ALLRESIST

Innovation
Creativity
Customer-specific solutions

HSQ negative resists AR-N 8400 (Medusa 84 SiH)

Precision for nanostructuring. Safer chemistry in the lab.

New product: **Choline-OH developer AR 300-41** for significantly lower toxic hazard

Characterisation

- Hydrogen silsesquioxane dissolved in butyl acetate
- Highest resolution e-beam resist
- Improved shelf life and stability, as casting solvent butyl acetate reduces gelling and particle formation
- Elimination of the presumably carcinogenic solvent MIBK
- Enhanced contrast with **metal-ion free** and **low toxic** Choline-OH developer **AR 300-41** (45% Ch-OH)
- Highest resolution and contrast with salty developer **AR 300-28** (1% NaOH + 4% NaCl)

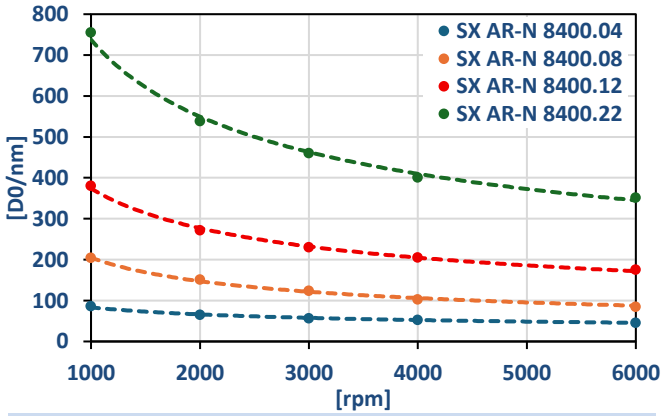
Properties I

Parameter / AR-N	8400.04	8400.08	8400.12	8400.22
Solids content (%)	4	8	12	22
Film thickness/ 4000rpm (nm)	50	100	200	400
Flash point (°C)	<35			
Storage temperature*	8-12 °C		From -18 °C	

* Storing in deep freezer/liquid nitrogen extends shelf life significantly.

Medusa 84 SiH must not be transferred to glass containers or filtered using a glass pre-filter, as this will cause it to gel irreversibly. The Medusa 84 SiH has to reach room temperature before opening the bottle. Condensing water can affect the shelf life, as the resist is sensitive to moisture.

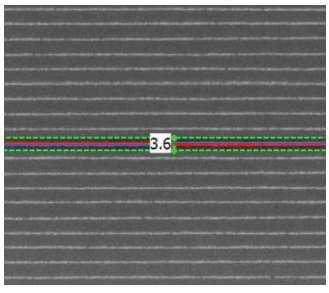
Spin curve



Properties II

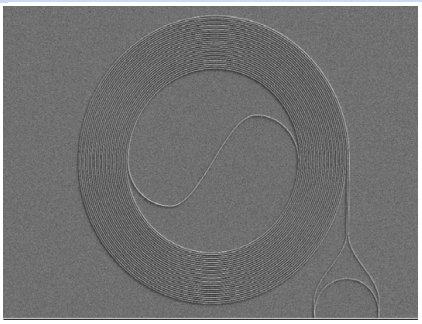
Dielectric constant	3.0	
Cauchy coefficients	N_0	1.409
	N_1	46
	N_2	0
Plasma etching rates (nm/min) 1 Pa reactor pressure 500 W ICP power –100 V bias substrate electrode 50 sccm of the respective process gas (42 sccm for CF_4 / 25 sccm each for $CF_4 + O_2$) 20 °C wafer temperature	Ar	34
	SF_6	146
	CF_4	175
	CF_4+O_2	82
	O_2	5.5
	Cl_2	64

Structure resolution



Single lines with a resolution of 3.6 nm and very low LER written with the RAITH Voyager EBL-System at 50kV, 120 pA, dose: 14.700 pC/cm, developer: KOH 1% 1 min.
© Raith Dortmund

Resist structures



100 nm line/space structures written on silicon at 1000 µC/cm² @ 100 kV and developed with AR 300-73 (6.5% TMAH solution).
© J. Hohmann, KIT-IMT Karlsruhe

Process parameters

Substrate	Si 4´´ wafer
Soft bake	90 °C, 60 s, hot plate
Exposure	e-beam only
Development	AR 300-41, 60-90 s, 21 °C

Process chemicals

Adhesion promoter	AR 300-80 new
Developer	AR 300-41, AR 300-28
Thinner	Butyl acetate VLSI-Grade
Stopper	DI-H_2O
Remover	BOE or 1% HF

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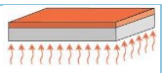
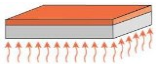
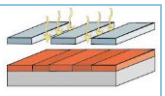
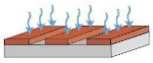
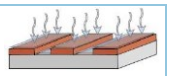
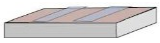
Process conditions

This diagram shows exemplary process steps for the resist series AR-N 8400. 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".

1. Coating		AR-N 8400.08 4000 rpm, 60s, 100nm
1. Soft bake		90 °C, 1 min hot plate or 90 °C, 5 min convection oven
2. Coating (optional)		Conductive coating AR-PC 5094.02 for insulation substrates (quartz, GaN)
2. Soft bake (optional)		90 °C, 1 min hot plate (only for the conductive coating AR-PC 5094)
E-beam exposure		50 kv: 250 µC/cm² (AR 300-41); 2 to 3 mC/cm² (AR 300-28) 100 kv: 500 µC/cm² (AR 400-41); 4 to 6 mC/cm² (AR 300-28)
Development Puddle or immersion		AR 300-41 (45% Ch-OH) or AR 300-28 (1% NaOH + 4% NaCl) 1-2 min for thin layers (>100 nm); up to 4 min for thicker layers
Rinse		DI-H_2O, 30 s
Post-bake (optional)		Not required
Customer-specific technologies		Generation of semiconductor properties
Removal		BOE 7/1 or 1% HF

Note on stability: Coated substrates can be stored under inert gas conditions and processed with minimal loss of sensitivity or resolution even after several weeks.

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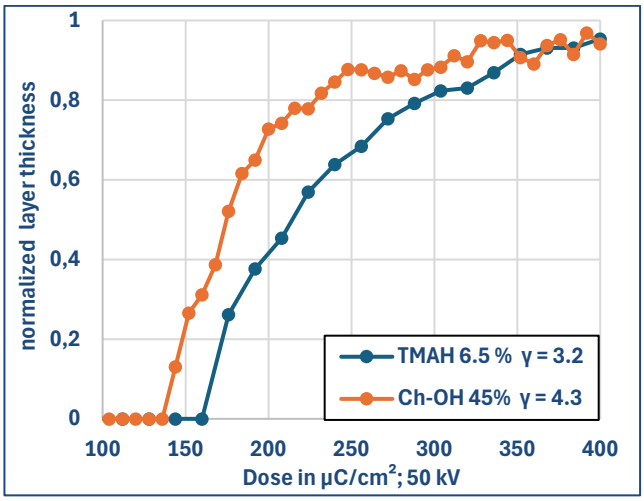
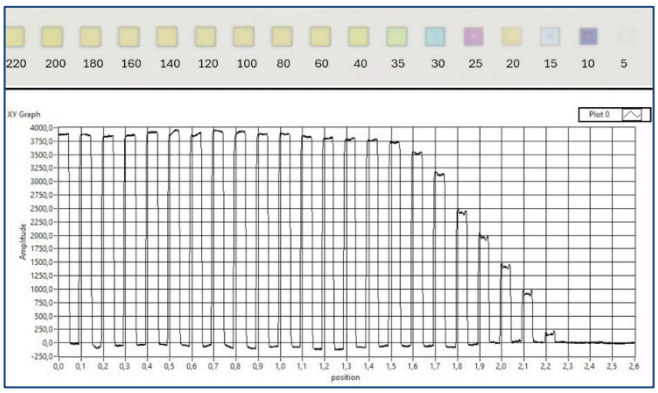
Contrast curve



AR-N 8400.08, 4k rpm, 100 °C 60s HP, 100 nm thickness, Immersion development for 60 sec.

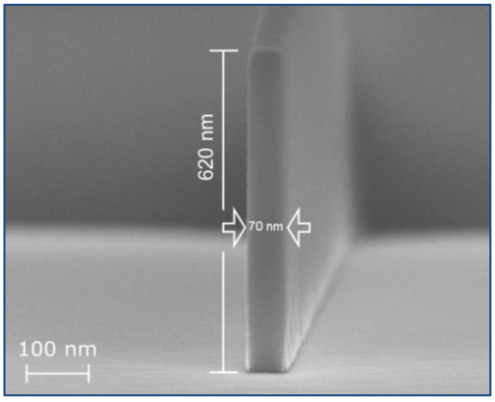
Dose-scale of 50K/ 200K systems

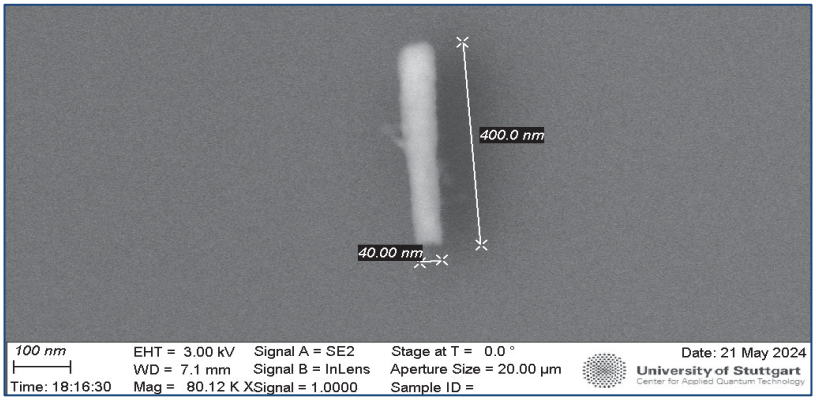


Grey scale structures written on silicon with 30 kV. The top row shows the squares with the dose used in µC/cm². The stylus profilometer shows the remaining height in Å after development with 2.38 % TMAH.

© Zsuzsanna Márton, ELI-ALPS Hungary

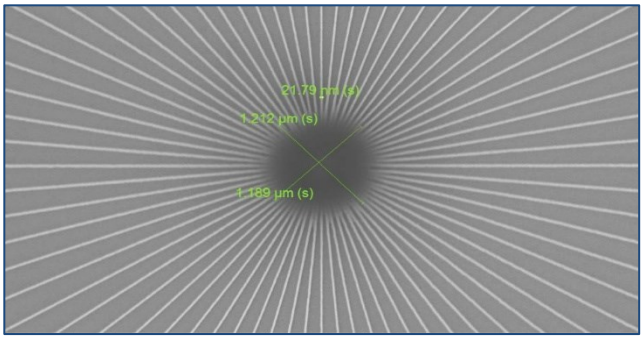
Structures with a high aspect ratio

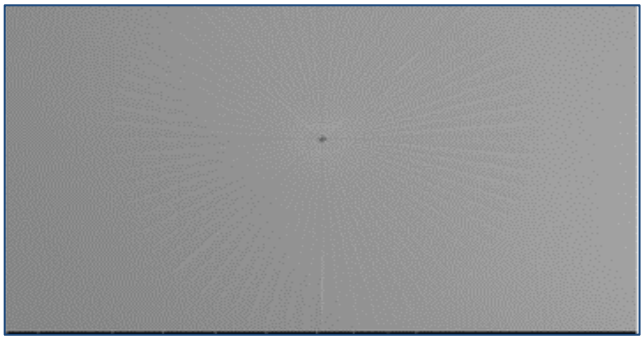




Left:Wall-structures written on GaAs with 600 µC/cm² @100 kV, 200 pA, developed with AR 300-73 (6.5% TMAH) for 60 s, PAB & PEB: 5 min @ 100 °C hotplate. © Yurii Kutovyi, FZ Jülich // **Right**: Nanorod written on silicon with 2000 µC/cm² @ 50kV and developed with AR 300-44 (2.38% TMAH). Aspect ratio of up to 10 was achieved. © R. Stöhr, ZAQuant University of Stuttgart.

Electra 94 as conductive coating for charge dissipation





Siemens star written on quartz with the new conductive coating Electra 94 (AR-PC 5094.02) spun on to prevent charge build-up.This variant of Electra 94 specially developed for HSQ, has excellent coating and adhesion properties.

© B. Drent, AMOLF NanoLab Amsterdam

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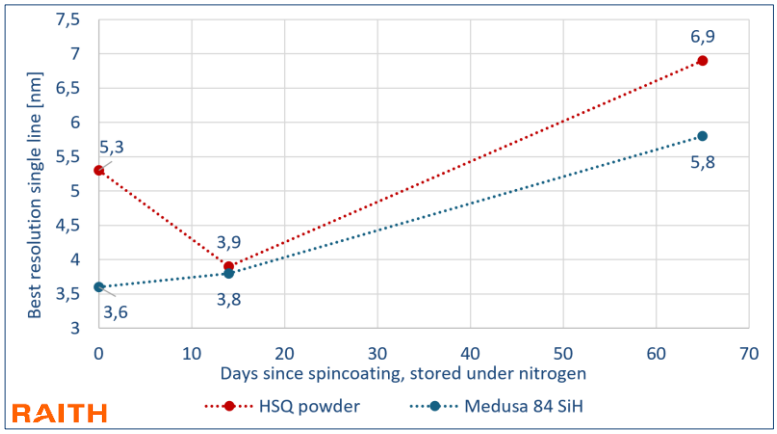
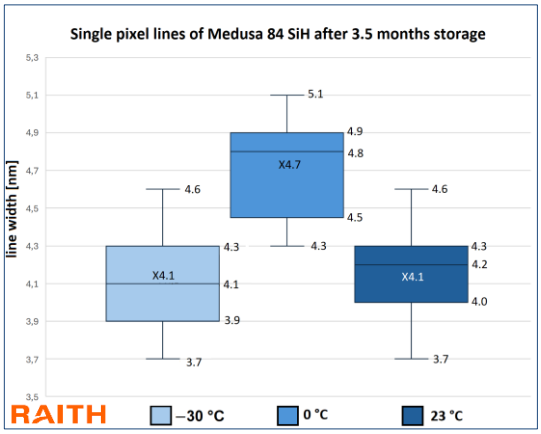
Process stability and storage under nitrogen atmosphere

The HSQ polymer, developed by Allresist, has a unique manufacturing and purification process. This results in the Medusa 84 SiH product being optimised in terms of its properties, such as minimum feature size, line edge roughness and process stability. This was confirmed in a study conducted by RAITH GmbH with their Voyager EBL-System at 50kV, 120 pA, base dose: 12.000 pC/cm, developer: KOH 1% 1 min. The Medusa 84 SiH was compared with an HSQ powder from another manufacturer, and the smallest possible line width was determined.

The highest achievable resolution of the Medusa 84 SiH is 3.6 nm on a freshly coated wafer (day 0), whereas the HSQ powder achieved significantly poorer values of 5.3 nm. Medusa 84 SiH also demonstrates a more consistent increase in achievable line width, with minimal change to 3.8 nm after 14 days. In contrast, the HSQ powder exhibited greater fluctuations throughout the entire observation period.

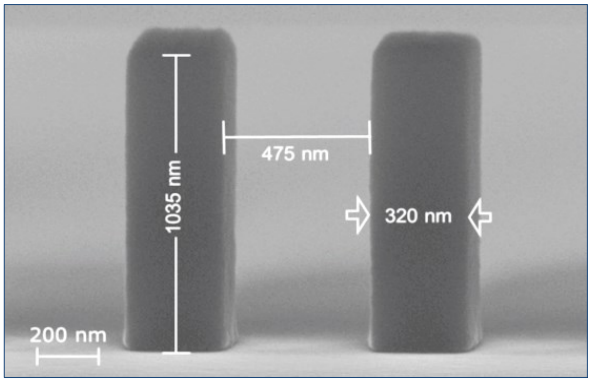




After 3.5 months, the effects of storing the Medusa 84 SiH resist solution at different temperatures (-30°C, 0°C and 23°C) showed only minor fluctuations. No degradation was observed despite storage temperatures exceeding the recommended range of 8-12 °C. The experiments were conducted at RAITH GmbH.

Double-coating for extended layer thickness range

Medusa 84 SiH allows for layer thicknesses of up to 1400 nm with double coating. This expands the range of applications for the thickest variant, SX AR-N 8400.22, which achieves a thickness of only 800 nm in a single coating at 1000 rpm. This improvement is achieved through the use of butyl acetate as a solvent instead of MIBK, as well as the high purity of the HSQ polymer in the solution.



© Yurii Kutovyi, FZ Jülich

The double coating process was demonstrated at FZ Jülich and requires precise control of the process fl ow. The final patterned structures of the double coating process are shown in the picture below. The process begins with a spin-coating step at 2,000 rpm using the SX AR-N 8400.22, followed by a 5-minute bake at 210 °C on a hotplate. It is critical that the wafer is allowed to cool for five minutes before the second spin-coating is applied. A second post-application bake is then carried out for 5 minutes at 130 °C (hotplate). Electron-beam exposure is then carried out at 100 kV with a beam current of 200 pA and a dose of 600 µC/cm². No post-exposure bake is required. Development is performed in AR 300-73 (6.5% TMAH) for seven minutes, followed by rinsing with deionised water and blow-dry.