



*Innovation
Creativity
Customer-specific solutions*

THE ALLRESIST GMBH

Company for chemical Products

E-Beam Resists

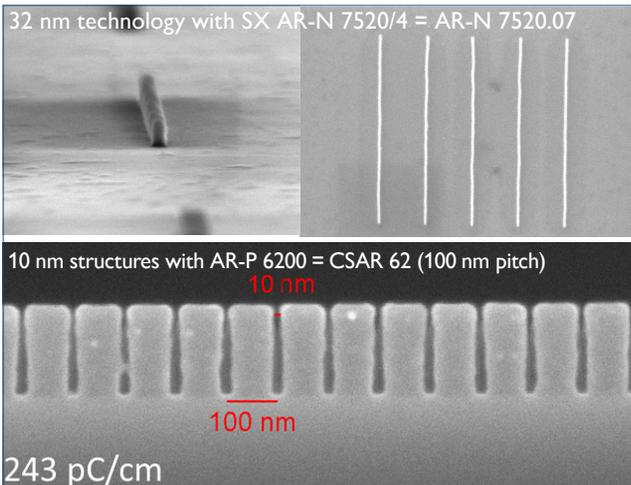


The executive board

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 Team

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 1/4 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.

WWW.ALLRESIST.COM

OUR NEWS

for Microstructuring

2017, 2018

Three further important new developments in principle allow new resist applications: very stable negative resist **Atlas 46 S** (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).

After further optimisation, the ready-to-use spray resists AR-P 1200, AR-N 2200 are in successful use.

The old AR-N 7520 providing a particularly high structural accuracy for very precise edges is offered again after numerous customer requests.

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.

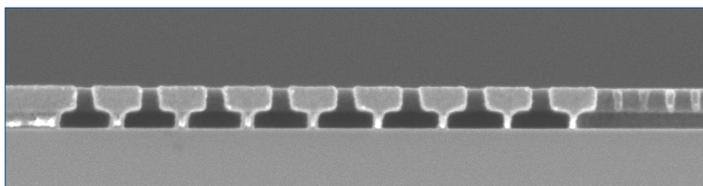
2014, 2015

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 $\mu\text{C}/\text{cm}^2$ 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 $\mu\text{C}/\text{cm}^2$.

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.

In future, **fluorinated polymers** (comparable to Cytop) will be available for organic semiconductors and flexible substrates.



Positive E-Beam Resists AR-P 610 series

E-Beam Resists

AR-P 617 e-beam resists for nanometer lithography

Copolymer resist series for the production of integrated circuits and masks

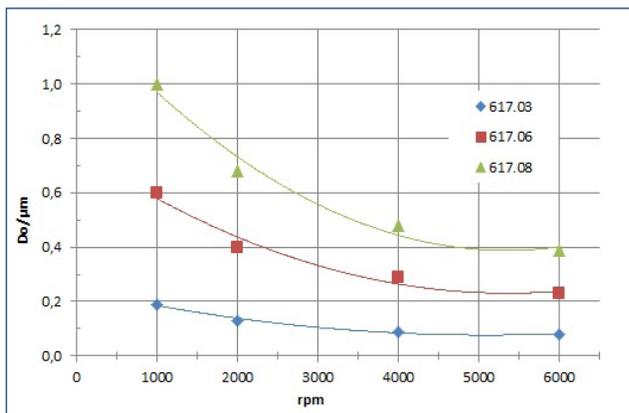
Characterisation

- 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 6 month (°C) | 10 - 22 | | |

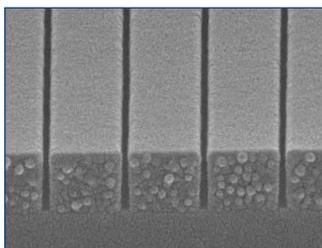
Spin curve



Properties II

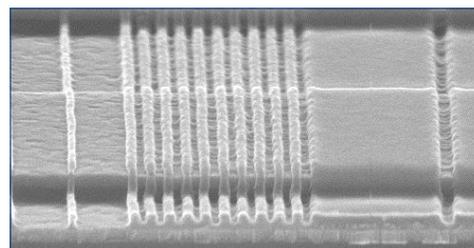
| | | |
|---|---|-------|
| Glass trans. temperature (°C) | 150 | |
| Dielectric constant | 2.6 | |
| Cauchy coefficients | N ₀ | 1.488 |
| | N ₁ | 44.0 |
| | N ₂ | 1.1 |
| Plasma etching rates (nm/min) (5 Pa, 240-250 V Bias) | Ar-sputtering: | 16 |
| | O ₂ | 291 |
| | CF ₄ | 56 |
| | 80 CF ₄ + 16 O 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 |

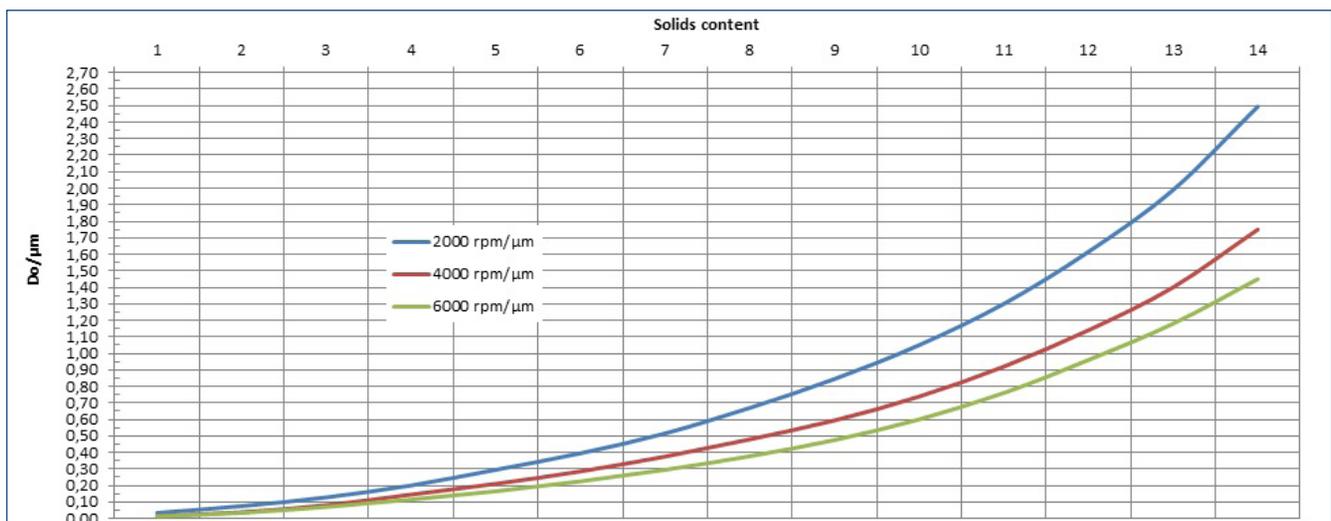
Positive E-Beam Resists AR-P 610 series

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 ($\pm 1\text{ }^{\circ}\text{C}$) | | 200 $^{\circ}\text{C}$, 25 min hot plate or 200 $^{\circ}\text{C}$, 60 min convection oven |
| E-beam exposure | | ZBA 21, 20 kV Exposure dose (E_0): 30 $\mu\text{C}/\text{cm}^2$, 500 nm space & lines |
| Development (21-23 $^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$) puddle | | AR 600-50, 60 s |
| Stopping | | AR 600-60, 30 s |
| Post-bake (optional) | | 130 $^{\circ}\text{C}$, 1 min hot plate or 130 $^{\circ}\text{C}$, 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





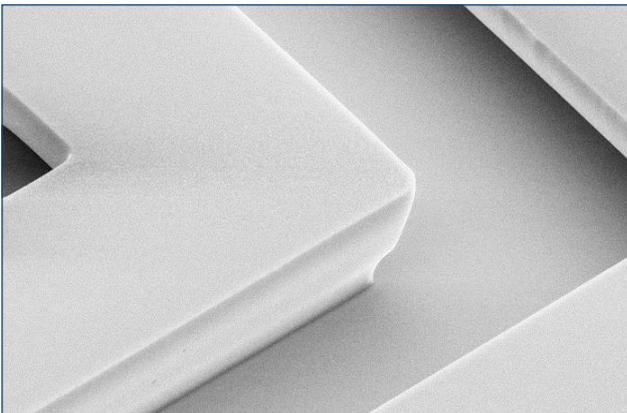
Positive E-Beam Resists AR-P 610 series

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.

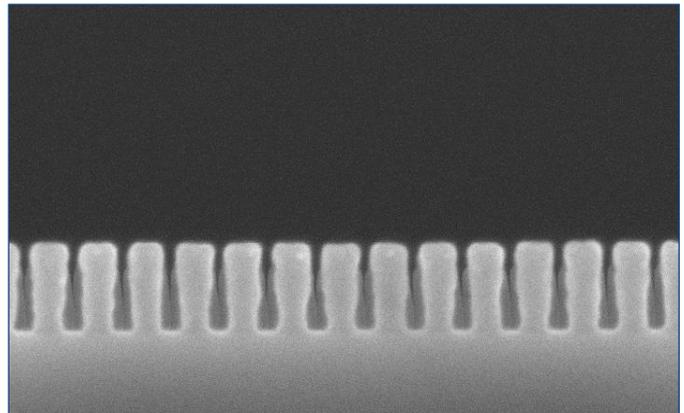
Due to differentiation processes, the lower layer is attacked faster by the developer and pronounced undercut structures are formed (lift-off). These lift-off structures can also be produced with the two-layer system PMMA/copolymer. At first AR-P 617 is coated and tempered at 190 °C, then the PMMA resist 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



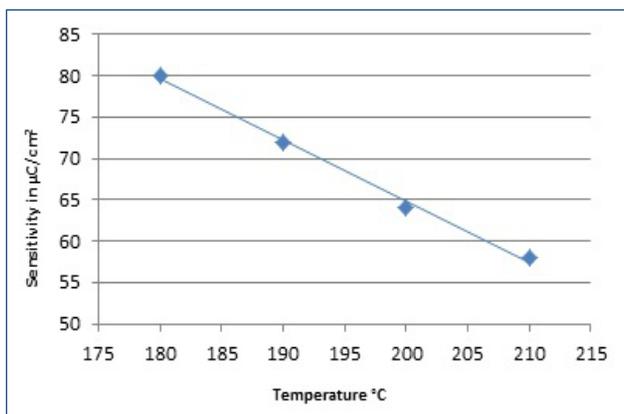
After development with AR 600-50
Bottom: AR-P 617.06, 400 nm thick, tempered at 200 °C
Top: AR-P 617.06, 500 nm thick, tempered at 180 °C

Undercut structure with PMMA/Copolymer



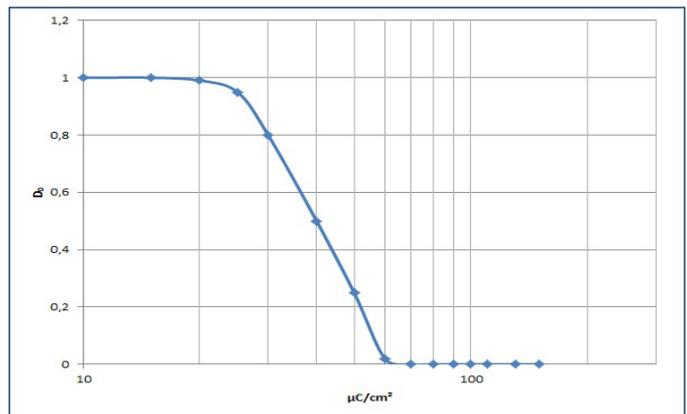
Two-layer system PMMA/copolymer after development
Bottom: AR-P 617.06, 400 nm thick, tempered at 190 °C
Top: AR-P 679.06, 180 nm thick, tempered at 150 °C

Dose vs. softbake temperature for AR-P 617



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

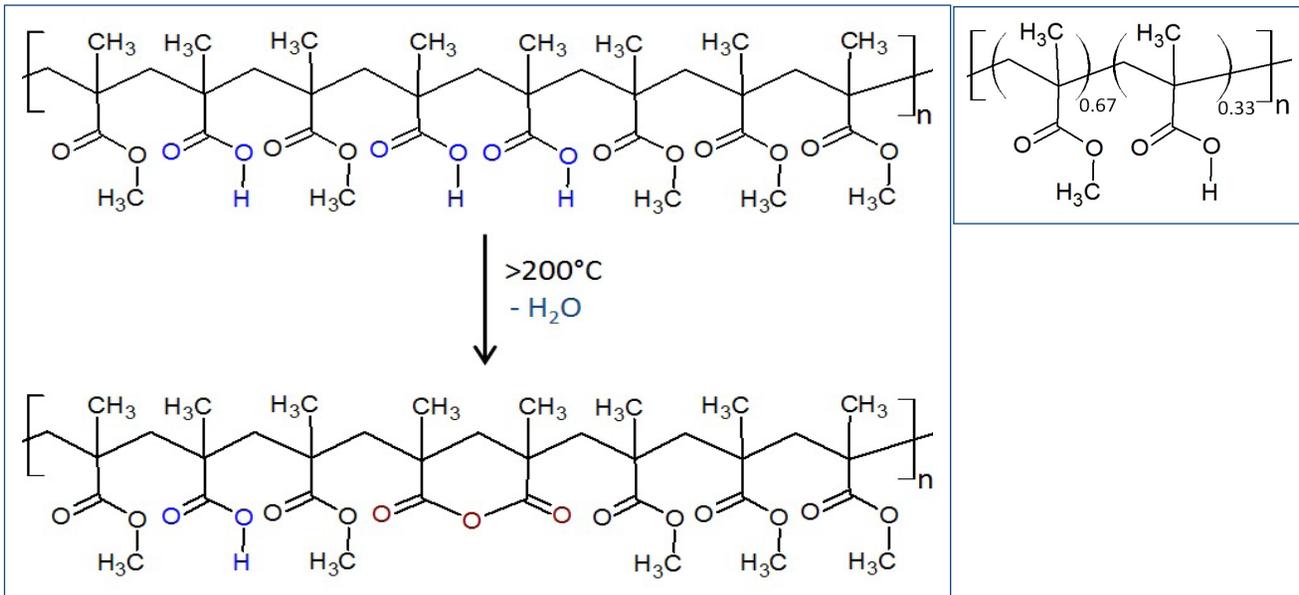
Gradation curve of AR-P 617



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

Positive E-Beam Resists AR-P 610 series

Sensitivity-enhancing reaction during tempering

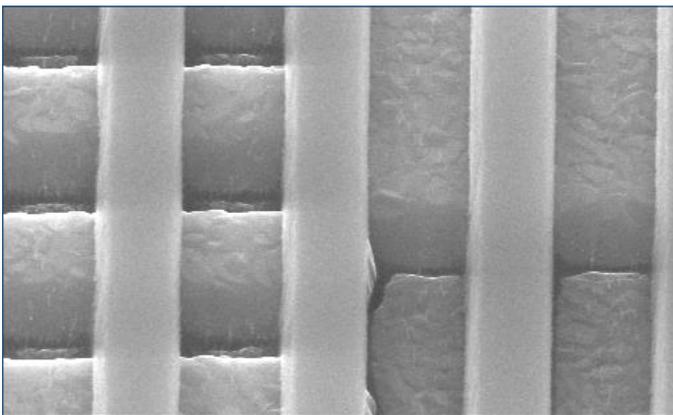


The copolymer composed of methyl methacrylate and methacrylic acid is, in contrast to pure PMMA products, able to form a 6-ring during thermal loading. In this case, 2 methacrylic acid groups have to be arranged adjacent to each other in the polymer chain (see large structural formula left), which statistically 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 it is 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

E-Beam Resists

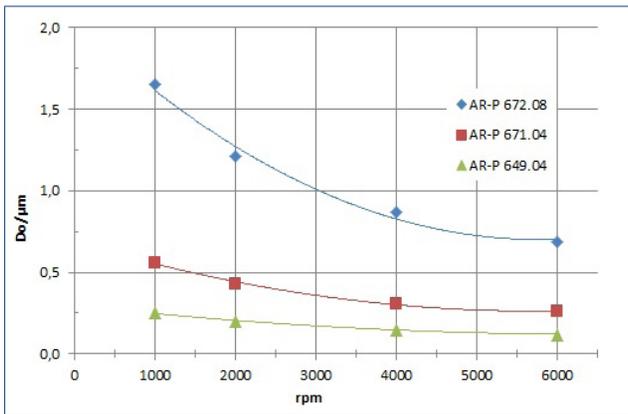
AR-P 631-679 e-beam resists for nanometer lithography

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

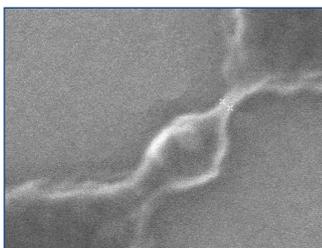
Characterisation

- 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 631-671 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

Spin curve

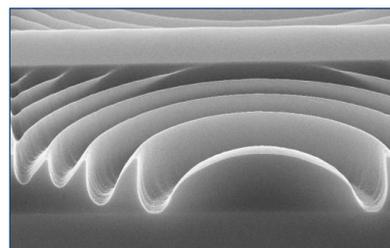


Structure resolution



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 | AR 600-01, -02, -09 |
| Stopper | AR 600-60 |
| Remover | AR 600-71, AR 300-76 |

Properties I

| Parameter / AR-P | 631-639 | 641-649 | 661-669 | 671-679 |
|---|-----------|-----------|-----------|-----------|
| PMMA type | 50K | 200K | 600K | 950K |
| 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 6 month (°C) | 10 - 22 | | | |

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) (5 Pa, 240-250 V Bias) | Ar-sputtering: | 21 |
| | O ₂ | 344 |
| | CF ₄ | 59 |
| | 80 CF ₄ + 16 O ₂ | 164 |

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

Process conditions

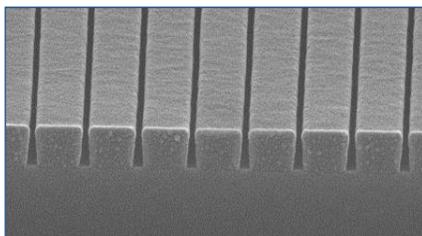
This diagram shows exemplary process steps for resists of the series AR-P 630 - 670. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, "Detailed instructions for optimum processing of e-beam resists". For recommendations 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 ($\pm 1\text{ }^\circ\text{C}$) | | 150 $^\circ\text{C}$, 3 min hot plate or 150 $^\circ\text{C}$, 60 min convection oven | |
| E-beam exposure | | ZBA 21, 20 kV Exposure dose (E_0): 95 $\mu\text{C}/\text{cm}^2$ | Raith Pioneer, 30 kV 770 $\mu\text{C}/\text{cm}^2$ |
| Development (21-23 $^\circ\text{C} \pm 1\text{ }^\circ\text{C}$) puddle | | AR 600-55 1 min | AR 600-56 3 min |
| Stopping | | AR 600-60, 30 s | |
| Post-bake (optional) | | 130 $^\circ\text{C}$, 1 min hot plate or 130 $^\circ\text{C}$, 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 | |

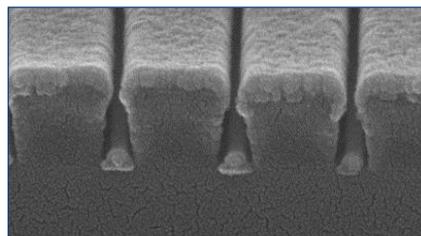
Processing instructions for coating

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 $^\circ\text{C}$.

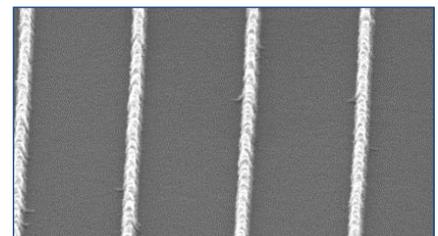
Recommendation: large undercut (low resolution): bottom layer 50K, upper layer 200K, 600K or 950K. High resolution (smaller undercut): bottom layer 600K, upper layer 950K.



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

Specifications of 50K, 200K, 600K and 950 K in chlorobenzene, anisole and ethyl lactate

| PMMA | E-beam resist AR-P | Solids content [%] | Viscosity [mPas] 25°C | Film thickness 1000 rpm [µm] | Film thickness 2000 rpm [µm] | Film thickness 4000 rpm [µm] | Film thickness 6000 rpm [µm] | Density [g/cm ³] 20°C |
|---------------|--------------------|--------------------|-----------------------|------------------------------|------------------------------|------------------------------|------------------------------|-----------------------------------|
| 50K | 631.01 | 1.0 | 0.9 | | 0.02 | 0.02 | 0.01 | 1.104 |
| | 631.04 | 4.0 | 1.3 | 0.02 | 0.13 | 0.09 | 0.08 | 1.107 |
| | 631.06 | 6.0 | 1.9 | | 0.23 | 0.17 | 0.14 | 1.110 |
| | 631.09 | 9.0 | 3.1 | 0.57 | 0.41 | 0.30 | 0.25 | 1.112 |
| | 632.01 | 1.0 | 1.2 | 0.20 | 0.02 | 0.02 | 0.01 | 0.992 |
| | 632.04 | 4.0 | 1.8 | 0.11 | 0.08 | 0.06 | 0.05 | 0.995 |
| | 632.06 | 6.0 | 2.3 | 0.21 | 0.16 | 0.11 | 0.09 | 0.997 |
| | 632.09 | 9.0 | 3.5 | 0.38 | 0.27 | 0.20 | 0.17 | 0.999 |
| | 632.12 | 12.0 | 5.1 | 0.60 | 0.42 | 0.31 | 0.25 | 1.001 |
| | 639.01 | 1.0 | 1.4 | 0.02 | 0.02 | 0.02 | 0.01 | 0.964 |
| 639.04 | 4.0 | 2.2 | 0.16 | 0.12 | 0.08 | 0.07 | 0.970 | |
| 200K | 641.01 | 1.0 | 1.4 | | 0.04 | 0.02 | 0.01 | 1.104 |
| | 641.04 | 4.0 | 4.4 | 0.33 | 0.23 | 0.16 | 0.13 | 1.108 |
| | 641.06 | 6.0 | 7.9 | | 0.38 | 0.28 | 0.26 | 1.110 |
| | 641.07 | 7.0 | 11.0 | 0.71 | 0.52 | 0.37 | 0.31 | 1.110 |
| | 641.09 | 9.0 | 17.4 | 1.13 | 0.83 | 0.59 | 0.48 | 1.112 |
| | 642.01 | 1.0 | 1.9 | 0.03 | 0.02 | 0.02 | 0.01 | 0.992 |
| | 642.03 | 3.0 | 4.8 | 0.13 | 0.09 | 0.07 | 0.05 | 0.994 |
| | 642.04 | 4.0 | 6.8 | 0.21 | 0.15 | 0.11 | 0.08 | 0.996 |
| | 642.06 | 6.0 | 12.8 | 0.41 | 0.29 | 0.21 | 0.17 | 0.997 |
| | 642.07 | 7.0 | 16.5 | 0.53 | 0.37 | 0.27 | 0.22 | 0.998 |
| | 642.09 | 9.0 | 30.3 | 0.85 | 0.59 | 0.41 | 0.35 | 0.999 |
| | 642.12 | 12.0 | 62.3 | 1.51 | 1.08 | 0.78 | 0.63 | 1.002 |
| | 649.01 | 1.0 | 1.9 | | 0.03 | 0.02 | 0.01 | 0.964 |
| 649.04 | 4.0 | 5.8 | 0.25 | 0.20 | 0.15 | 0.12 | 0.970 | |
| 600K | 661.01 | 1.0 | 2.2 | | 0.04 | 0.03 | 0.02 | 1.104 |
| | 661.04 | 4.0 | 13.7 | 0.43 | 0.32 | 0.23 | 0.19 | 1.108 |
| | 661.06 | 6.0 | 28.2 | | 0.67 | 0.48 | 0.39 | 1.110 |
| | 661.08 | 8.0 | 76.0 | | 1.29 | 0.93 | 0.74 | 1.120 |
| | 661.09 | 9.0 | 105 | 2.58 | 1.75 | 1.25 | 1.00 | 1.113 |
| | 662.01 | 1.0 | 2.6 | 0.03 | 0.02 | 0.02 | 0.01 | 0.991 |
| | 662.04 | 4.0 | 12.2 | 0.28 | 0.22 | 0.14 | 0.09 | 0.995 |
| | 662.06 | 6.0 | 31.2 | 0.59 | 0.41 | 0.29 | 0.25 | 0.998 |
| | 662.09 | 9.0 | 82.5 | 1.27 | 0.91 | 0.62 | 0.54 | 1.003 |
| | 662.11 | 11.0 | 158.8 | 2.14 | 1.47 | 1.04 | 0.88 | 1.005 |
| | 669.01 | 1.0 | 2.5 | | 0.03 | 0.02 | 0.02 | 0.965 |
| | 669.04 | 4.0 | 15.6 | 0.46 | 0.31 | 0.22 | 0.18 | 0.970 |
| 669.06 | 6.0 | 68.0 | 0.99 | 0.74 | 0.52 | 0.42 | 0.975 | |
| 669.07 | 7.0 | 128 | 1.66 | 1.07 | 0.74 | 0.60 | 0.978 | |

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

Specifications of 50K, 200K, 600K and 950 K in chlorobenzene, anisole and ethyl lactate

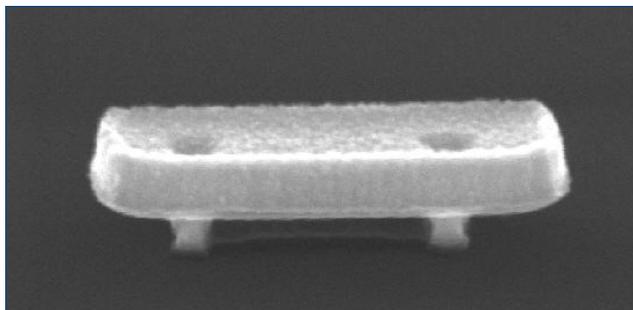
| PMMA | E-beam resist AR-P | Solids content [%] | Viscosity [mPas] 25°C | Film thickness 1000 rpm [µm] | Film thickness 2000 rpm [µm] | Film thickness 4000 rpm [µm] | Film thickness 6000 rpm [µm] | Density [g/cm ³] 20°C |
|------|--------------------|--------------------|-----------------------|------------------------------|------------------------------|------------------------------|------------------------------|-----------------------------------|
| 950K | 671.01 | 1.0 | 3.2 | 0.05 | 0.04 | 0.03 | 0.02 | 1.105 |
| | 671.02 | 2.0 | 7.3 | 0.19 | 0.13 | 0.09 | 0.07 | 1.106 |
| | 671.04 | 4.0 | 23.2 | 0.56 | 0.43 | 0.31 | 0.26 | 1.108 |
| | 671.05 | 5.0 | 57.0 | 0.95 | 0.69 | 0.49 | 0.39 | 1.109 |
| | 671.06 | 6.0 | 86.0 | | 0.97 | 0.68 | 0.54 | 1.110 |
| | 671.07 | 7.0 | 135 | | 1.37 | 0.97 | 0.78 | 1.111 |
| | 671.09 | 9.0 | 285 | 3.70 | 2.40 | 1.70 | 1.34 | 1.113 |
| | 672.01 | 1.0 | 3.8 | 0.05 | 0.04 | 0.03 | 0.02 | 0.998 |
| | 672.02 | 2.0 | 8.8 | 0.12 | 0.09 | 0.07 | 0.06 | 0.991 |
| | 672.03 | 3.0 | 15.5 | 0.22 | 0.17 | 0.13 | 0.10 | 0.994 |
| | 672.045 | 4.5 | 46.2 | 0.41 | 0.32 | 0.23 | 0.19 | 0.998 |
| | 672.05 | 5.0 | 63.1 | 0.65 | 0.45 | 0.32 | 0.26 | 1.000 |
| | 672.06 | 6.0 | 76.2 | 0.83 | 0.63 | 0.45 | 0.36 | 1.001 |
| | 672.08 | 8.0 | 211 | 1.65 | 1.21 | 0.87 | 0.69 | 1.005 |
| | 672.11 | 11.0 | 503 | 3.94 | 2.82 | 1.87 | 1.42 | 1.007 |
| | 679.01 | 1.0 | 3.4 | 0.05 | 0.04 | 0.03 | 0.02 | 0.965 |
| | 679.02 | 2.0 | 7.8 | 0.12 | 0.10 | 0.07 | 0.06 | 0.967 |
| | 679.03 | 3.0 | 16.4 | 0.31 | 0.23 | 0.16 | 0.12 | 0.968 |
| | 679.04 | 4.0 | 43.4 | 0.63 | 0.40 | 0.27 | 0.22 | 0.970 |

chlorobenzene
 anisole
 ethyl lactate

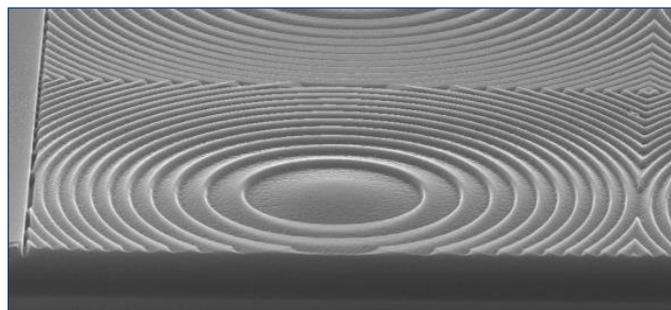
Resist printed in bold are standard variants whose prices are listed in the price list. Further solids contents are possible in amounts from ¼ l onwards and are charged with a surcharge of 10 % in relation to the next higher solids content.

Allresist has significantly extended its anisole and ethyl lactate product range and aims to gradually reduce chlorobenzene resists as of 2014 in agreement with our customers due to health and environmental concerns.

Applications for PMMA resists



Fabrication of a PMMA bridge with AR-P 679.04 by exploiting the limited penetration depth at low acceleration voltage



Fresnel lenses with AR-P 671.09



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

E-Beam Resists

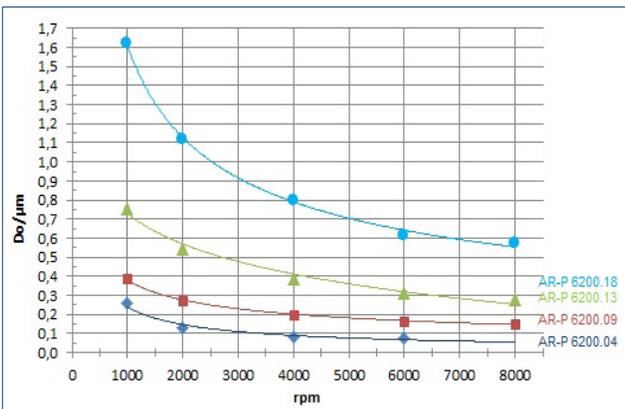
Characterisation

- e-beam; layer thckn. 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 6 month (°C) | 10-22 | | | |

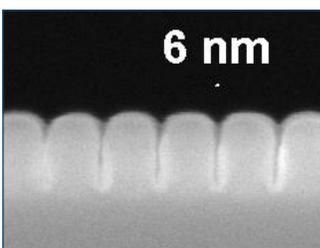
Spin curve



Properties II

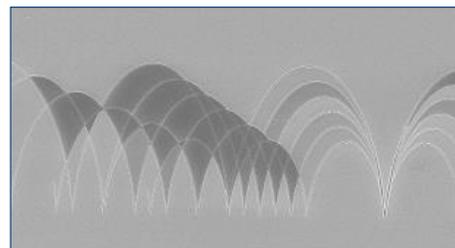
| | | |
|---|---|-------|
| Glass trans. temperature (°C) | 128 | |
| Dielectric constant | 2.8 | |
| Cauchy coefficients | N ₀ | 1.543 |
| | N ₁ | 71.4 |
| | N ₂ | 0 |
| Plasma etching rates (nm/min) (5 Pa, 240-250 V Bias) | Ar-sputtering | 10 |
| | O ₂ | 180 |
| | CF ₄ | 45 |
| | 80 CF ₄ + 16 O ₂ | 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 |

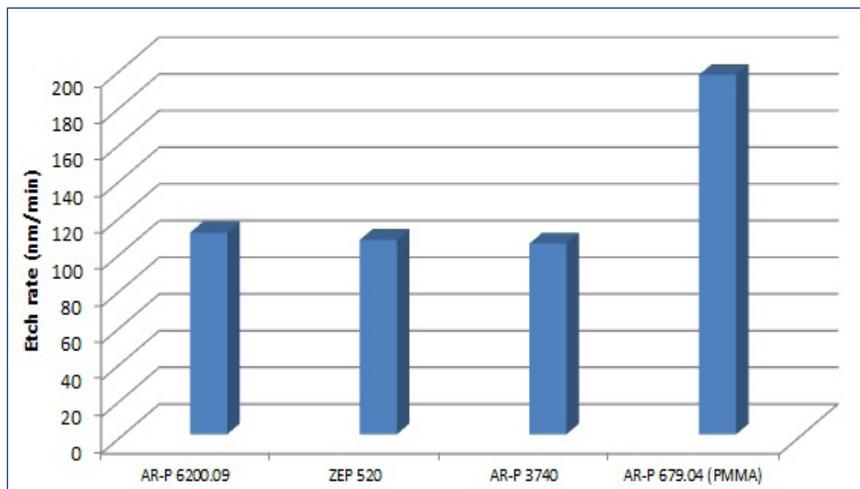
Positive E-Beam Resists AR-P 6200 (CSAR 62)

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 ₂ O, 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 CF₄ + O₂ plasma.



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

E-Beam Resists

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 $\mu\text{C}/\text{cm}^2$ (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.

An additional increase in sensitivity due to addition of sensitivity-enhancing components occurs already during exposure. A post-exposure bake is thus not required.

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

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 $\mu\text{C}/\text{cm}^2$. 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.

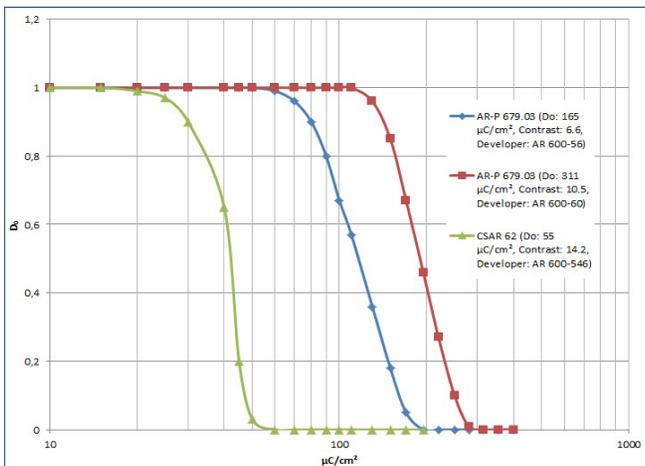
For immersion development, generally development times of 30 - 60 seconds are recommended. If developer AR 600-546 is used, even after 10 minutes at room temperature no erosion of unexposed areas is detected.

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).

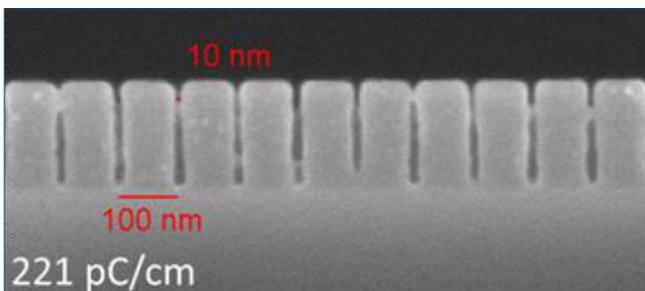
The development procedure should be stopped quickly. For this purpose, the substrate is moved for 30 seconds in stopper AR 600-60. Optionally, the substrate may thereafter be rinsed for 30 seconds with DI water to remove all residual solvent.

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

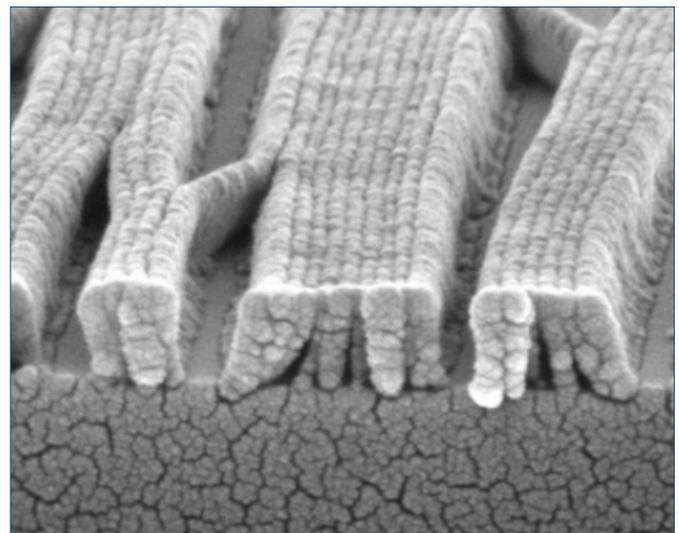
A post-bake for special working steps at max. 130 °C results in a slightly improved etching stability during wet-chemical and plasma-chemical processes.



Comparison D_0 and contrast CSAR 62 and PMMA



Maximum resolution CSAR 62 of 10 nm (180 nm)



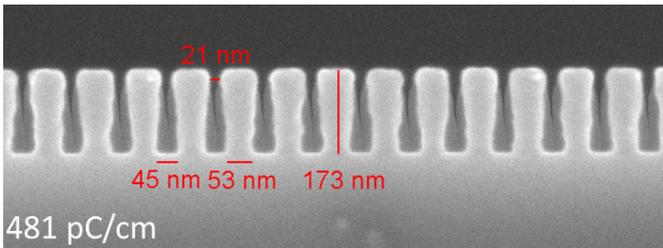
Danger of collapsed lines after too rigid rinsing

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

Processing instructions

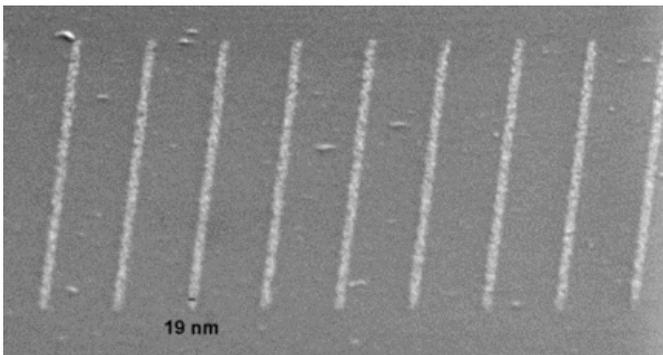
Lift-off structures:

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.

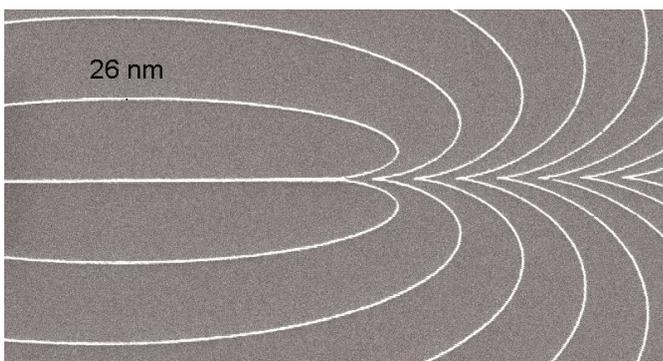


Undercut structures obtained with increased exposure dose

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



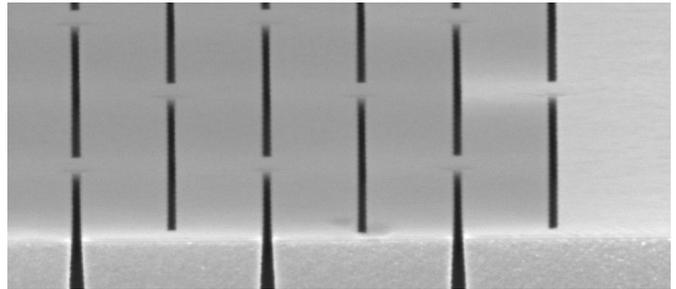
19-nm metal lines after lift-off process with AR-P 6200.09



CrAu test structures with a line width of 26 nm

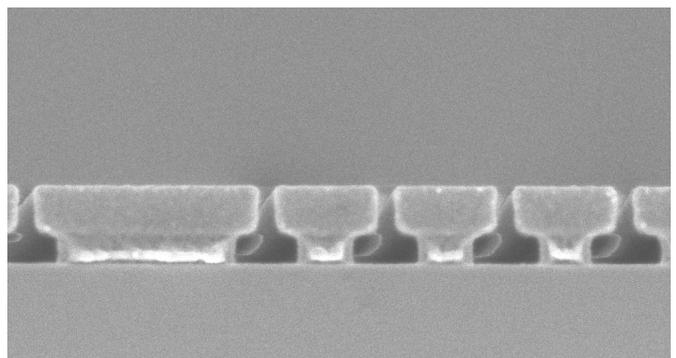
High layers for special applications:

Films with a thickness of up to 800 nm can be produced with AR-P 6200.13, and even 1.5- μm films are possible with experimental sample SX AR-P 6200/10.



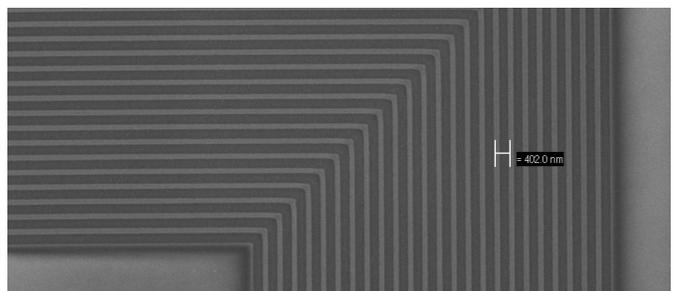
AR-P 6200.13: 100-nm trenches in 830-nm thick layer

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 which are coated with our resist and offered by our partners:



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 $\mu\text{C}/\text{cm}^2$ (20 kV, AR 600-548).

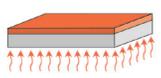
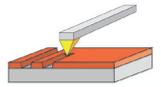
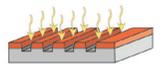
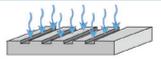


Thermally structurable positive resist AR-P 8100

E-Beam Resists

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 ($\pm 1\text{ }^\circ\text{C}$) |  | 90 °C, 3 min hot plate or 90 °C, 20 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.

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 ($\pm 1\text{ }^{\circ}\text{C}$) | | 200 $^{\circ}\text{C}$, 20 min hot plate or 200 $^{\circ}\text{C}$, 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 ($\pm 1\text{ }^{\circ}\text{C}$) | | 90 $^{\circ}\text{C}$, 3 min hot plate or 90 $^{\circ}\text{C}$, 20 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

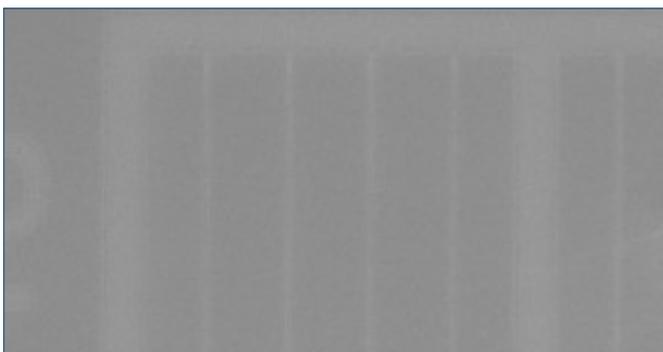
E-Beam Resists

Application examples

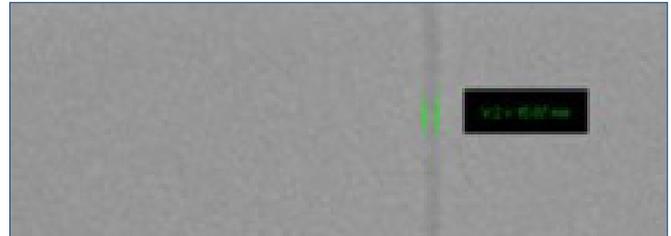
Patterning of PPA with e-beam lithography

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 $\mu\text{C}/\text{cm}^2$), 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.

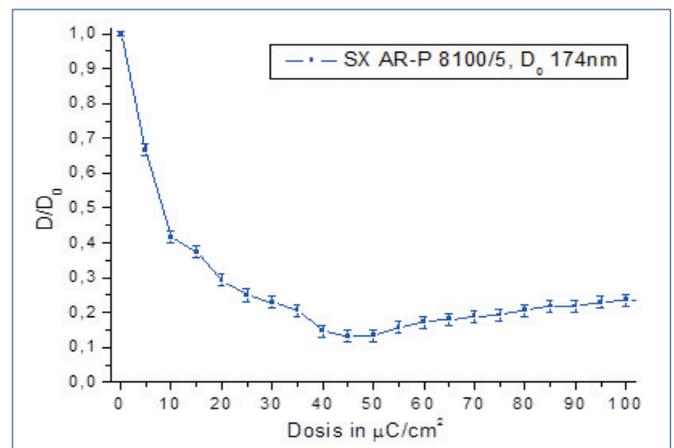


Lines written in PPA (resist AR-P 8100)



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.

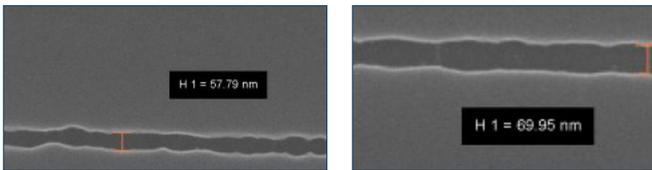


Gradation of SX AR-P 8100/5 after PEB at 98 °C

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

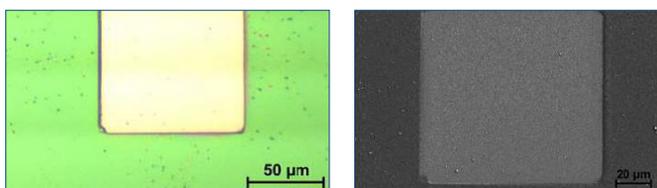
PPA layers can also be structured directly by means of photolithography. Irradiation with UV-light of a wavelength of < 300 nm results in a cleavage of the polymer chains to form volatile components.

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.

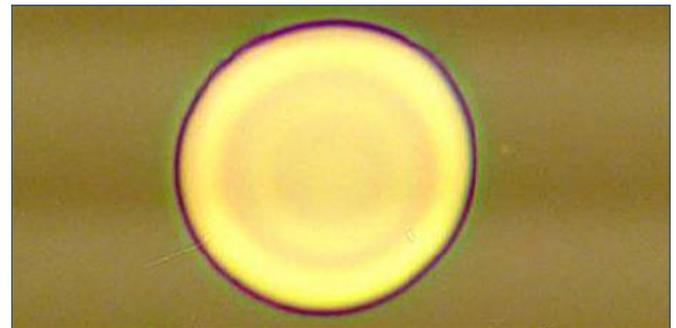
Structuring with laser (pulse)

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.



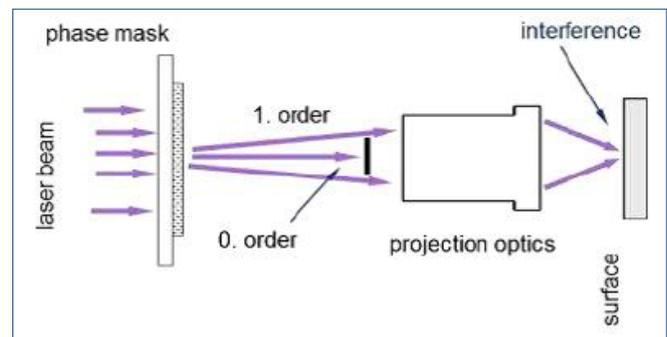
0.5 J/cm² 248 nm, 20 ns, double pulse exposure, 700 nm PPA on Si-wafer

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.

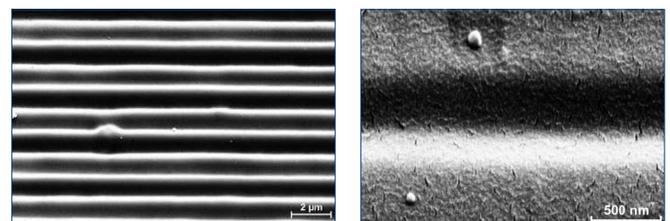


0.1 J/cm² 355 nm ps-laser, single-pulse exposure, 700 nm PPA on Si-wafer

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 7520

E-Beam Resists

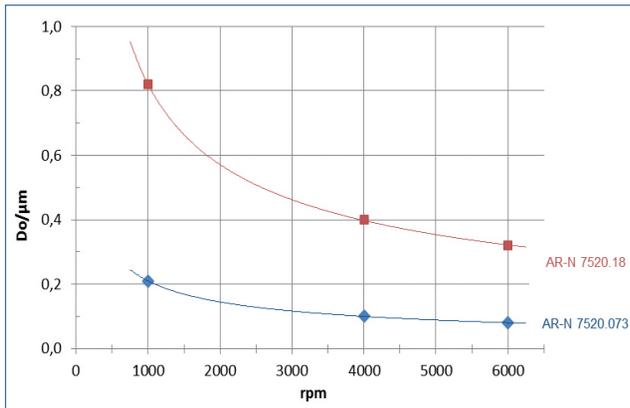
AR-N 7520 e-beam resists for mix & match

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

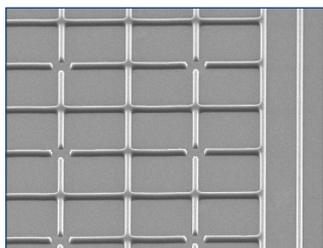
Characterisation

- 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

Spin curve



Structure resolution



400 nm lines with AR-N 7520.073

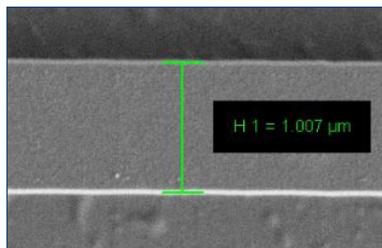
Properties I

| 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 6 month (°C) | 10 - 18 | |

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) (5 Pa, 240-250 V Bias) | Ar-sputtering | 8 |
| | O ₂ | 169 |
| | CF ₄ | 41 |
| | 80 CF ₄ + 16 O ₂ | 90 |

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".

| | | | |
|--|--|--|--|
| Coating | | AR-N 7520.18 4000 rpm, 60 s, 0.4 µm | AR-N 7520.073 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/cm ² 300 µC/cm ² | |
| Development (21-23 °C ± 0,5 °C) puddle Rinse | | AR 300-47, 4 : 1 90 s | AR 300-47, 4 : 1 50 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.



Protective Coating PMMA Electra 92 (AR-PC 5090)

E-Beam Resists

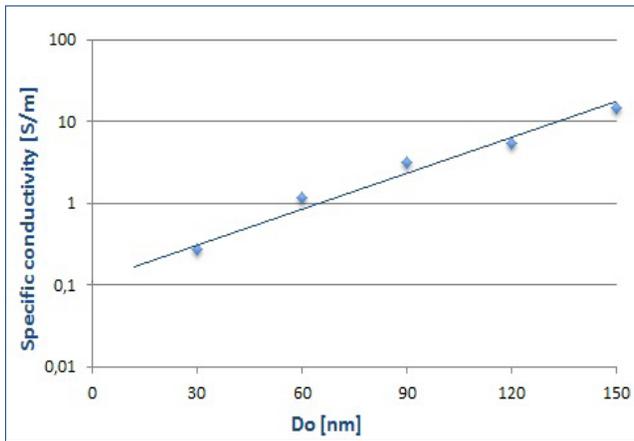
Conductive protective coating for non-novolak-based e-beam resists

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

Conductivity



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

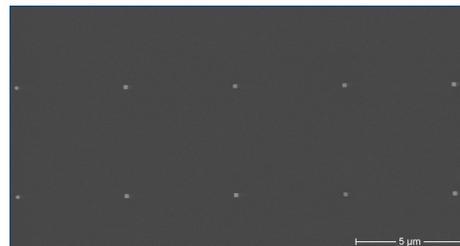
Properties I

| 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 6 month (°C) | 8 - 12 |

Properties II

| | | |
|---|---|-----|
| Conductivity in layer 60 nm (S/m) | 1.2 | |
| Cauchy-Koeffizienten | N ₀ | - |
| | N ₁ | - |
| | N ₂ | - |
| Plasma etching rates (nm/min) (5 Pa. 240-250 V Bias) | Ar-sputtering | - |
| | 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 |

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 ($\pm 1\text{ }^{\circ}\text{C}$) | | 150 $^{\circ}\text{C}$, 2 min hot plate or 150 $^{\circ}\text{C}$, 30 min convection oven |
| 2. Coating | | AR-PC 5090.02 2000 rpm, 60 s, 60 nm |
| 2. Tempering ($\pm 1\text{ }^{\circ}\text{C}$) | | 90 $^{\circ}\text{C}$, 2 min hot plate or 85 $^{\circ}\text{C}$, 25 min convection oven |
| E-beam exposure | | ZBA 21, 20 kV Exposure dose (E_0): 110 $\mu\text{C}/\text{cm}^2$ (AR-P 662.04, 140 nm) |
| Removal | | AR-PC 5090.02 DI-water, 60 s |
| Development (21-23 $^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$) puddle | | AR-P 662.04 AR 600-56, 2 min |
| Stop | | AR 600-60, 30 s |
| Post-bake (optional) | | 130 $^{\circ}\text{C}$, 1 min hot plate or 130 $^{\circ}\text{C}$, 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.



Protective Coating Novolac Electra 92 (AR-PC 5091)

E-Beam Resists

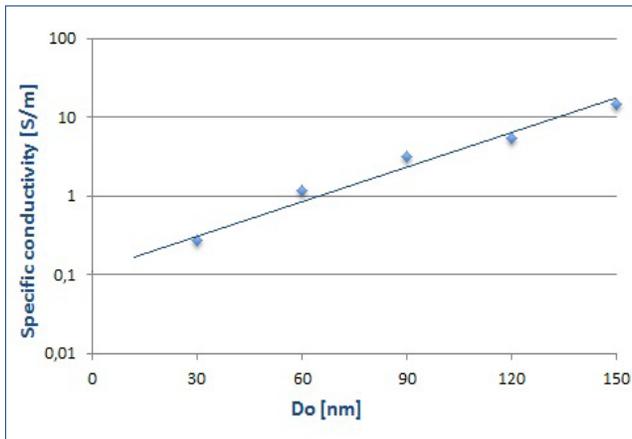
Conductive protective coating for novolac-based e-beam resists

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

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".

Process parameters

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

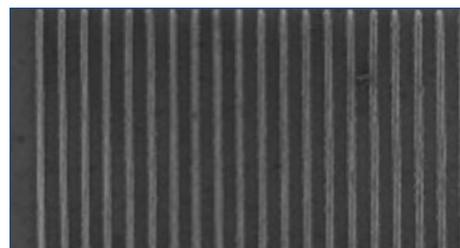
Properties I

| | |
|------------------------------|---------|
| 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 6 month (°C) | 8 - 12 |

Properties II

| | | |
|---|---|-----|
| Conductivity in layer 60 nm (S/m) | 1.2 | |
| Cauchy-Koeffizienten | N ₀ | - |
| | N ₁ | - |
| | N ₂ | - |
| Plasma etching rates (nm/min) (5 Pa. 240-250 V Bias) | Ar-sputtering | - |
| | 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 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 ($\pm 1\text{ }^{\circ}\text{C}$) | | 85 $^{\circ}\text{C}$, 2 min hot plate or 85 $^{\circ}\text{C}$, 30 min convection oven |
| 2. Coating | | SX AR-PC 5000/91.2 2000 rpm, 50 s, 50 nm |
| 2. Soft bake ($\pm 1\text{ }^{\circ}\text{C}$) | | 50 $^{\circ}\text{C}$, 2 min hot plate or 45 $^{\circ}\text{C}$, 25 min convection oven |
| E-beam exposure | | Raith Pioneer, acceleration voltage 30 kV Exposure dose (E_0): 30 $\mu\text{C}/\text{cm}^2$, 100 nm spaces & lines |
| Removal optional | | AR-PC 5091.02 (The removal step can also be carried out simultaneously with the subsequent development step.) DI-H ₂ O, 60 s |
| Development (21-23 $^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$) puddle Rinse | | AR-N 7520.07 new AR 300-47, 50 s DI-H ₂ O, 30 s |
| Post-bake (optional) | | 85 $^{\circ}\text{C}$, 1 min hot plate or 85 $^{\circ}\text{C}$, 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.

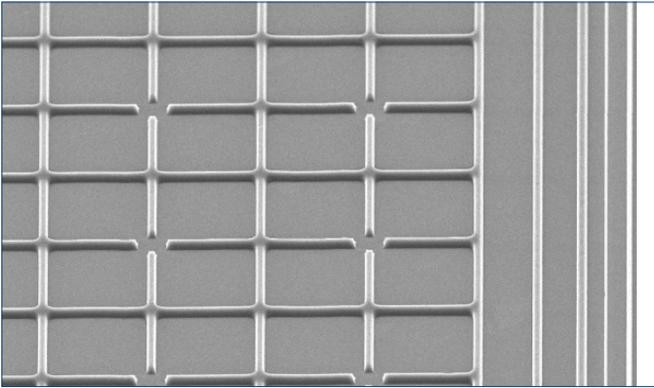


Protective Coating Electra 92

E-Beam Resists

Application examples for PMMA-Electra 92

Shelf live of Electra 92

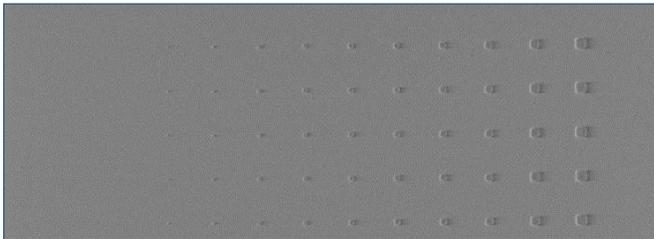


Conductivity properties of differently aged Electra 92 batches

The conductivity was determined as a function of the measured temperature. At temperatures < 100 °C, both resists show a virtually identical conductivity. Electra 92 is thus characterised by a very long shelf life. 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.

30 – 150 nm squares of CSAR 62 on glass

CSAR 62 on glass with Electra 92 for deriving



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.

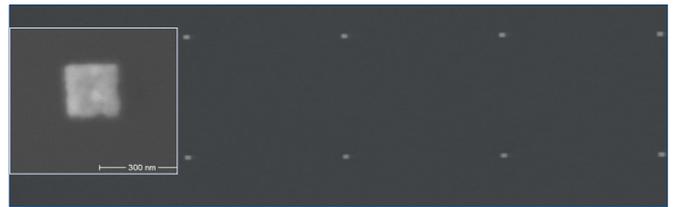
CSAR 62 and Electra 92 on glass

| | |
|------------------------|---|
| 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/cm ² |
| 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.

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

PMMA Lift-off on glass with Electra 92



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.

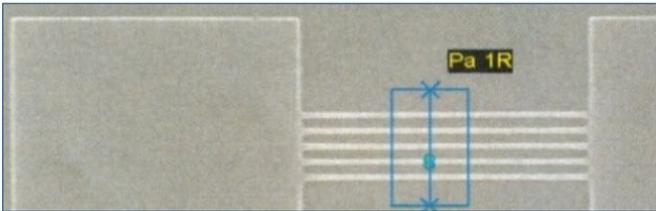
PMMA-Lift-off auf Glas mit Electra 92

| | |
|-----------------------|---|
| 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/cm ² |
| 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

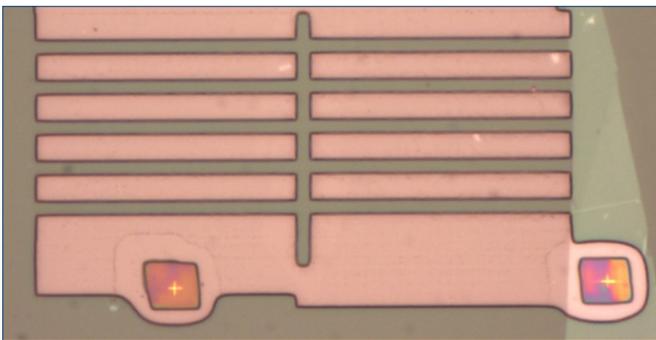


20 nm bars of HSQ, prepared on quartz AR-PC 5090.02

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 $4300 \mu\text{C}/\text{cm}^2$.

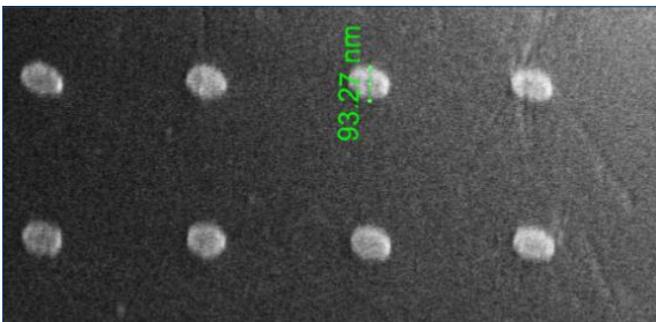
SX AR-PC 5000/90.2 was subsequently completely removed within 2 minutes with warm water and no residues could be detected. After development of the HSQ resist, the structures with high-precision 20 nm bars remained.

Lift-off structures on garnet



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

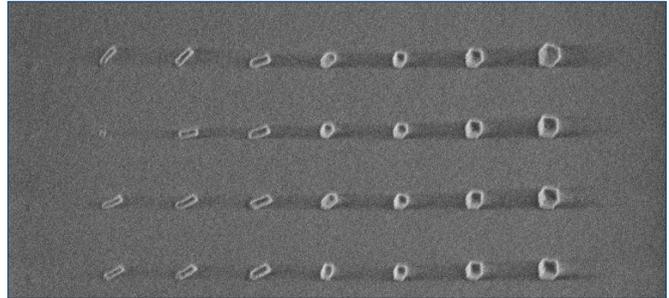
Plasmonic structures on quartz



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

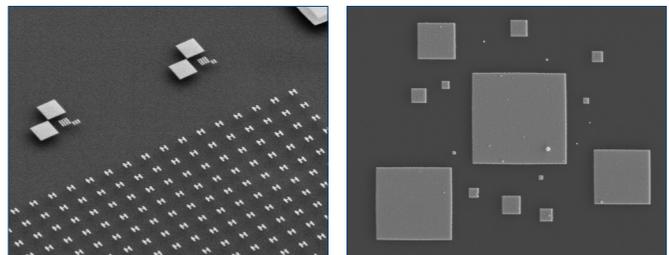


60 – 150 nm squares (100 nm height) on glass with AR-N 7700.08 and AR-P 5091.02

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

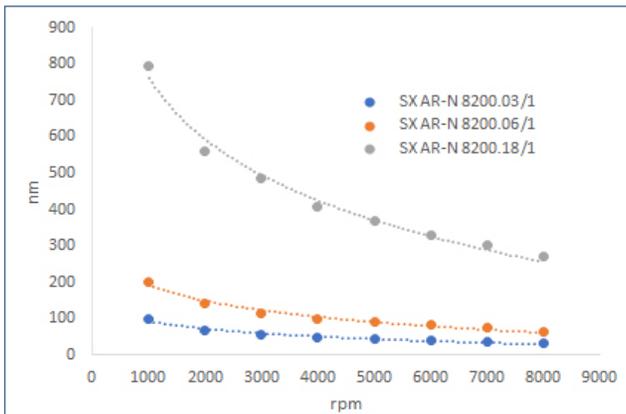
Etch-stable e-beam resists SX AR-N 8200/1

Experimental sample/custom-made product

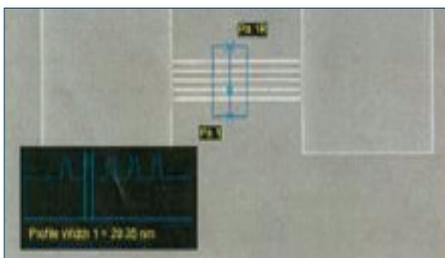
Characterization

- 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

Spin curve



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 |

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 (µm) | | 50 | 100 | 400 |
| Resolution (nm) | | 10 | 13 | 20 |
| Contrast | | 5 | 5 | 5 |
| Flash point (°C) | | 38 | | |
| Storage 6 month (°C) | | 8 - 12 | | |

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 |

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 ($\pm 1\text{ }^{\circ}\text{C}$) | | 150 $^{\circ}\text{C}$, 10 min, hot plate | | |
| E beam exposure | | Raith Pioneer, acceleration voltage 30 kV Exposure dose (E0): 1300 $\mu\text{C}/\text{cm}^2$ | | 2000 $\mu\text{C}/\text{cm}^2$ |
| Hardbake (optional) | | To enhance the sensitivity 170 $^{\circ}\text{C}$, 10 min, hot plate 60 $\mu\text{C}/\text{cm}^2$ | | 85 $\mu\text{C}/\text{cm}^2$ |
| Development (21-23 $^{\circ}\text{C} \pm 0,5\text{ }^{\circ}\text{C}$) Puddle Rinse | | AR 300-44 90 s DI water, 30 s | | |
| Customer-specific Technologies | | | | |
| Removing | | 2 n NaOH | | |

Note on stability: Liquid Medusa resists are stable for up to 6 months if kept refrigerated at least 8 - 12 $^{\circ}\text{C}$. 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

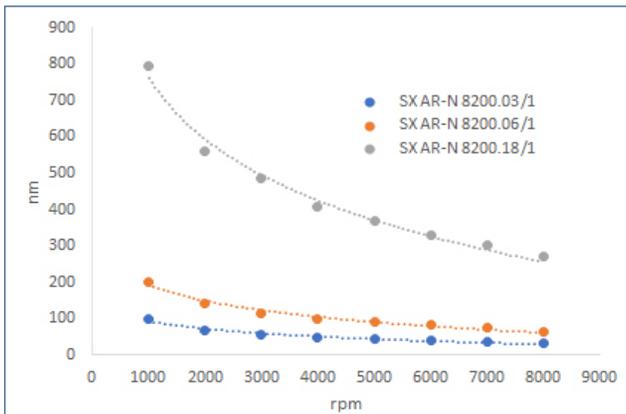
Etch-stable, high-resolution e-beam resists SX AR-N 8250/1

Experimental sample/custom-made product

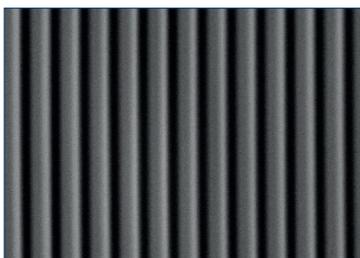
Characterization

- 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

Spin curve



Strukturauflösung



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

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 6 month (°C) | | 8 - 12 | | |

Properties II

| | | |
|---|--|-------|
| Glass trans. temperature (°C) | | |
| Dielectric constant | | |
| Cauchy coefficients | N0 | 1,461 |
| | N1 | 72 |
| | N2 | 0 |
| Plasma etching rates (nm/min) (1 Pa, 240-250 V Bias) | Ar sputter | |
| | O ₂ | 7 |
| | CF ₄ | |
| | 30 CF ₄ + 5 O ₂ | 240 |

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 |

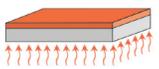
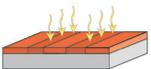
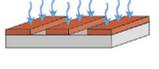
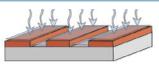
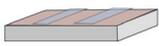
Process chemicals

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

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 ($\pm 1\text{ }^{\circ}\text{C}$) |  | 150 $^{\circ}\text{C}$, 10 min, hot plate | | |
| E beam exposure |  | Raith Pioneer, acceleration voltage 30 kV Exposure dose (E0): 60 $\mu\text{C}/\text{cm}^2$ | | 85 $\mu\text{C}/\text{cm}^2$ |
| Hardbake (optional) |  | Hardbake can be omitted since no further sensitivity increase is achieved. | | |
| Development (21-23 $^{\circ}\text{C} \pm 0,5\text{ }^{\circ}\text{C}$) Puddle |  | AR 300-44 90 s | | |
| Rinse | | DI-Wasser, 30 s | | |
| Customer-specific Technologies |  | | | |
| Removing |  | 2 n NaOH | | |

Note on stability: Liquid Medusa resists are stable for up to 6 months if kept refrigerated at 8 - 12 $^{\circ}\text{C}$. 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 $1300 \mu\text{C}/\text{cm}^2$ is sufficient at 30 kV, this value increases to $4000 \mu\text{C}/\text{cm}^2$ 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.

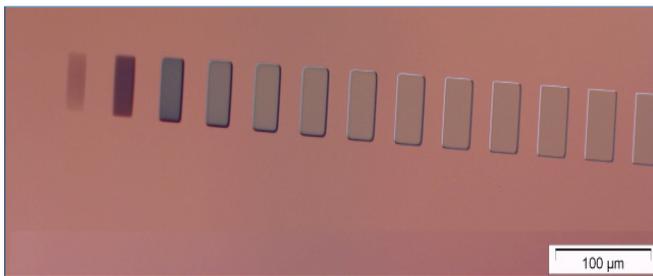


Figure 1: Dose scale ($400 - 5000 \mu\text{C}/\text{cm}^2$) Medusa 82. Resist: SX AR-N 8200.06/1 - 100 nm; coating: 60 s 4000 rpm; soft-bake: 15 min @ 120 °C; exposure: Raith Pioneer, 30 kV; development: 90 s AR 300-44; 23 °C; stopping: 30 s DI water

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 $690 \mu\text{C}/\text{cm}^2$, while AR 300-73 results in a contrast of 4.6 at a required dose of $785 \mu\text{C}/\text{cm}^2$ under otherwise equal conditions.

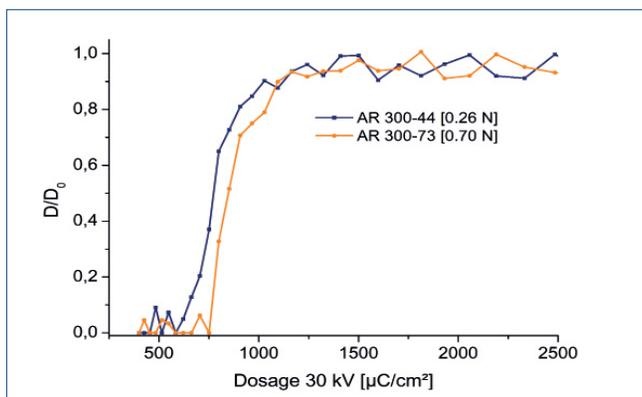


Figure 2: Influence of developer concentration on contrast and dose

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.

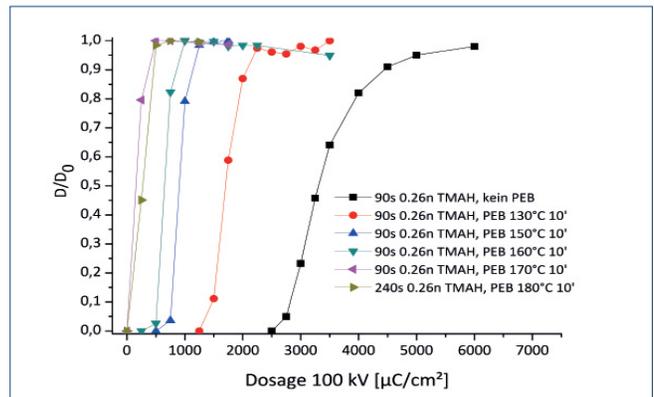


Figure 3: Influence of post exposure bake temperature on the dose. Resist: SX AR-N 8200.06/1; coating: 60 s 4000 rpm; soft-bake: 10 min; exposure: 100 kV; post exposure bake 10 min; development: 90 s AR 300-44; 23 °C; stopping: 30 s DI water

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:

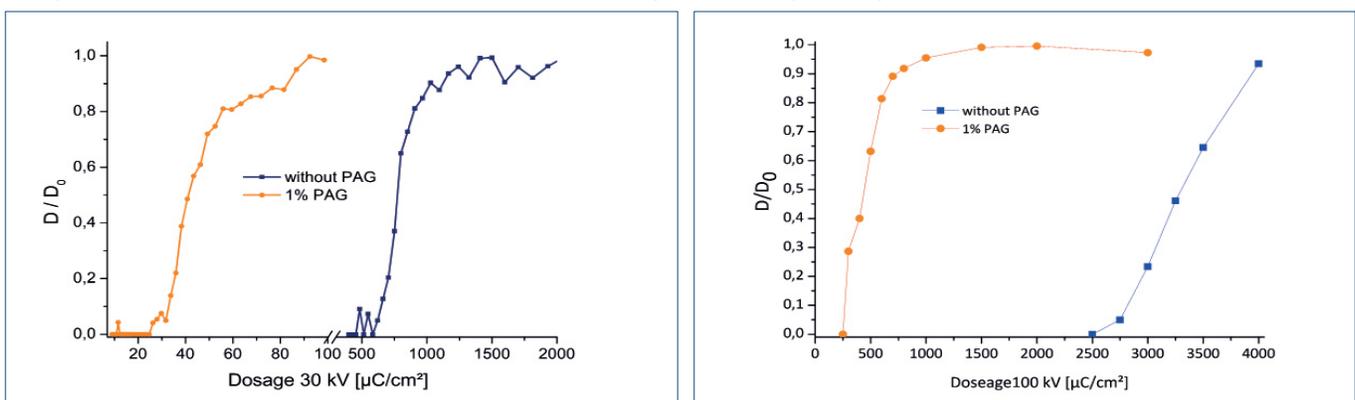


Figure 4: Comparison of the sensitivity of SX AR-N 8200.06/1 (blue) and SX AR-N 8250.06/2 (orange); on the left side at 30 kV, on the right at 100 kV acceleration voltage. Development was performed in AR 300-44, 90 s, 23 °C and without post exposure bake.

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

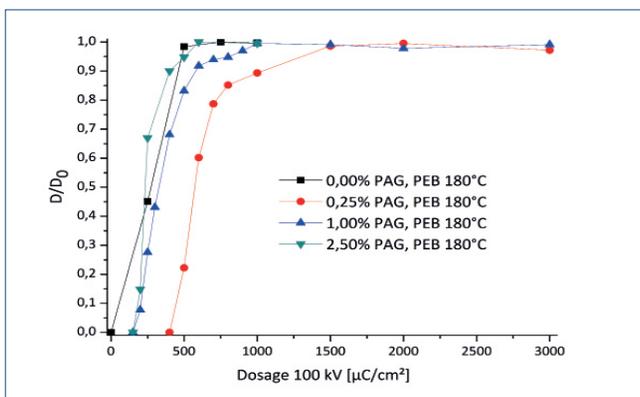


Figure 5: Combination of post exposure bake and photoacid addition

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.