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

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

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

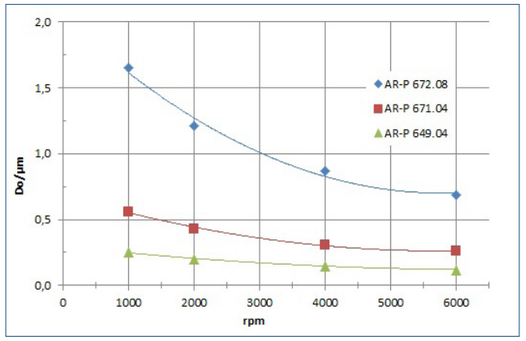
Characterisation

- e-beam, deep UV (248 nm)
- very good adhesion to glass, silicon and metals
- 50K 20 % more sensitive than 950K
- for planarization and multi-layer processes
- highest resolution, high contrast
- poly(methyl methacrylate) with diff. molecular weights
- AR-P 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

Properties I

Parameter / AR-P	631-639	641-649	661-669	671-679
PMMA type	50 K	200 K	600 K	950 K
Film thickness/ 4000 rpm (nm) according to solids content	0.02-0.31	0.02-0.78	0.02-1.04	0.03-1.87
Solids content (%)	1-12	1-12	1-11	1-11
Resolution best value (nm)	6			
Contrast	7			
Storage 6 month (°C)	10 - 22			

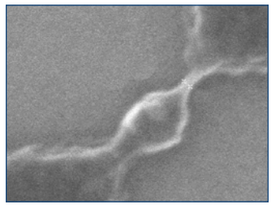
Spin curve



Properties II

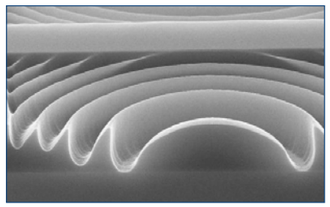
Glass trans. temperature (°C)	105	
Dielectric constant	2.6	
Cauchy coefficients	N_0	1.478
	N_1	47.3
	N_2	0
Plasma etching rates (nm/min) (5 Pa, 240-250 V Bias)	Ar-sputtering:	21
	O_2	344
	CF_4	59
	80 CF_4 + 16 O_2	164

Structure resolution



AR-P 679.02
Structural resolution: 6.2 nm gap, 65 nm high

Resist structures



AR-P 671.09
diffractive optics, thickness of 4.4 µm

Process parameters

Substrate	Si 4“ waver
Tempering	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
Developer	AR 600-55, AR 600-56
Thinner	AR 600-01, -02, -09
Stopper	AR 600-60
Remover	AR 600-71, AR 300-76

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Process conditions

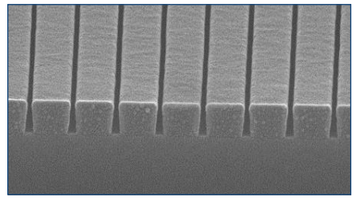
This diagram shows exemplary process steps for resists of the series AR-P 630 - 670. All specifications are guideline values which have to be adapted to own specific conditions. For further information on processing, ☞ “Detailed instructions for optimum processing of e-beam resists”. For recommendations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

Coating	AR-P 632.06	AR-P 671.05
	4000 rpm, 60 s, 110 nm	2000 rpm, 60 s, 690 nm
Tempering (± 1 °C)	150 °C, 3 min hot plate or	
	150 °C, 60 min convection oven	
E-beam exposure	ZBA 21, 20 kV	Raith Pioneer, 30 kV
	Exposure dose (E_0):	
	95 µC/cm²	770 µC/cm²
Development (21-23 °C ± 1 °C) puddle	AR 600-55 1 min	AR 600-56 3 min
Stopping	AR 600-60, 30 s	
Post-bake (optional)	130 °C, 1 min hot plate or 130 °C, 25 min convection oven for slightly enhanced plasma etching resistance	
Customer-specific technologies	Generation of semiconductor properties	
Removal	AR 300-76 or O_2 plasma ashing	

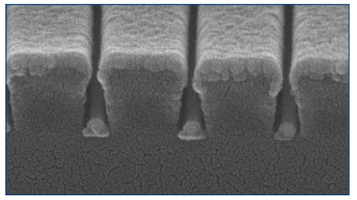
Processing instructions for coating

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

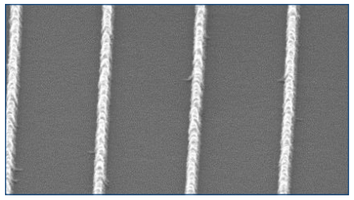
Recommendation: large undercut (low resolution): bottom layer 50K, upper layer 200K, 600K or 950K. High resolution (smaller undercut): bottom layer 600K, upper layer 950K.



After development (AR 600-56)



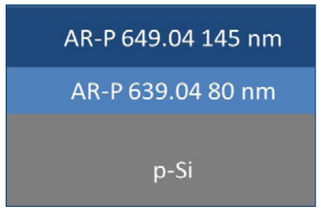
Structures coated with metal films



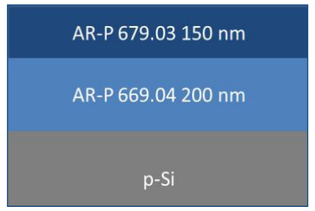
Lifted 30 nm metal lines

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

Investigations of 2-layer PMMA lift-off structures



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



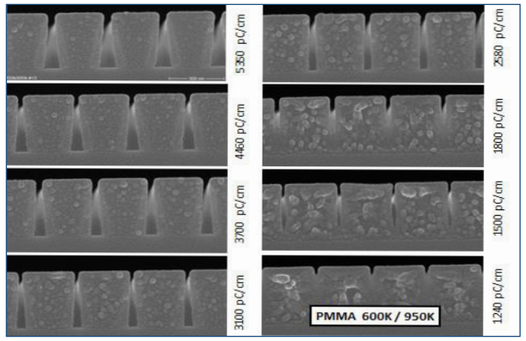
Layer structure of the two-layer system 600K/950K

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

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

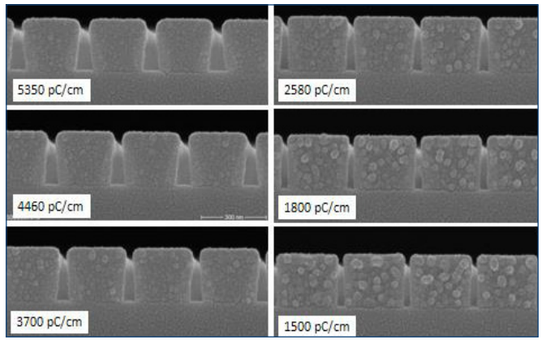
Dose sequence of the 600K/950K system

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



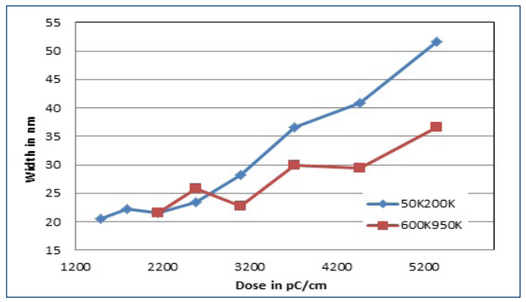
Not yet completely developed at 1800 pC/cm

Dosisstaffel des 50K/ 200K-Systems



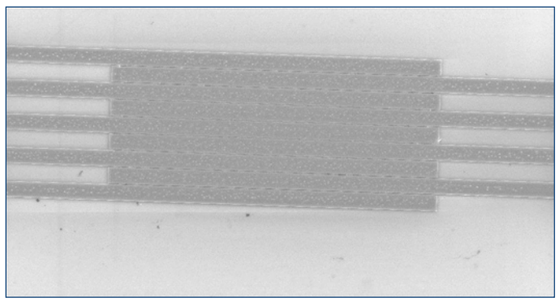
Constantly increasing undercut

Formation of undercut vs. exposure dose



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

Application example



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

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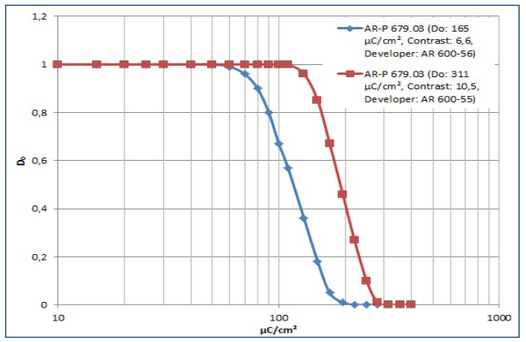
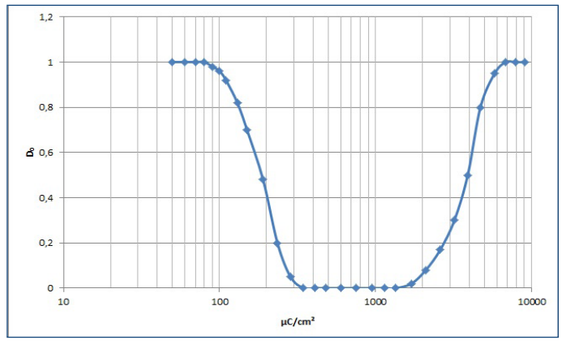
Sensitivity of a PMMA resist



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

Gradation curve PMMA



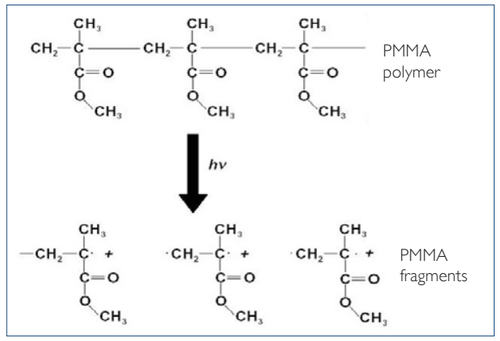
Gradation curve up to maximum dose

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

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

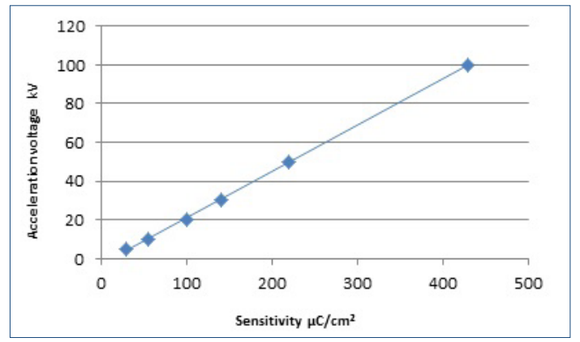
Upon electron irradiation of PMMA resists, the main chain is cleaved and the molecular mass drops from initially 950 000 g/mol (950K) to 5.000 – 10.000 g/mol. This main chain scission is primarily due to radical processes (see figure below). At an optimal dose, radicals recombine and form molecules with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

Depolymerisation opon exposure



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

Dose versus acceleration voltage



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

Positive 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/cm³] 20°C
50 K	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**
200 K	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**
600 K	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**

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

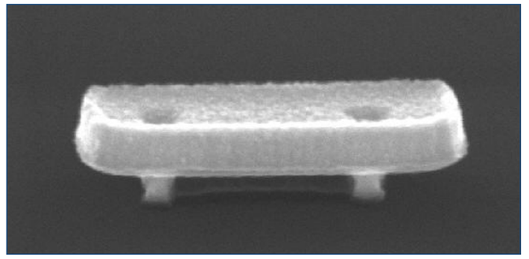
PMMA	E-beam resist AR-P	Solids content [%]	Viscosity [mPas] 25°C	Film thickness 1000 rpm [µm]	Film thickness 2000 rpm [µm]	Film thickness 4000 rpm [µm]	Film thickness 6000 rpm [µm]	Density [g/cm³] 20°C
950 K	**671.01**	**1.0**	**3.2**	**0.05**	**0.04**	**0.03**	**0.02**	**1.105**
	671.02	**2.0**	**7.3**	**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

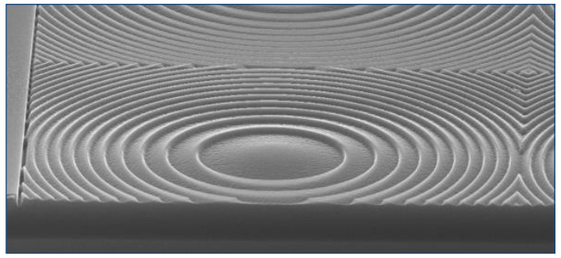
Resist printed in bold are standard variants whose prices are listed in the price list. Further solids contents are possible in amounts from ¼ l onwards and are charged with a surcharge of 10 % in relation to the next higher solids content.

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