

**New high etch resistant high resolution silsesquioxane based
resist for DUV/EUV and e-beam lithography as long
shelf-life and more sensitive alternative for HSQ
Medusa 82**

MNE 2019, Rhodes



Medusa, by Caravaggio (1595)

Matthias Schirmer
Allresist GmbH

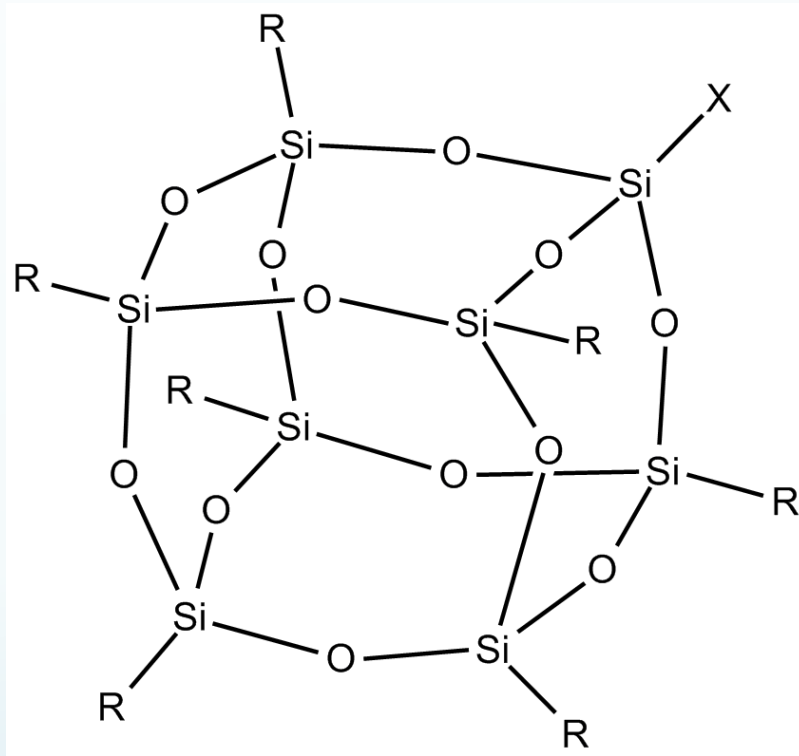
Rhodes, 26th September 2019

Short introduction of Allresist GmbH

- Founded 16th October in 1992
- Located in Strausberg, Brandenburg in Germany
- Quality management system ISO 9001:2015 and ISO 14001:2015
- 43 years experience in resist research & development
- 38 scientific projects completed successfully

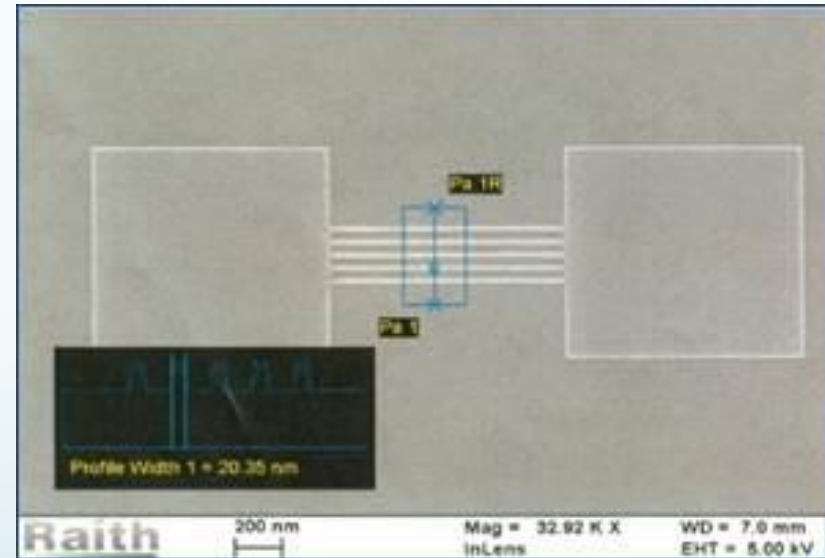


Introduction



R = H

Hydrogen silsesquioxane (HSQ)



20 nm bars of HSQ, prepared on quartz with Electra 92 conductive coating as top layer

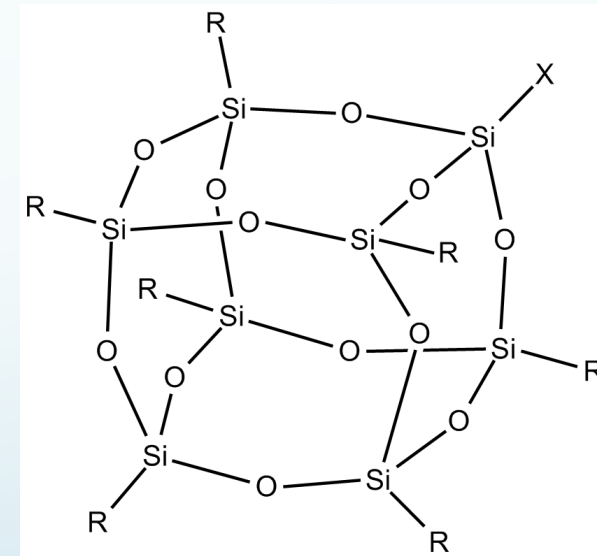
Motivation

Main goals

- Standard HSQ process
- High etch resistant
- Comparable sensitivity

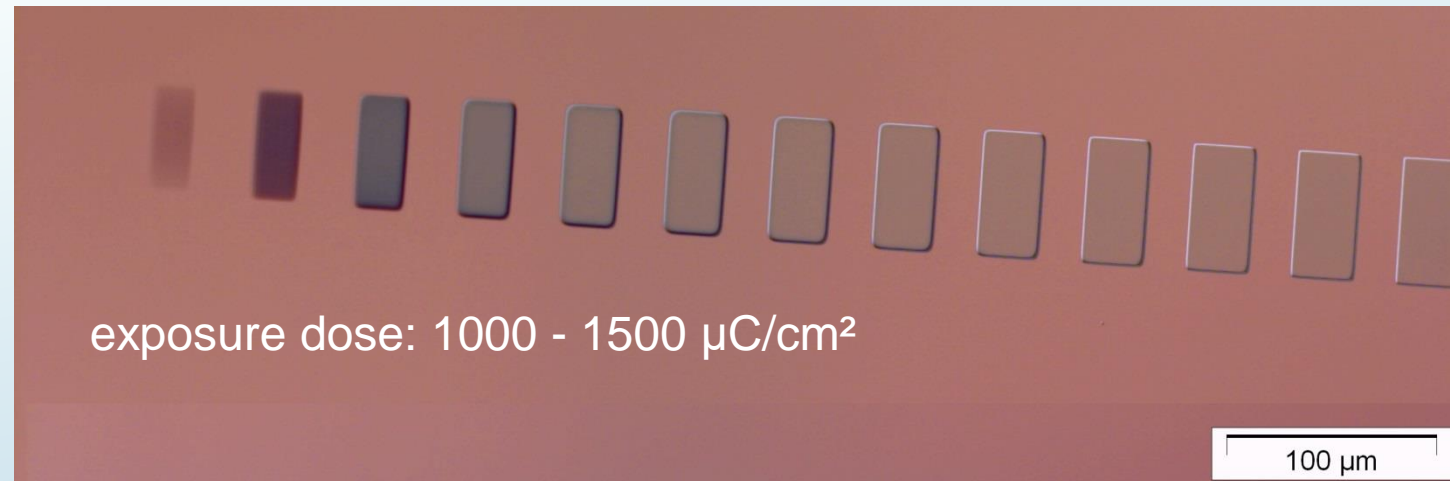
Additionally

- Try to find a robust and more stable system
- Try to increase the sensitivity
- Check compatibility with other processes
 - Ideally photolithography
 - Gray tone lithography



Early compatibility tests @ 30kV

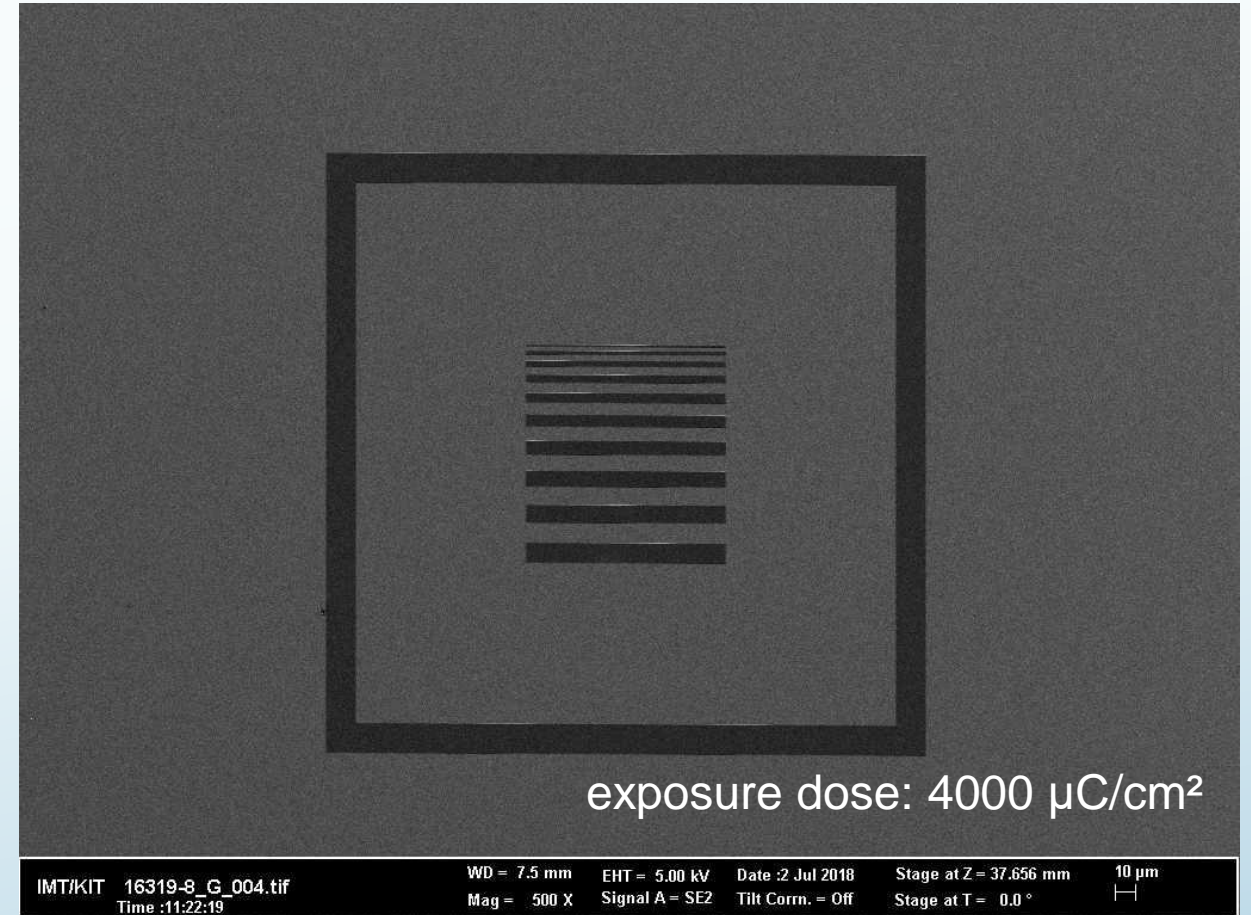
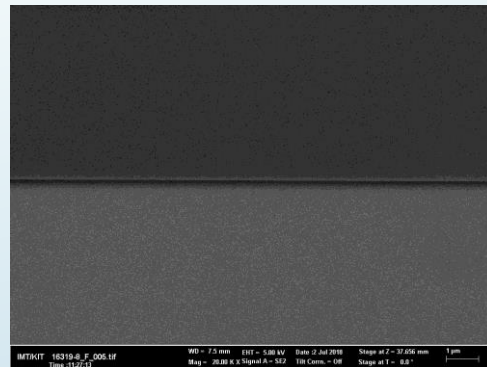
- Resist: SX AR-N 8200.06/1 - 100 nm
- Coating: 60 s 4000 rpm
- Soft-bake: 15 min @ 120°C
- Exposure: Raith Pioneer, 30 kV
- Development: 90 s AR 300-44; 23°C
- Stopping: 30 s DI-water



With special thanks to F. Heyroth and G. Schmidt, Institute for Physics, Martin-Luther-University, Halle (Saale)

Early compatibility tests @ 100kV

- Resist: SX AR-N 8200.06/1 - 100 nm
- Coating: 60 s 4000 rpm
- Soft-bake: 15 min @ 120°C
- Exposure: Raith Pioneer, 100 kV
- Development: 90 s AR 300-44; 23°C
- Stopping: 30 s DI-water



With special thanks to L. Hahn, Institute of Microstructure Technology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen Aachen

Medusa 82 is available (AR-N 8200)

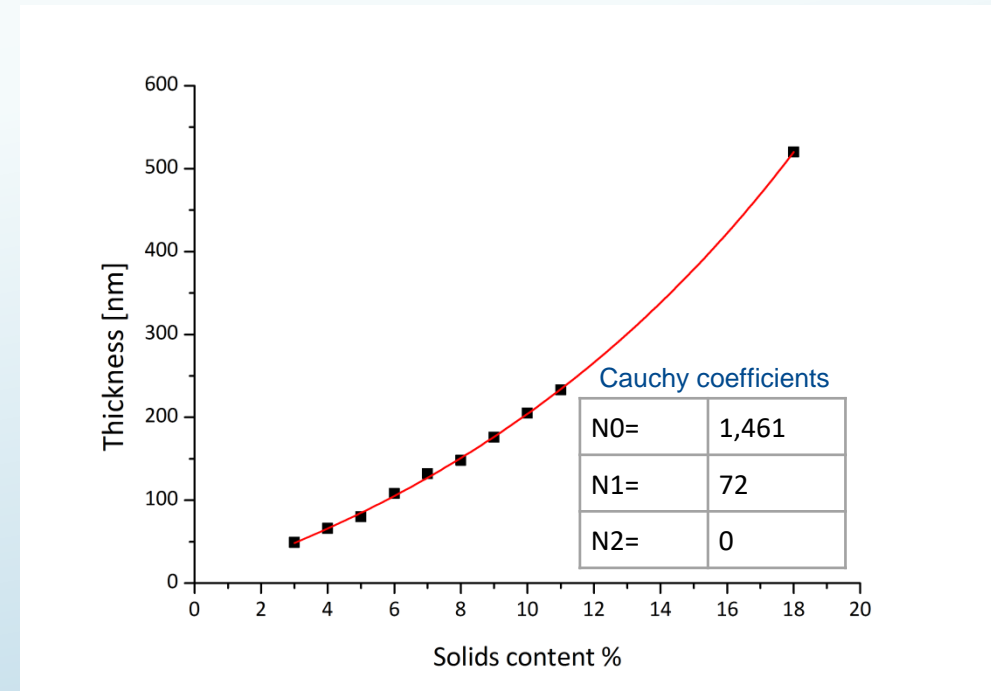
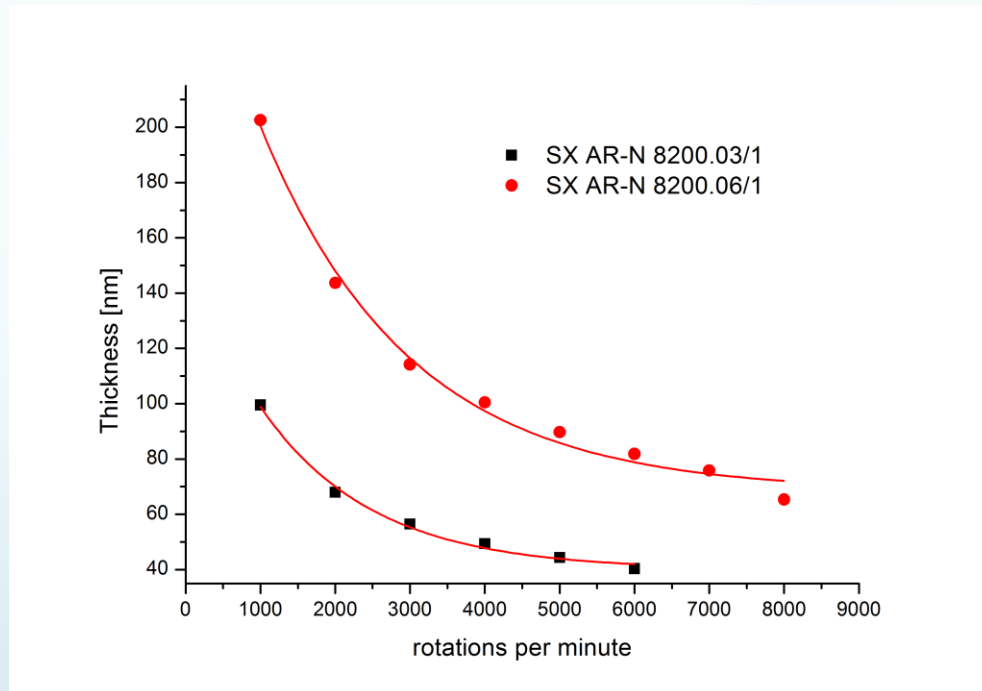
Stability of the liquid resist: Storage by 4 – 10 °C for the time being 6 month

Delivery time in Europe: 3 – 4 days

SX AR-N 8200.06 - 100 nm

SX AR-N 8200.03 - 50 nm

Up to 1 μm layers can realized @1000 rpm



Resolution

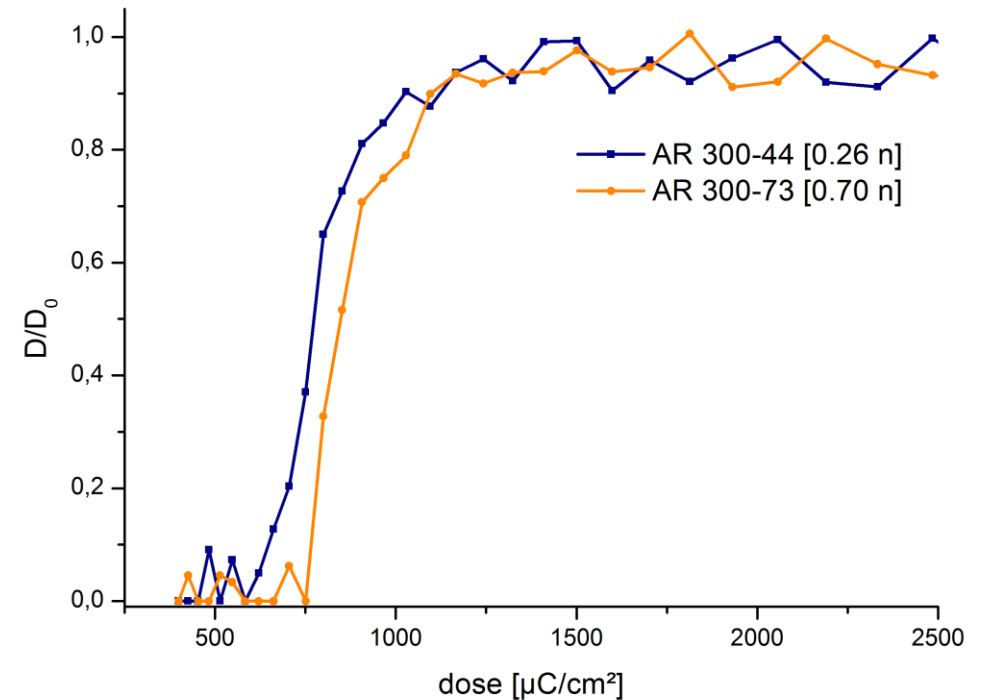
- Resist: SX AR-N 8200.03/1 - 50 nm
- Coating: 60 s 4000 rpm
- Soft-bake: 10 min @ 120°C
- Exposure: Raith Pioneer, 30 kV
 - 0 to 22 days delay
- Development: 90 s AR 300-44; 23°C
- Stopping: 30 s DI-water



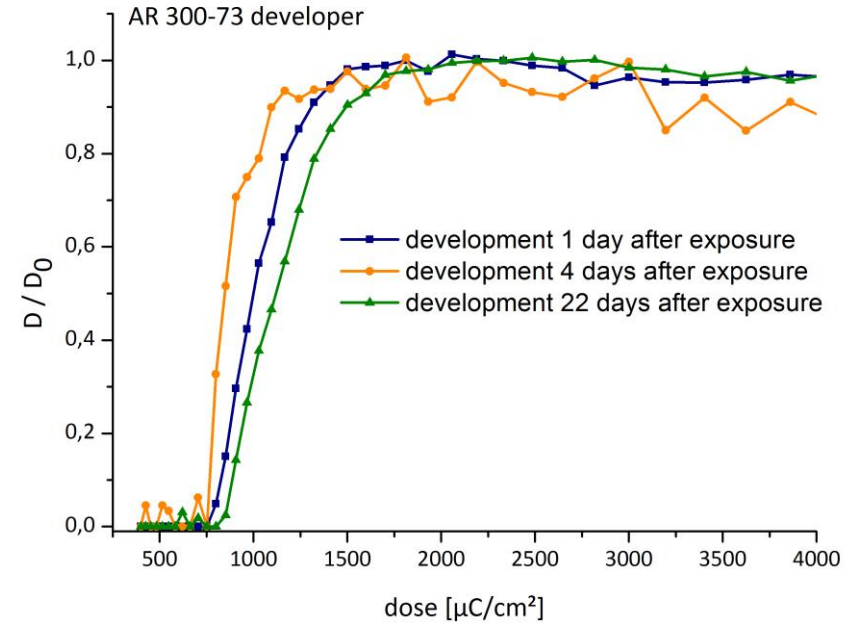
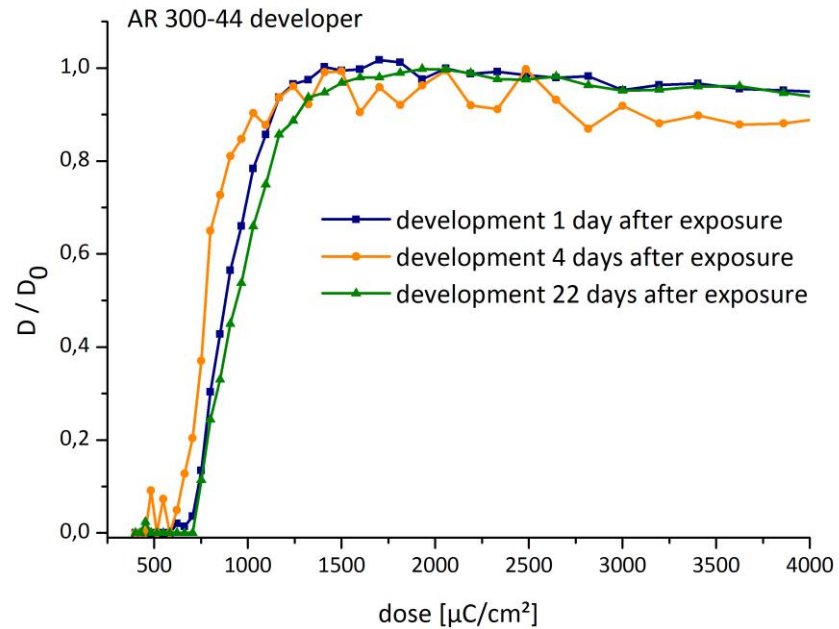
With special thanks to N. Pyka, Raith GmbH, Dortmund

Influence of developer's concentration

- Resist: SX AR-N 8200.06/1 - 100 nm
- Coating: 60 s 4000 rpm
- Soft-bake: 15 min @ 120°C
- Exposure: Raith Pioneer, 30 kV
- Development: 90 s AR 300-44; 23°C
- Stopping: 30 s DI-water

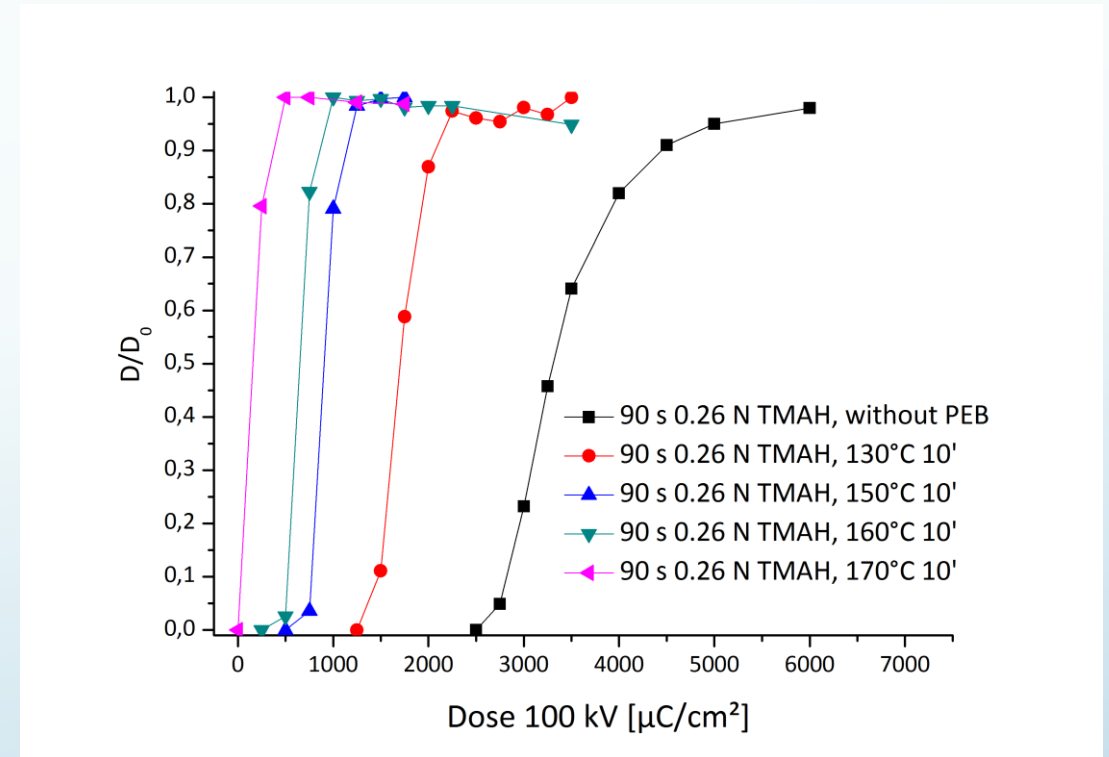
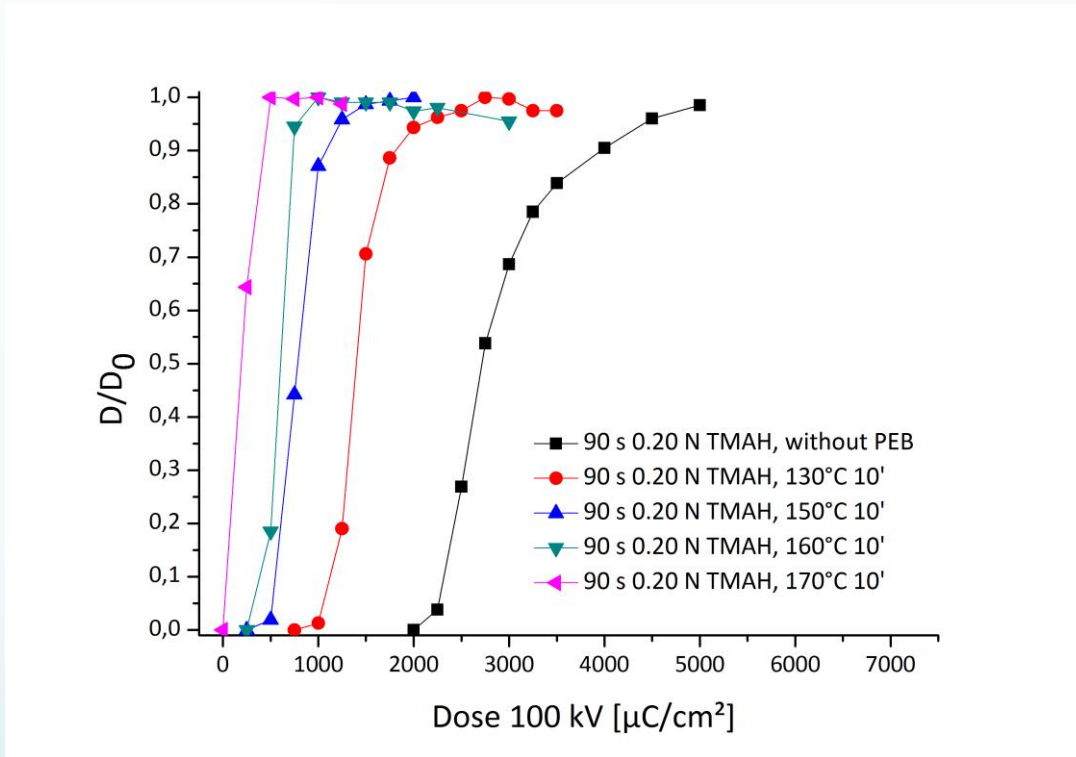


Influence of time after exposure



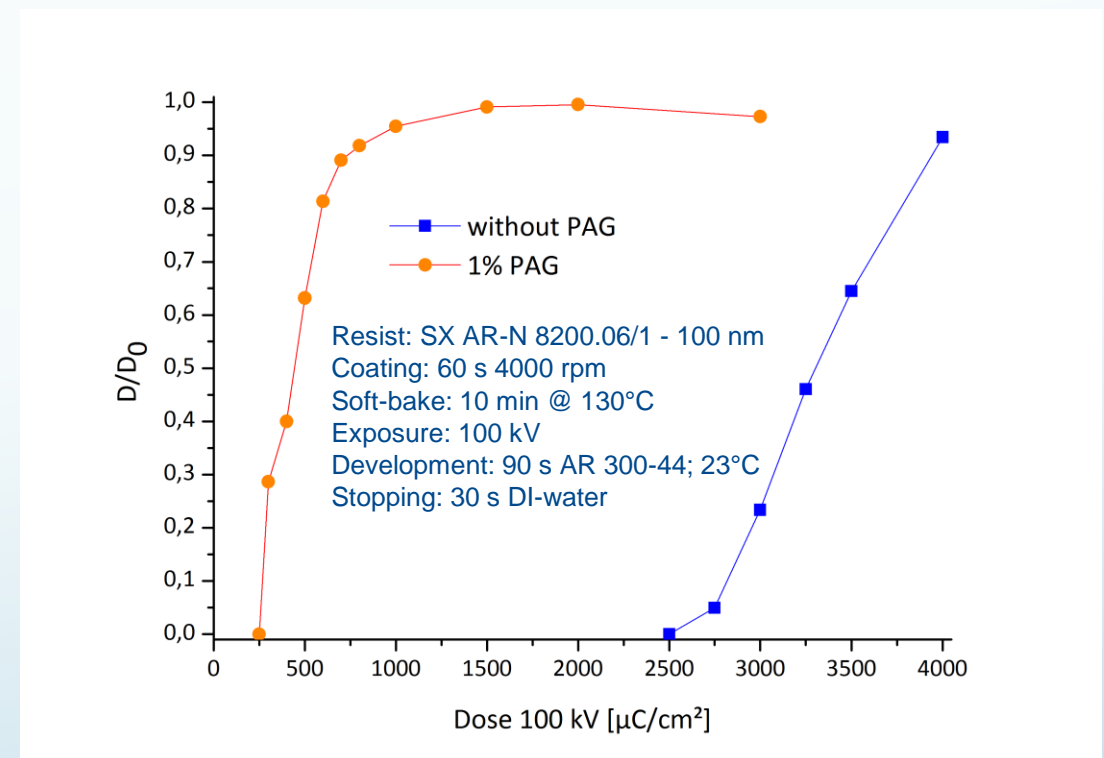
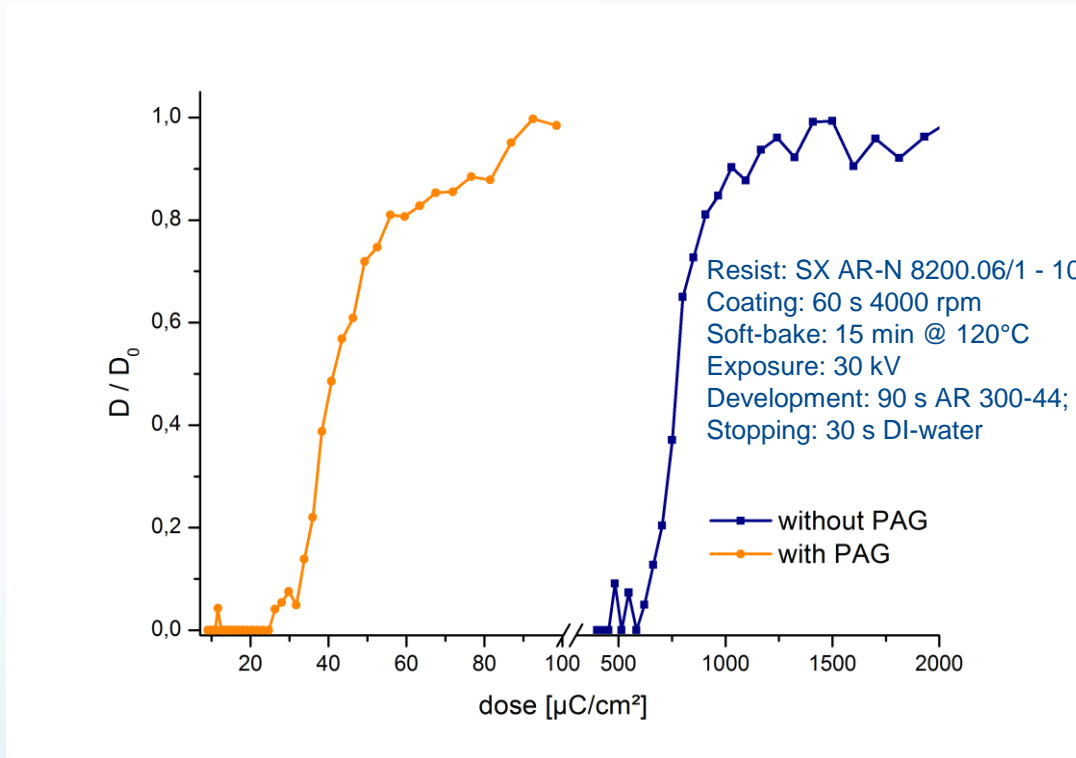
Time [days]	300-44	0.26 N	300-73	0.70 N
	Contrast	Dose [$\mu\text{C}/\text{cm}^2$]	Contrast	Dose [$\mu\text{C}/\text{cm}^2$]
1	4.7	690	4.6	785
22	3.9	688	4.2	793

Increasing sensitivity by temperature



Increasing sensitivity with PAG (AR-N 8250)

The silsesquioxane used for Medusa can cross-linked by very strong acids.

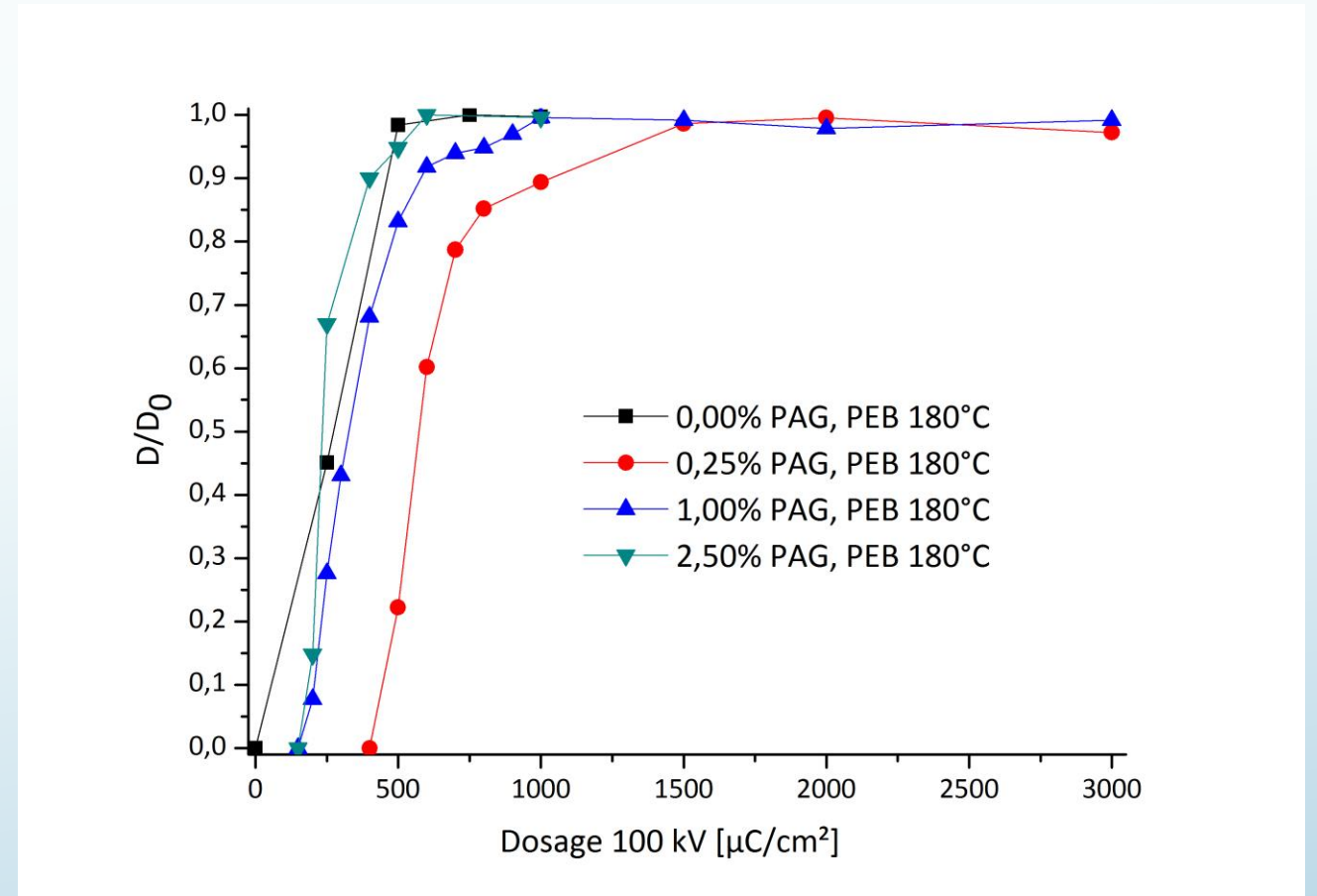


20x higher for 30 kV and 5x higher for 100 kV

It was shown, Medusa UV (8250) is principally suitable for i-line photolithography, but further experiments are necessary.

Increase sensitivity additionally by PAG and temperature?

- Both processes enhance sensitivity
- Combination does not further improve sensitivity

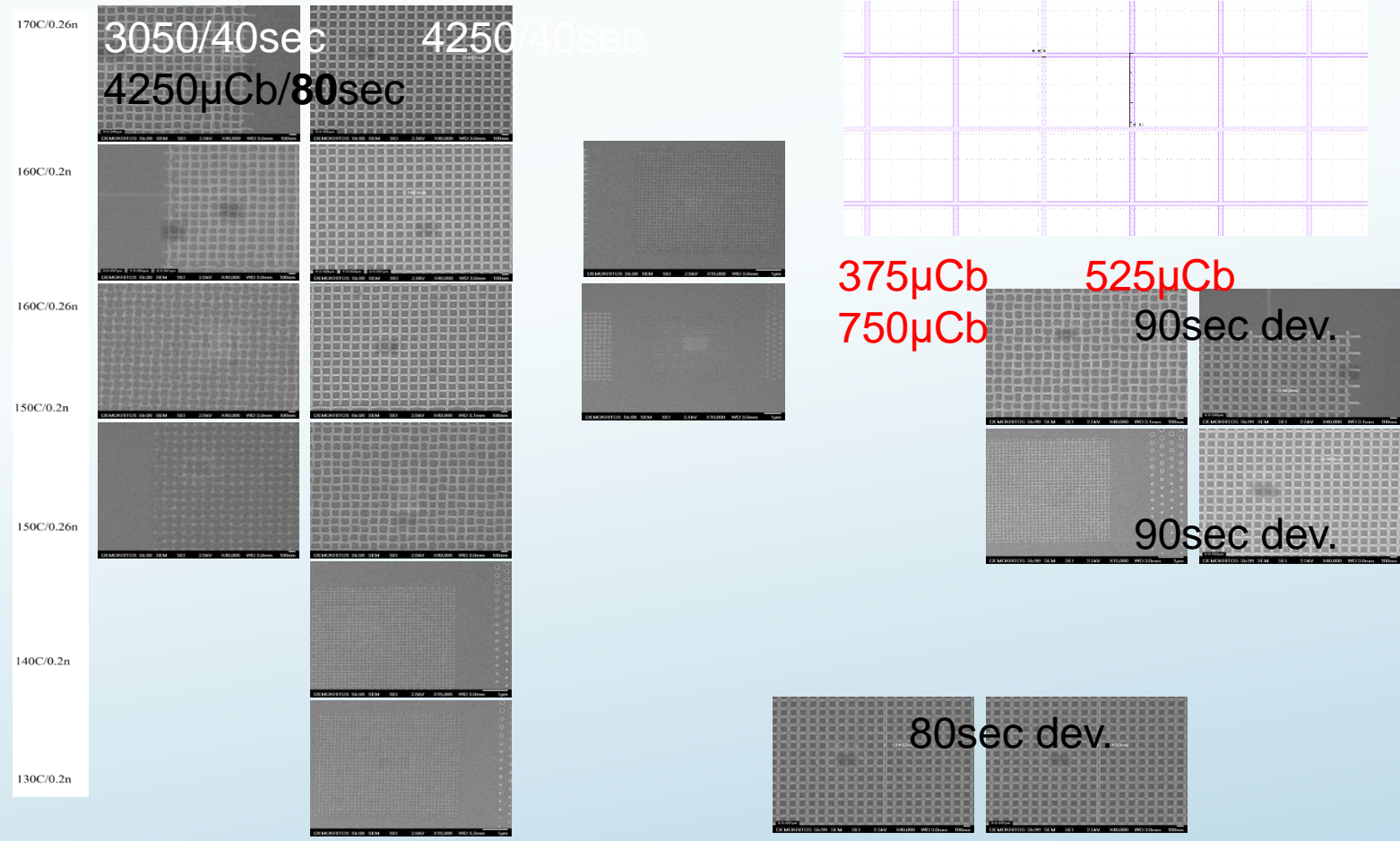


Optimizing of the process parameters

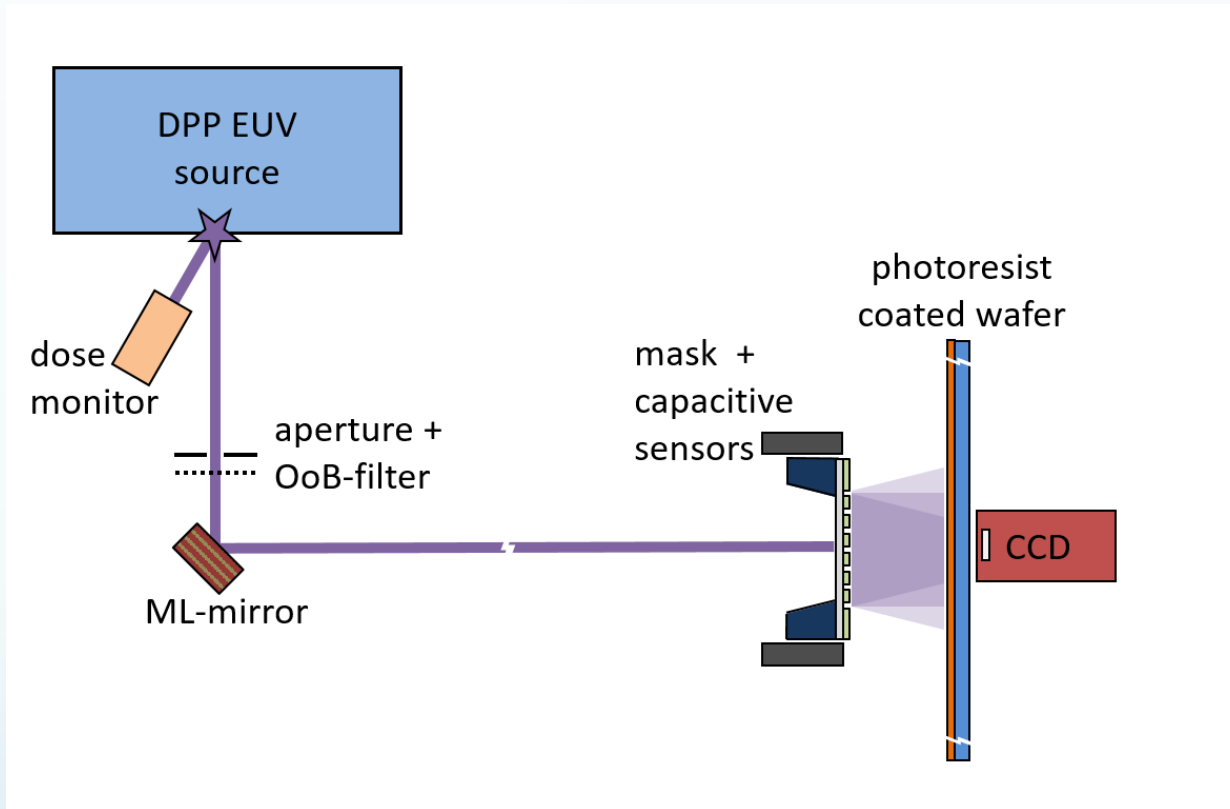
EBL: dose, processing and development influence on both resists' lithographic performance

Many parameters are investigated

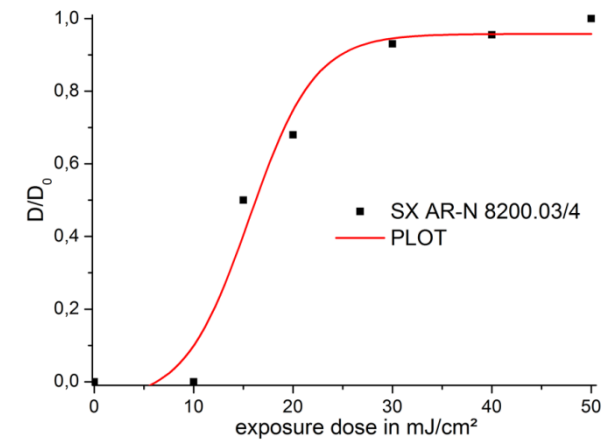
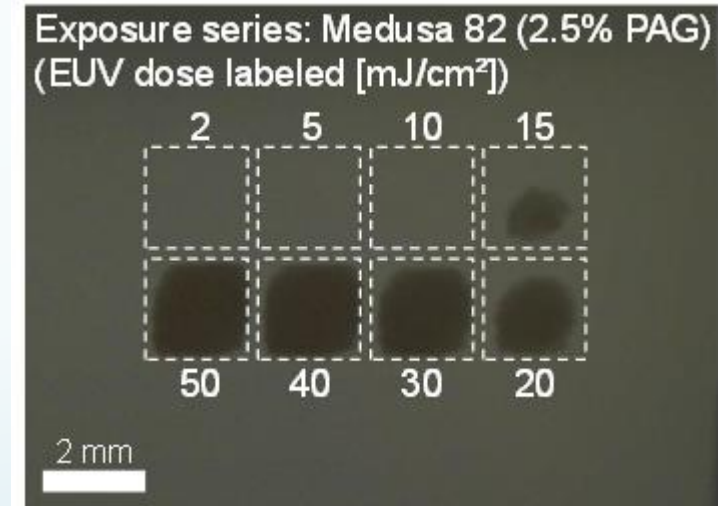
- Dissolution rate un-/exposed
- Contrast curves variation:
 - Bake temperature
 - Bake time
 - Developer concentration
 - Developer time
 - Contrast curves analysis
- dose and processing influence on resist lithographic performance



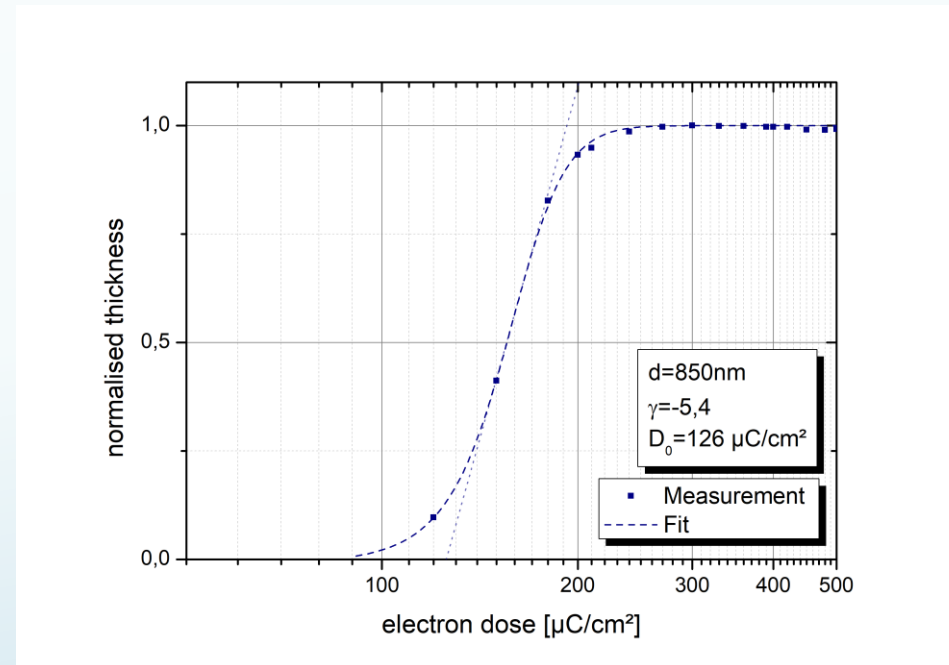
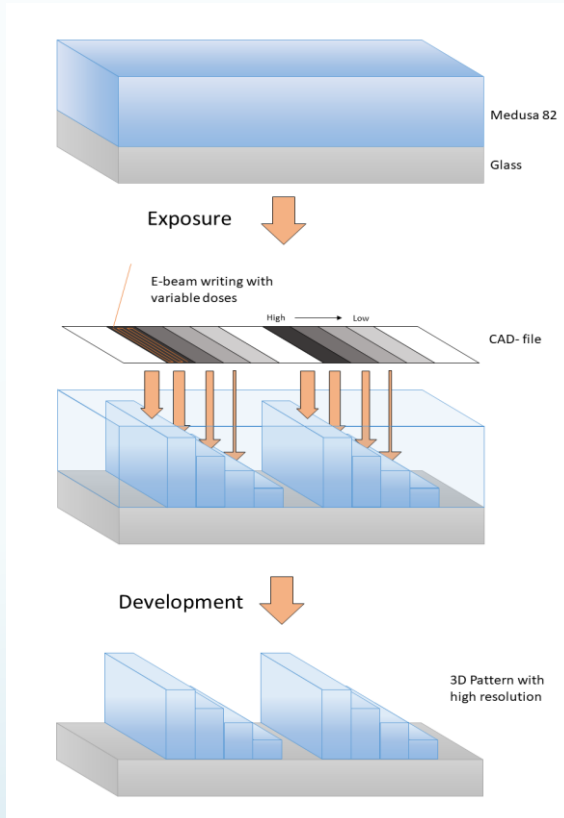
Deep-UV compatibility



With special thanks to S. Brose, RWTH Aachen, Chair of Technology Optical Systems TOS, Aachen



Medusa 82 for gray-scale lithography



Contrast curve of Medusa 82

- Resist: **SX AR-N 8250.18/1**
- E_0 : 50 keV
- Temp. (HP): 10 min 150 °C
- Contrast: -5
- D_0 : 126 $\mu\text{C}/\text{cm}^2$
- Development: 60 s AR300-44

→ Contrast suitable for gray tone

Principle of gray tone lithography

Medusa 82 for gray-scale lithography



10-level blazed grating

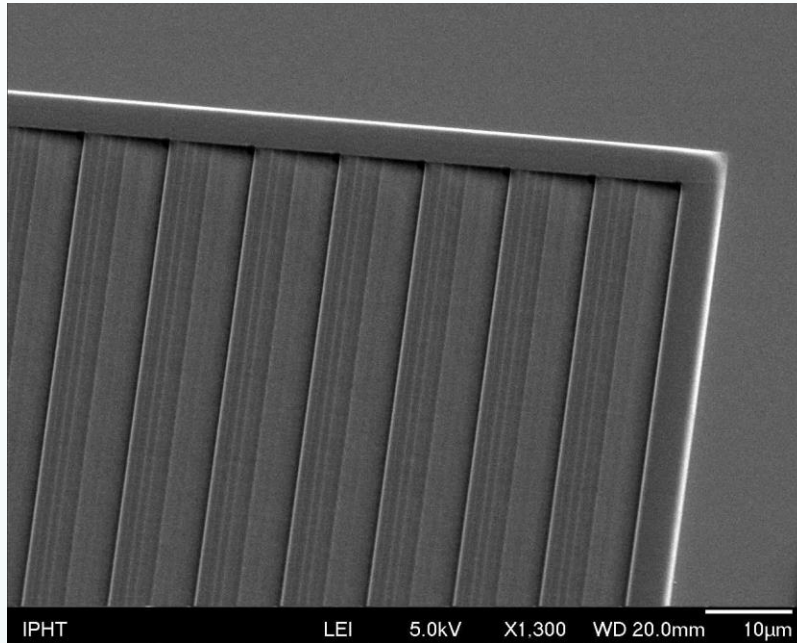
Blazed grating (10-level)

Resist thickness: 900 nm

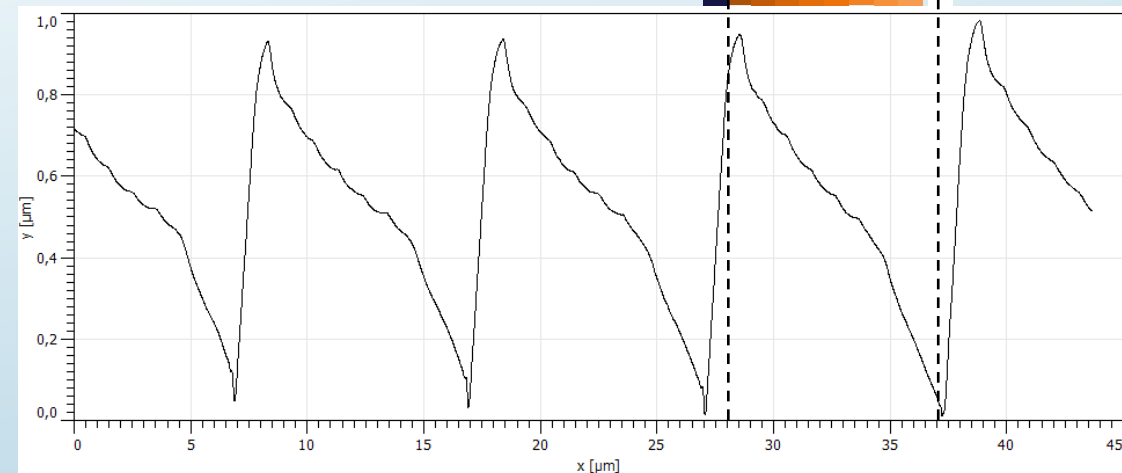
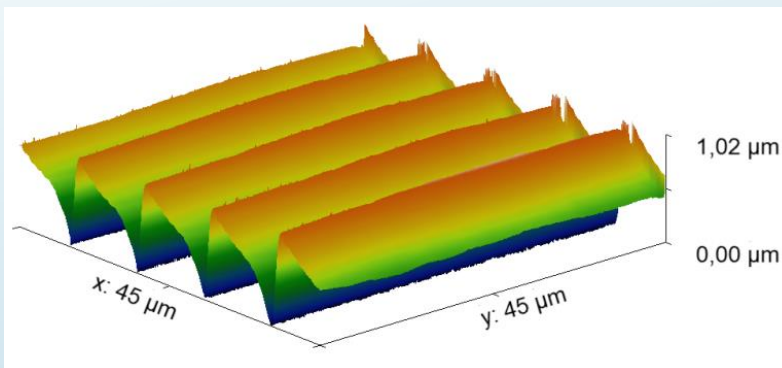
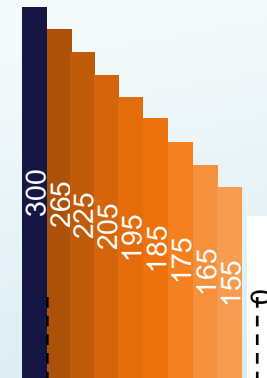
Grating pitch: 10 μm

Smallest feature size: 1 μm

Dose levels: from 155 to 300 $\mu\text{C}/\text{cm}^2$
(see sketch)

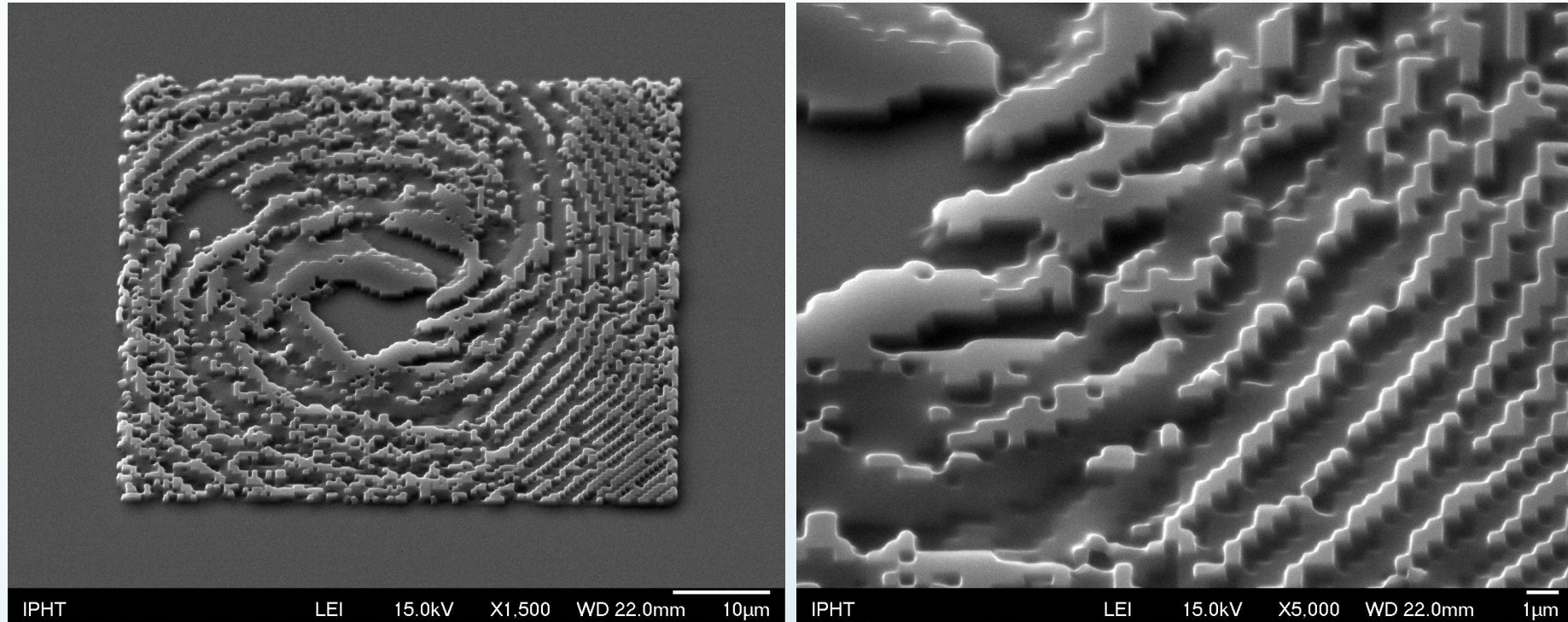


Electron dose in [$\mu\text{C}/\text{cm}^2$]



Medusa 82 for gray-scale lithography

3-level hologram (DOE-pixel)



SEM-micrograph of a 3-level DOE-pixel (tilt 25°) made in 800 nm Medusa 82 UV

DOE-pixel (3-level hologram)

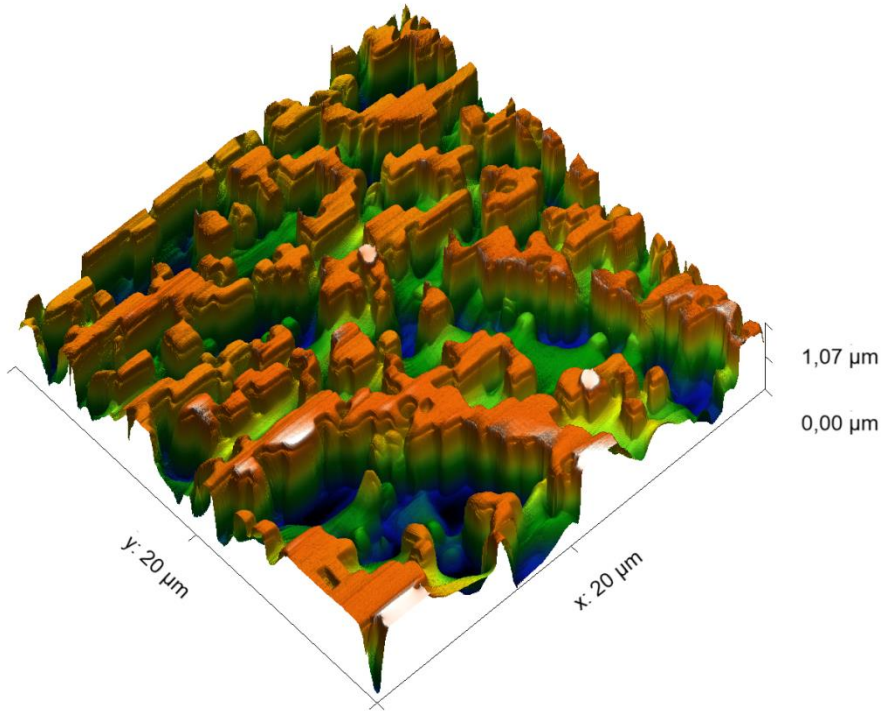
Resist thickness: 800 nm

Smallest feature size: 500 nm

Dose level: 0 $\mu\text{C}/\text{cm}^2$, 210 $\mu\text{C}/\text{cm}^2$, 450 $\mu\text{C}/\text{cm}^2$

Medusa 82 for gray-scale lithography

3-level hologram (DOE-pixel)



Standard technology

- Hard mask layer
- E-beam lithography
- Structuring hard mask
- ICP- etching in quartz
- Removing of hard mask

Process with Medusa 82

- only e-beam lithography of Medusa 82

With special thanks to U. Hübner and P. Voigt, Leibnitz-Institute of Photonic Technology G, Jena

AFM measurement of a section of the DOE pixel

AFM: FRT Microprof

All experiments over several weeks were made with resist from the same bottle.
Storage: fridge 4 – 10 °C

Conclusion

- Medusa 82 as alternative to HSQ with comparable properties
- Medusa 82 can be processed with the HSQ standard conditions
- The storage is possible by 4 – 10 °C for 6 month
- Broader process window
- Increasing the sensitivity by 2 ways: added PAG or make a PEB
- Compatible with Deep-UV (30 mJ/cm² @ 13,5 nm)
- Gray scale lithography is possible with Medusa 82
- Easy process for 3-level hologram (DOE-pixel)