

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 $\leq 20 \mu\text{m}$

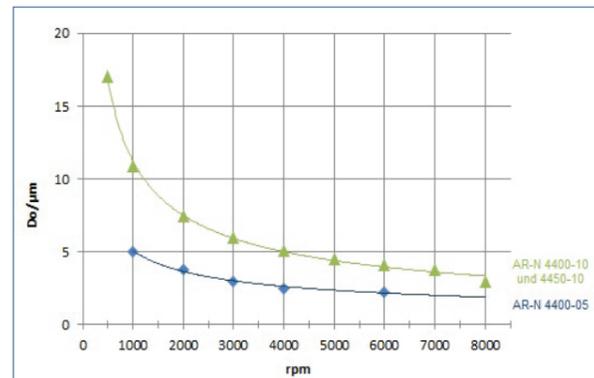
Characterisation

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

Properties I

Parameter / AR-N	4400-05	4400-10	4450-10
Solids content (%)	33	45	45
Film thickness/1000 rpm (μm)	5	10	10
Resolution (μm)	1.0	2.0	3.5
Contrast	4.0	4.0	10
Flash point ($^{\circ}\text{C}$)	42		
Storage 6 month ($^{\circ}\text{C}$)	10 - 18		

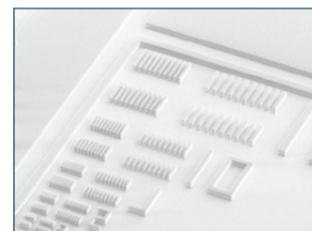
Spin curve



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
	$80 \text{ CF}_4 + 16 \text{ O}_2$	81

Structure resolution



AR-N 4400-10
 $3 \mu\text{m}$ resolution at a film thickness of $15 \mu\text{m}$

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
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 $\geq 50 \mu\text{m}$

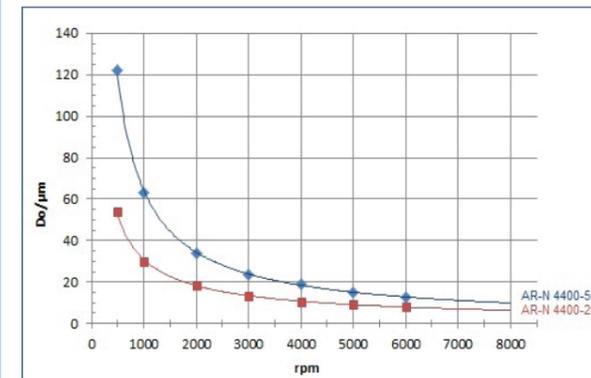
Characterisation

- i-, g-line, e-beam, X-ray, synchrotron, broadband UV
- chemically enhanced, very good adhesion, electroplating-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 $50 \mu\text{m}$ (250 rpm)
- 4400-50 for highest film thicknesses up to $100 \mu\text{m}$
- 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 ($^{\circ}\text{C}$)	42	
Storage 6 month ($^{\circ}\text{C}$)	10 - 18	

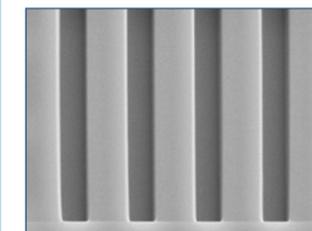
Spin curve



Properties II

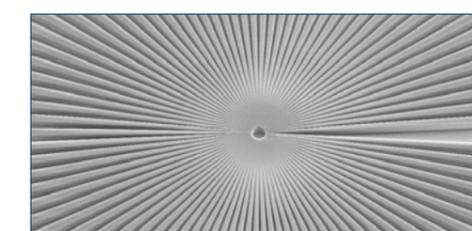
Glass transition temperature	102	
Dielectric constant	3.1	
Cauchy coefficients	N_0	1.615
	N_1	77.6
	N_2	64.1
Plasma etching rates (nm/min) (5 Pa, 240-250 V Bias)	Ar-sputtering	3
	O_2	122
	CF_4	31
	$80 \text{ CF}_4 + 16 \text{ O}_2$	81

Structure resolution



AR-N 4400-25
 $5 \mu\text{m}$ trenches at a film thickness of $40 \mu\text{m}$

Resist structures



Siemens star produced with AR-N 4400-25 ($30 \mu\text{m}$ thickness)

Process parameters

Substrate	Si 4" wafer
Tempering	95°C , 10 min, hot plate
Exposure	Maskaligner I 50
Development	AR 300-44, undil., 90 min, 22°C

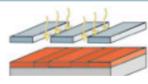
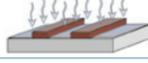
Process chemicals

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, see "Detailed instructions for optimum processing of photoresists". For recommendations on waste water treatment and general safety instructions, see "General product information on Allresist photoresists".

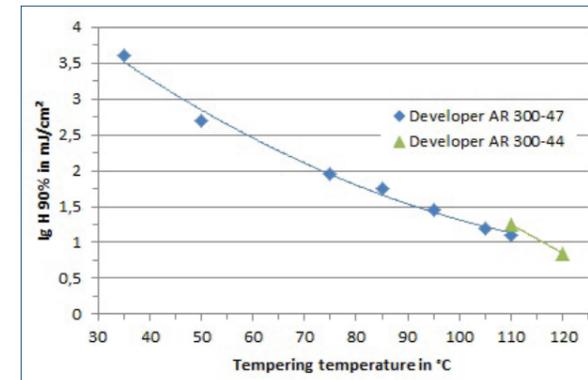
Coating (open chuck) 	4400-05	4400-10 4450-10	4400-25	4400-50
	1000 rpm 5 µm	1000 rpm 10 µm	1000 rpm 25 µm	1000 rpm 50 µm
Tempering (± 1 °C) 	H* 90 °C 4 min	90 °C 10 min	90 °C 45 min	90 °C 90 min
H* = Hot plate or C* = Convection oven	C* 85 °C 30 min	85 °C 60 min	85 °C 4 h	85 °C 7 h
UV exposure 	Maskaligner, broadband UV Exposure dose (E ₀ , broadband UV): 22 mJ/cm ² 26/ 90 mJ/cm ² 33 mJ/cm ² 52 mJ/cm ²			
Crosslinking bake (+/- 1 °C) 	H* 100 °C 5 min	100 °C 10 min	100 °C 10 min	100 °C 10 min
H* = Hot plate or C* = Convection oven	C* 95 °C 30 min	95 °C 40 min	95 °C 60 min	95 °C 80 min
Development (21-23 °C ± 0,5 °C) puddle 	300-47, 3 : 2 2 min	300-47 4 min	300-46 9 min	300-44 18 min
Rinse	DI-H ₂ O, 30 s and dry with caution			
Hardening of structures up to 300 °C (optional)	Flood exposure 100 mJ/cm ² ; bake 120 °C, 5 min hot plate			
Customer-specific technologies 	Generation of e.g. semiconductor properties or lift-off (4450-10)			
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	AR-N 4400-10, 4500-10	AR-N 4400-25	AR-N 4400-50
AR 300-44	3-10 µm	5-20 µm	13-25 µm	25-100 µm
AR 300-46	-	-	-	8 : 1 to undil.
AR 300-47	6 : 1 to undil.	3 : 2 to undil.	undil.	-
AR 300-475	undil.	-	-	-

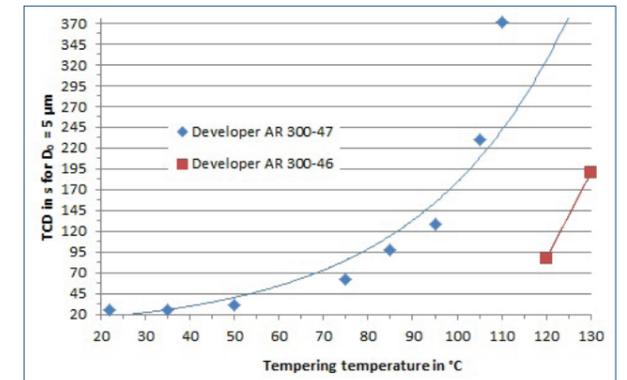
Negative Photoresists AR-N 4400 (CAR 44)

Sensitivity of AR-N 4400-05



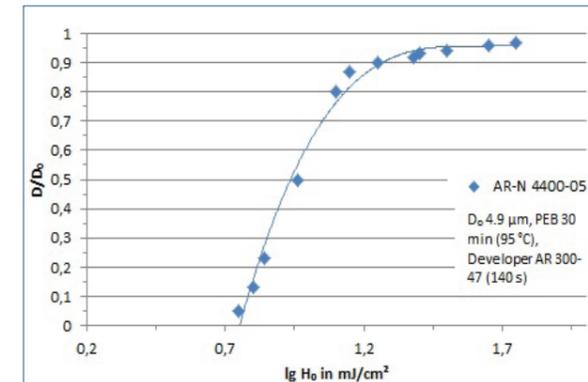
The sensitivity increases constantly with increasing bake temperatures (broadband UV Maskaligner, thickness 5.0 µm)

Time for complete development of AR-N 4400-05



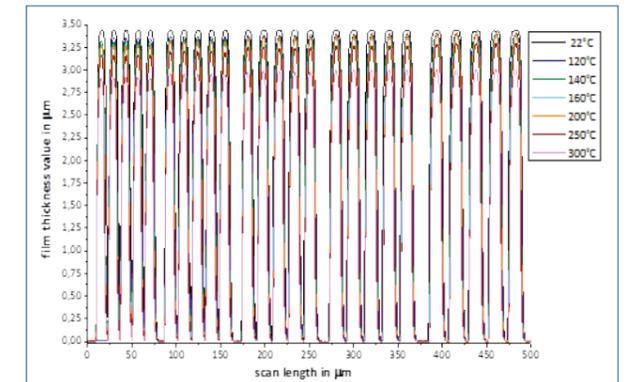
With increasing temperature, the TCD increases considerably. > 130 °C, no development is possible even if strong developers (AR 300-44) are used.

Gradation curve of AR-N 4400-05



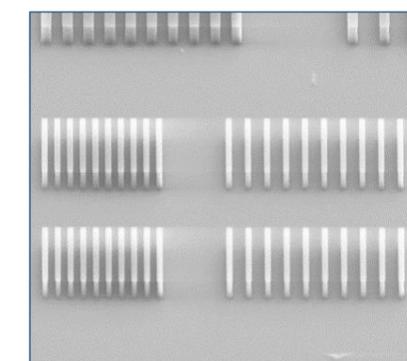
The gradation (contrast) is 3.5, the sensitivity was determined to 21.5 mJ/cm² for a structure buildup of 90 % (H₀90).

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



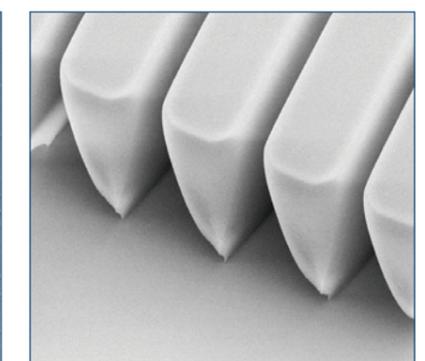
At a film thickness of 5 µm, 1.0 µm bars were produced

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 4450-10)



Negative Photoresists AR-N 4400 (CAR 44)

Processing instructions for the handling 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 at 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 temperatures lead to a slower development.

Development: longer development times with weaker developer provide a higher imaging quality. For AR-N 4450-10, 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	✗