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# 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

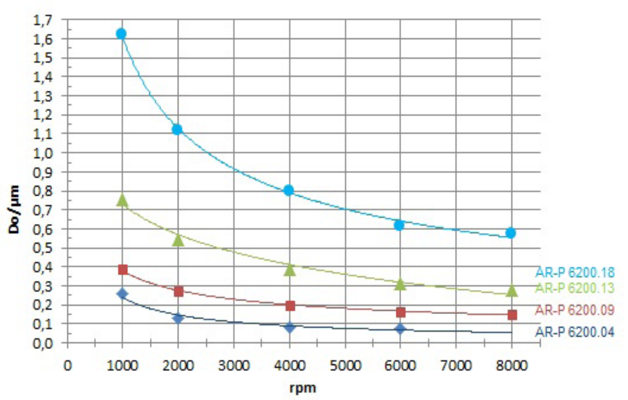
### Characterisation

- 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 methyl ester) and an enhancer of sensitivity
- 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) | 8 - 12 | | | |

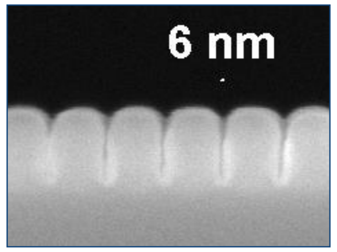
### Spin curve




### Properties II

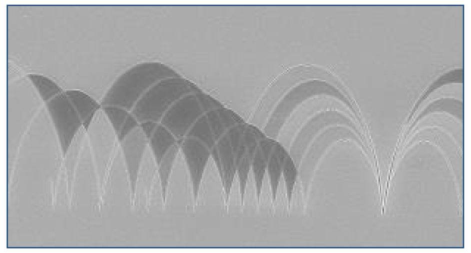
| | | |
|---|---|---|
| Glass trans. temperature (°C) | 128 | |
| Dielectric constant | 2.8 | |
| Cauchy coefficients | $N_0$ | 1.543 |
| | $N_1$ | 71.4 |
| | $N_2$ | 0 |
| Plasma etching rates (nm/min) | Ar-sputtering | 10 |
| (5 Pa, 240-250 V Bias) | $O_2$ | 180 |
| | $CF_4$ | 45 |
| | 80 $CF_4$ + 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 |
| Tempering | 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 |
| Developer | AR 600-546, 600-549 |
| Thinner | AR 600-02 |
| Stopper | AR 600-60 |
| Remover | AR 600-71, 300-76 |

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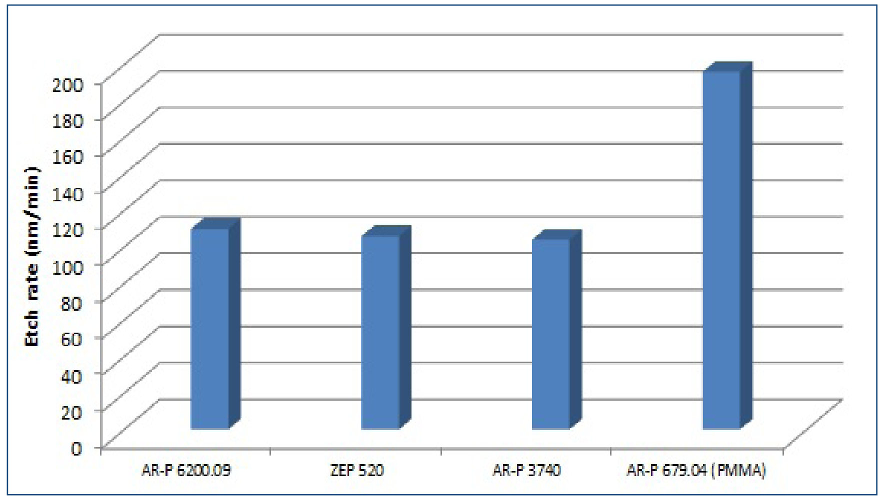
## Process conditions

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<br>4000 rpm, 60 s<br>0.2 µm |
| Tempering (± 1 °C) | 150 °C, 1 min hot plate or<br>150 °C, 30 min convection oven |
| E-beam exposure | Raith Pioneer, 30 kV<br>Exposure dose ($E_0$): 65 µC/cm² |
| Development (21-23 °C ± 0,5 °C) puddle | AR 600-546<br>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.

As of January 2014

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

## Processing instructions

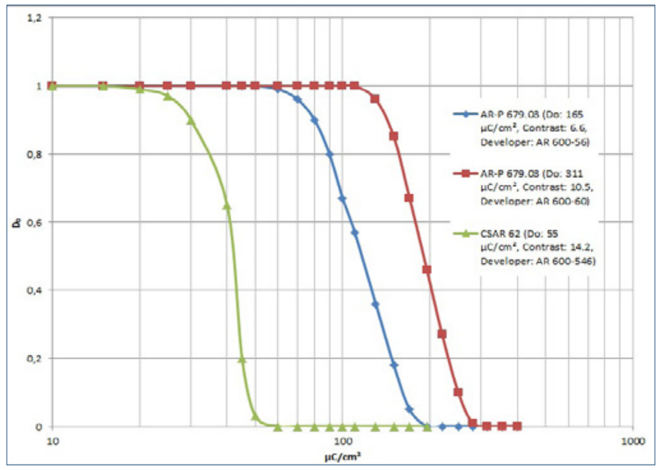
E-beam exposure: The required e-beam exposure dose for structural imaging mainly depends on the desired minimum structure size, the developer, the acceleration voltage (1 - 100 kV), and the film thickness.

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.

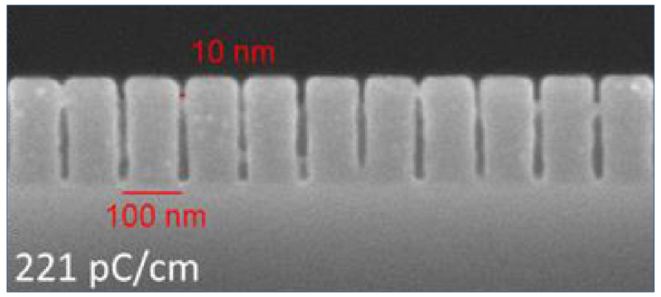
CSAR 62 is thus 3x more sensitive as compared to the standard PMMA resist AR-P 679.03 (developed in AR 600-56), or 6x more sensitive if developed in AR 600-60. Also the contrast is higher by a factor of 2 and 1.4, respectively.

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, 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.

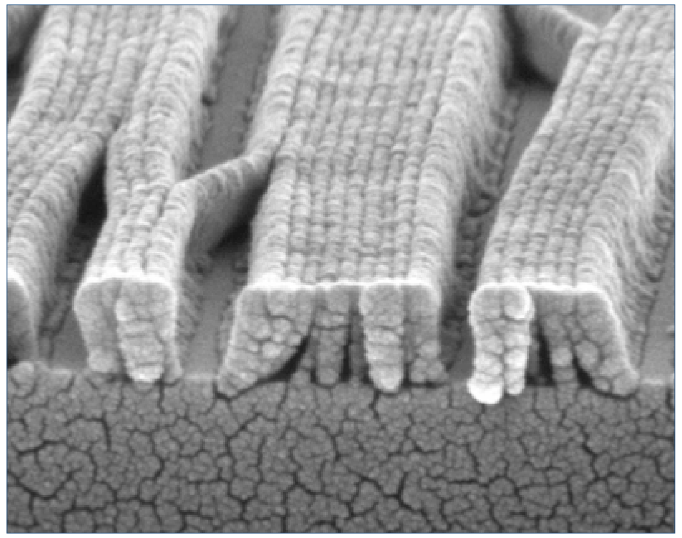
For immersion development, generally development times of 30 - 60 seconds are recommended. If developer AR 600-546 is used, even after 10 minutes at room temperature no erosion of unexposed areas is detected.

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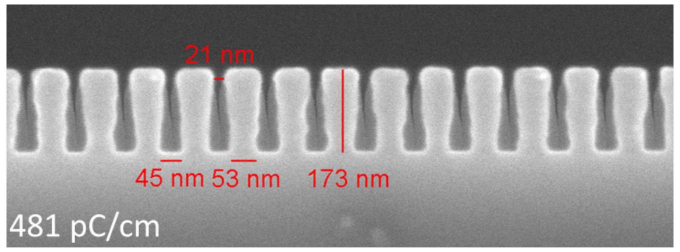
# Positive E-Beam Resists AR-P 6200 (CSAR 62)

## Processing instructions

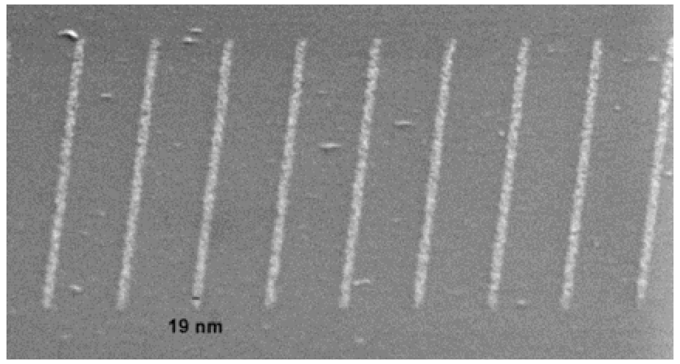
Lift-off structures:

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.

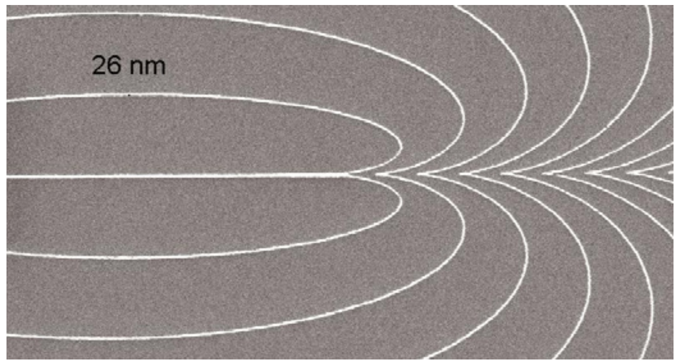



Undercut structures obtained with increased exposure dose

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



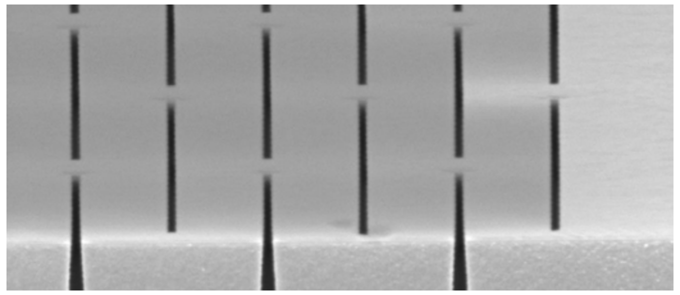

19-nm metal lines after lift-off process with AR-P 6200.09




CrAu test structures with a line width of 26 nm

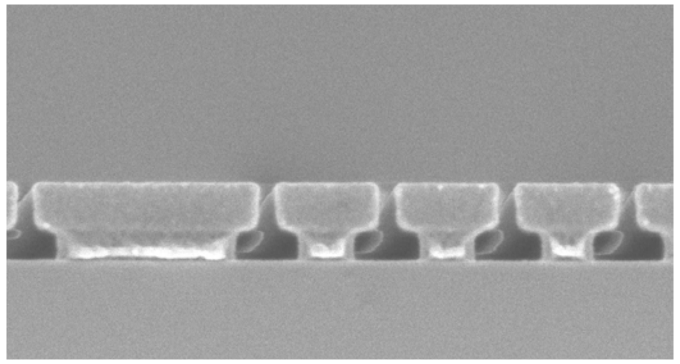
High layers for special applications:

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



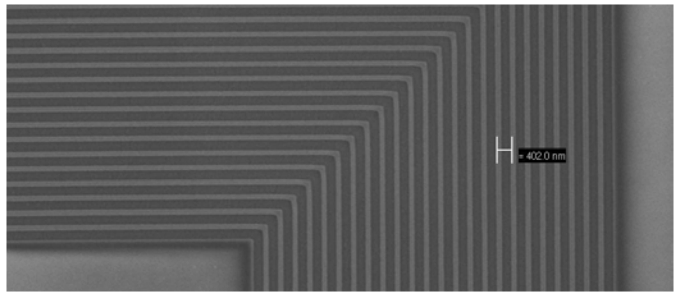
AR-P 6200.13: 100-nm trenches in 830-nm thick layer

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 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.

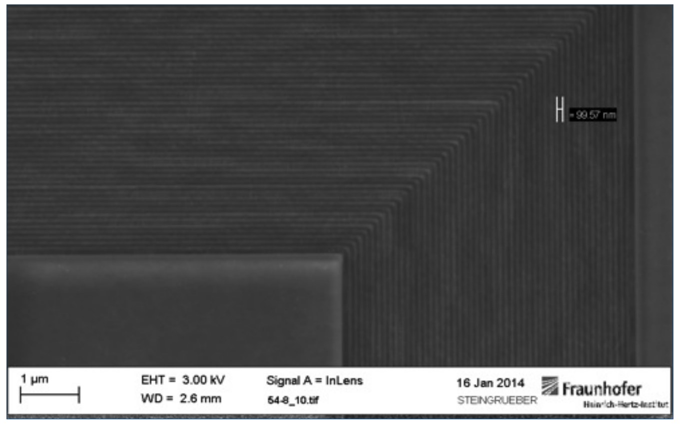



Fig. 1 CSAR 62 test structure on a mask blank with 50 nm lines and 50 nm trenches; pitch line & space here 99.57 nm

### Fabrication of plasmonic nanomaterials

The working group “Quantum Detection” at the Aarhus University Denmark which has already for many years successfully promoted electron beam projects for nanostructuring emphasised in particular the high process stability of CSAR 62 in comparison with ZEP 520.

CSAR 62 is able to balance out small process fluctuations and still reliably provides the desired high resolution. The new Allresist product furthermore showed 1.5-fold higher contrast values than ZEP in comparative measurements (☞ Fig. 2).

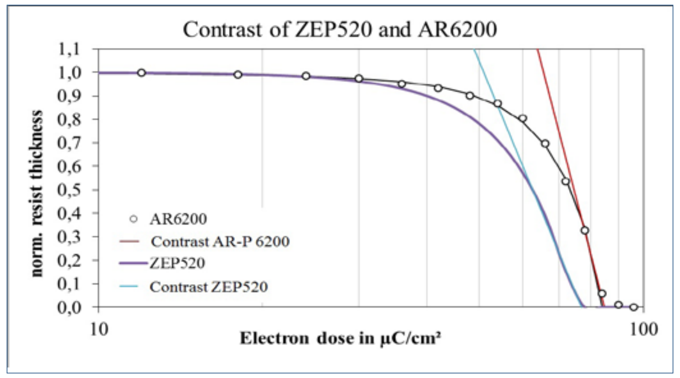



Fig. 2 Contrast curves AR-P 6200 and ZEP 520A, 50kV, substrate: Si; ZEP 520A, film thickness 220 nm, 60 s ZED N-50, contrast 6; AR-P 6200, film thickness 260 nm, 60 s AR 600-546, contrast 9

### 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:

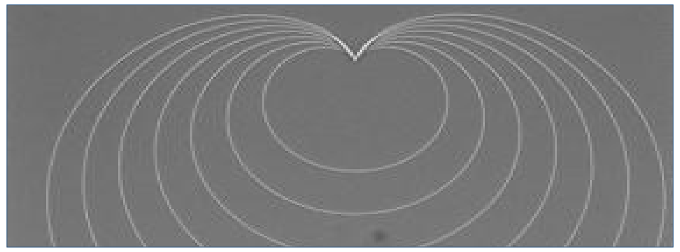


Fig. 3 Chrome structures with 20 nm lines after lift-off

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:

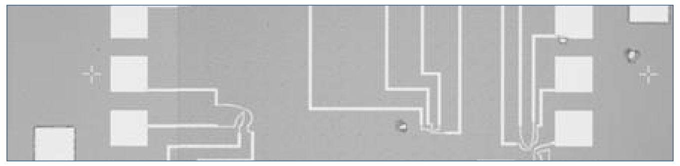


Fig. 4 Typical structure for contacting nanowires. Large areas are mixed with small details





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

## Application examples for CSAR 62

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.

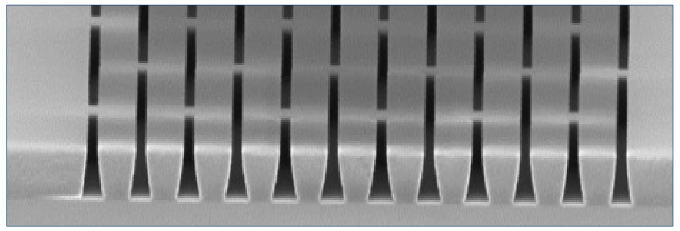
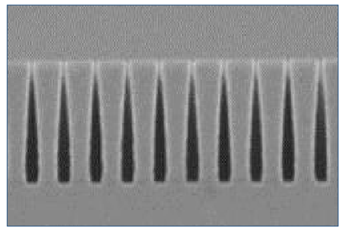


Fig. 5 Lift-off structures with large undercut at a film thickness of 800 nm

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.



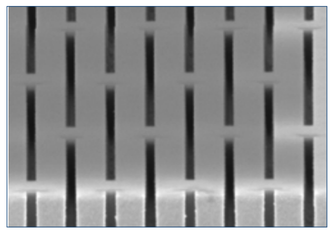


Fig. 6 AR-P 6200.13, 823 nm layer, dose: 1440 pC/cm

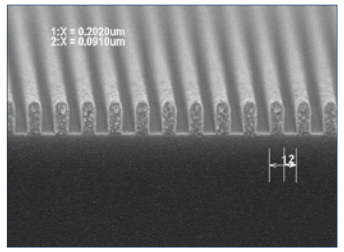
Fig. 7 Vertical structures at an area dose of 120 µC/cm² for nanowires

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).

### Comparison CSAR 62 vs. ZEP 520A

A leading company for electron-beam devices conducted a comparison of CSAR 62 and ZEP 520A. Using the current e-beam system SB 250, three comparative studies of CSAR 62 (AR-P 6200.09) and ZEP 520A were carried out which focused on the parameters structural resolution, contrast and sensitivity in the respective native developers:

1. Structural resolution: The comparison of 90 nm lines of both resists (☞ Fig. 8 and 9) in the centre of a silicon wafer with a film thickness of 200 nm shows that both CSAR and ZEP are characterised by an excellent structural resolution (trench width of 91 nm, pitch 202 nm) and comparable broad process windows:



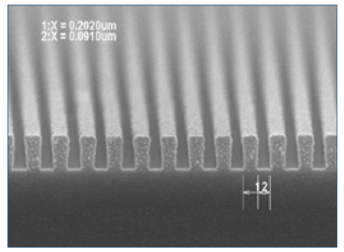


Fig. 8 left ZEP 520A, 200 nm, ZED N50, 50kV, 80 µC/cm²

Fig. 9 right AR-P 6200.09, 200 nm, AR 600-546, 50 kV, 85 µC/cm²

2. Contrast: The diagram (Fig. 10) illustrates a comparison of the contrast of both resists: ZEP 520A in the native developer ZED-N50 and CSAR in two native developers, AR 600-546 and 600-549.

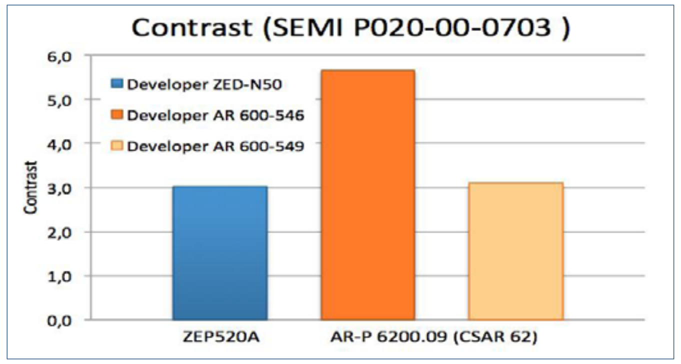



Fig. 10 Contrast ZEP 520A, 200 nm, ZED N50 as well as AR-P 6200.09, 200 nm, AR 600-546 and AR 600-549

While systems ZEP-ZED-N50 and CSAR-AR 600-549 yield almost equally good contrast values, the contrast of CSAR in developer AR 600-546 (which was specifically optimised for this purpose) is almost doubled. CSAR is thus also predestined for highest resolutions (see Fig. 10).

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

## Application examples for CSAR 62

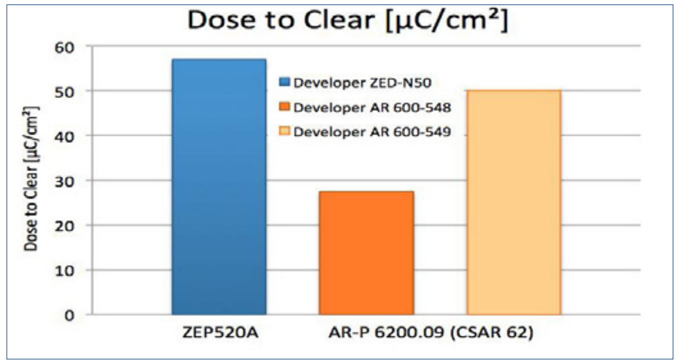



Fig. 11 Sensitivity ZEP 520 A, 200 nm, ZED-N50 as well as AR-P 6200.09, 200 nm, AR 600-548 and 600-549

3. Sensitivity (dose to clear): The diagram (☞ Fig. 11) demonstrates a good range for the required dose for both resists. Again however, the CSAR resist-developer systems (with AR 600-549 12 % and AR 600-548 51 %) are more sensitive than the ZEP resist-developer system. All three studies come to the conclusion that CSAR 62 can very well compete with ZEP 520 and partly has even more favourable application parameters which also result from the variety of suitable developers.

### 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“.

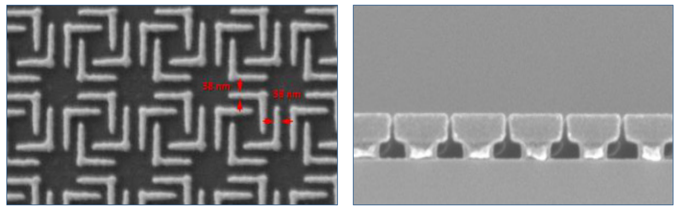


Fig. 12 High-precision L-shaped structures, produced with the two-layer system AR-P 6200.09 / AR-P 617.06; right 2 Layer sytems

### 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).

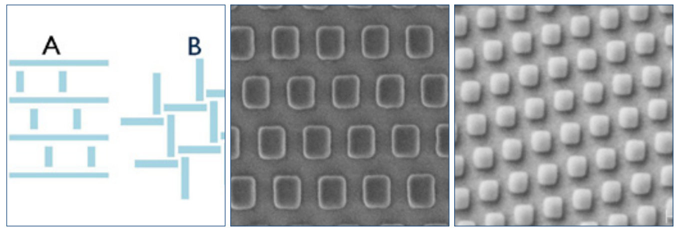



Fig. 13 Different irradiation designs and resulting square structures (centre: A; right: B)

### 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. The doses used (e.g. #1 = 45 µC/cm²) are listed in the table in Fig. 17.



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## Application examples for CSAR 62

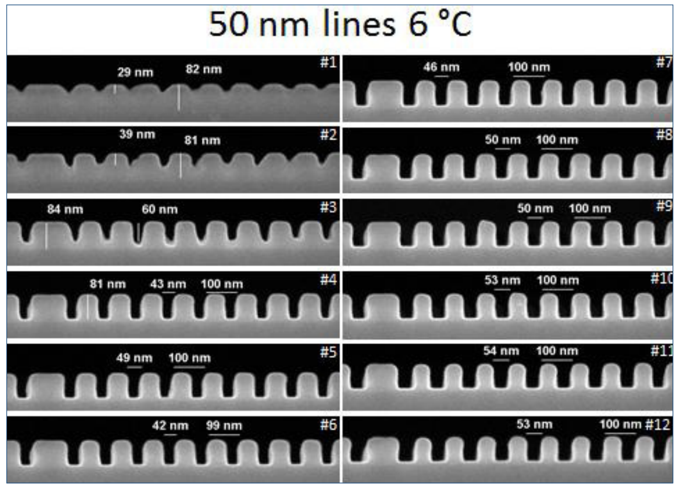


Fig. 14 CSAR 62 structures at 6 °C, opt. dose 195 pC/cm

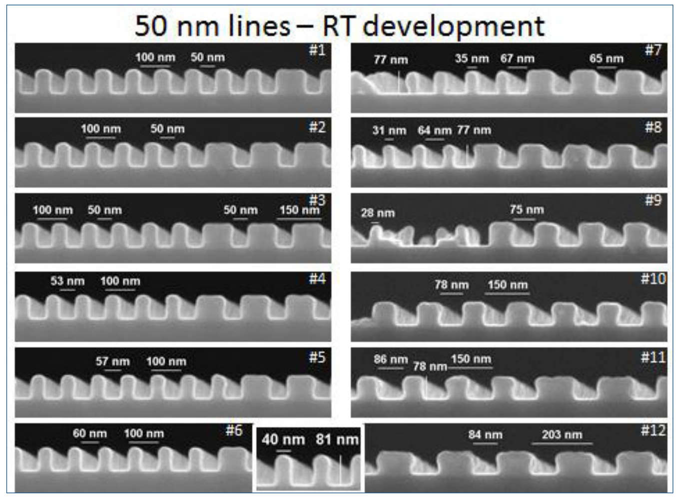


Fig. 15 CSAR 62 structures at 21 °C, opt. dose 121 pC/cm

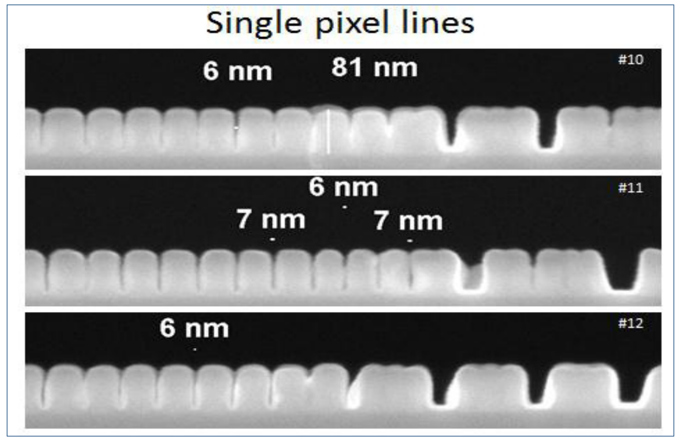


Fig. 16 Max. resolution of 6 nm at 235 pC/cm and 6 °C

### Number to Dose Conversion

| 20 & 50 nm wide lines | | single pixel lines | |
|---|---|---|---|
| number | Dose | number | Dose |
| # | µC/cm² | # | pC/cm |
| 1 | 45.0 | 1 | 100.0 |
| 2 | 49.5 | 2 | 110.0 |
| 3 | 54.5 | 3 | 121.0 |
| 4 | 59.9 | 4 | 133.1 |
| 5 | 65.9 | 5 | 146.4 |
| 6 | 72.5 | 6 | 161.1 |
| 7 | 79.7 | 7 | 177.2 |
| 8 | 87.7 | 8 | 194.9 |
| 9 | 96.5 | 9 | 214.4 |
| 10 | 106.1 | 10 | 235.8 |
| 11 | 116.7 | 11 | 259.4 |
| 12 | 128.4 | 12 | 285.3 |

Fig. 17 Dose values for Fig. 14-15