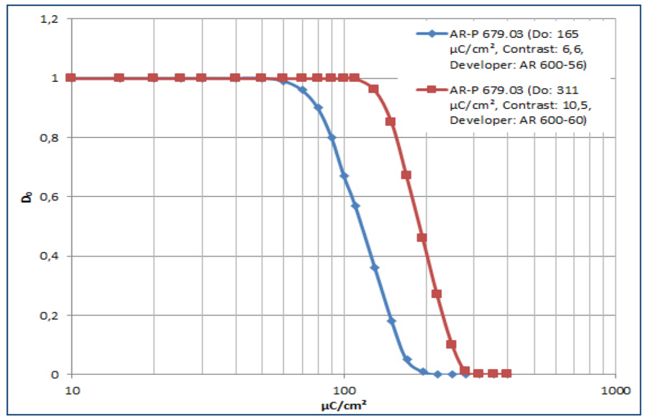
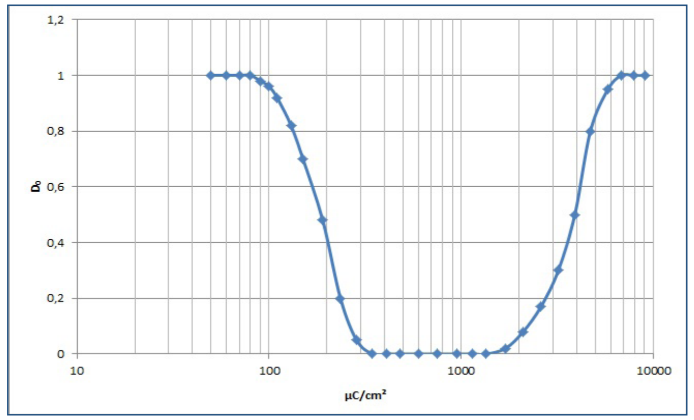
Positive PMMA E-Beam Resists AR-P 630 – 670 series

Sensitivity of a PMMA resist



Comparison of developer AR 600-55 and AR 600-56

Gradation curve PMMA



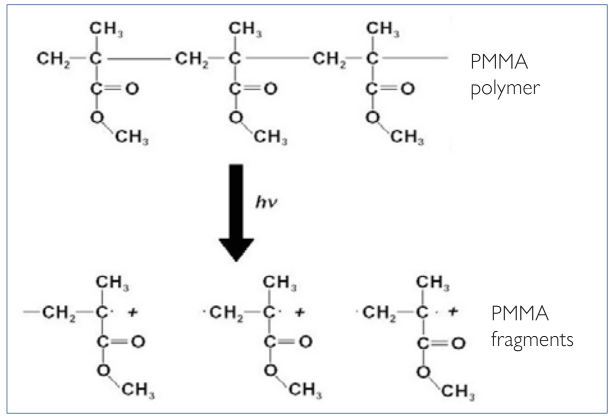
Gradation curve up to maximum dose

The left diagram shows a comparison of the sensitivity of AR-P 679.03 in two different developers. Under otherwise identical conditions (30 kV, 165 nm film thickness), the sensitivity is almost twice as high if the standard developer AR 600-55 is used as compared to AR 600-60 (IPA). A development with IPA however results in a considerably higher contrast (10.5 : 6.6). This developer is thus predestined for higher resolutions. Experience furthermore shows that the process window is significantly larger as compared to faster developers.

Dose deviations of e.g. 10 % are tolerated without any quality loss.

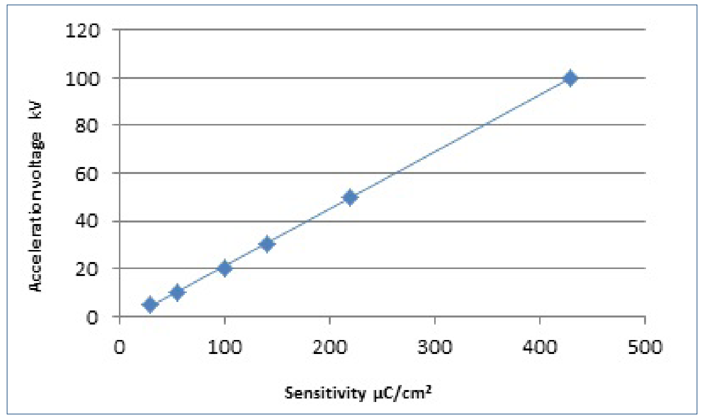
Upon electron irradiation of PMMA resists, the main chain is cleaved and the molecular mass drops from initially 950 000 g/mol (950K) to 5.000 – 10.000 g/mol. This main chain scission is primarily due to radical processes (see figure below). At an optimal dose, radicals recombine and form molecules with a molecular mass of about 5 000 g/mol. If however the dose is drastically increased, a large number of radicals are produced and undergo crosslinking so that molecules with higher molecular masses are obtained. The PMMA is turned into a negative resist. This effect is depicted in the diagram on the right which shows the gradation curve of a standard process (AR-P 671.05, 490 nm film thickness, 30 kV, developer AR 600-56). High exposure doses convert the resist into a negative resist.

Depolymerisation opon exposure



The main chain of the PMMA is cleaved into many radical fragments

Dose versus acceleration voltage



The sensitivity of a PMMA resist (AR-P 671.05) strongly depends on the acceleration voltage. At 100 kV a major part of the energy passes the resist without any interaction and the resist is consequently less sensitive. At 5 kV however, all electrons are absorbed.

Positive E-Beam Resists AR-P 6200 (CSAR 62)

AR-P 6200 e-beam resists with highest resolution

High-contrast e-beam resists for the production of integrated circuits and masks

Characterisation

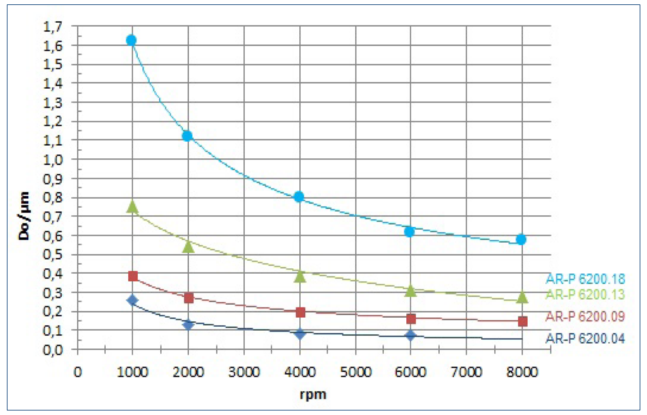
- e-beam; layer thickn. 0,05-1,6 µm (6000-1000 rpm)
- high sensitivity which can be adjusted via the developer
- highest resolution (< 10 nm) and very high contrast
- highly process-stable, high plasma etching resistance
- easy fabrication of lift-off structures
- poly(α-methyl styrene-co-α-chloroacrylate methylester)
- safer solvent anisole

Properties I

Parameter / AR-P 6200	.18	.13	.09	.04
Solids content (%)	18	13	9	4
Viscosity 25 °C (mPas)	29	11	6	2
Film thickness/4000 rpm (µm)	0.80	0.40	0.20	0.08
Resolution best value (nm)	6			
Contrast	14			
Flash point (°C)	44			
Storage temperature (°C) *	10-22			

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

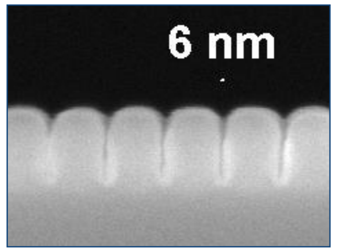
Spin curve



Properties II

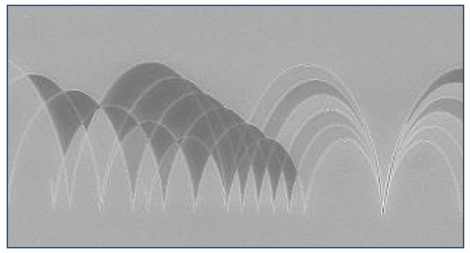
Glass trans. temperature (°C)	128	
Dielectric constant	2.8	
Cauchy coefficients	N_0	1.543
	N_1	71.4
	N_2	0
Plasma etching rates (nm/min)	Ar-sputtering	10
(5 Pa, 240-250 V Bias)	O_2	180
	CF_4	45
	80 CF_4 + 16 O_2	99

Structure resolution



AR-P 6200.04
Resolution of up to 6 nm at film thickness of 80 nm

Resist structures



AR-P 6200.09
25-nm structures, film thickness of 180 nm, artwork

Process parameters

Substrate	Si 4" waver
Soft bake	150 °C, 60 s, hot plate
Exposure	Raith Pioneer, 30 kV
Development	AR 600-546, 60 s, 22 °C

Process chemicals

Adhesion promoter	AR 300-80 new
Developer	AR 600-546, 600-549
Thinner	AR 600-02
Stopper	AR 600-60
Remover	AR 600-71, 300-76

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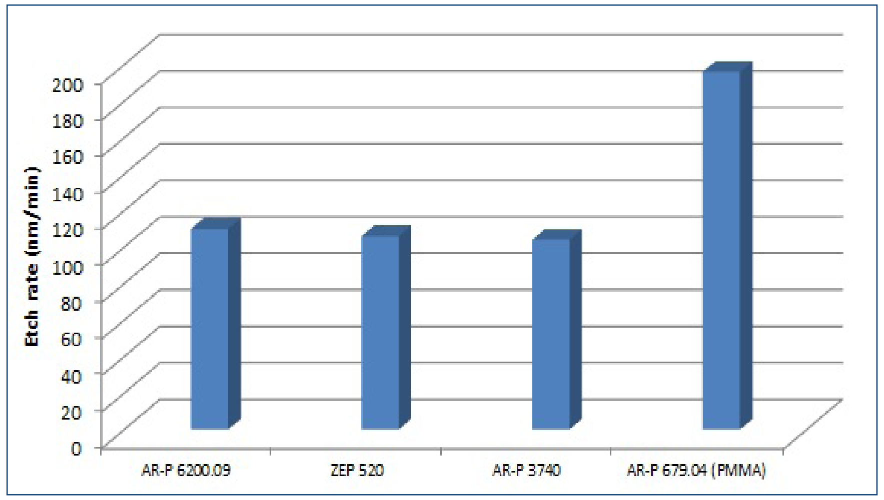
Positive E-Beam Resists AR-P 6200 (CSAR 62)

Process conditions

This diagram shows exemplary process steps for AR-P 6200 resists. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

Coating	AR-P 6200.09 4000 rpm, 60 s 0.2 µm
Soft bake (± 1 °C)	150 °C, 1 min hot plate or 150 °C, 30 min convection oven
E-beam exposure	Raith Pioneer, 30 kV Exposure dose (E_0): 65 µC/cm^2
Development (21-23 °C ± 0,5 °C) puddle	AR 600-546 1 min
Stopping / Rinse	AR 600-60, 30 s / DI-H_2O, 30 s
Post-bake (optional)	130 °C, 1 min hot plate or 130 °C, 25 min convection oven for slightly enhanced plasma etching resistance
Customer-specific technologies	Generation of semiconductor properties
Removal	AR 600-71 or O_2 plasma ashing

Plasma etching resistance



CSAR 62 is characterized by a high plasma etching resistance. In this diagram, plasma etching rates of AR-P 6200.09 are compared with those of AR-P 3740 (photoresist), AR-P 679.04 (PMMA resist) and ZEP 520A in CF_4 + O_2 plasma.

Positive E-Beam Resists AR-P 6200 (CSAR 62)

Processing instructions

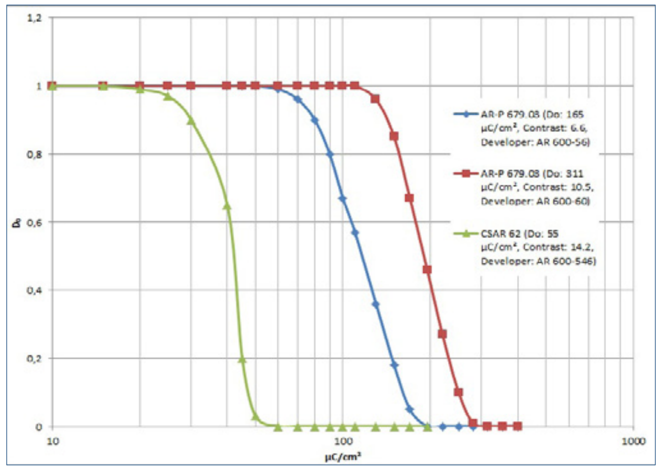
E-beam exposure: The required e-beam exposure dose for structural imaging mainly depends on the desired minimum structure size, the developer, the acceleration voltage (1 - 100 kV), and the film thickness.

The exposure dose for AR-P 6200.09 was in this experiment (☞ diagram comparison of CSAR 62 and PMMA) 55 μC/cm² (dose to clear D_0, 30 kV, 170 nm layer, developer AR 600-546, si wafer). The contrast was determined here to 14.2.

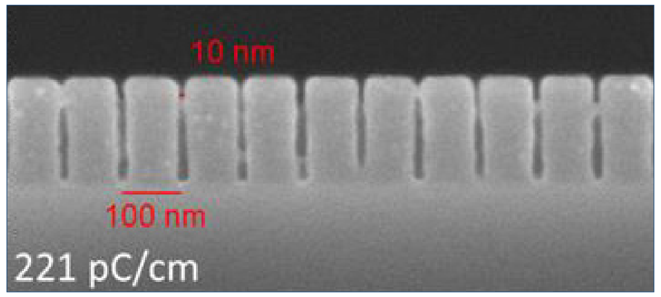
CSAR 62 is thus 3x more sensitive as compared to the standard PMMA resist AR-P 679.03 (developed in AR 600-56), or 6x more sensitive if developed in AR 600-60. Also the contrast is higher by a factor of 2 and 1.4, respectively.

Upon irradiation, long-chain polymers are radically cleaved. A post-exposure bake is thus not required.

For the fabrication of 10-nm trenches (174 nm film, 100n pitch), AR 6200.09 requires a dose of approx. 220 pC/cm (30 kV, developer AR 600-546)



Comparison D_0 and contrast CSAR 62 and PMMA



Maximum resolution CSAR 62 of 10 nm (180 nm)

Development: For the development of exposed resist films, developers AR 600-546, 600-548 and 600-549 are recommended. As weaker developer, AR 600-546 provides a wider process window. If the stronger developer AR 600-548 is used, the sensitivity can be increased 6-fold to < 10 μC/cm². The intermediate developer AR 600-549 renders the CSAR 62 twice as sensitive as compared to AR 600-546, it shows also no dark erosion and has a contrast of 4.

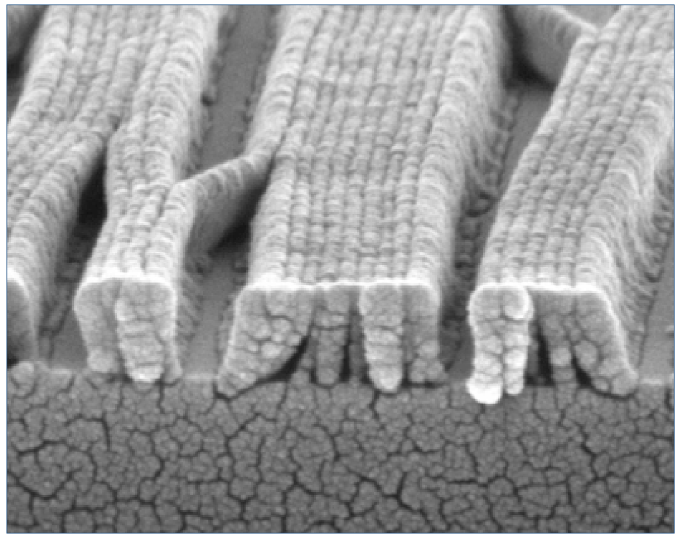
For immersion development, generally development times of 30 - 60 seconds are recommended. If developer AR 600-546 is used, even after 10 minutes at room temperature no erosion of unexposed areas is detected.

Developer AR 600-548 in contrast attacks resist surfaces already after two minutes visibly. If however the development process is carried out at temperatures of approx. 0 °C, no dark erosion is observed even after 5 minutes (which is however associated with a reduction of sensitivity).

The development procedure should be stopped quickly. For this purpose, the substrate is moved for 30 seconds in stopper AR 600-60. Optionally, the substrate may thereafter be rinsed for 30 seconds with DI water to remove all residual solvent.

Note: Please take into account that rigid rinsing procedures may lead to a collapse of smaller structures (☞ see image below).

A post-bake for special working steps at max. 130 °C results in a slightly improved etching stability during wet-chemical and plasma-chemical processes.



Danger of collapsed lines after too rigid rinsing

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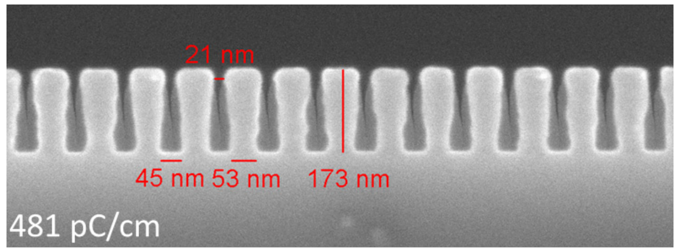
Positive E-Beam Resists AR-P 6200 (CSAR 62)

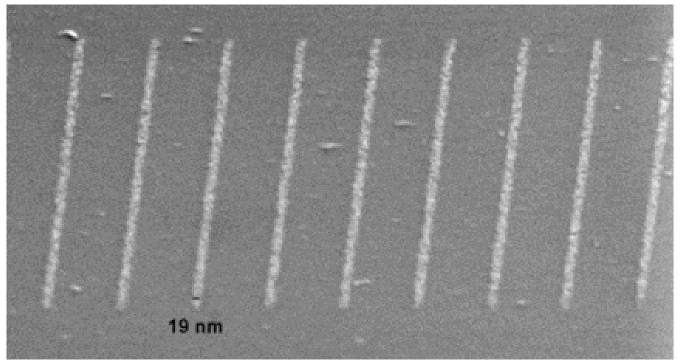
Processing instructions

Lift-off structures:
Resist CSAR 62 is well suited to generate lift-off structures with a resolution of up to 10 nm. If the dose is increased by a factor of 1.5 - 2, narrow trenches with defined undercut can be fabricated with AR-P 6200.09.

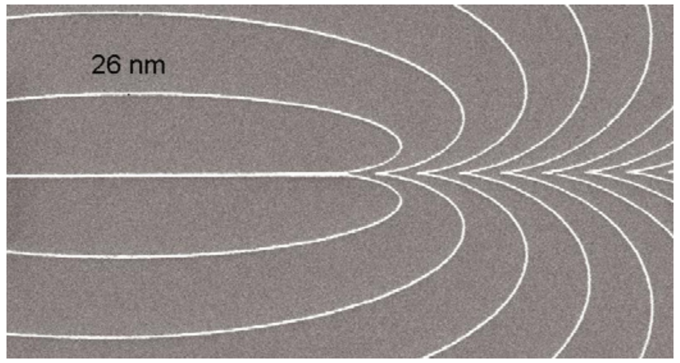


Undercut structures obtained with increased exposure dose

After vapour-deposition of metal and subsequent easy lift-off, metal structures remain

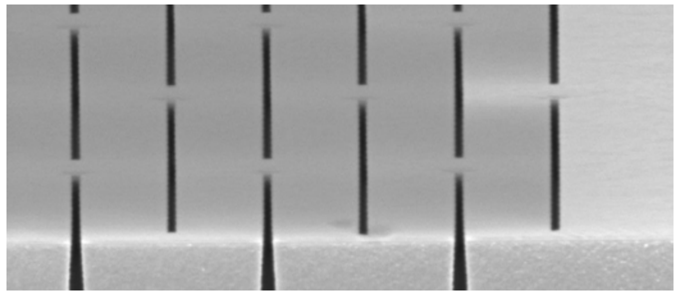


19-nm metal lines after lift-off process with AR-P 6200.09



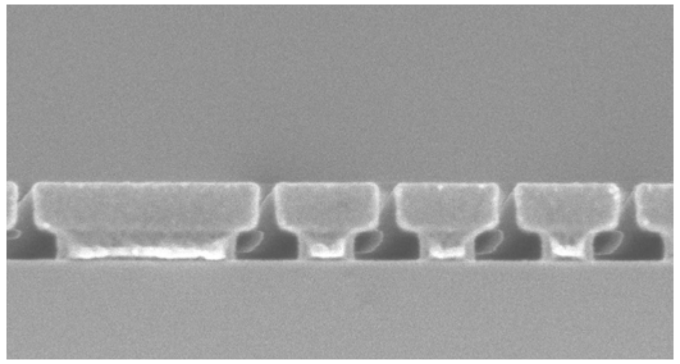
CrAu test structures with a line width of 26 nm

High layers for special applications:
Films with a thickness of up to 800 nm can be produced With AR-P 6200.13, and even 1.6-μm films are possible with experimental sample SX AR-P 6200/10.



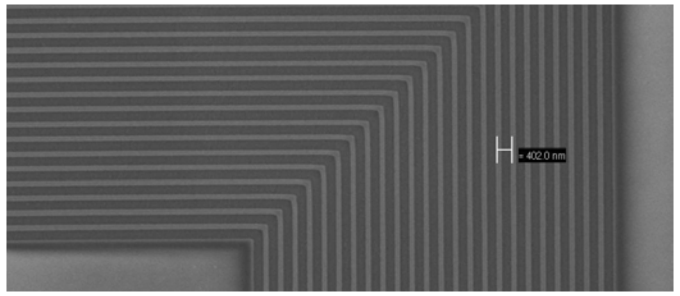
AR-P 6200.13: 100-nm trenches in 830-nm thick layer

CSAR 62 is also applied in various two-layer systems and can be used both as bottom and as top resist.



AR-P 6200.09 as top resist for extreme lift-off applications

Another field of application for CSAR 62 is the production of mask blanks .



At a film thickness of 380 nm, 100-nm lines and spaces can be obtained on a chrome mask with AR-P 6200.13. The sensitivity is 12 μC/cm² (20 kV, AR 600-548).

Positive E-Beam Resists AR-P 6200 (CSAR 62)

Application examples for CSAR 62

Circuits for the 5 GHz range which are primarily needed for wireless Bluetooth or Wi-Fi technologies can in future be produced with CSAR 62. E-beam lithography is also required for the research on nanomaterials like graphene, for three-dimensional integrated circuits as well as for optical and quantum computers. The computing power or memory density is constantly increased in each of these technologies. Applications with the highest demands on computing power (supercomputers), e.g. in computational fluid dynamics or in space applications, thus also demand microchips with highest integration density.

CSAR 62 on mask blanks

Experts at the HHI Berlin have already tested CSAR 62 on mask blanks (☞ Fig. 1). They immediately achieved a resolution of 50 nm which is an excellent value for masks. To date, 100 nm lines and above are used on masks. Currently test coatings of mask blanks with CSAR 62 are conducted, and samples will be offered by our partners to all customers in the near future.

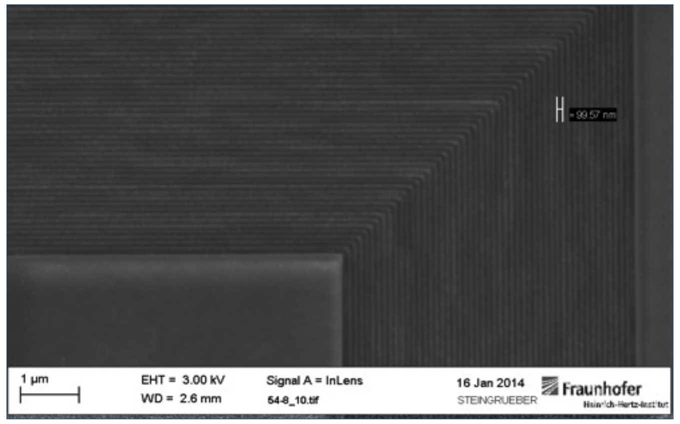


Fig. 1 CSAR 62 test structure on a mask blank with 50 nm lines and 50 nm trenches; pitch line & space here 99.57 nm

CSAR 62 for highest-resolution lithography

In the work group for nanostructured materials of the MLU Halle, CSAR 62 is mainly used in highest-resolution lithography for the lift-off and as etching mask for dry chemical etching processes. The new resist offers several specific advantages. It achieves the high resolution of PMMA, but at a much lower dose. Due to the high contrast, vertical resist edges are generated which allow a reliable lift-off even with thinner films and ensure a uniform lift-off up to 20 nm:

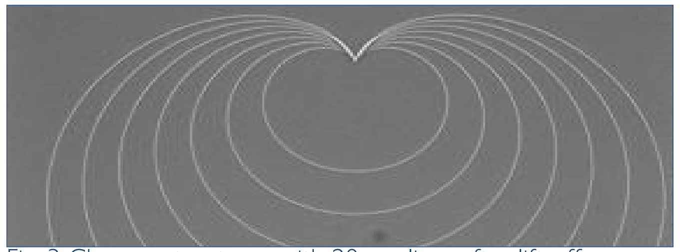


Fig. 3 Chrome structures with 20 nm lines after lift-off

The goal in the lift-off of metal structures is however not always to go beyond the limits of resolution. Typical applications for example in the contacting of nanowires rather require dimensions in a range of 30-50 nm, which can also be realised with other resists. The „resolution reserve" of CSAR 62 however allows for significantly improved structure accuracy and faster design with less iteration:

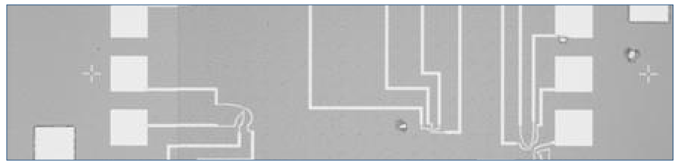


Fig. 4 Typical structure for contacting nanowires. Large areas are mixed with small details

During dry chemical etching, for example in the structuring of silicon nitride, CSAR combines the best of two worlds: It not only allows the use as a high resolution positive resist similar to PMMA, but also offers a stability which is comparable to novolacs.

This facilitates the production of pattern with sharp edges that provide the required etch stability without the disturbing faceting at the edges which otherwise occurs frequently. CSAR 62 is normally used for films with thickness values between 50 and 300 nm. Intense plasma etching for the fabrication of deep etch structures however requires significantly thicker resist layers and places special demands on resolution and contrast. Resist AR-P 6200.18 was thus designed for high layer thicknesses of 0.6-1.6 µm and is particularly well suited for the realisation of high metal structures with lift-off, deep plasma etching processes or nanowires.

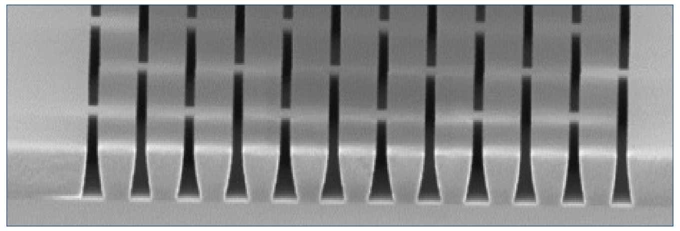


Fig. 5 Lift-off structures with large undercut at a film thickness of 800 nm

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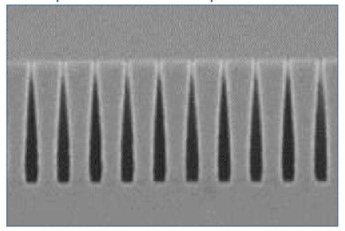
Positive E-Beam Resists AR-P 6200 (CSAR 62)

Application examples for CSAR 62

It is nonetheless possible to produce trenches with a width of < 100 nm at a film thickness of 800 nm. The high contrast is made possible through the use of our developer AR 600-546. By increasing the irradiation dose, the degree of the generated undercut can be adjusted specifically (Fig. 5 + 6). Each user can thus select the most favourable profile for his specific lift-off process.



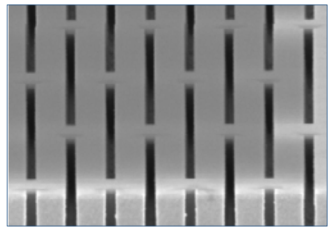


Fig. 6 AR-P 6200.13, 823 nm layer, dose: 1440 pC/cm

Fig. 7 Vertical structures at an area dose of 120 µC/cm² for nanowires

If circles are irradiated and developed in such thick layers, columns (nanowires) can be produced due to a high metal deposition (evaporation, sputtering or electroplating) (see vertical edges in Fig. 7).

High-precision lift-off structures with the two-layer system CSAR 62/AR-P 617

The task in the IAP of the Friedrich Schiller University of Jena was to produce very small, high-precision rectangular structures. For this purpose, a two-layer system composed of AR-P 6200.09 as top layer and AR-P 617.06 as bottom layer was established. After exposure with e-beam writer Vistec SB 350OS, CSAR 62 was patterned with developer AR 600-546. The bottom layer was subsequently developed with developer AR 600-55, followed by coating with gold. The lift-off was performed with a mixture of acetone and isopropanole. The resulting structures are shown in Fig. 12. The structure sizes are 38 nm with structure intervals of approximately 40 nm. In particular to be regarded positively are the small radii of curvature at the corner of the inside of the „L".

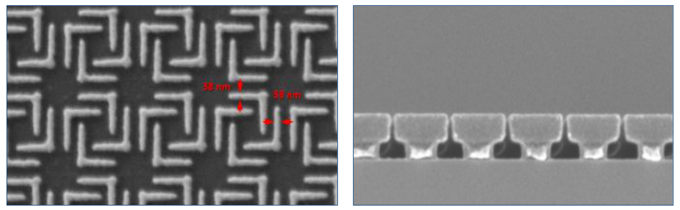


Fig. 12 High-precision L-shaped structures, produced with the two-layer system AR-P 6200.09 / AR-P 617.06; right 2 Layer sytems

CSAR 62 – High-precision square structures

A similar objective was pursued by this working group with respect to the fabrication of square structures. The aim was again to obtain corners with particularly high resolution. For this purpose a CSAR 62 film with a thickness of 100 nm was irradiated with 50 kV and developed with developer AR 600-546. In addition to the excellent properties of CSAR 62, also the irradiation design is of vital importance (see Fig. 13, centre: A; right: B).

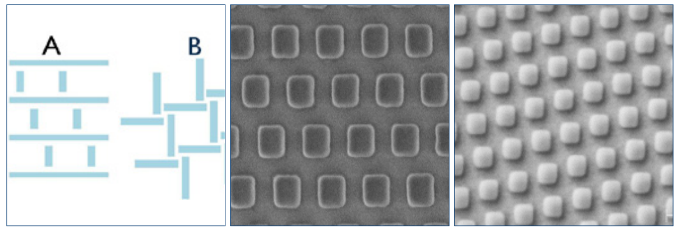


Fig. 13 Different irradiation designs and resulting square structures (centre: A; right: B)

CSAR 62 – Development at lower temperatures

The sensitivity of CSAR 62 is strongly influenced by the choice of the developer. In comparison to the standard developer AR 600-546, the sensitivity can almost be increased tenfold if AR600-548 is used which is however accompanied by an incipient erosion of unexposed resist areas. This is tolerable to a certain extent: If, for example, always 10 % of the layer is lost, can this effect be compensated for in advance. Erosion can also be avoided if the development is carried out at lower temperatures, but this is again associated with a certain loss of the previously gained sensitivity. It thus comes down to the fact that an optimisation of the process is required. The lower temperatures offer, due to the more gentle development step, the possibility to increase the contrast or reduce the edge roughness.

Fig. 14-16 show the sensitivities and resolutions of AR-P 6200.04 at 6 °C and 21 °C (room temperature). Due to the high contrast at 6 °C, a resolution of 6 nm could be achieved.

Positive E-Beam Resists AR-P 6200 (CSAR 62)

Application examples for CSAR 62

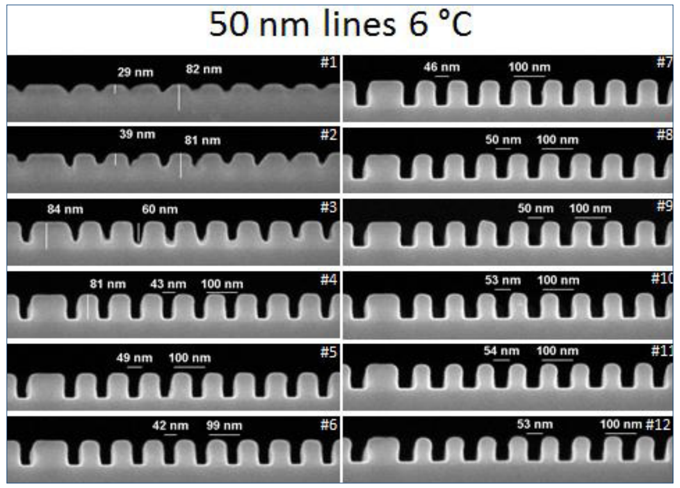


Fig. 14 CSAR 62 structures at 6 °C, opt. dose 195 pC/cm

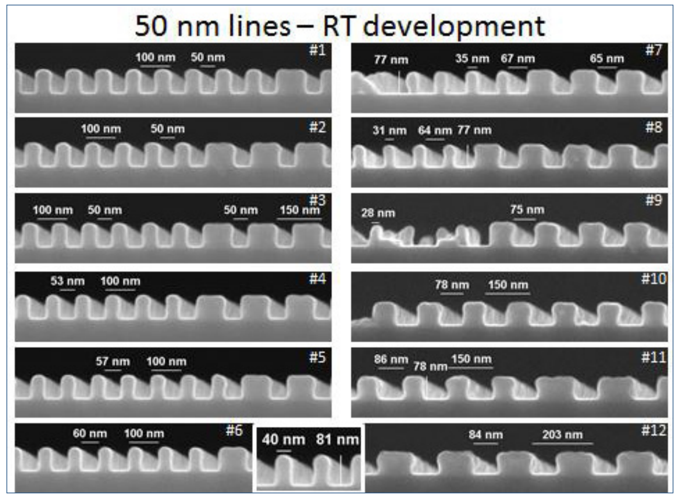


Fig. 15 CSAR 62 structures at 21 °C, opt. dose 121 pC/cm

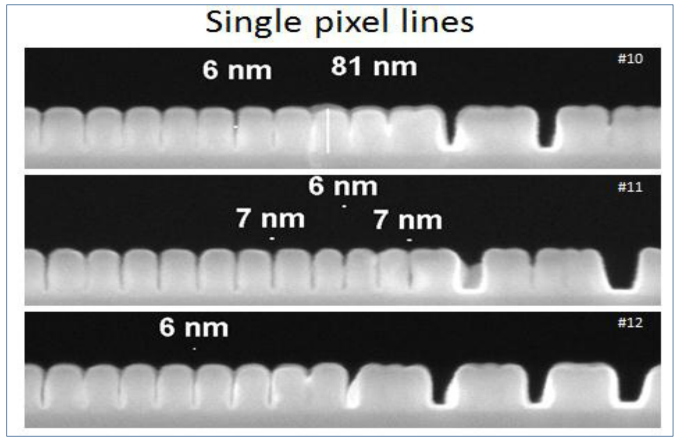


Fig. 16 Max. resolution of 6 nm at 235 pC/cm and 6 °C

CSAR 62 nanostructures written with 100 kV

At the Karlsruhe Institute of Technology, the suitability of CSAR 62 for the fabrication of complex architectures was investigated in detail. CSAR 62 layers were irradiated with e-beam writer EBPG5200Z at 100 kV and developed with developer AR 600-546. The results are shown in the figures below.

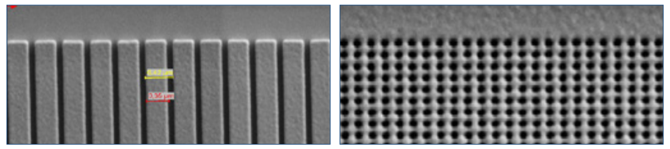


Fig. 17 SEM images (gold-sputtered): CSAR 62 nanostructures, parameters: film thickness 200 nm, dose 225 µC/cm², 100 kV, developer AR 600-546, 3 min, stopper AR 600-60

A particular challenge is the writing and development of nano-sized hole structures. Using CSAR 62, a diameter of remarkable 67 nm could be realised, whereby the sophisticated structural element shows a very regular pattern.

Developer for T-gate applications with AR-P 617

X AR 600-50/2 is a new, sensitive and highly selective developer for high-tempered AR-P 617 layers (SB>180 °C). PMMA or CSAR 62 layers are not attacked, which is of particular importance for multilayer processes e.g. in the manufacture of T-gates.

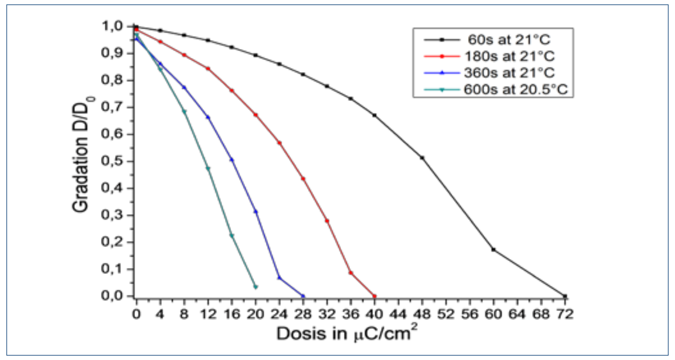


Fig. 18 AR-P 617, film thickness: ~1 µm, SB 10 minutes at 200 °C, 50 kV, dose variations, dependence of the sensitivity on the development time with developer X AR 600-50/2 at room temperature, stopper AR 600-60

The sensitivity can easily be controlled via the duration of the development. At a development time of 60 s, the dose to clear is about 70 µC/cm², after 3 minutes of development about 40 µC/cm², after 6 minutes 25 µC/cm², and after 10 minutes about 20 µC/cm²! The amount of dark erosion is very low, even at longer development times.

Positive E-Beam Resists AR-P 6200 (CSAR 62)

Fluorescent films with CSAR 62 and PMMA

Fluorescent dyes can be embedded into positive-tone e-beam resists like CSAR 62 and PMMA. For this purpose, both PMMA and CSAR 62 polymers were prepared in a solvent mixture which also dissolves the fluorescent dyes to a sufficient extent. The use of different fluorescent dyes allows a defined adjustable emission in various wavelength ranges. These dyes are highly process-stable, and structuring is performed in the same manner as in corresponding standard processes with uncoloured e-beam resists. By embedding dyes into CSAR 62, resist films could be generated which optionally show violet, blue, yellow, orange or red fluorescence. The intense fluorescence is retained even after tempering at 180 °C.

Fig. 21 Yellow fluorescent PMMA-based resist architectures

Fig. 19 Intensely fluorescing films of CSAR 62 on glass.

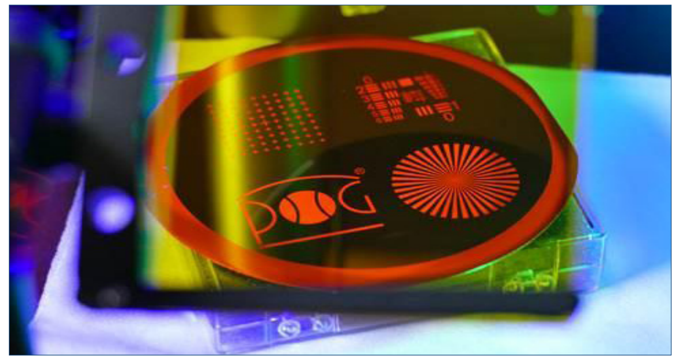


Fig. 22 Red fluorescent PMMA-based resist architectures

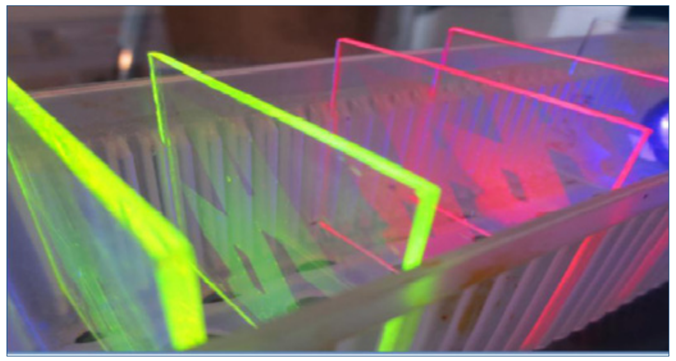


Fig. 20 Fluorescent structures (UV irradiation with a wavelength < 250 nm, developer AR 600-546)

Due to the properties of these e-beam resists, resolutions up to the 10 - 20 nm range are possible. The main field of this application is in optical industry; these materials are e.g. required for night vision devices. Fluorescent resist films are furthermore used for applications in microscopy.

Fluorescent PMMA architectures were produced by Precision Optics Gera GmbH via electron beam lithography. These structures could be developed residue-free using an optimized developer. If these resist structures are excited with UV light (as shown in the two pictures), they begin to glow intensely.

Positive E-Beam Resists AR-P 6500

AR-P 6510 e-beam resists for high film thicknesses

Thick positive resists for the production of microcomponents

Characterisation

- e-beam (no yellow light required)
- excellent image quality
- solvent-based developer
- film thickness values of 10 µm to 100 µm
- process-stable
- high molecular weight poly(methyl methacrylate)
- safer solvent PGMEA

Properties I

Parameter / AR-P 6510	.15	.17
Solids content (%)	15	17
Viscosity 25 °C (Pas)	12.2	24.5
Film thickness/200 rpm (µm)	45	95
Resolution best value (µm)	1	
Contrast	10	
Flash point (°C)	42	
Storage temperature (°C)*	10-22	

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

Film thickness values

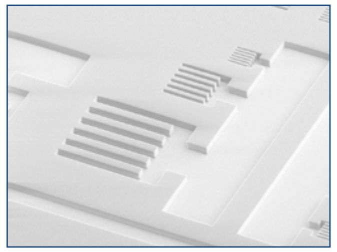
2 min / 30 s	.15	.17
200 / 350 rpm (µm)	45	95
350 / 500 rpm (µm)	28	56

These resists are designed for high film thicknesses which can only be obtained with low spin speeds. At spin numbers of < 1000 rpm, resists tend to form strings (candy floss effect). Thinner films can be realised if dilutions are used.

Properties II

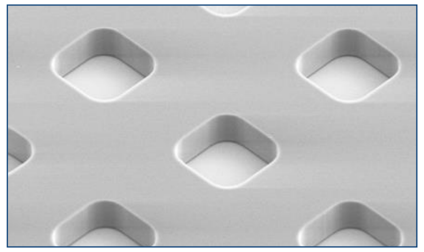
Glass trans. temperature (°C)	105	
Dielectric constant	2.6	
Cauchy coefficients	N_0	1.480
	N_1	41.9
	N_2	0
Plasma etching rates (nm/min)	Ar-sputtering	22
(5 Pa, 240-250 V Bias)	O_2	350
	CF_4	61
	80 CF_4 + 16 O_2	169

Structure resolution



AR-P 6510.17
Film thickness 40 µm,
structures up to 5 µm

Resist structures



AR-P 6510.17 (diluted), exposure with e-beam (developer AR 600-55), film thickness 5 µm

Process parameters

Substrate	Si 4" waver
Soft bake	100 °C, 4 h, convection oven
Exposure	e-beam
Development	AR 600-56, 20 min
Stopper	AR 600-60, 3 min

Process chemicals

Adhesion promoter	AR 300-80 new
Developer	AR 600-56
Thinner	AR 300-12
Stopper	AR 600-60
Remover	AR 600-71, AR 300-76

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Positive E-Beam Resists AR-P 6500

E-Beam Resists

Process conditions

This diagram shows exemplary process steps for AR-P 6500 resists. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

Coating	AR-P 6510.17 350 rpm, 5 min 45 µm
Soft bake (± 1 °C)	95 °C, 60 min hot plate (temperature ramps recommended) 90 °C, 3 h convection oven (temperature ramps recommended)
E-beam exposure	e-beam Exposure dose (E_0): 5000 µC/cm²
Development (21-23 °C ± 1 °C) Immersion	AR 600-56 15 min
Stopping / Rinse	AR 600-60, 30 s / DI-H_2O, 30 s
Post-bake (optional)	100 °C, 10 min hot plate or 95 °C, 60 min, convection oven for complete drying and slightly enhanced plasma etching resistance
Customer-specific technologies	LIGA procedures or the fabrication of X-ray masks
Removal	AR 300-71 or O_2 plasma ashing

Processing instructions for coating

Prior to spin coating it is recommended to remove gases which may possibly be present. The highly viscous resist should therefore rest a few hours before use. A warming of resist bottles in a water bath to 50 °C max. to reduce the viscosity and the utilisation of ultrasound support the removal of gas bubbles. Resist deposition should be performed as carefully as possible to avoid any additional introduction of air bubbles. Slow spin speeds and low exposure times are advantageous (200 to 350 rpm, > 3 min). Edge bead formation can be reduced if the rotational speed is briefly increased towards the end of the coating procedure (for 10 s to max. 500 rpm). The amount of resist will also influence the film thickness; for 4 inch-wafers, the use of at least 10 g of resist are recommended. In order to obtain optimum film qualities, own experiments of each user are required.

Thermally structurable positive resist AR-P 8100

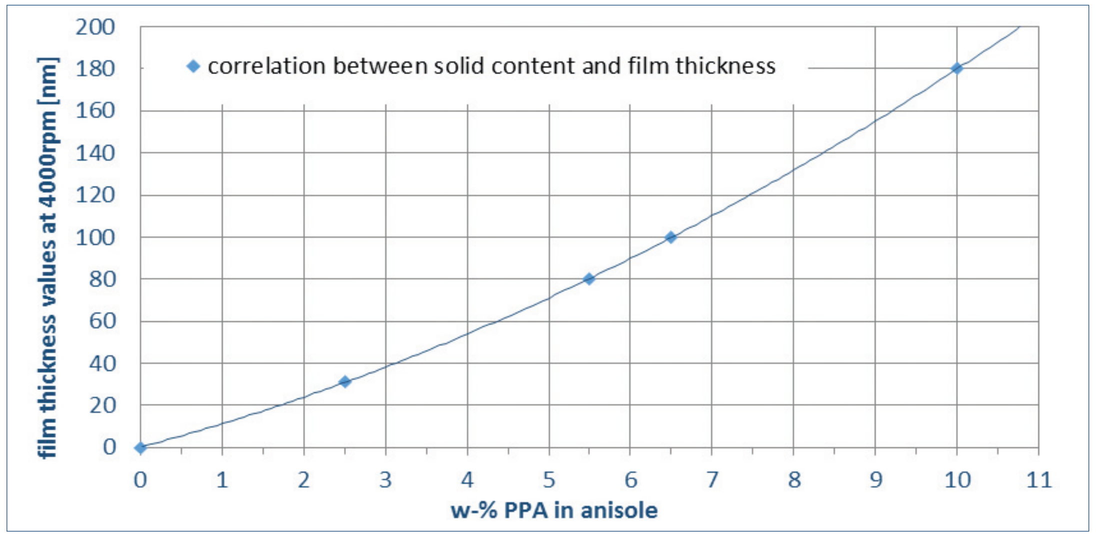
Information on PPA, the base polymer of Phoenix 81

Anionically polymerized polyphalaldehyde (PPA), the base polymer for the thermo-structurable resist Phoenix 81, is a white powder which is storage-stable for at least 4 weeks at room temperature. PPA can thus be shipped with standard shipping and does not require the highly cost-intensive refrigerated transport of PPA solutions.

When stored in a refrigerator (8 - 12 °C), the PPA polymer is stable for at least 6 months. For long-term-storage, we recommend temperatures of -18 °C since this ensures that PPA remains stable for at least one year.

The polymer PPA dissolves easily in anisole. By varying the polymer concentration, solutions can be produced flexibly to realize different film thicknesses values. The film thicknesses can furthermore be varied by changing the spin speeds. This is exemplarily shown for AR-P 8100.03 (solids content: 2.5 %) and AR-P 8100.06 (solids content: 5.5%) in the table "Properties I".

The following graph shows the relationship between polymer concentration and resulting film thickness.



Dependency of film thickness on solids content (anionic PPA in anisole, 4000 rpm, 30 s, open chuck)

Preparation and use of PPA solutions

1. To prepare the PPA solutions, the weighed quantity of PPA is given into a suitable vial before the calculated amount of anisole is added. The mixture is stirred or shaken at room temperature until after about 10 minutes a clear, homogeneous solution results.
2. The PPA solution is transferred into a syringe of appropriate size and filtered using a 0.2 µm syringe filter into a dry and clean bottle.

Formulation example for 2.5 % solution

2.5 g PPA + 97.5 g anisole = 100.0 g of 2.5 % 0.2 µm filtrated polymer solution. This corresponds to AR-P 8100.03 with respect to the properties. Please note: 2.5 % is rounded up to 3 % in the product designation.

Storage

PPA solutions are only stable at low temperatures; we thus recommend storage at -18 °C. In this case, solutions are stable for at least 6 months. Prior to use, solution should be warmed to room temperature to avoid condensation of moisture. Short-term use of PPA solutions at room temperature (up to 3 hours) will still ensure the high product quality.

Thermally structurable positive resist AR-P 8100

AR-P 8100 (Phoenix 81) for NanoFrazor applications

High-contrast, thermolabile resist for integrated circuits and holographic structures

Characterisation

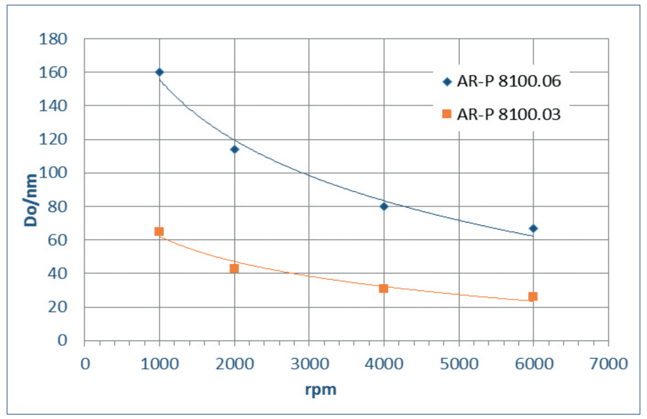
- for tSPL (thermal Scanning Probe Lithography)
- film thickness 20 - 160 nm
- high resolution (< 10 nm) and very high contrast
- very process-stable
- not photosensitive > 300 nm
- well suited for two-layer processes (lift-off)
- for the production of „overlay-patterns"
- application in grey-tone & e-beam lithography
- solution of PPA in safer solvent anisole

Properties I

Parameter / AR-P	8100.03	8100.06
Solids content (%)	3	6
Film thickness/4000 rpm (nm)	30	80
Resolution (nm)	10	
Contrast (adjustable)	1 - 10	
Flash point (°C)	44	
Storage temperature (°C)*	-18	

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

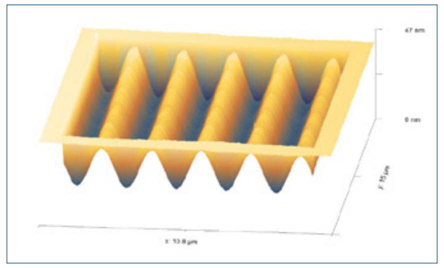
Spin curve



Properties II

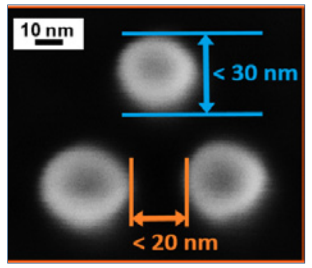
Glass trans. temperature (°C)	Decomposition > 120°C	
Cauchy coefficients	N_0	1,563
	N_1	81,9
	N_2	0
Plasma etching rates (nm/min) (20 mbar, 120 V Bias, 400 W (ICP), 20 W (RF))	90 H_2 + 10 Ar	42

Structure of grey-tone interferenz



Etched sinus pattern

Resist structures



Plasmonic trimer of 30 nm gold discs with 20 nm distance

Process parameter

Substrate	Si waver
Soft bake	110 °C, 2 min, hot plate
Structuring	NanoFrazor

Process chemicals

Adhesion promoter	AR 300-80 neu, HMDS
Thinner	AR 600-02
Remover	AR 600-01, AR 600-02

Thermally structurable positive resist AR-P 8100

Process conditions

This diagram shows exemplary process steps for AR-P 8100 resists. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

Coating	AR-P 8100.03 4000 rpm, 60 s, 30 nm	AR-P 8100.06 4000 rpm, 60 s, 80 nm
Soft bake (± 1 °C)	110 °C, 2 min hot plate or 110 °C, 10 min convection oven	
Structuring	tSPL (NanoFrazor), E-Beam	
Customer-specific technologies	Generation of semiconductor properties, etching	
Removal	AR 600-02 or O_2 plasma ashing	

NanoFrazor technology

Polyphthalaldehydes (PPA) are thermally structurable resists which were mainly developed for tSPL applications with the NanoFrazor (SwissLitho AG). Key element of this device is a hot needle scanning the resist surface. With each tip, the thermally sensitive PPA evaporates, thereby transferring the desired structures into the layer. Both 10 nm-lines as well as sophisticated three-dimensional structures can be written in this way.

The NanoFrazor technology allows writing structures without vacuum conditions. Due to the specific technology, it is also possible to set up the device in a clean laboratory. A cleanroom is required for the coating the substrates with resist Phoenix 81. The write speed of the NanoFrazor is comparable to the speed of simple electron beam devices for the realization of high-resolution structures.

Processing recommendations

Phoenix 81 is not storage-stable at room temperature and should thus be kept cooled at -18 °C. To ensure our high quality demands, this product is only shipped in powder form as PPA polymer á 1g.

Prior to coating, the PPA solution should be adjusted to room temperature. Brief heating has no significant influence on the stability. PPA layers are thermally sensitive, but significant decomposition processes are only observed above temperatures of 120 °C.

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Thermally structurable positive resist AR-P 8100

Two-layer process

1. Coating (bottom resist)	AR-P 617.03 4000 rpm, 60 s, 90 nm	
1. Soft bake (± 1 °C)	200 °C, 20 min hot plate or 200 °C, 30 min convection oven	
2. Coating (top resist)	AR-P 8100.03 4000 rpm, 60 s, 30 nm	AR-P 8100.06 4000 rpm, 60 s, 80 nm
2. Soft bake (± 1 °C)	110 °C, 2 min hot plate or 110 °C, 10 min convection oven	
Structuring (top resist)	tSPL (NanoFrazor), E-Beam	
Development (bottom resist)	AR 600-50, 30-60 s	
Customer-specific technologies	Generation of semiconductor properties, lift-off	
Removal	AR 300-76, AR 600-71 or O_2 plasma ashing	

Additional information concerning positive two-layer systems

Coating

At first, AR-P 617.03 is coated and tempered. After cooling to room temperature, Phoenix 81 is applied as top resist. The layer thickness can be varied in a range between 20 nm and 160 nm. Subsequently, the two-layer system is tempered. The thickness ratio of both layers influences the structural geometry. To obtain a strong lift-off effect, a thin PPA layer and a thick bottom layer is recommended. For a dimensionally accurate pattern transfer however, both layers should be approximately equal in thickness. The entire system has to be optimized with regard to the respective application.

Development

Development of the lower layer exclusively takes place in those areas which were exposed by the NanoFrazor. PPA layers are not attacked by developer AR 600-50. The development is isotropic and proceeds with defined speed. Both the duration of the development and the developer temperature strongly influence the extent of the undercut. The longer the developer exerts its influence and the higher the developer temperature, the more pronounced is the undercut obtained.

Lift-off / Removing

Suitable for the final lifting are remover AR 300-76 or AR 600-71.

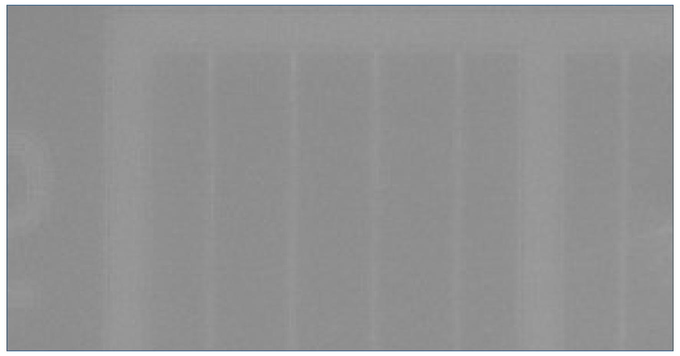
Thermally structurable positive resist AR-P 8100

Application examples

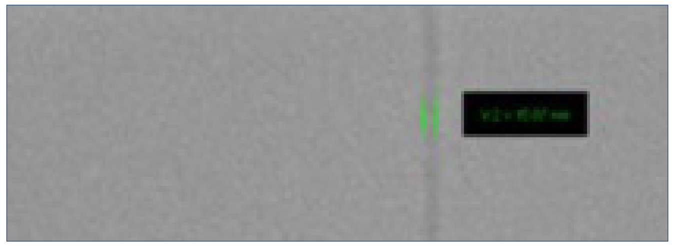
Patterning of PPA with e-beam lithography

PPA layers can also be positively patterned directly by electron irradiation. Similar to the irradiation of commonly used e-beam resists like CSAR 62 or PMMA, electron beam exposure induces fragmentation of the polymer chains. Polymer fragments resulting from PPA are however unstable and decompose into the volatile ortho-phthalaldehyde.

Only very small amounts of monomeric phthalaldehyde are directly released in the device during e-beam exposure; only the subsequent PEB leads to an almost complete thermal development. But even in the range of the dose to clear (approx. 30 - 40 µC/cm^2), a resist layer with a thickness of a few nanometres will remain. A residue-free substrate surface can nevertheless be obtained if a short plasma etching step is added. The gradation passes through a minimum, but with increasing dose, also the concurrent cross-linking processes become increasingly important. This undesirable side reaction is due to radicals which are generated during electron irradiation and stabilise the layer by cross-linking. These effects also occur in PMMA layers, but only at much higher exposure doses, and are here used to produce negative PMMA architectures. To determine the resolution limits of AR-P 8100, line patterns were examined in detail at the company Raith. Lines of different width were written into the PPA layer. After PEB and subsequent platinum metallisation, metal bridges of < 20 nm width were obtained. The highest resolution that could be achieved was 16 nm.

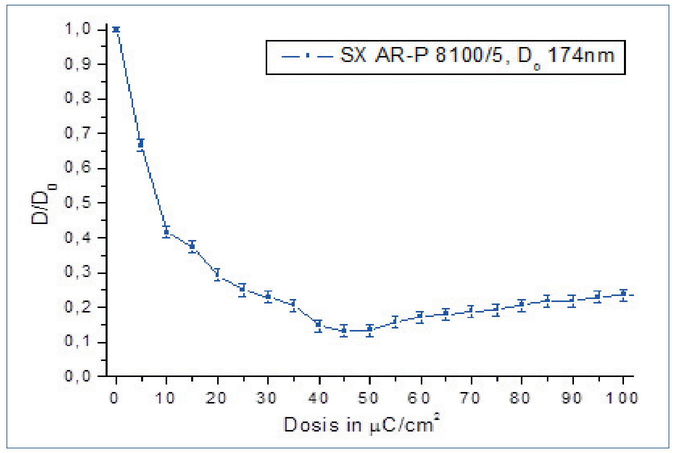


Lines written in PPA (resist AR-P 8100)



Bridge with width of 16 nm, obtained after sputter coating with platinum (film thickness: 4 nm)

Adding PAGs (photo acid generator) to PPA (sample SX AR-P 8100/5) can increase the sensitivity and allow a better control of the gradation. The exposure causes a release of acid in situ which decomposes the PPA layer at 95 - 100 °C during the following PEB (positive development). The thermally induced, solvent-free development proceeds almost completely. Despite the addition of PAGs, a very thin residual resist layer however remains.

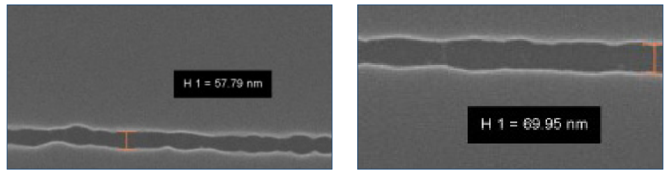


Gradation of SX AR-P 8100/5 after PEB at 98 °C

If PAG-containing resists are used together with AR-P 617 in two-layer process, the thin remaining resist layer will not disturb the further process sequence since it is dissolved during the subsequent development. After e-beam exposure and PEB, bottom resist AR-P 617 is selectively developed with developer AR 600-50. The undercut is adjusted specifically by varying the duration of the development step. Reliably processable lift-off resist architectures can thus be produced. This method allows the realisation of metal bridges (platinum):

Thermally structurable positive resist AR-P 8100

Application examples



Platinum bridges realised with two-layer process, width 58 nm (left), 70 nm (right)

The process window is however quite narrow; already small variations of the dose affect the obtained line width considerably.

Patterning of PPA with photolithography

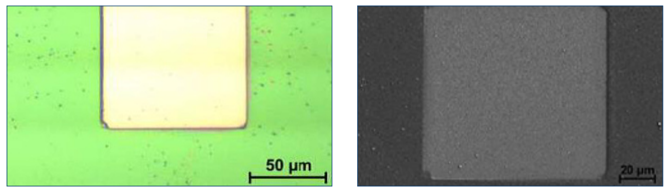
PPA layers can also be structured directly by means of photolithography. Irradiation with UV-light of a wavelength of < 300 nm results in a cleavage of the polymer chains to form volatile components.

By adding PAGs (photo acid generators), the photosensitivity can be significantly increased. The exposure releases acid in situ which then decomposes the PPA layer at 95 - 100 °C during the subsequent PEB (positive development).

The thermally induced, solvent-free development step proceeds almost completely. Cross-linking processes which are also induced by UV-exposure may however cause a thin, only a few nanometres thick residual resist layer. A residue-free substrate surface is obtained after addition of a short plasma etching step.

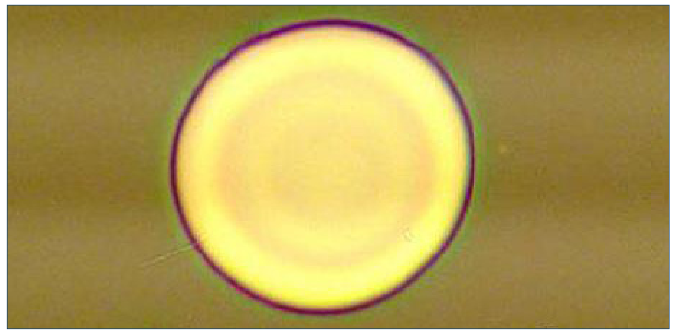
Structuring with laser (pulse)

PPA layers can also be structured by laser ablation. Substrates coated with AR-P 8100 were patterned at the IOM Leipzig with pulsed laser light at different wavelengths. This enabled the realisation of architectures with very low edge roughness. In the absorption range of PPA (at 248 nm), complete ablation was achieved without damage of the silicon substrate.



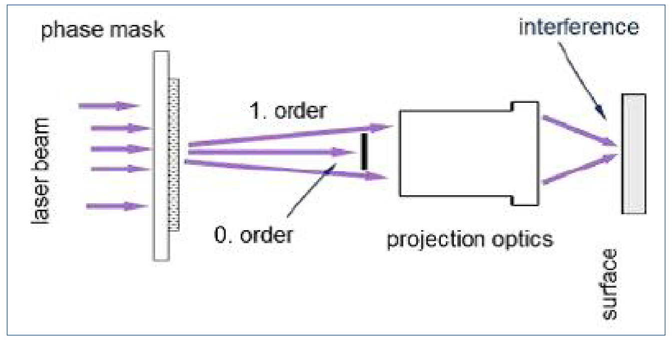
0.5 J/cm^2, 248 nm, 20 ns, double pulse exposure, 700 nm PPA on Si-wafer

Even though PPA shows only a very low absorption at a wavelength of 355 nm, a selective ablation with comparatively high sensitivity is nevertheless possible. The structures realised here are again characterised by very smooth edges.

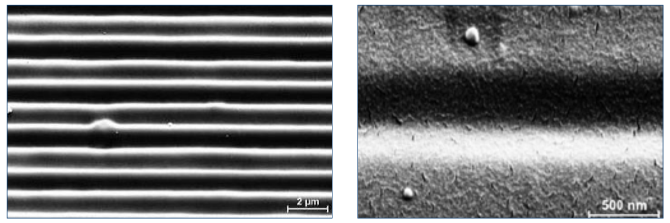


0.1 J/cm^2, 355 nm ps-laser, single-pulse exposure, 700 nm PPA on Si-wafer

The laser beam can also be used to generate 3D structures. Interference projection through a phase mask allows the production of lattice structures with sinusoidal shape and very low surface roughness.



Experimental setup of interference projection



SEM-image of PPA lattice with sinusoidal progression (period ~750 nm); 248 nm, 20 ns pulses, number of pulses: 10; 700 nm PPA on Si-wafer

Negative E-Beam Resists AR-N 7500

AR-N 7500 e-beam resists for mix & match

High-resolution e-beam resists for the production of integrated circuits

Characterisation

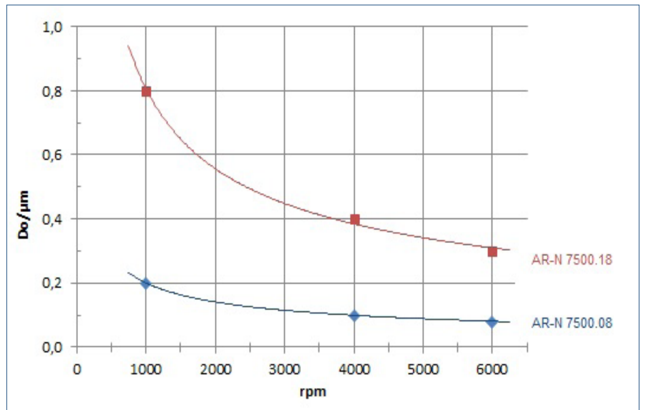
- e-beam, deep UV, i-line, g-line
- intermediate sensitivity
- mix & match-processes between e-beam and UV exposure 310 - 450 nm, positive or negative depending on the exposure wavelength chosen
- high resolution, process-stable (no CAR)
- plasma etching resistant, temp.-stable up to 120 °C
- novolac, naphthoquin. diazide, organic crosslink. a.
- safer solvent PGMEA

Properties I

Parameter / AR-N	7500.18	7500.08
Solids content (%)	18	8
Viscosity 25 °C (mPas)	4	2
Film thickness/4000 rpm (µm)	0.4	0.1
Resolution best value (nm)	40	
Contrast	5	
Flash point (°C)	42	
Storage temperature (°C) *	10-18	

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

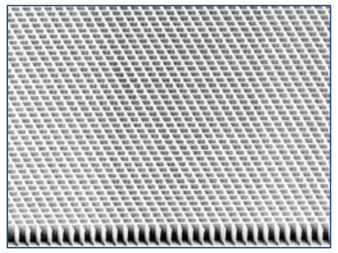
Spin curve



Properties II

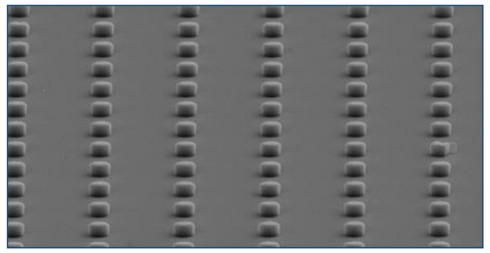
Glass trans. temperature (°C)	108	
Dielectric constant	3.1	
Cauchy coefficients	N_0	1.614
	N_1	157.1
	N_2	0
Plasma etching rates (nm/min)	Ar-sputtering	8
(5 Pa, 240-250 V Bias)	O_2	170
	CF_4	40
	80 CF_4 + 16 O_2	90

Structure resolution



AR-N 7500.18
Film thickness 400 nm
Lattice with 70 nm lines

Resist structures



AR-N 7500.18, rows of cylinders with a diameter of 500 nm

Process parameters

Substrate	Si 4" waver
Soft bake	85 °C, 90 s, hot plate
Exposure	ZBA 21, 30 kV
Development	AR 300-47, 4 : 1, 60 s, 22 °C

Process chemicals

Adhesion promoter	AR 300-80 new
Developer	AR 300-46, 300-47
Thinner	AR 300-12
Remover	AR 300-76, AR 300-73

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Negative E-Beam Resists AR-N 7500

Process conditions

This diagram shows exemplary process steps for AR-N 7500 resists. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

Process step	AR-N 7500.18
Coating	4000 rpm, 60 s, 0.4 µm
Soft bake (± 1 °C)	85 °C, 2 min hot plate or 85 °C 30 min convection oven
E-beam exposure	ZBA 21, 20 kV Exposure dose (E_0): 180 µC/cm²
Development (21-23 °C ± 0,5 °C) puddle	AR 300-47, 4 : 1 60 s
Rinse	DI-H_2O, 30 s
Post-bake (optional)	120 °C, 1 min hot plate or 120 °C, 25 min convection oven for enhanced plasma etch resistance
Customer-specific technologies	Generation of semiconductor properties
Removal	AR 300-76 or O_2 plasma ashing

Developments recommendations

optimal suitable

Developer	AR 300-26	AR 300-35	AR 300-47
AR-N 7500.18 ; .08	1 : 4 ; 1 : 7	4 : 1 ; 1 : 1	4 : 1

Processing instructions

These resists are predestined for e-beam exposure, but also suitable for UV exposure. Mix & match processes are possible, if both exposure methods are carefully coordinated. During e-beam exposure, the resist works in a negative mode. If these resists are exposed to UV, they also work in a negative mode if image-wise exposure is performed at 310 to 365 nm, followed by flood exposure at > 365 nm (optimum g-line). The exposure dose is in this case roughly 100 mJ/cm² (i-line) for a film thickness of 400 nm. With an additional tempering step (85 °C, 2 min hot plate) after image-wise exposure, the sensitivity can be slightly increased. A positive image is obtained after image-wise UV exposure at 365 - 450 nm without subsequent flood exposure. The developer dilution should be adjusted with DI water in such a way that the development time is in a range of 30 and 120 s at 21 – 23 °C.

Negative E-Beam Resists AR-N 7520 new

AR-N 7520 new e-beam resists for mix & match

with highest resolution and highly sensitive for the production of integrated circuits

Characterisation

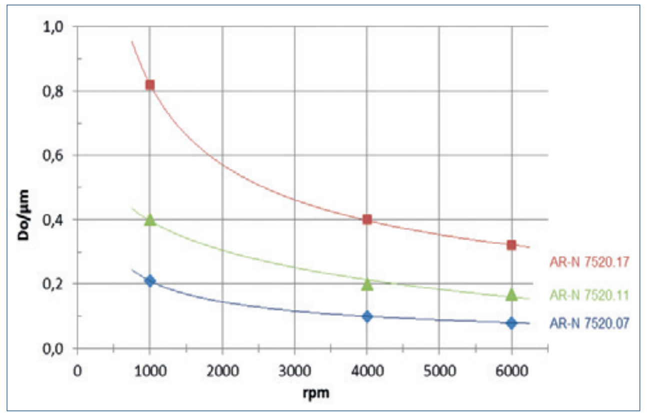
- e-beam, deep UV, i-line (formerly SX AR-N 7520/4)
- short writing times, very high contrast
- mix & match processes between e-beam and UV exposure 248-365 nm, negative in the UV range
- highest resolution, very process-stable (no CAR)
- plasma etching resistant, temp.-stable up to 140 °C
- novolac, organic crosslinking agent
- safer solvent PGMEA

Properties I

Parameter / AR-N new	7520.17	7520.11	7520.07
Solids content (%)	17	11	7
Viscosity 25 °C (mPas)	4	3	2
Film thickness/4000 rpm (µm)	0.4	0.2	0.1
Resolution best value (nm)	28		
Contrast	10		
Flash point (°C)	42		
Storage temperature (°C)*	10 - 18		

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

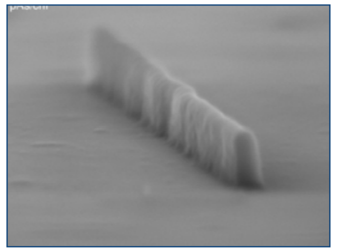
Spin curve



Properties II

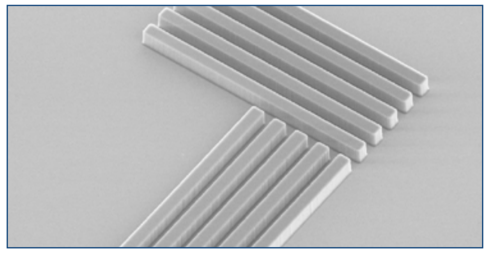
Glass trans. temperature (°C)	102	
Dielectric constant	3.1	
Cauchy coefficients	N_0	1.622
	N_1	123.2
	N_2	0
Plasma etching rates (nm/min)	Ar-sputtering	8
(5 Pa, 240-250 V Bias)	O_2	169
	CF_4	41
	80 CF_4 + 16 O_2	90

Structure resolution



AR-N 7520.07 new
30-nm lines at a film thickness of 90 nm

Resist structures



AR-N 7520.17 new
400- and 600-nm lines, film thickness 400 nm

Process parameters

Substrate	Si 4" waver
Soft bake	85 °C, 90 s, hot plate
Exposure	Raith Pioneer, 30 kV
Development	AR 300-47, 60 s, 22 °C

Process chemicals

Adhesion promoter	AR 300-80
Developer	AR 300-47, AR 300-46
Thinner	AR 300-12
Remover	AR 300-73, AR 300-76

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Negative E-Beam Resists AR-N 7520 new

Process conditions

This diagram shows exemplary process steps for AR-N 7520 new resists. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

	AR-N 7520.17 new	AR-P 7520.07 new
Coating	4000 rpm, 60 s, 0.4 µm	4000 rpm, 60 s, 0.1 µm
Soft bake (± 1 °C)	85 °C, 1 min hot plate or 85 °C 30 min convection oven	
E-beam exposure	Raith Pioneer, 30 kV Exposure dose (E_0): 30 µC/cm², 100 nm space & lines	
Development (21-23 °C ± 0,5 °C) puddle	AR 300-46 90 s	AR 300-47 50 s
Rinse	DI-H_2O, 30 s	
Post-bake (optional)	85 °C, 1 min hot plate or 85 °C, 25 min convection oven for enhanced plasma etch resistance	
Customer-specific technologies	Generation of semiconductor properties	
Removal	AR 300-73 or O_2 plasma ashing	

Development recommendations

optimal suitable

Developer	AR 300-26	AR 300-35	AR 300-40
AR-N 7520.17, .11; .07 new	3 : 1 ; 1 : 1	-	300-46 ; 300-47

Processing instructions

These resists are predestined for e-beam exposure, but also suitable for UV exposure. Mix & match processes are possible if both exposure methods are carefully coordinated. During e-beam exposure, the resist works in a negative mode.

The resist works also in a negative mode with deep UV (248-270 nm) or mid-UV (290-365) exposure. If a further tempering step (85 °C, 2 min hot plate) is added after image-wise exposure, the sensitivity can be slightly enhanced.

The developer dilution should be adjusted with DI water such that the development time is in a range between 20 s and 120 s. By dilution of the developer, contrast and development rate can be influenced to a large degree. A stronger dilution results in an increased contrast and a reduced development rate.

Negative E-Beam Resists AR-N 7520

AR-N 7520 e-beam resists for mix & match

E-beam resists with highest resolution for the production of integrated circuits

Characterisation

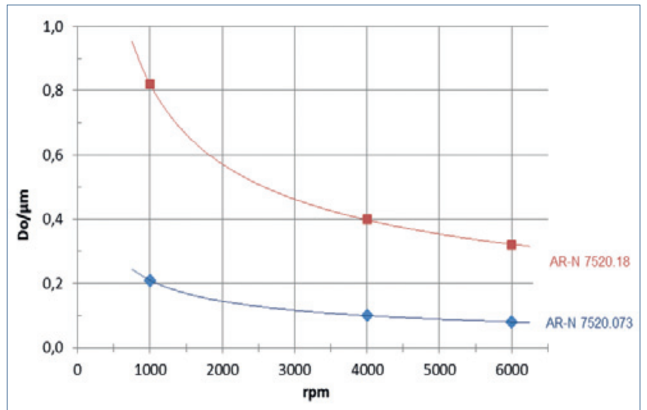
- e-beam, deep UV, i-line
- very high contrast, excellent transfer of structures, high-precision edges
- mix & match processes between e-beam and UV exposure 248-365 nm
- highest resolution, very process-stable (no CAR)
- plasma etching resistant, temp.-stable up to 140 °C
- novolac, organic crossl. agent, safer solvent PGMEA

Properties I

Parameter / AR-N	7520.18	7520.073
Solids content (%)	18	7.3
Viscosity 25 °C (mPas)	4.2	2.3
Film thickness/4000 rpm (µm)	0.4	0.1
Resolution best value (nm)	28	
Contrast	10	
Flash point (°C)	42	
Storage temperature (°C) *	10 - 18	

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

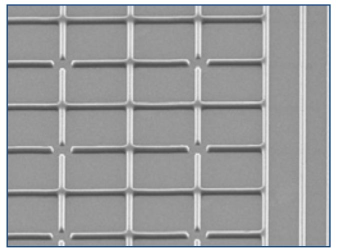
Spin curve



Properties II

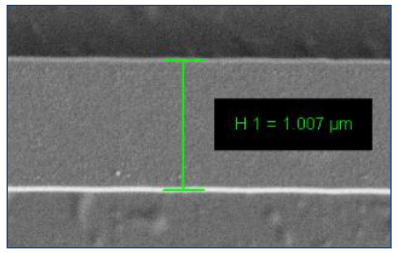
Glass trans. temperature (°C)	102	
Dielectric constant	3.1	
Cauchy coefficients	N_0	1.63
	N_1	122.0
	N_2	0
Plasma etching rates (nm/min)	Ar-sputtering	8
(5 Pa, 240-250 V Bias)	O_2	169
	CF_4	41
	80 CF_4 + 16 O_2	90

Structure resolution



400 nm lines with AR-N 7520.073

Resist structures



1 µm line with high-precision edges, AR-N 7520.18, Resist thickness 340 nm, 1.400 µC/cm², 100 kV

Process parameters

Substrate	Si 4" waver
Soft bake	85 °C, 90 s, hot plate
Exposure	Raith Pioneer, 30 kV
Development	AR 300-47, 4 : 1, 60 s, 22 °C

Process chemicals

Adhesion promoter	AR 300-80
Developer	AR 300-47, AR 300-26
Thinner	AR 300-12
Remover	AR 300-76, AR 300-73

Negative E-Beam Resists AR-N 7520

Process conditions

This diagram shows exemplary process steps for AR-N 7520 resists. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

	AR-N 7520.18	AR-N 7520.073
Coating	4000 rpm, 60 s, 0.4 µm	4000 rpm, 60 s, 0.1 µm
Soft bake (± 1 °C)	85 °C, 2 min hot plate or 85 °C, 30 min convection oven	
E-beam exposure	Raith Pioneer, 30 kV	
	Exposure dose (E_0): 100 nm space & lines	
	500 µC/cm²	300 µC/cm²
Development (21-23 °C ± 0,5 °C) puddle	AR 300-47, 4 : 1 90 s	AR 300-47, 4 : 1 50 s
Rinse	DI-H_2O, 30 s	
Post-bake (optional)	85 °C, 1 min hot plate or 85 °C, 25 min convection oven for enhanced plasma etch resistance	
Customer-specific technologies	Generation of semiconductor properties	
Removal	AR 300-76 or O_2 plasma ashing	

Development recommendations

optimal suitable

Developer	AR 300-26	AR 300-35	AR 300-40
AR-N 7520.18, 7520.073	2 : 3 ; 1 : 3	2 : 1; pur	300-47, 4 : 1

Processing instructions

These resists are predestined for e-beam exposure, but also suitable for UV exposure. Mix & match processes are possible if both exposure methods are carefully coordinated. During e-beam exposure, the resist works in a negative mode. (For details on Mix & Match, see AR-N 7520 new). Due to their composition, resists AR-N 7520 are approximately 8 x more insensitive than resists of the series AR-N 7520 new. The required higher dose predestines these resists for the production of very precise structural edges, since due to the high electron density edges are perfectly reproduced. For the very high imaging quality however, longer writing times have to be accepted.

The developer dilution should be adjusted with DI water such that the development time is in a range between 20 s and 120 s. By dilution of the developer, contrast and development rate can be influenced to a large degree. A stronger dilution results in an increased contrast and a reduced development rate.

Negative E-Beam Resists AR-N 7700

AR-N 7700 e-beam resists with steep gradation

High-resolution e-beam resists for the production of integrated circuits

Characterisation

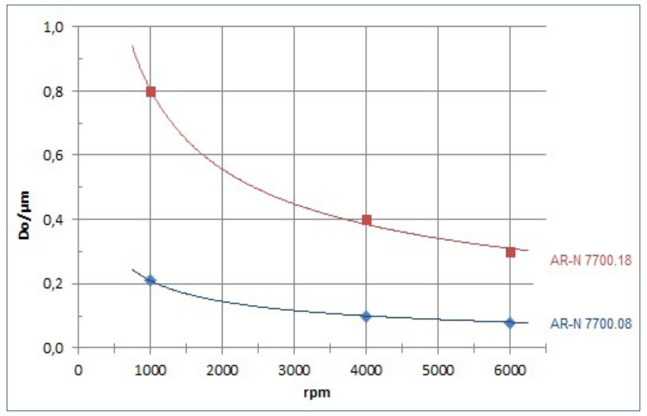
- e-beam, deep UV; chemically enhanced (CAR)
- 7700: high contrast for digital reproduction with excellent sensitivity
- negative-tone with high resolution in the UV range 248-265 nm and 290-330 nm
- plasma etching resistant, temp. stable up to 140 °C
- novolac, acid generator, crosslinking agent
- safer solvent PGMEA

Properties I

Parameter / AR-N	7700.18	7700.08
Solids content (%)	18	8
Viscosity 25 °C (mPas)	4	2
Film thickness/4000 rpm (µm)	0.4	0.1
Resolution best value (nm)	80	
Contrast	5	
Flash point (°C)	42	
Storage temperature (°C) *	8 - 12	

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

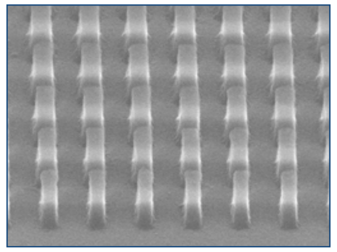
Spin curve



Properties II

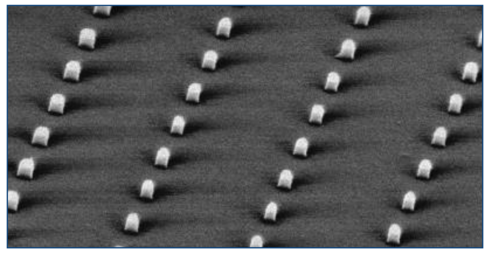
Glass trans. temperature (°C)	102	
Dielectric constant	3.1	
Cauchy coefficients	N_0	1.596/ 1.604
not crosslinked / crosslinked	N_1	77.0 / 85.5
	N_2	65.0 / 56.9
Plasma etching rates (nm/min)	Ar-sputtering	8
(5 Pa, 240-250 V Bias)	O_2	168
	CF_4	38
	80 CF_4 + 16 O_2	89

Structure resolution



AR-N 7700.18
112 x 164 squares, film thickness of 400 nm

Resist structures



AR-N 7700
500-nm dots, written with a dose of 12 µC/cm² (30 kV).

Process parameters

Substrate	Si 4" waver
Soft bake	85 °C, 90 s, hot plate
Exposure	ZBA 21, 30 kV
Development	AR 300-46, 60 s, 22 °C

Process chemicals

Adhesion promoter	AR 300-80 new
Developer	AR 300-46, 300-26
Thinner	AR 300-12
Remover	AR 300-73, AR 300-76

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Negative E-Beam Resists AR-N 7700

Process conditions

This diagram shows exemplary process steps for AR-N 7700 resists. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

Process step	AR-N 7700.18	AR-N 7700.08
Coating	4000 rpm, 60 s 0.4 µm	4000 rpm, 60 s 0.1 µm
Sopft bake (± 1 °C)	85 °C, 2 min hot plate or 85 °C, 30 min convection oven	
E-beam exposure	ZBA 21, 30 kV	
	E-beam exposure dose (E_0):	
	12 µC/cm²	8 µC/cm²
UV exposure (optional)	UV exposure dose: (E_0):	for mix & match
	30 mJ/cm²	24 mJ/cm²
Crosslinking bake	105 °C, 2 min hot plate or 100 °C, 60 min convection oven	
Development (21-23 °C ± 0,5 °C) puddle	AR 300-46 60 s	AR 300-46, 4 : 1 60 s
Rinse	DI-H_2O, 30 s	
Post-bake (optional)	120 °C, 1 min hot plate or 120 °C, 25 min convection oven for slightly enhanced plasma etching resistance	
Customer-specific technologies	Generation of semiconductor properties	
Removal	AR 300-73 or O_2 plasma ashing	

Development recommendations

optimal suitable

Developer	AR 300-26	AR 300-35	AR 300-40
AR-N 7700.18 ; 7700.08	2 : 1 ; 1 : 3	undil. up to 3 : 1	300-46 undil. ; 300-46, 4 : 1

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Negative E-Beam Resists AR-N 7700

Processing instructions

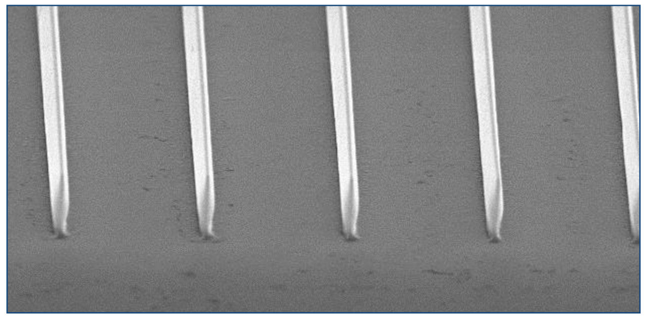
These resists are predestined for e-beam exposure, but also suitable for UV exposure. During e-beam exposure, the resist works in a negative mode. The exposure dose mainly depends on the acceleration voltage, the substrate and the film thickness. The resist also work in a negative mode after deep UV exposure if the image-wise exposure is performed at a wavelength of 248-265 and 290-330 nm. A bake step is mandatory after exposure (e-beam/UV) to induce the required crosslinking.

Contrast and development rate strongly depend on the tempering. Recommended is a temperature of 105 °C (hot plate, 2 min), with possible variation of ± 5°C. Higher crosslinking temperatures require stronger developers. Contrast and development rate can be influenced to a large degree if developer strength and tempering temperature are coordinated accordingly. The general rule is: the weaker the developer, the higher is the contrast and the lower the development rate. The development time ideally is about 60 s (30 … 120 s) at 21 – 23 °C. Shorter times for complete development will attack the crosslinked structures.

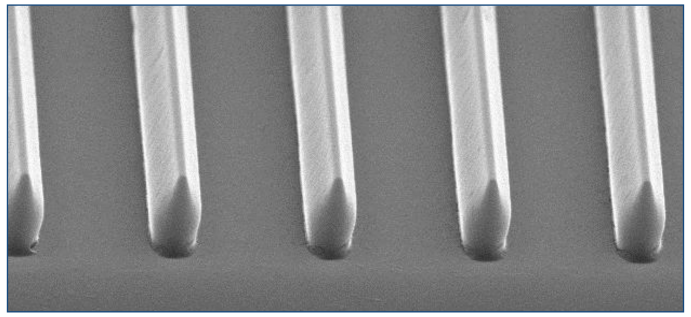
Proximity effect

If electrons are used for the irradiation of resist films, always a certain amount of scattered radiation will occur, either as forward scattering due to an interaction with the resist material or as backscattering from the substrate (wafer). This phenomenon is called proximity effect and results in undesirable changes of the structures. The proximity effect is significantly more pronounced if sensitive resists (CAR) as compared to e.g. PMMA resists are used.

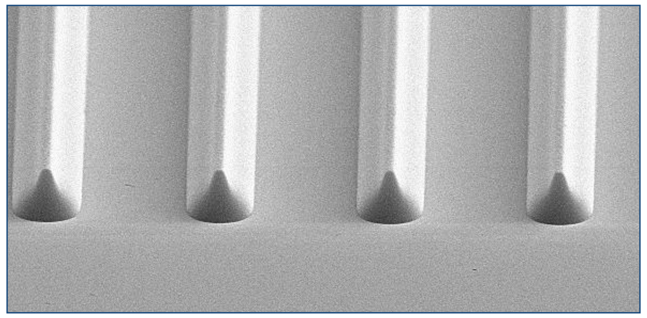
In the following example, AR-N 7700.18 was applied by spin coating to yield a film thickness of 1100 nm, tempered (85 °C, 2 min, hot plate) and irradiated with different doses (20 kV). The crosslinking bake was carried out at 105 °C, 3 min on a hot plate. After development (AR 300-46 undil., 2 min), the following structures were obtained. Clearly visible is an increased widening of the 250-nm bars with higher exposure doses.



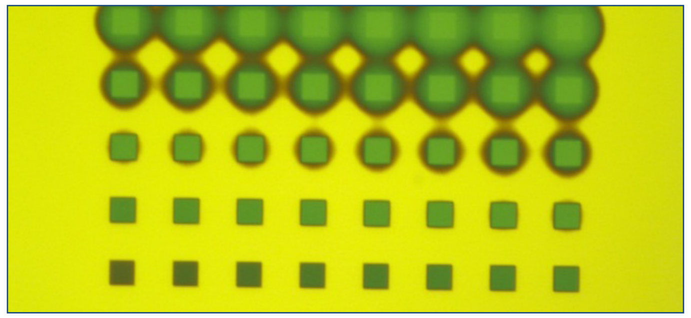
AR-N 7700.18 dose 19.5 μC/cm²



AR-N 7700.18 dose 37.0 μC/cm²



AR-N 7700.18 dose 63.5 μC/cm²



Dose sequence of AR-N 7700.08 : Squares were written with a dose of 1.0 – 90 μC/cm². The proximity effect at higher doses is quite apparent.

Negative E-Beam Resists AR-N 7720

AR-N 7720 e-beam resists with flat gradation

High-resolution e-beam resists for the production of diffractive optics

Characterisation

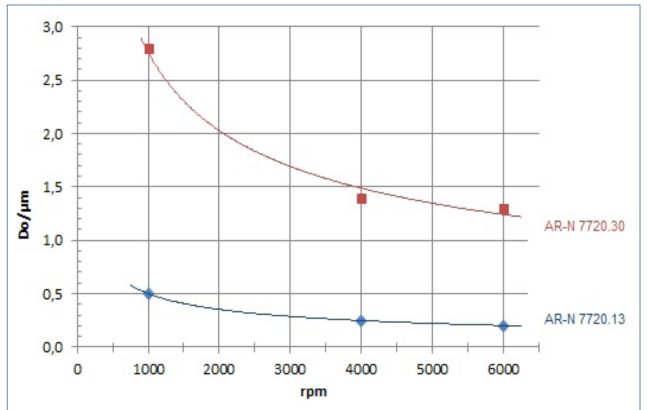
- e-beam, deep UV; chemically enhanced (CAR)
- flat gradation for three-dimensional resist profiles for diffractive optics and holograms
- negative-tone with high resolution in the UV-range 248-265 nm and 290-330 nm
- plasma etching resistant, temperature-stable up to 140 °C
- novolac, acid generator, crosslinking agent
- safer solvent PGMEA

Properties I

Parameter / AR-N	7720.30	7720.13
Solids content (%)	30	13
Viscosity 25 °C (mPas)	20	3
Film thickness/4000 rpm (µm)	1.4	0.25
Resolution best value (nm)	80	
Contrast	< 1	
Flash point (°C)	42	
Storage temperature (°C) *	8 - 12	

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

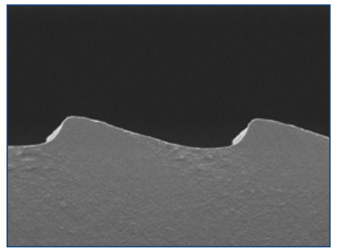
Spin curve



Properties II

Glass trans. temperature (°C)	102	
Dielectric constant	3.1	
Cauchy coefficients not crosslinked / crosslinked	N_0	1.595 / 1.602
	N_1	69.9 / 85.3
	N_2	64.9 / 56.8
Plasma etching rates (nm/min)	Ar-sputtering	8
(5 Pa, 240-250 V bias)	O_2	168
	CF_4	38
	80 CF_4 + 16 O_2	89

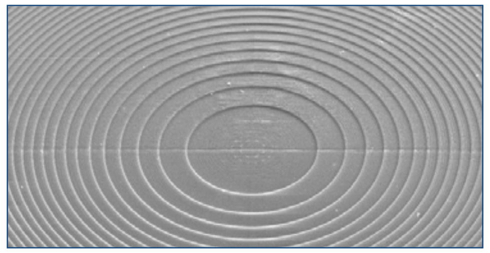
Three-dimensional structure



AR-N 7720.13

Sinusoidal structures

Applications of AR-N 7720



Diffractive optic transferred with AR-N 7720.30 into silicone

Process parameters

Substrate	Si 4" wafer
Soft bake	85 °C, 90 s, hot plate
Exposure	Vistec Lion, 12.5 kV
Development	AR 300-47, 4 : 1, 60 s, 22 °C

Process chemicals

Adhesion promoter	AR 300-80 new
Developer	AR 300-47, 300-26
Thinner	AR 300-12
Remover	AR 300-76, AR 300-72

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Negative E-Beam Resists AR-N 7720

Process conditions

This diagram shows exemplary process steps for AR-N 7720 resists. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of e-beam resists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist e-beam resists".

Process step	AR-N 7720.30	AR-N 7720.13
Coating	4000 rpm, 60 s 1.4 µm	4000 rpm, 60 s 0.25 µm
Soft bake (± 1 °C)	85 °C, 2 min hot plate or 85 °C 30 min convection oven	
E-beam exposure	Vistec Lion, acceleration voltage 12.5 kV E-beam exposure dose (E_0):	
	100 µC/cm²	35 µC/cm²
Crosslinking bake	105 °C, 1 min hot plate or 100 °C, 60 min convection oven	
Post-bake	70 °C, 20 min, hot plate or 70 °C, 120 min convection oven for preventive avoidance of roughnesses	
Development (21-23 °C ± 0,5 °C) puddle	AR 300-47 90 s	AR 300-47, 4 : 1 60 s
Rinse	DI-H_2O, 30 s	
Post-bake (optional)	120 °C, 1 min hot plate or 120 °C, 25 min convection oven for slightly enhanced plasma etching resistance	
Customer-specific technologies	Fabrication of holograms or diffractive optics	
Removal	AR 300-76 or O_2 plasma ashing	

Development recommendations

optimal · suitable

Developer	AR 300-26	AR 300-35	AR 300-40
AR-N 7720.30 ; 7720.13	1 : 2 ; 1 : 3	-	300-47 undil. ; 300-47, 4 : 1

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Negative E-Beam Resists AR-N 7720

Processing instructions

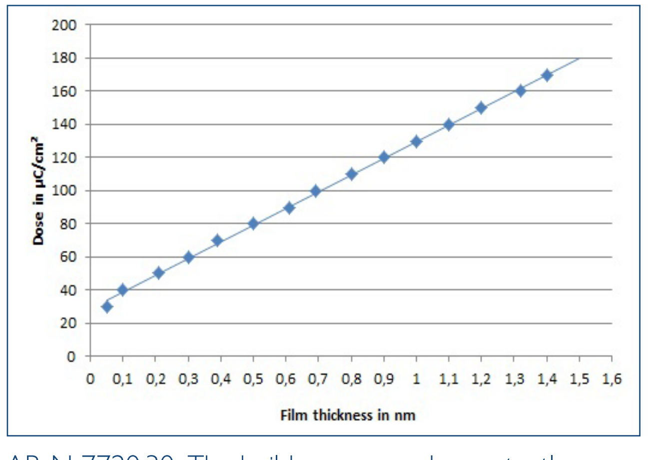
These resists are predestined for e-beam exposure, but also suitable for UV exposure. During e-beam exposure, the resist works in a negative mode. The exposure dose mainly depends on the acceleration voltage, the substrate and the film thickness. The resist also work in a negative mode after deep UV exposure if the image-wise exposure is performed at a wavelength of 248-265 and 290-330 nm. A bake step is mandatory after exposure (e-beam/UV) to induce the required crosslinking. Contrast and development rate strongly depend on the tempering. Recommended is a temperature of 105 °C (hot plate, 2 min), with possible variation in a range of ± 5°C. Higher crosslinking temperatures require stronger developers.

For resist AR-N 7720 it is recommended to add a further tempering step at 60 – 70 °C for 1-3 h in the oven prior to development to avoid possibly occurring roughnesses of the structures to be developed. Contrast and development rate can be influenced to a large degree if developer strength and tempering temperature are coordinated accordingly. The general rule is: the weaker the developer, the higher is the contrast and the lower the development rate. The development time ideally is about 60 s (30 … 120 s) at 21 – 23 °C. Shorter times for complete development will attack the crosslinked structures. Own tests with respect to the development process are required.

Three-dimensional, “analogous” structures

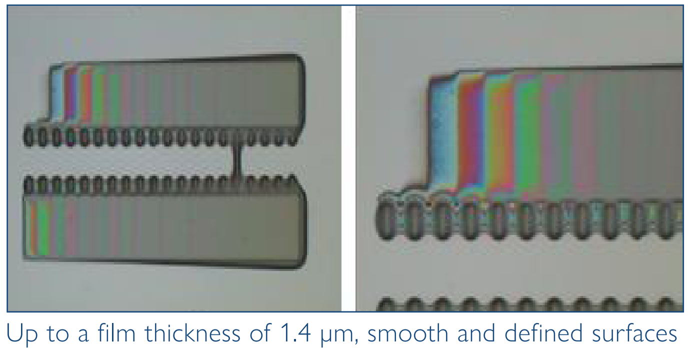
For most applications, a high contrast is desired to obtain a high resolution. For the production of holograms, diffractive optics or curved surfaces however, in particular resists with low contrast are predestined. Resist AR-N 7720 was specifically designed for these applications. The active components acid generator and crosslinking agent were both substantially reduced as compared to “digital” resists, which results in lower crosslinking efficiency. With increasing exposure dose, consequently a defined increase of the film thickness is obtained (see diagram below).

Film build-up and dose dependency



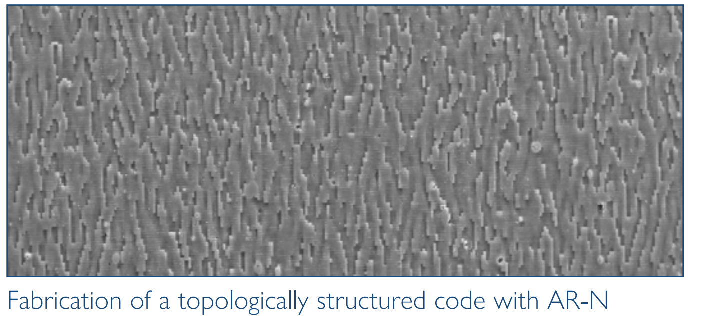
AR-N 7720.30: The build-up proceeds constantly across the entire dose range as indicated. Film thickness 1.4 µm, acceleration voltage 12.5 kV, crosslinking bake 100 °C, 3 min, postbake 70 °C, 4 h convection oven, developer AR 300-47 (4 :1 dilution).

Dose sequence of AR-N 7720.30



Up to a film thickness of 1.4 µm, smooth and defined surfaces are obtained.

Application AR-N 7720



Fabrication of a topologically structured code with AR-N 7720.30

Protective Coating PMMA Electra 92 (AR-PC 5090)

Conductive protective coating for non-novolak-based e-beam resists

Top layer for the dissipation of e-beam charges on insulating substrates

Characterisation

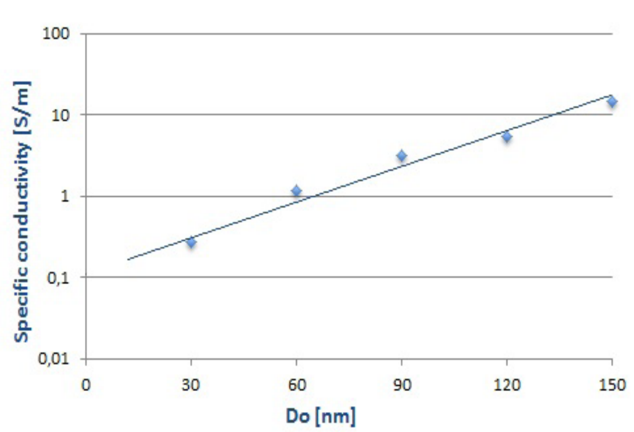
- as protective coating, this resist is not sensitive to light / radiation
- thin, conductive layers for the dissipation of charges during electron exposure
- coating of non-novolac PMMA, CSAR 62, HSQ et al.
- longterm-stable
- easy removal with water after exposure
- polyaniline-derivative dissolved in water and IPA

Properties I

Parameter / AR-PC	5090.02
Solids content (%)	2
Viscosity 25°C (mPas)	1
Film thickness/4000 rpm (nm)	42
Film thickness/1000 rpm (nm)	100
Resolution (µm) / Contrast	-
Flash point (°C)	28
Storage temperature (°C)*	8 - 12

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

Conductivity

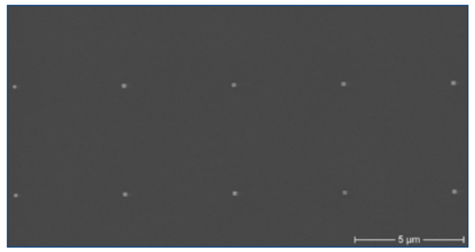


Conductivity measurements of AR-PC 5090.02 layers obtained after spin deposition. For thinner films, the resistance increases and the conductivity decreases.

Properties II

Conductivity in layer 60 nm (S/m)	1.2	
Cauchy-Koeffizienten	N_0	-
	N_1	-
	N_2	-
Plasma etching rates (nm/min)	Ar-sputtering	-
(5 Pa. 240-250 V Bias)	O_2	185
	CF_4	68
	80 CF_4 + 16 O_2	120

REM dissipation of charges



200 nm-squares written on quartz without distortion caused by charges with AR-P 662.04 and AR-PC 5090.02

Process parameters

Substrate	4“ wafer quartz with AR-P 662.04
Coating	2000 rpm, 60 nm
Soft bake	85 °C

Process chemicals

Adhesion promoter	-
Developer	-
Thinner	-
Remover	DI-water

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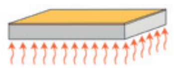
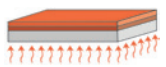
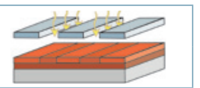
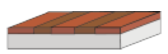
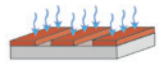
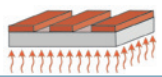
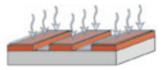
Protective Coating PMMA Electra 92 (AR-PC 5090)

Process conditions

This diagram shows exemplary process steps for resist Electra 92 - AR-PC 5090.02 and PMMA-resist AR-P 664.04. All specifications are guideline values which have to be adapted to own specific conditions.

1. Coating		AR-P 662.04 on insulating substrates (quartz, glass, GaAs) 4000 rpm, 60 s, 140 nm
1. Soft bake (± 1 °C)		150 °C, 2 min hot plate or 150 °C, 30 min convection oven
2. Coating		AR-PC 5090.02 2000 rpm, 60 s , 60 nm
2. Tempering (± 1 °C)		90 °C, 2 min hot plate or 85 °C, 25 min convection oven
E-beam exposure		ZBA 21, 20 kV Exposure dose (E_0): 110 µC/cm² (AR-P 662.04, 140 nm)
Removal		AR-PC 5090.02 DI-water, 60 s
Development (21-23 °C ± 0.5 °C) puddle		AR-P 662.04 AR 600-56, 2 min
Stop		AR 600-60, 30 s
Post-bake (optional)		130 °C, 1 min hot plate or 130 °C, 25 min convection oven for slightly enhanced plasma etching stability
Customer-specific technologies		Generation of e.g. semi-conductor properties, etching, sputtering
Removal		AR 600-71 or O_2 plasma ashing

Processing instructions

The conductivity may be varied by adjusting the thickness with different rotational speeds. Thicker layers of 90 nm thus have a 2.5 times higher conductivity as compared to 60 nm thick layers.

For the build-up of an even conductive layer, the substrate should be wetted with the resist solution before the spin process is started. After a certain storage time at room temperature, the coating pattern of Electra may change slightly. To restore the coating pattern, treatment with ultrasound and filtration (0.2 µm) can then be carried out.

Protective Coating Novolac Electra 92 (AR-PC 5091)

Conductive protective coating for novolac-based e-beam resists

Top layer for the dissipation of e-beam charges on insulating substrates

Characterisation

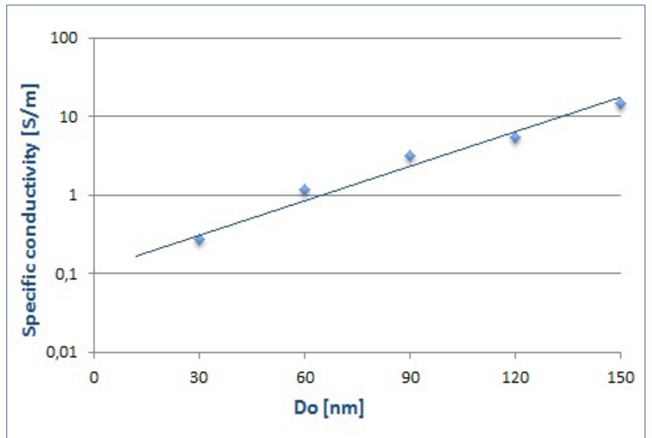
- as protective coating, this resist is not sensitive to light / radiation
- thin, conductive layers for the dissipation of charges during electron exposure
- coating of novolac-based e-beam resist AR-N 7000
- longterm-stable
- easy removal with water after exposure
- polyaniline-derivative dissolved in water and IPA

Properties I

Parameter / AR-PC	5091.02
Solids content (%)	2
Viscosity 25°C (mPas)	1
Film thickness/4000 rpm (nm)	31
Film thickness/1000 rpm (nm)	80
Resolution (µm) / Contrast	-
Flash point (°C)	39
Storage temperature (°C)*	8 - 12

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

Conductivity



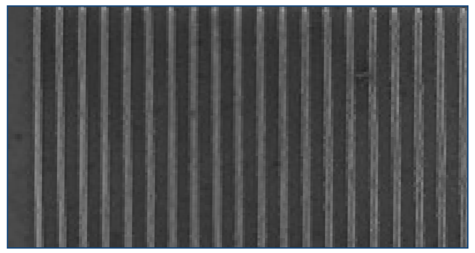
Resistance measurements of AR-PC 5091.02 layers obtained after spin deposition. For thinner films, the resistance increases and the conductivity decreases.

Note: Novolac-based e-beam resists possess other surface properties than CSAR 62 or PMMA. AR-PC 5091 was thus developed with a different solvent mixture. In all other respects however, the polymer composition of AR-PC 5090 and AR-PC 5091 is identical so that both resists are referred to as "Electra 92".

Properties II

Conductivity in layer 60 nm (S/m)	1.2	
Cauchy-Koeffizienten	N_0	-
	N_1	-
	N_2	-
Plasma etching rates (nm/min)	Ar-sputtering	-
(5 Pa. 240-250 V Bias)	O_2	185
	CF_4	68
	80 CF_4 + 16 O_2	120

REM dissipation of charges



50 nm lines written on glass at a pitch of 150 nm with AR-N 7520.07 and AR-PC 5091.02

Process parameters

Substrate	4" wafer quarz with AR-N 7520.07 neu
Coating	2000 rpm, 60 nm
Soft bake	50 °C

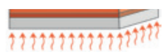
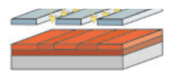
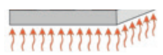
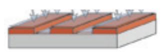
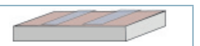
Process chemicals

Adhesion promoter	-
Developer	-
Thinner	-
Remover	DI-water

Protective Coating Novolac Electra 92 (AR-PC 5091)

Process conditions

This diagram shows exemplary process steps for resist Electra 92 (AR-PC 5091.02) and e-beam resist AR-N 7520.07 new. All specifications are guideline values which have to be adapted to own specific conditions.

1. Coating		AR-N 7520.07 new on insulating substrates (quartz, glass, GaAs) 4000 rpm, 60 s, 100 nm
1. Soft bake (± 1 °C)		85 °C, 2 min hot plate or 85 °C, 30 min convection oven
2. Coating		SX AR-PC 5000/91.2 2000 rpm, 50 s , 50 nm
2. Soft bake (± 1 °C)		50 °C, 2 min hot plate or 45 °C, 25 min convection oven
E-beam exposure		Raith Pioneer, acceleration voltage 30 kV Exposure dose (E_0): 30 µC/cm², 100 nm spaces & lines
Removal optional		AR-PC 5091.02 (The removal step can also be carried out simul- DI-H_2O, 60 s taneously with the subsequent development step.)
Development (21-23 °C ± 0.5 °C) puddle		AR-N 7520.07 new AR 300-47, 50 s
Rinse		DI-H_2O, 30 s
Post-bake (optional)		85 °C, 1 min hot plate or 85 °C, 25 min convection oven for slightly enhanced plasma etching stability
Customer-specific technologies		Generation of e.g. semi-conductor properties, etching, sputtering
Removal		AR 600-70 or O_2 plasma ashing

Processing instructions

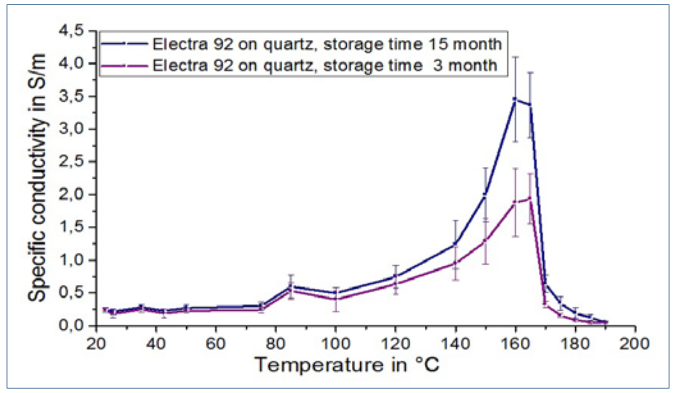
The conductivity may be varied by adjusting the thickness with different rotational speeds. Thicker layers of 90 nm thus have a 2.5 times higher conductivity as compared to 60 nm thick layers. In the case that crack formation is observed after tempering of the protective coating, the tempering step can be omitted.

For the build-up of an even conductive layer, the substrate should be wetted with the resist solution before the spin process is started. After a certain storage time at room temperature, the coating pattern of Electra may change slightly. To restore the coating pattern, treatment with ultrasound and filtration (0.2 µm) can then be carried out.

Protective Coating Electra 92

Application examples for PMMA-Electra 92

Conductivity Electra 92 as a function of Temperature

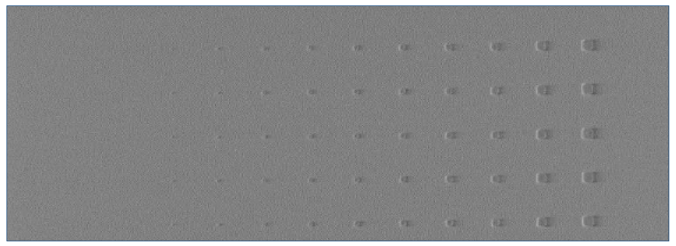


Conductivity properties of differently aged Electra 92 batches

The conductivity was determined as a function of the measured temperature. At temperatures < 100 °C, both resists show a virtually identical conductivity.

Conductivity measurements up to a temperature of 160 °C which were performed directly on a hotplate showed a large increase of the conductivity by a factor of 10 (see diagram). This fact is due to the complete removal of water from the layer. After a few hours of air humidity absorption under room conditions, the conductivity decreases again to the initial value. In the high vacuum of e-beam devices, the water is also completely removed and the conductivity thus increases accordingly. This effect has been demonstrated in direct conductivity measurements under mediate vacuum conditions. Temperatures above 165 °C destroy the polyaniline irreversibly and no conductivity is observed any more.

CSAR 62 on glass with Electra 92 for deriving



30 – 150 nm squares of CSAR 62 on glass

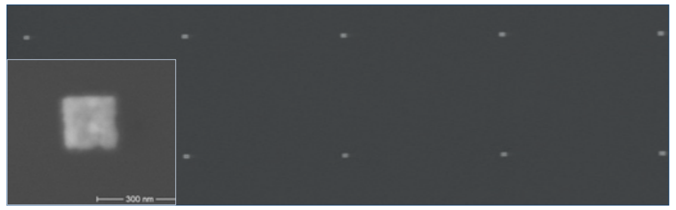
The combination of CSAR 62 with Electra 92 - AR-PC 5090.02 offers the best options to realise complex e-beam structuring processes on glass or semi-insulating substrates like e.g. gallium arsenide. The excellent sensitivity and highest resolution of the CSAR are complemented harmoniously by the conductivity of Electra 92.

CSAR 62 and Electra 92 on glass

Substrate	Glas 24 x 24 mm
Adhesion AR 300-80	4000 rpm; 10 min, 180 °C hot plate
Coating AR-P 6200.09	4000 rpm; 8 min, 150 °C hot plate
Copating AR-PC 5090.02	4000 rpm; 5 min, 105 °C hot plate
E-beam-irradiation	Raith Pioneer; 30 kV, 75 µC/cm²
Removal Electra 92	2 x 30 s water, dipping bath
Bath (drying)	30 s AR 600-60
Development CSAR 62	60 s AR 600-546
Stopping	30 s AR 600-60

At a CSAR 62 film thickness of 200 nm, squares with an edge length of 30 nm could reliably be resolved on glass.

PMMA Lift-off on glass with Electra 92



200 nm squares produced with 2-layer PMMA lift-off

Initially, the PMMA resist AR-P 669.04 (200 nm thickness) was coated on a quartz substrate and tempered. The second PMMA resist AR-P 679.03 was then applied (150 nm thickness) and tempered, followed by coating with Electra 92. After exposure, Electra 92 was removed with water, the PMMA structures were developed (AR 600-56) and the substrate vaporised with titanium/gold. After a liftoff with acetone, the desired squares remained on the glass with high precision.

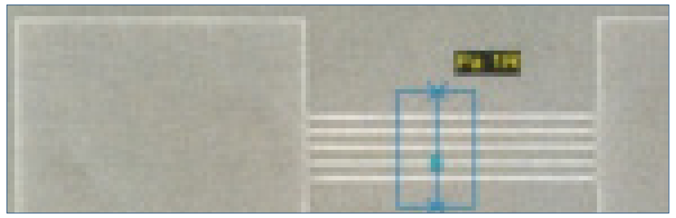
PMMA-Lift-off auf Glas mit Electra 92

Substrate	Glas 25 x 25 mm
Coating AR-P 669.04	4000 rpm; 3 min, 150 °C hot plate
Coating AR-P 679.03	4000 rpm; 3 min, 150 °C hot plate
Coating AR-PC 5090.02	2500 rpm; 5 min, 105 °C hot plate
E-beam irradiation	Raith Pioneer; 30 kV, 75 µC/cm²
Removal Electra 92	2 x 30 s water
Development PMMAs	60 s AR 600-56
Stopping	30 s AR 600-60
Steaming	titanium/gold

Protective Coating Electra 92

Application examples for PMMA Electra 92

Electra 92 with HSQ on quartz

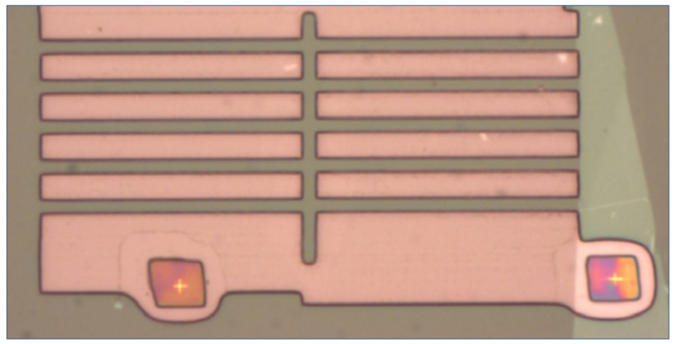


20 nm bars of HSQ, prepared on quartz AR-PC 5090.02

After a coating of Electra 92 on an HSQ resist, even this resist can be patterned on a quartz substrate with very high quality. The HSQ resist (20 nm thickness) was irradiated with the required area dose of 4300 µC/cm².

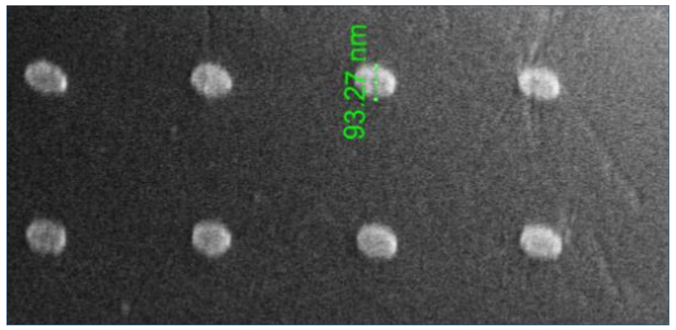
SX AR-PC 5000/90.2 was subsequently completely removed within 2 minutes with warm water and no residues could be detected. After development of the HSQ resist, the structures with high-precision 20 nm bars remained.

Lift-off struktures on garnet



Lift-off structures on garnet (University of California, Riverside, Department of Physics and Astronomy)

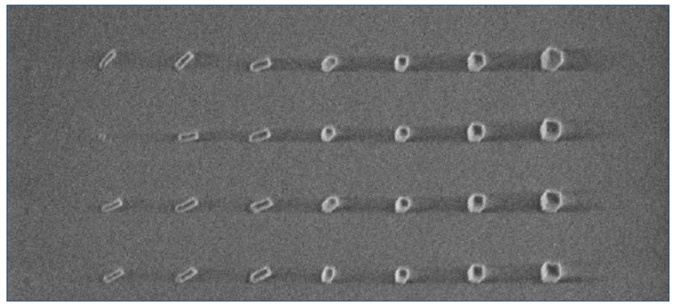
Plasmonic structures on quartz



Silver nanoparticles on quartz, generated with AR-P 672.11 and AR-PC 5090.02 (Aarhus University, Denmark)

Application examples for Novolac Electra 92

Electra 92 and AR-N 7700 on glass

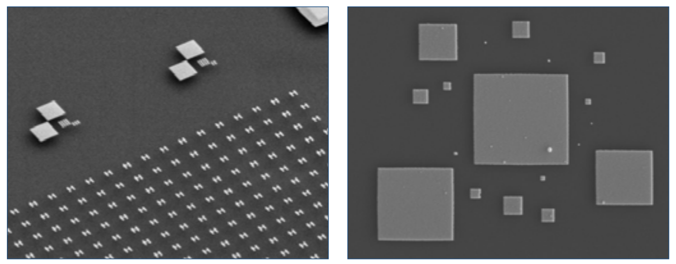


60 – 150 nm squares (100 nm height) on glass with AR-N 7700.08 and AR-P 5091.02

Novolac-based e-beam resists possess other surface properties than CSAR 62 or PMMA. For this reason, AR-PC 5091.02 was designed with a different solvent composition. E-beam resist AR-N 7700.08 was at first spincoated on glass, dried, coated with Electra 92 and baked at 50 °C. After irradiation, the Electra layer was removed within 1 minute with water and the e-beam resist then developed. The resulting resolution of 60 nm is very high for chemically amplified resists.

On highly insulating substrates for SEM applications

Electrostatic surface charges caused by a deflection of the incident electron beam can be extremely disturbing and interfere with a correct imaging. To avoid this effect, e.g. gold is evaporated onto the sample which however also entails disadvantages since some structures change irreversibly due to thermal effects. Studies demonstrated that the conductive coating Electra 92 can be used as alternative. The coating on electrically highly insulating polymers or glass also enables high-quality images of nanostructures in SEM:



SEM images: Highly insulating polymer structures coated with AR-PC 5090.02

After SEM investigation, the conductive coating was completely removed with water, and structures could still be used further.

High-resolution negative resists Medusa 82

Etch-stable e-beam resists SX AR-N 8200

Experimental sample/custom-made product

Characterization

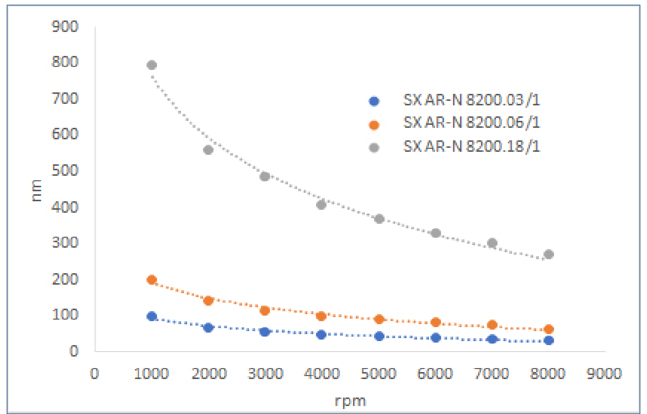
- high-resolution e-beam resist (10 nm)
- etch-stable resist structures available in two film thicknesses
- comparable to HSQ, but higher process stability, easier to remove, considerably higher shelf life
- sensitivity is increased by a factor of 20 if an additional tempering step is applied
- silsesquioxane dissolved in 1-methoxy-2-propanol

Properties I

Parameter SX AR-N	8200.03	8200.06	8200.18
Solids content (%)	3,0	6,0	18,0
Viscosity 25°C (mPas)	2,3	2,5	3,2
Film thickness/4000 rpm (nm)	50	100	400
Resolution (nm)	10	13	20
Contrast	5	5	5
Flash point (°C)	38		
Storage temperature (°C) *	8 - 12		

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

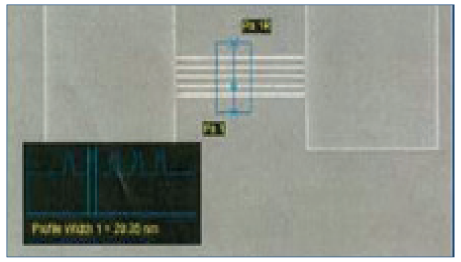
Spin curve



Properties II

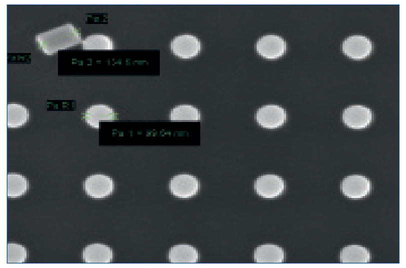
Glass trans. temperature (°C)	-	
Dielectric constant	-	
Cauchy coefficients	N0	1,461
	N1	72
	N2	0
Plasma etching rates (nm/min) (1 Pa, 230 W Bias)	Ar sputtern	
	O_2	6
	CF_4	
	30 CF_4 + 5 O_2	220

Structure resolution



11 nm structures produced with SX AR-N 8200.03/1

Resist structures



100 nm bars with SX AR-N 8200.06/1

Process parameter

Substrate	Si 4" wafer
Softbake	150 °C, 10 min, hot plate
Exposure	Raith Pioneer 30 KV
Development	AR 300-44, 90 s, 23 °C

Process chemicals

Developer	AR 300-44
Thinner	AR 600-07
Stopper	DI water
Remover	2n NaOH, BOE

Innovation
Creativity
Customer-specific solutions

High-resolution negative resists Medusa 82

Process conditions

This diagram shows exemplary process steps for resist SX AR-N 8200. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ "Detailed instructions for optimum processing of photoresists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist photoresists".

Coating	SX AR-N 8200.03 4.000 rpm, 50 nm	SX AR-N 8200.06 4.000 rpm, 100 nm	SX AR-N 8200.18 4.000 rpm, 400 nm
Softbake (± 1 °C)	150 °C, 10 min, hot plate		
E beam exposure	Raith Pioneer, acceleration voltage 30 kV Exposure dose (E0): 1300 µC/cm²		2000 µC/cm²
Hardbake (optional)	To enhance the sensitivity 170 °C, 10 min, hot plate 60 µC/cm²		85 µC/cm²
Development (21-23 °C ± 0,5 °C) Puddle	AR 300-44 90 s		
Rinse	DI water, 30 s		
Customer-specific Technologies	Plasma etching steps		
Removing	2 n NaOH		

<u>Note on stability:</u> Liquid Medusa resists are stable for up to 6 months if kept refrigerated at least 8 - 12 °C. Coated substrates can be stored under normal conditions and processed without any loss of sensitivity or resolution even after several weeks. Current studies show that irradiated substrates can be processed even after 21 days without significant loss of sensitivity.

High sensitive negative resists Medusa 82 UV

Etch-stable, high-resolution e-beam resists SX AR-N 8250

Experimental sample/custom-made product

Characterization

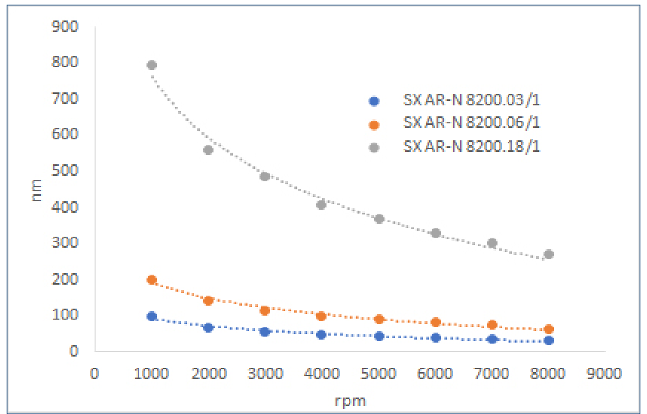
- high-resolution e-beam resist, also sensitive in EUV (13.5 nm) and DUV (250 nm) range
- comparable to HSQ, but with by a factor of 20 higher sensitivity, easier to remove
- considerably higher shelf life
- silsesquioxane and acid generator dissolved in 1-methoxy-2-propanol

Properties I

Parameter SX AR-N	8250.03	8250.06	8250.18
Solids content (%)	3,0	6,0	18,0
Viscosity 25°C (mPas)	2,3	2,5	3,2
Film thickness/4000 rpm (µm)	50	100	400
Resolution (nm)	15	15	20
Contrast	8	8	8
Flash point (°C)	38		
Storage temperature (°C) *	8 - 12		

* Products have a guaranteed shelf life of 6 months from the date of sale if stored correctly and can also be used without guarantee until the date indicated on the label.

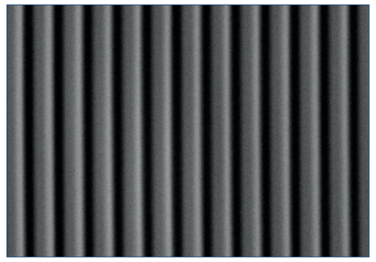
Spin curve



Properties II

Glass trans. temperature (°C)	-	
Dielectric constant	-	
Cauchy coefficients	N0	1,461
	N1	72
	N2	0
Plasma etching rates (nm/min)	Ar sputtern	
(1 Pa, 240-250 V Bias)	O_2	7
	CF_4	
	30 CF_4 + 5 O_2	240

Strukturauflösung



200 nm bars, written at 100 kV with SX AR-N 8200.03/1

Resist structures

Medusa 82 UV structure with higher sensitivity

Process parameter

Substrate	Si 4“ wafer
Softbake	150 °C, 10 min, hot plate
Exposure	Raith Pioneer 30 KV
Development	AR 300-44, 90 s, 23 °C

Process chemicals

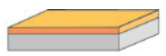
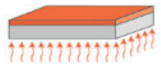
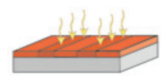
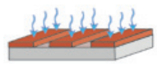
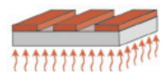
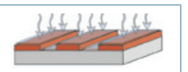
Developer	AR 300-44
Thinner	AR 600-07
Stopper	DI water
Remover	2n NaOH, BOE

ALLRESIST
Innovation
Creativity
Customer-specific solutions

High sensitive negative resists Medusa 82 UV

Process conditions

This diagram shows exemplary process steps for resist SX AR-N 8250. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ “Detailed instructions for optimum processing of photoresists”. For recommendations on waste water treatment and general safety instructions, ☞ ”General product information on Allresist photoresists”.

Coating		SX AR-N 8250.03 4.000 rpm, 50 nm	SX AR-N 8250.06 4.000 rpm, 100 nm	SX AR-N 8250.18 4.000 rpm, 400 nm
Softbake (± 1 °C)		150 °C, 10 min, hot plate		
E beam exposure		Raith Pioneer, acceleration voltage 30 kV Exposure dose (E0): 60 µC/cm²	 85 µC/cm²	
Hardbake (optional)		Hardbake can be omitted since no further sensitivity increase is achieved.		
Development (21-23 °C ± 0,5 °C) Puddle		AR 300-44 90 s		
Rinse		DI-Wasser, 30 s		
Customer-specific Technologies		Plasma etching steps		
Removing		2 n NaOH		

Note on stability: Liquid Medusa resists are stable for up to 6 months if kept refrigerated at 8 - 12 °C. Coated substrates can be stored under normal conditions and processed without any loss of sensitivity or resolution even after several weeks. Current studies show that irradiated substrates can be processed even after 21 days without significant loss of sensitivity.

High-resolution negative resists Medusa 82

Processing instructions

The sensitivity changes in dependence on the acceleration voltage. While 1300 µC/cm² is sufficient at 30 kV, this value increases to 4000 µC/cm² at 100 kV. Figure 1 shows the corresponding dose scale (90 s AR 300-44, 23 °C). Recommended are development times of 60-90 s.

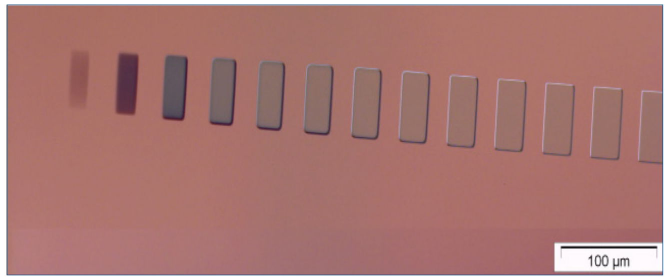


Figure 1: Dose scale (400 – 5000 µC/cm²) Medusa 82. Resist: SX AR-N 8200.06/1 - 100 nm; coating: 60 s 4000 rpm; soft-bake: 15 min @ 120 °C; exposure: Raith Pioneer, 30 kV; development: 90 s AR 300-44; 23 °C; stopping: 30 s DI water

Also AR 300-46, AR 300-47 and AR 300-73 can be used for development, but the different developer concentrations affect the required development time and the dose. AR 300-44 results in a contrast of 4.7 at a required dose of 690 µC/cm², while AR 300-73 results in a contrast of 4.6 at a required dose of 785 µC/cm² under otherwise equal conditions.

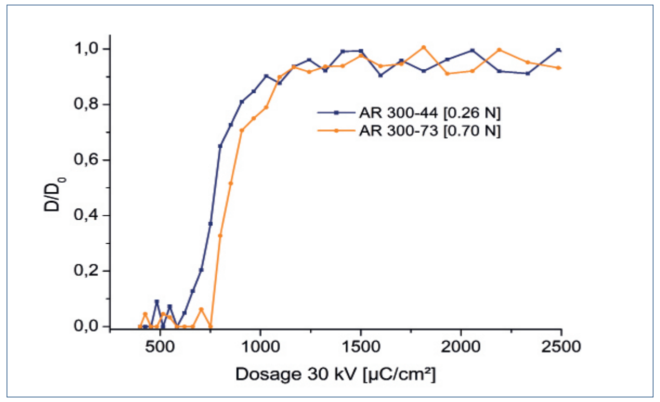


Figure 2: Influence of developer concentration on contrast and dose

To increase sensitivity, a post exposure bake may be required after irradiation, which increases the sensitivity the increases by a factor of 8 at 100 kV and even by a factor of 20 at 30 kV. In addition, also the contrast is increased.

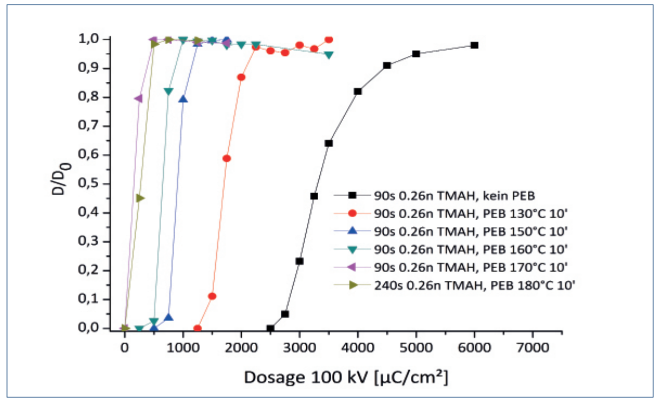


Figure 3: Influence of post exposure bake temperature on the dose. Resist: SX AR-N 8200.06/1; coating: 60 s 4000 rpm; soft-bake: 10 min; exposure: 100 kV; post exposure bake 10 min; development: 90 s AR 300-44; 23°C; stopping: 30 s DI water

High sensitive negative resists Medusa 82 UV

Processing instructions

Medusa 82 and Medusa 82 UV can both be processed under similar conditions (annealing, development, removal), but they differ with respect to their sensitivity. Resist Medusa 82 UV contains a photoacid generator to increase the sensitivity and is already 20 times more sensitive if normal process conditions (without post exposure bake) are used. This is especially important für sensitive substrates which might be damaged by an additional heat treatment. Fig. 4 shows a comparison of both resists at different acceleration voltages without post exposure bake:

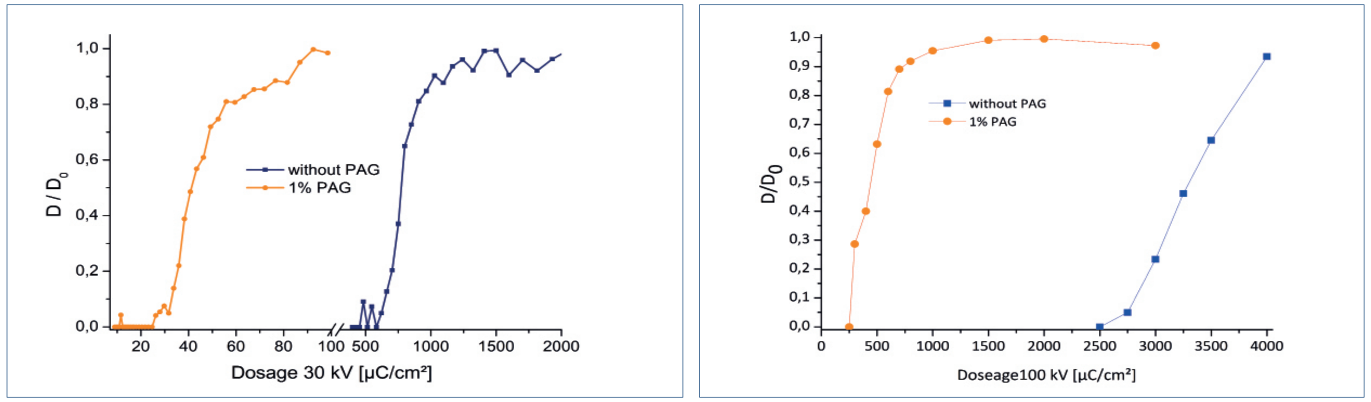


Figure 4: Comparison of the sensitivity of SX AR-N 8200.06/1 (blue) and SX AR-N 8250.06/2 (orange); on the left side at 30 kV, on the right at 100 kV acceleration voltage. Development was performed in AR 300-44, 90 s, 23 °C and without post exposure bake.

For Medusa 82 UV, an additional tempering step after exposure does not result in a further increase in sensitivity:

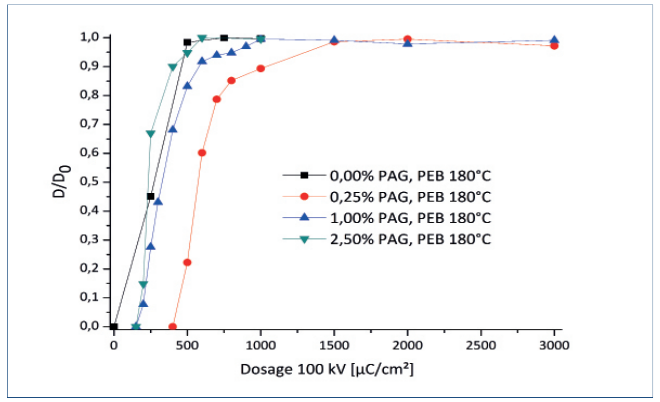


Figure 5: Combination of post exposure bake and photoacid addition

Also AR 300-46, AR 300-47 or AR 300-73 can be used for the development of Medusa 82 UV. The different developer concentrations however influence the required development time and the required dose.

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