Negative Photoresists AR-N 4400 (CAR 44)

AR-N 4400 photoresist series for high film thickness values

Thick negative resists for electroplating, microsystems technology and LIGA ≤ 20 µm

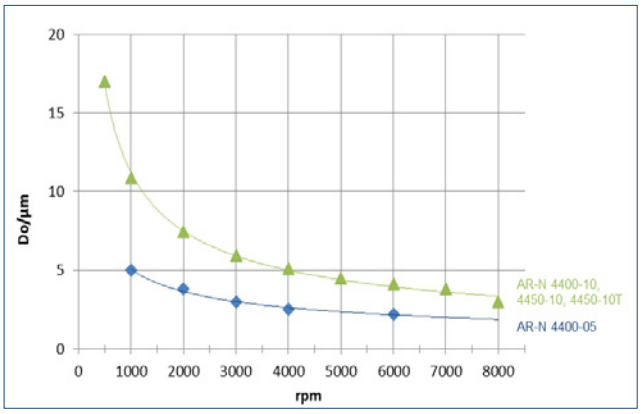
Characterisation

- i-, g-line, e-beam, X-ray, synchrotron, broadband UV
- chemically enhanced, very good adhesion, electro plating-stable
- very high sensitivity, easy removal
- profiles with high edge steepness for excellent resolution, covering of topologies
- 4400-05/-10 for films up to 10 µm/ 20 µm (250 rpm)
- 4450-10T for film thicknesses up to 20 µm and lift-off
- novolac, crosslinking agent, amine-based acid generator
- safer solvent PGMEA

Properties I

Parameter / AR-N	4400 -05	4400 -10	4450 -10T
Solids content (%)	33	45	41
Film thickness/1000 rpm (µm)	5	10	10
Resolution (µm)	1.0	2.0	3.5
Contrast	4.0	4.0	10
Flash point (°C)	42		
Storage 6 month (°C)	10 - 18		

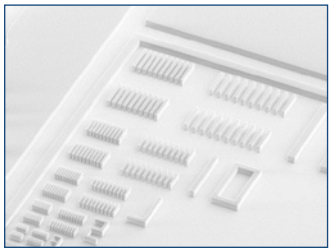
Spin curve



Properties II

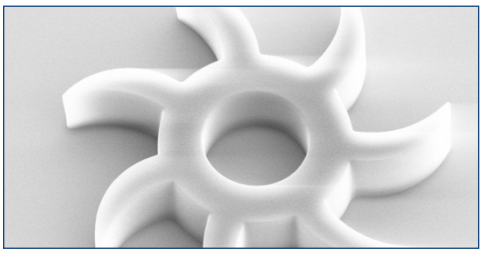
Glass transition temperature	102	
Dielectric constant	3.1	
Cauchy coefficients	N_0	1.615
	N_1	77.6
	N_2	64.1
Plasma etching rates (nm/min) (5 Pa, 240-250 V Bias)	Ar-sputtering	3
	O_2	122
	CF_4	31
	80 CF_4 + 16 O_2	81

Structure resolution



AR-N 4400-10
3 µm resolution at a film thickness of 15 µm

Resist structures



Turbine wheel produced with AR-N 4400-10

Process parameters

Substrate	Si 4“ wafer
Tempering	95 °C, 10 min, hot plate
Exposure	Maskaligner MJB 3, contact exposure
Development	AR 300-47, undil., 3 min, 22 °C

Process chemicals

Adhesion promoter	AR 300-80
Developer	AR 300-47, AR 300-44
Thinner	AR 300-12
Remover	AR 600-71, AR 600-70

Negative Photoresists AR-N 4400 (CAR 44)

AR-N 4400 photoresist series for high film thickness values

Thick negative resists for electroplating, microsystems technology and LIGA ≥ 50 µm

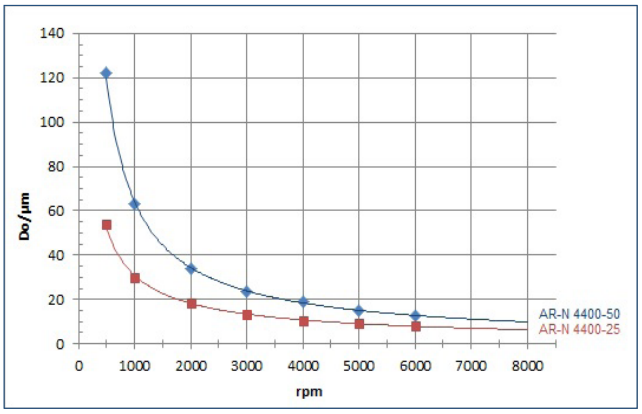
Characterisation

- i-, g-line, e-beam, X-ray, synchrotron, broadband UV
- chemically enhanced, very good adhesion, electro plating-stable
- very high sensitivity, easy removal
- profiles with high edge steepness for excellent resolution, covering of topologies
- 4400-25 for very thick films up to 50 µm (250 rpm)
- 4400-50 for highest film thicknesses up to 100 µm
- novolac, crosslinking agent, amine-based acid generator
- safer solvent PGMEA

Properties I

Parameter / AR-N	4400 -25	4400 -50
Solids content (%)	52	58
Film thickness/1000 rpm (µm)	25	50
Resolution (µm)	3.5	5.0
Contrast	5.0	6.0
Flash point (°C)	42	
Storage 6 month (°C)	10 - 18	

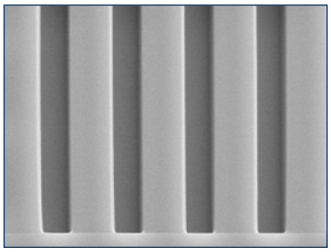
Spin curve



Properties II

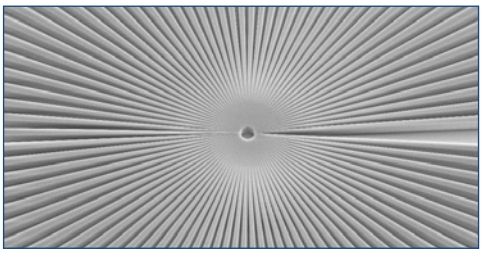
Glass transition temperature	102	
Dielectric constant	3.1	
Cauchy coefficients	N_0	1.615
	N_1	77.6
	N_2	64.1
Plasma etching rates (nm/min) (5 Pa, 240-250 V Bias)	Ar-sputtering	3
	O_2	122
	CF_4	31
	80 CF_4 + 16 O_2	81

Structure resolution



AR-N 4400-25
5 µm trenches at a film thickness of 40 µm

Resist structures



Siemens star produced with AR-N 4400-25 (30 µm thickness)

Process parameters

Substrate	Si 4“ wafer
Tempering	95 °C, 10 min, hot plate
Exposure	Maskaligner 150
Development	AR 300-44, undil., 90 min, 22 °C

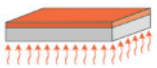
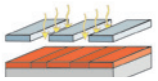
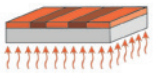
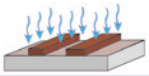
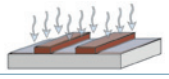
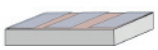
Process chemicals

Adhesion promoter	AR 300-80
Developer	AR 300-46, AR 300-44
Thinner	AR 300-12
Remover	AR 600-71, AR 600-70

Negative Photoresists AR-N 4400 (CAR 44)

Process conditions

This diagram shows exemplary process steps for AR-N 4400 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 photoresists". For recommendations on waste water treatment and general safety instructions, ☞ "General product information on Allresist photoresists".

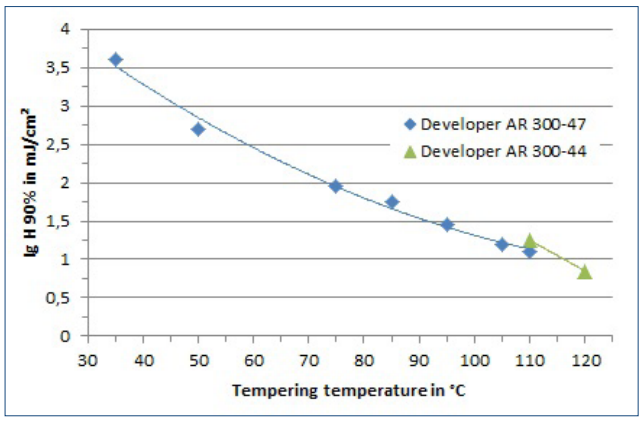
		4400-05	4400-10	4400-25	4400-50	4450-10T
Coating (open chuck) 		1000 rpm 5 µm	1000 rpm 10 µm	1000 rpm 25 µm	1000 rpm 50 µm	1000 rpm 10 µm
Tempering (± 1 °C)  H* = Hot plate or C* = Convection oven	H*	90 °C 4 min	90 °C 15 min	90 °C 30 min	90 °C 90 min	90 °C 15 min
	C*	85 °C 30 min	85 °C 60 min	85 °C 2 h	85 °C 3 h	85 °C 60 min
UV exposure 		Maskaligner, broadband UV				
		Exposure dose (E_0, broadband UV):				
		22 mJ/cm²	26 mJ/cm²	33 mJ/cm²	52 mJ/cm²	95 mJ/cm²
Crosslinking bake (+/- 1 °C)  H* = Hot plate or C* = Convection oven	H*	100 °C 5 min	100 °C 10 min	100 °C 10 min	100 °C 10 min	100 °C 10 min
	C*	95 °C 30 min	95 °C 40 min	95 °C 60 min	95 °C 80 min	95 °C 40 min
Development (21-23 °C ± 0,5 °C) puddle 		300-47 1 min	300-47 4 min	300-46 9 min	300-44 18 min	300-44 3 min
Rinse		DI-H_2O, 30 s and dry with caution				
Hardening of structures up to 300 °C (optional)		Flood exposure 100 mJ/cm²; bake 120 °C, 5 min hot plate				
Customer-specific technologies 		Generation of e.g. semiconductor properties or lift-off (4450-10T) and galvanic, MEMS				
Removal 		AR 300-76 for low crosslink density, AR 600-71 for high crosslink density, O_2 plasma ashing is also possible for high film thicknesses.				

Development recommendations

Resist / Developer	AR-N 4400-05 3-10 µm	AR-N 4400-10 5 - 20 µm	AR-N 4400-25 13 - 25 µm	AR-N 4400-50 25 - 100 µm	AR-N 4450-10T 5 - 20 µm
AR 300-44	-	-	-	8 : 1 to undil.	undil.
AR 300-46	-	-	5 : 1 to undil.	undil.	-
AR 300-47	6 : 1 to undil.	3 : 2 to undil.	undil.	-	-
AR 300-475	undil.	-	-	-	-

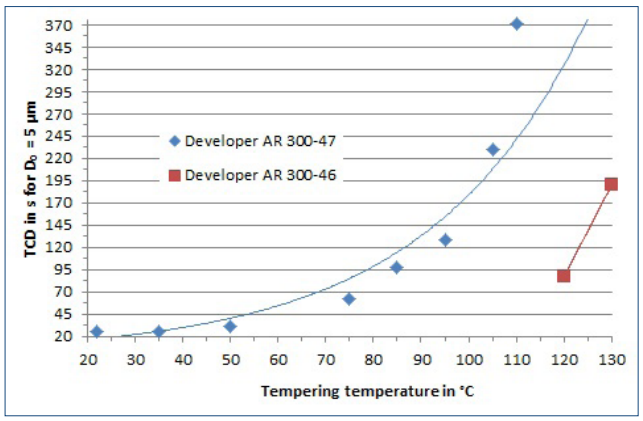
Negative Photoresists AR-N 4400 (CAR 44)

Sensitivity of AR-N 4400-05



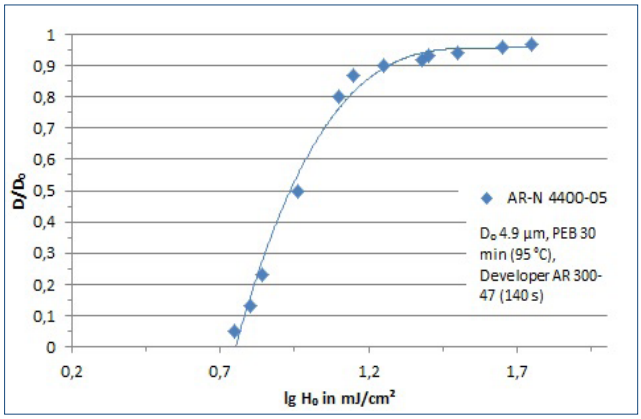
The sensitivity increases constantly with increasing bake temperatures (broadband UV Maskeliner, thickness 5.0 µm)

Time for complete development of AR-N 4400-05



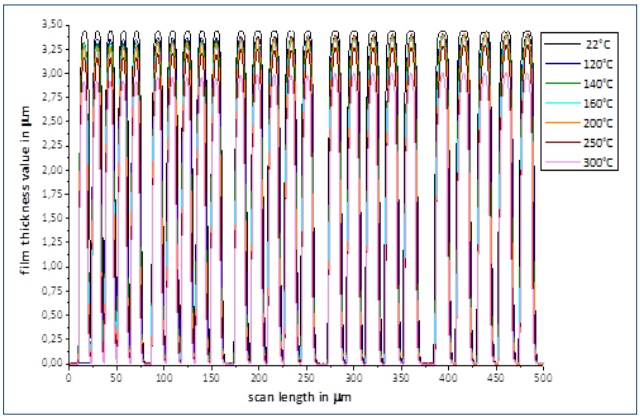
With increasing temperature, the TCD increases considerably. > 130 °C, no development is possible even if strong developers (AR 300-44) are used.

Gradation curve of AR-N 4400-05



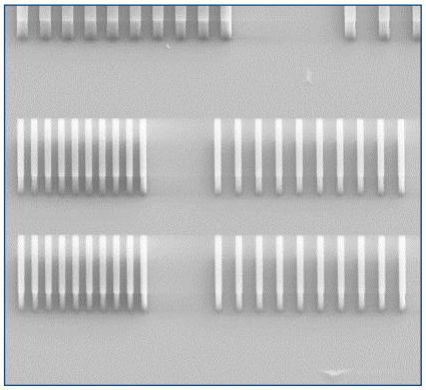
The gradation (contrast) is 3.5, the sensitivity was determined to 21.5 mJ/cm² for a structure buildup of 90 % ($H_0$90).

Thermal stability and shrinking up to 300 °C



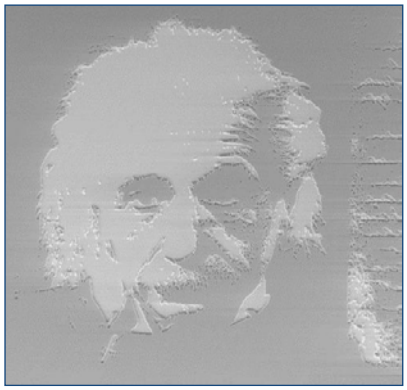
Developed lines with a width of 10 – 20 µm were hardened by flood exposure and subsequent bake step. These lines were tempered stepwise until 300 °C. Up to a temperature of 200 °C, structures remain more or less unchanged.

Resolution of AR-N 4400-05



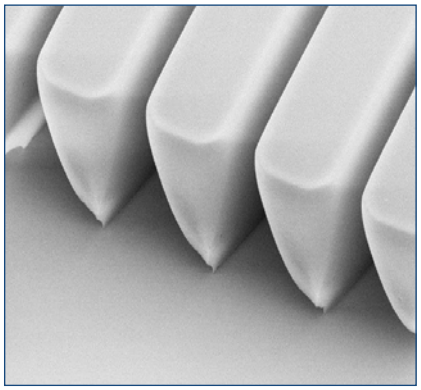
At a film thickness of 5 µm, 1.0 µm bars were produced

Picture of Albert Einstein



Test structure produced on the occasion of the "Einsteinjahr" in 2006

Lift-off structures



Undercuts produced with low exposure dose (AR-N 4450-10T)

Negative Photoresists AR-N 4400 (CAR 44)

Processing instructions for the handing of thick films

Coating: In order to avoid the formation of bubbles, the resist should be left undisturbed for at least one day prior to processing. For resist with higher viscosity from AR-N 4400-25 onwards, degassing with ultrasound or vacuum is advisable.

The resist should be applied slowly, from a low height and always using the same amount of resist (e.g. 100 ml for 4-inch-wafers) onto the standing wafer. Subsequently, a formation for 10 s a low rotational speed (250 - 400 rpm) is recommended, followed by slow increase of the spin speed up to the desired final speed. To achieve a high resist film quality, rotational speeds above 2000 rpm should be avoided for the highly viscous AR-N 4400-50.

☞ Shorter coating times at final spin speed will increase the film thickness.

Multiple coating steps (up to 4 x) are possible for film thicknesses between 50 and 150 µm. A particularly high edge steepness of structures results in this case from an improved drying procedure. After each coating step, the resist is dried at 85 °C (hot plate) or 90 °C (convection oven) according to the specifications as given in the process conditions.

Tempering: The required tempering times are highly dependent on the respective film thickness:

Drying times hot plate/convection oven:

10 µm: 10 min/1h; 25 µm: 45 min/4 h; 50 µm: 90 min/7 h. The use of temperature ramps is highly recommended, since too fast cooling may lead to tension cracks.

☞ Long intensive drying procedures result in decreased sensitivities and prolonged development times.

Crosslinking: The crosslinking temperature can be varied in the range from 85 °C to 105 °C. The bake can be performed a few days after exposure without loss of sensitivity.

☞ Higher temperaturs lead to a slower development.

Development: longer development times with weaker developer provide a higher imaging quality. For AR-N 4450-10T, the undercut (lift-off) of resist structures can be achieved by extending the development time at the minimum required exposure dose.

Removal: Crosslinked structures can easily be removed by wet- or plasma chemical procedures using removers AR 600-71 and AR 300-76. Complicated electroplating structures as well as substrates treated with high temperatures require removers AR 600-71 or AR 600-70.

Comparison CAR44 and SU-8

CAR 44	Resist properties – Suitability	SU-8
✓	thick films	✓✓
✓	high resolution	✓
✓	excellent aspect ratio	✓
✓	high sensitivity at i-line, deep UV, e-beam, X-ray	✓✓
✓	good sensitivity at g-line	×
✓	low-stress tempering – easy handling	×
✓	aqueous-alkaline development	×
✓	easy removal	×