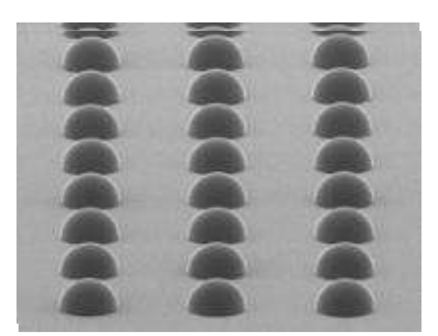
Photoresists for direct writing lithography

Dr. Anja Voigt

micro resist technology GmbH,
Berlin, Germany

2nd OPTIMAL WS @ JOR

November 20, 2025



Content

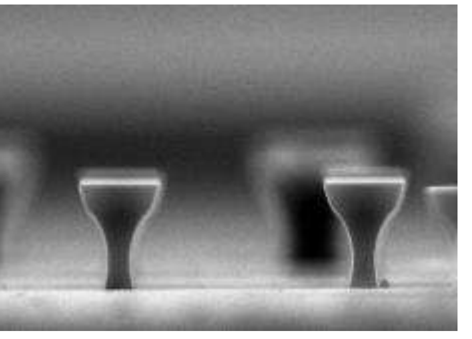
1 Company information

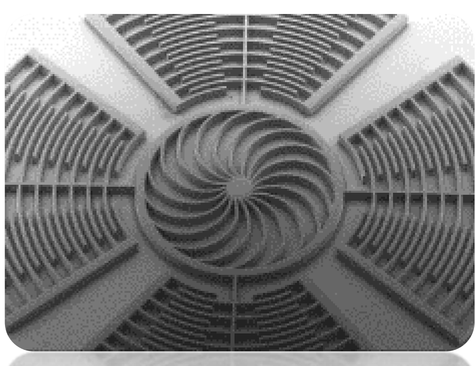
2 Negative resists
and application examples

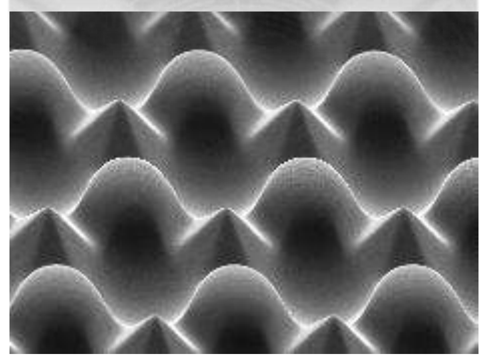
3 Positive resists
and application examples

4 Hybrid polymers
and application examples

5 Summary







micro resist technology GmbH – who we are…

Specialized in providing **innovative resists, polymers, photopolymers and ancillaries**,
we support our high-tech customers with high performance materials, technologies and process solutions.

- *Established:* 1993 (since March, 1st 2025 wholly owned subsidiary by TOKYO OHKA KOGYO CO., LTD.)
- *Employees:* ~55 (2025)

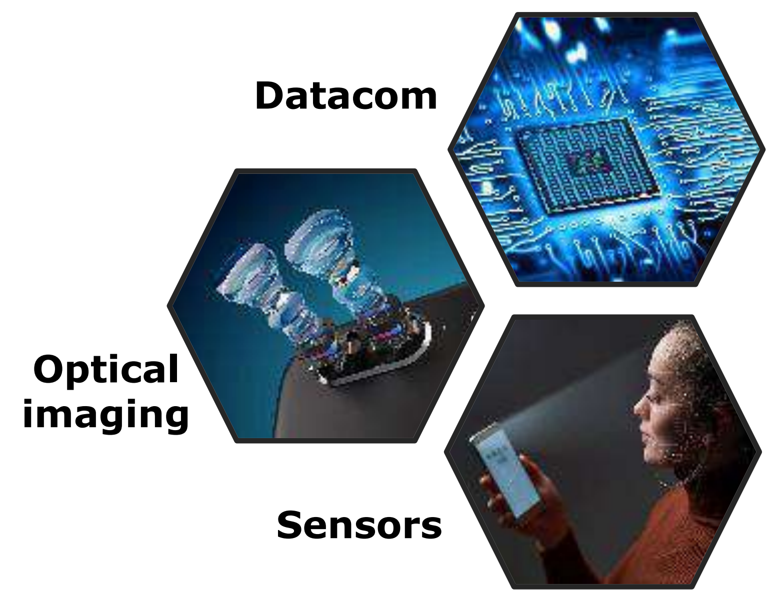
- *Location:* Berlin, Germany
  (Corporate office, logistics and manufacturing)
- *Facility*: 3.450 m^2 incl. clean room (300 m^2)
- *Certifications:*
  ISO 9001:2015
  ISO 14001:2015

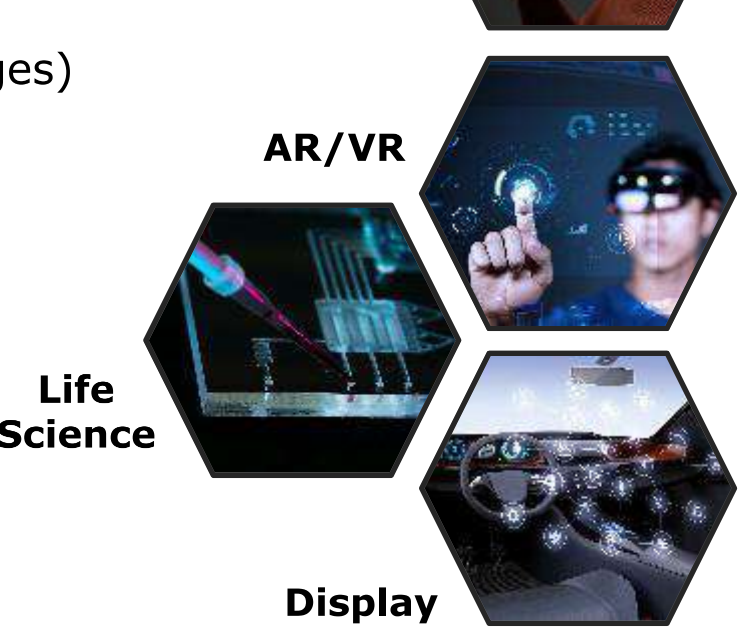
- *Fields of business activities:*
  - Manufacturing: formulation / synthesis
  - Distributorship (products of partner companies)
  - Researching advanced materials and processes
  - Lithographic Services

KAYAKU ADVANCED MATERIALS
DUPONT
DJ MICROLAMINATES, Inc
Shin-Etsu

micro resist technology GmbH – Application and end-use industry

Consumer Electronics **Automotive / Mobility**	▪Micro-electronics ▪Sensors Technology ▪Micro-optics & Photonic Components ▪Display & Immersive Technology
Lighting & Telecommunication Technology	▪LED & Laser Lighting ▪Photonic Integrated Circuits ▪Opto-Electronics
Security Features	▪Physical Security Feature (Holographic images) ▪Decorative elements (packaging / labels)
Health Care / Medical **Life-Sciences**	▪Mechanical Microcomponents ▪Microfluidics & Point-of-Care ▪Lab-on-Chip
Others	▪3D Printing & Additive Manufacturing ▪Emerging Technologies



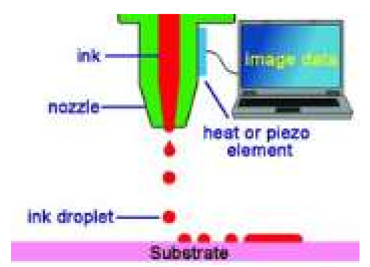


Photoresists for direct writing lithography

Direct writing lithography ⇒ mask-less patterning technology

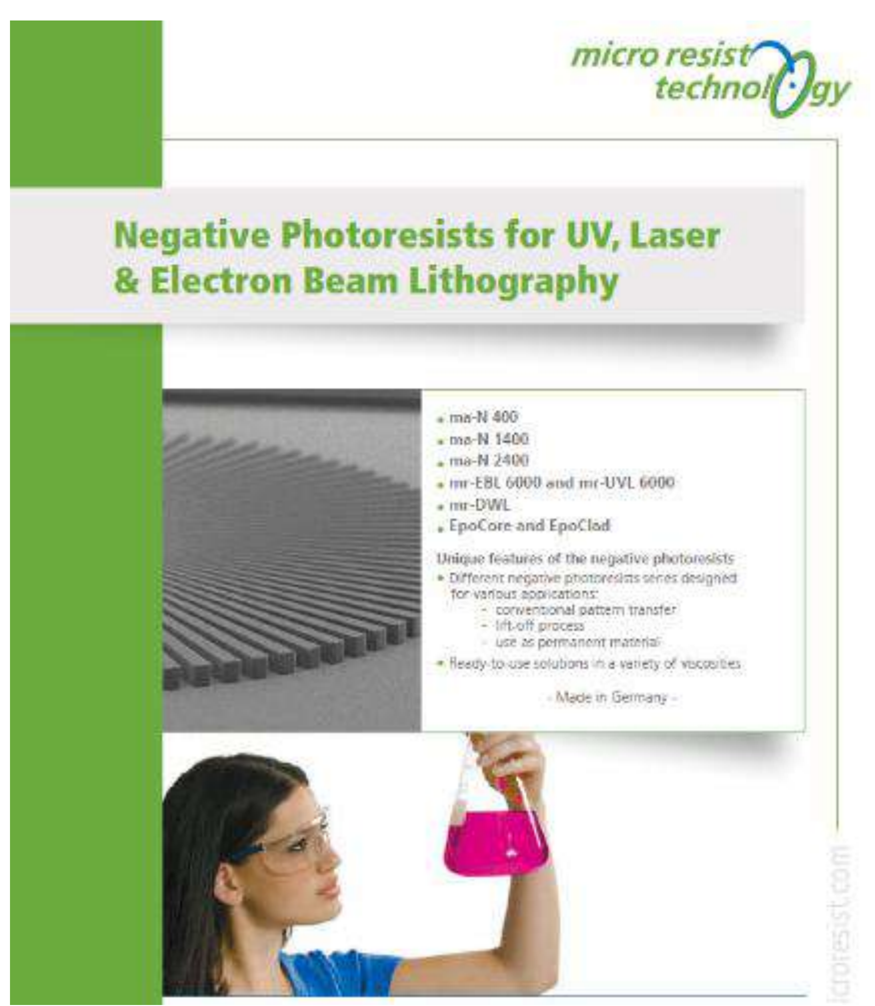
Beam based patterning: ⇒ e-beam
⇒ Laser : 1PL, 2 or MPL, LIL

Direct deposition: inkjet printing



⇒ Useful to generate 2D, 2.5 D and 3 D patterns

Negative resists



- For E-Beam lithography
  ma-N 2400 & **mr-EBL 6000**

- Mix & match approach
  ma-N 1400 & **mr-EBL 6000**

- For laser based lithography
  mr-DWL

Negative resists – for E-Beam lithography

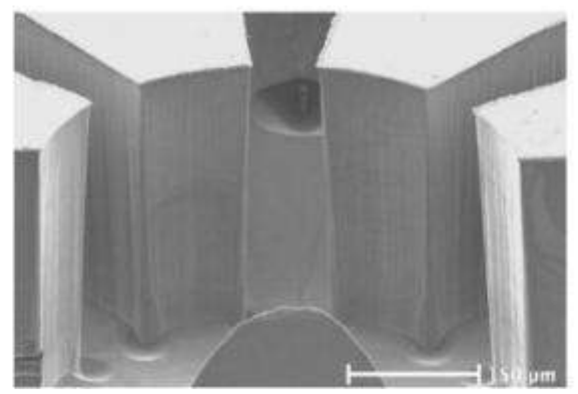
ma-N 2400 series

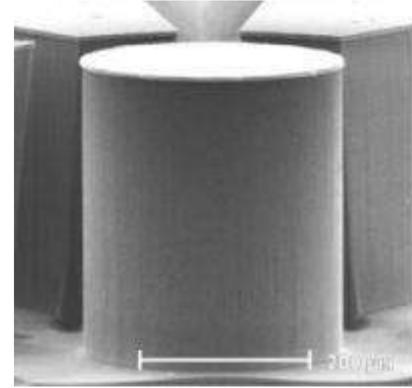
- Non-CAR
- Aqueous alkaline development

Applications:

- Micro- and nanoelectronics
- Etch mask for semiconductors and metals

Pattern transfer via RIE





Resist mask (bright top layer) on Si pattern after
RIE (CHF_3) plasma (high etch selectivity of resist to Si)

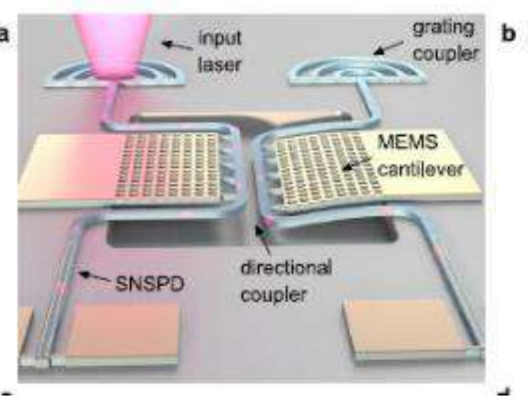
Blideran et al Microelectron. Eng. 86 (2009) 769 – 772
Schuster et al AnalBioanalChem (2008)

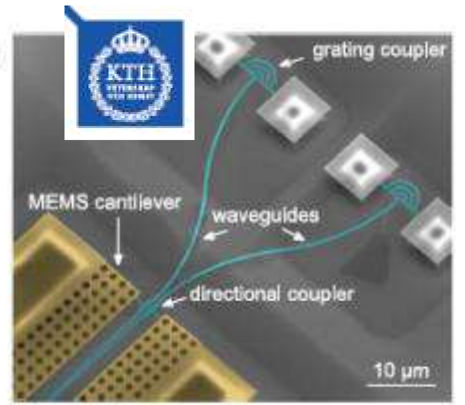
Cryogenic RIE: SF6:O2, @ -120 °C,
etching depth of 3.0 ± 0.1 µm (Si), Selectivity of 9.7

P. Yousefi et al, Nuclear Inst.&Methods in Phys.Res.Sec. A: Vol. 909, 2018, 221
P. Yousefiet et al , Optics Letters , Vol. 44, No. 6 (2019)

Patter transfer via RIE/Lift-off

Gyger at al_Nature Communications 2021, https://doi.org/10.1038/s41467-021-21624-3

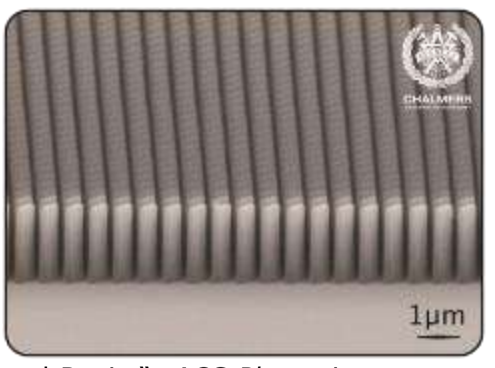




Reconfigurable photonics with on-chip single-photon detectors
- Cr/ Au marker lift-off (ma-N 2400)
- CHF_3 RIE (ma-N 2400) → Si_3N_4 WG device

Patterning for permanent applications

High AR patterns on Si, glass or PET,
FT: 1.9 µm;
400µC/cm² (EPRG200, 100 keV)



D. Andrén et al „Large-Scale Metasurfaces Made by an Exposed Resist“, *ACS Photonics* 2020, 7, 4, 885-892, https://doi.org/10.1021/acsphotonics.9b01809

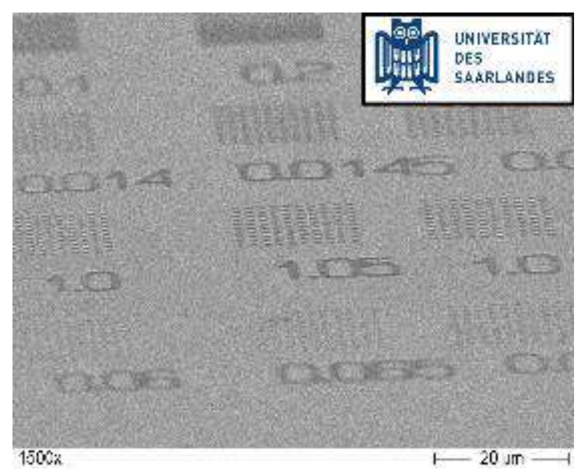
mr-EBL 6000 series

- CAR
- Solvent development

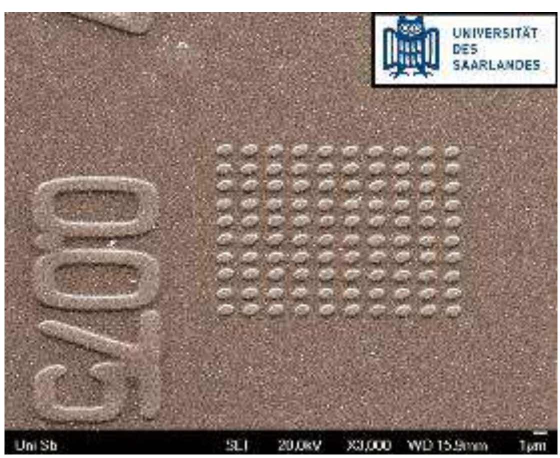
Applications:

- Micro- and nanoelectronics
- Etch mask for semiconductors and metals

Pattern transfer via RIE

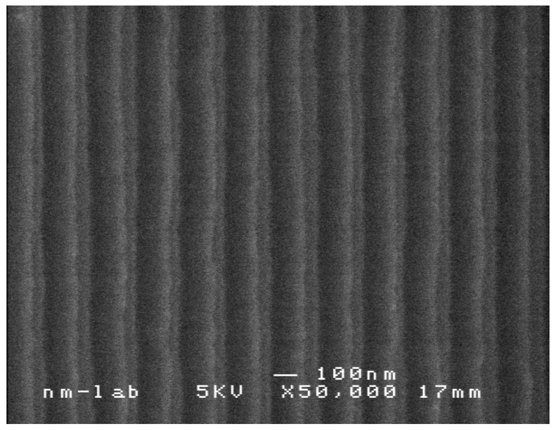


120 nm thick mr-EBL 6000,
Resolution < 100 nm



98 nm SiC dots (FT: 70 nm)
after ICP RIE SF_6 & resist removal

Permanent app: Fabrication of stamps for NIL



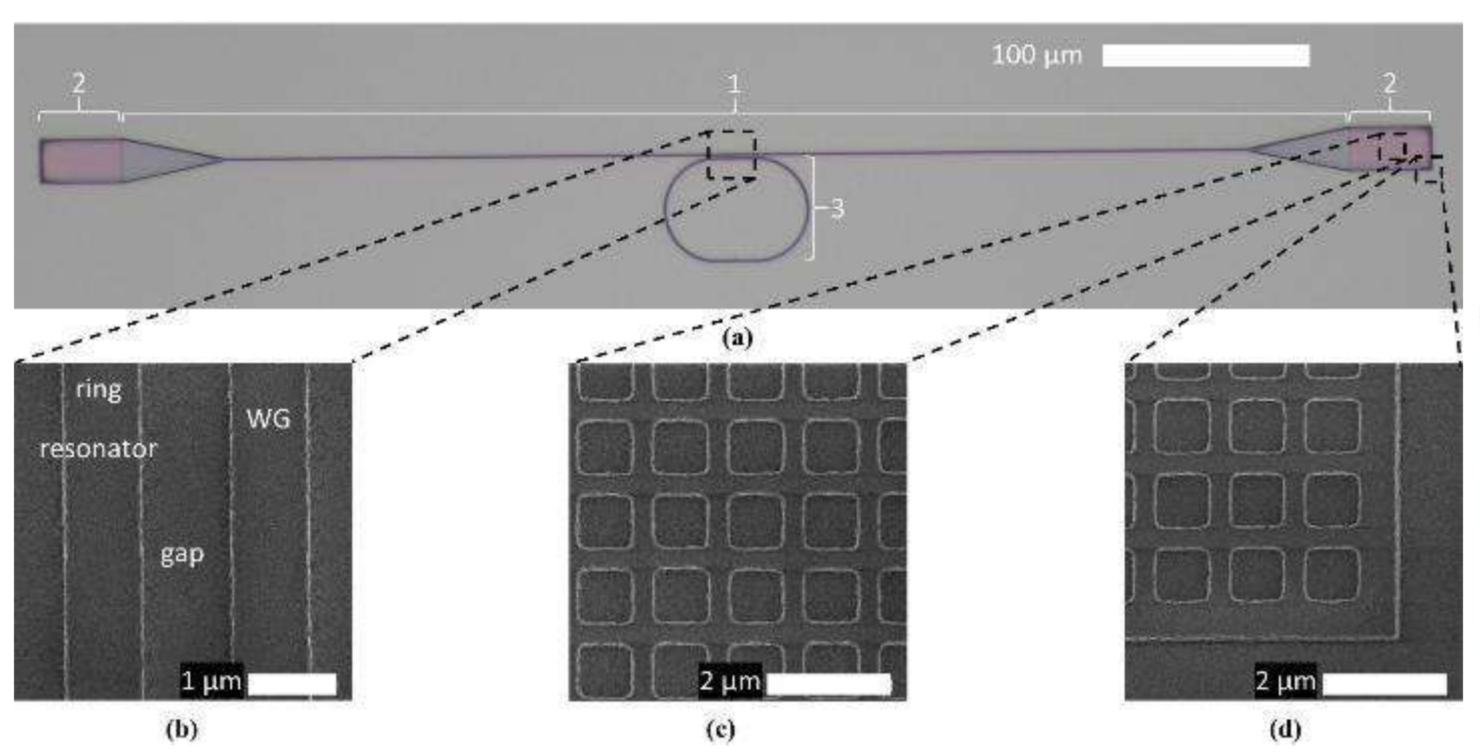
mr-EBL 6000 stamp,
100 nm thick, 100 nm L/S

Maximov et al. Poster Nanotech (2002)

Negative resists – for a Mix & Match approach

mr-EBL 6000 series **E-Beam & i-line stepper (ILM&M)**

Fabrication of photonic integrated circuit (PIC) related waveguides (WG), ring resonators and coupling structures (for etching in LP-Si_3N_4)

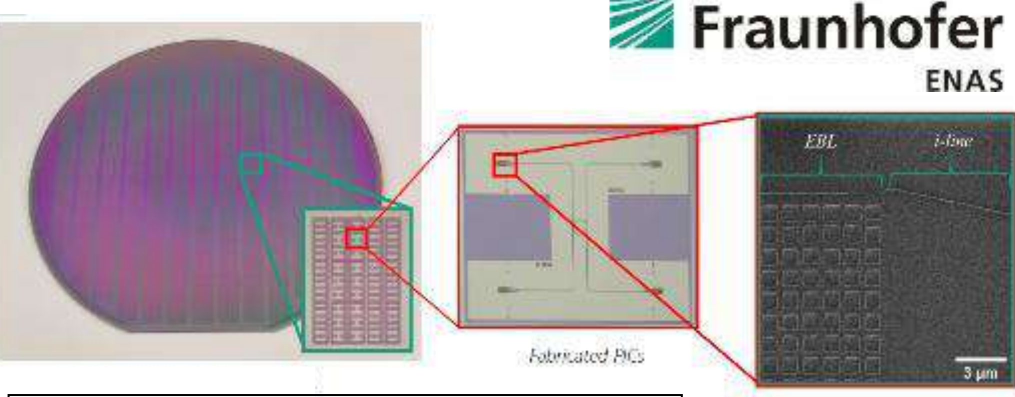


Optical microscope image of: FT: 500 nm, (1) WG (900 nm width),
(2) coupling structures (hole array, 800nm square holes, 400 nm line bars),
(3) ring resonator (900 nm width, 0.5µm/ 1 µm gap to WG)

i-line stepper exposure (365 nm):
→ Preliminary PIC pattern

e-beam lithography (50 keV):
→ Fine tuning pattern accuracy

Fraunhofer ENAS



6” wafer, 150 Chips, 72 PICs:
2.5 h e-beam + 3 min i-line
(compared to 14 h e-beam only)

M. Reinhardt et al, Proc. SPIE 12802, EMLC 2023, https://doi.org/10.1117/12.2675558

S. Schermer et al, Oral presentation @ MNE 2023
Ch. Helke et al oral presentaion @ EIPBN 2024

Negative resists – for a Mix & Match approach

ma-N 1400 (UV-resist)

E-beam (50 keV) & i-line stepper

Device1 — 25 µm, 4 µm, 1 µm

Device2 — 25 µm, 20 µm, 5 µm

Device3 — 25 µm, 10 µm, 2 µm

6” wafer:
2 h e-beam + 5 min i-line
(compared to 10 h e-beam only)

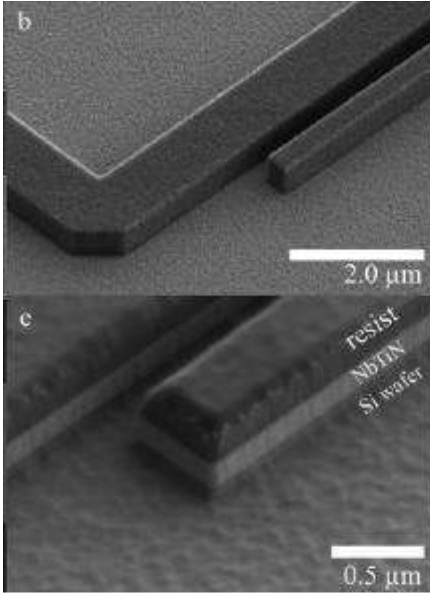
Optical & SEM images of devices: 200 nm thick ma-N 1400, smallest resolution: 55 nm by EBL & 350 nm by i-line stepper

Fraunhofer ENAS · Technische Universität Chemnitz · ZfM Zentrum für Mikrotechnologien

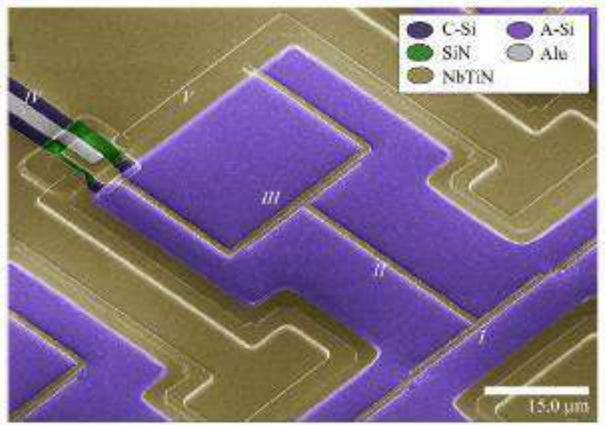
E-beam (100 keV) & MA (i-line)

500 nm thick ma-N 1400,
Pattern dimensions:
1 µm + 0.45 µm, gap 300 nm

(smallest resolution by EBL: 100 nm L)



On-chip terahertz spectrometer: SF_6/O_2 etch of NbTiN



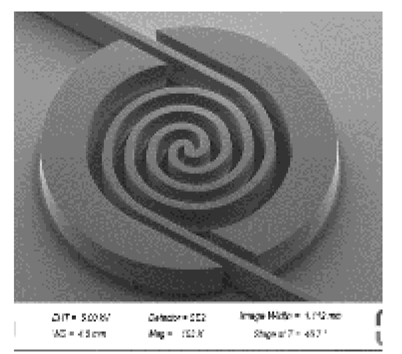
D. J. Thoen et al, J.Vac.Sci.Technol. B 40, 052603 (2022); doi.org/10.1116/6.0001918

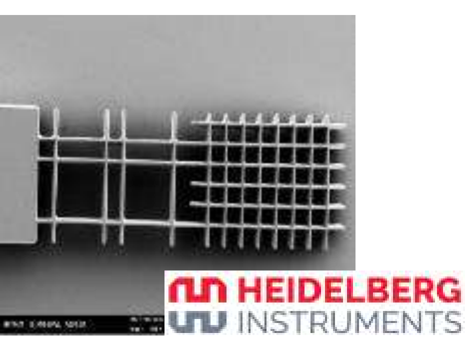
a) Canpolat-Schmidt at al, Proc. SPIE 12472, 37th EMLC, 124720J (2022); doi:10.1117/12.2639447
b) C. Helke et al, *Micro and Nano Engineering, Volume 19 (2023) 100189* doi.org/10.1016/j.mne.2023.100189
c) Helke et al @ EIPBN 2024

Negative resists – for a laser direct writing

mr-DWL

Features & Applications:
- UV sensitive until 405 nm
- fast and contactless prototyping with DWL

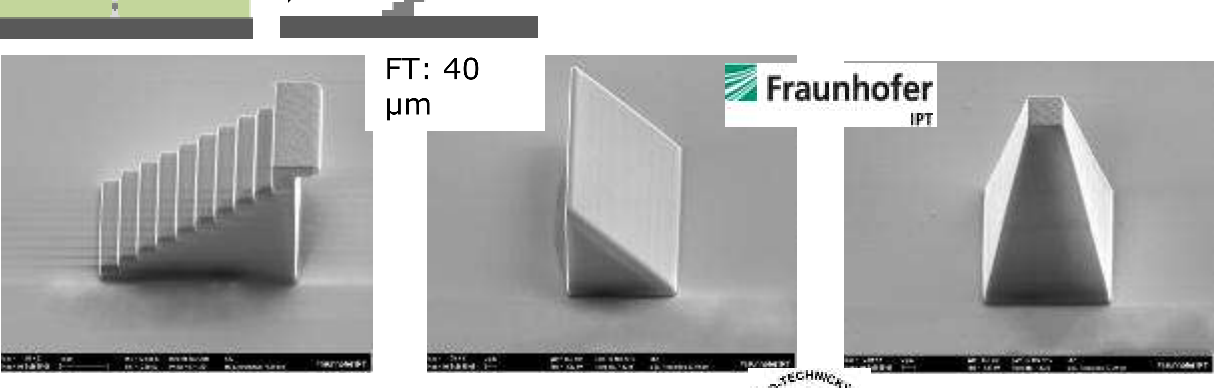




FT: 50 µm, AR: 10 FT: 80 µm FT: 150 µm

LDW with Diode laser (DWL66FS) @ 405 nm (200 mW)

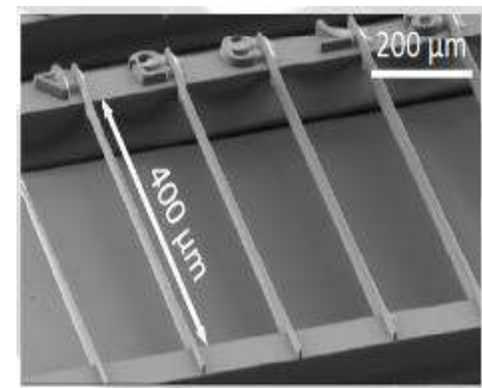
2 Photon Polymerization (2PP)



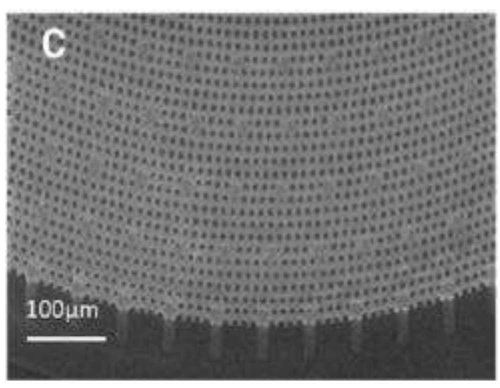
2 Layer litho with 2 laser emission wavelengths

(one developing step)

Generation of suspended micro structures of mr-DWL on SU-8

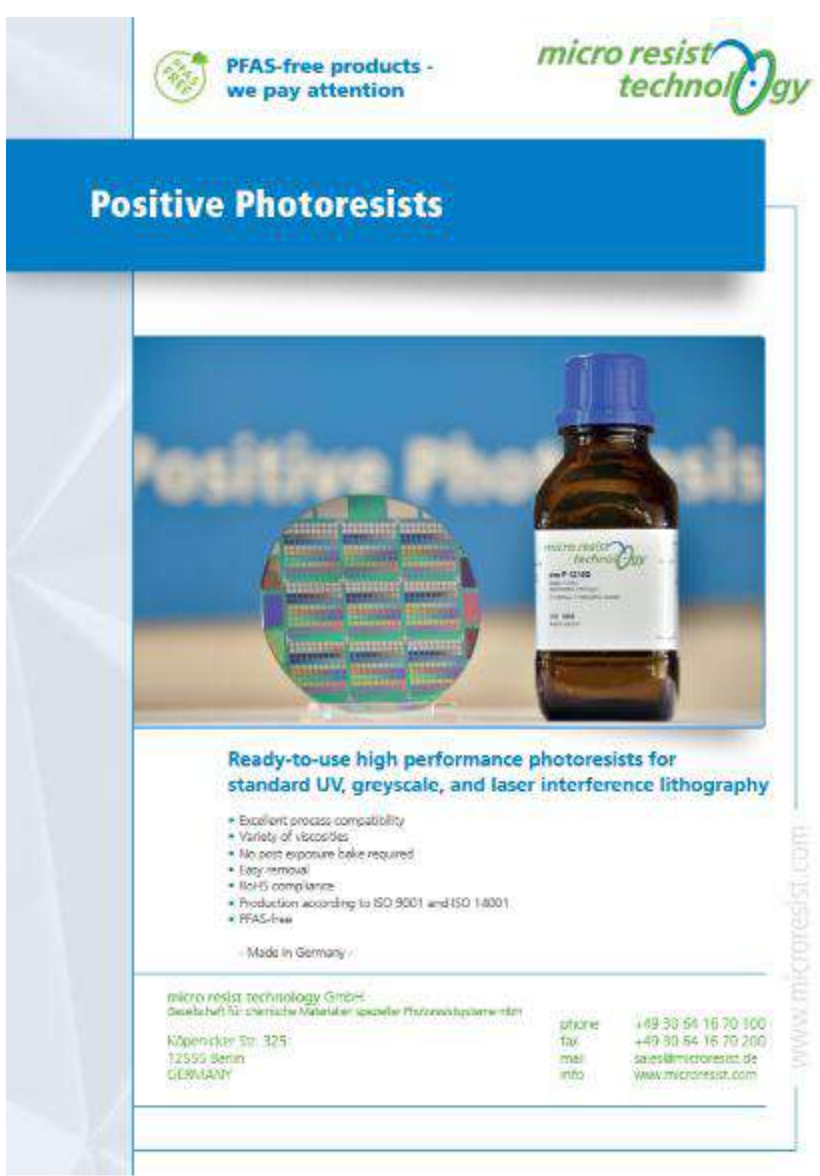


V. Cadarso Poster EIBPN 2012



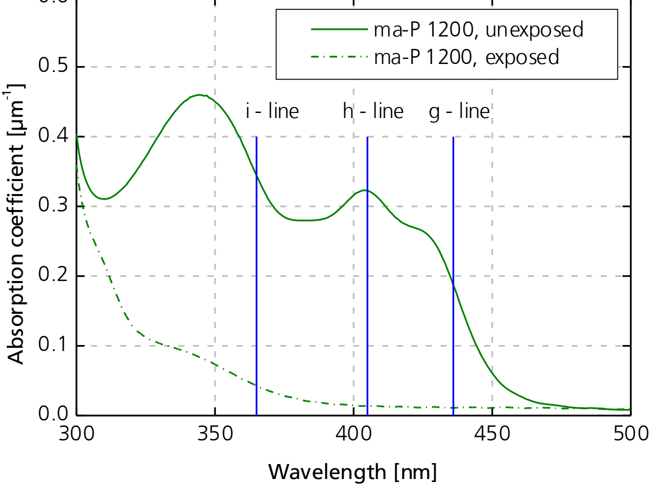
S. Hemanth et al. MicroelecEng 176 (2017) 40–44

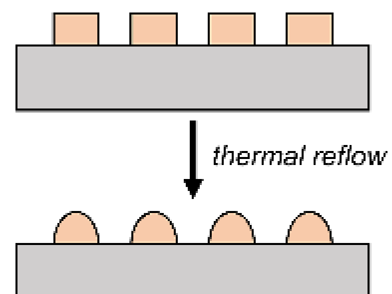
Positive resists

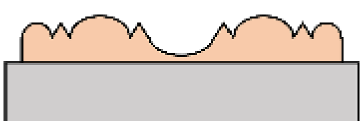


- For – thin & thick – gray scale/ 2,5 D lithography

ma-P 1200G & **mr-P 22G_XP**
ma-P 1200LIL







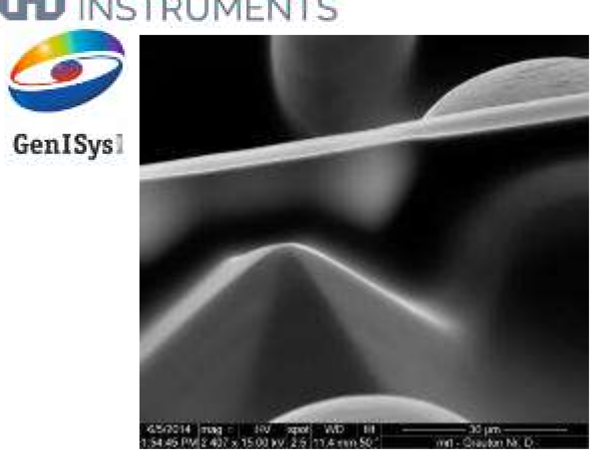
Positive resists – for gray scale lithography

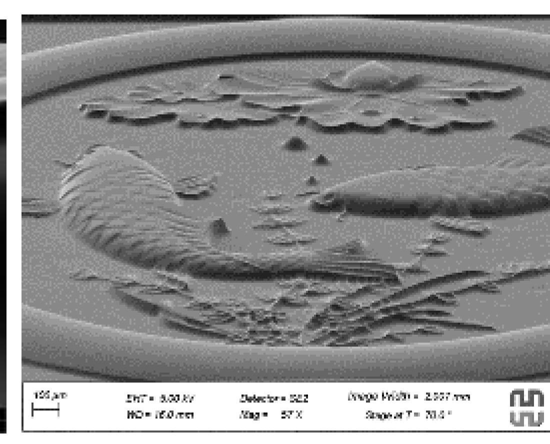
ma-P 1200G

- Up to 60 µm (single), 120 µm (double) film thickness
- Max. grayscale exposure depth: 70-90 µm with LDW @ 405 nm
- Smooth surface after development in TMAH
- (Patterning via UV- and LIL demonstrated)

HEIDELBERG INSTRUMENTS Laser direct writing @ 405 nm

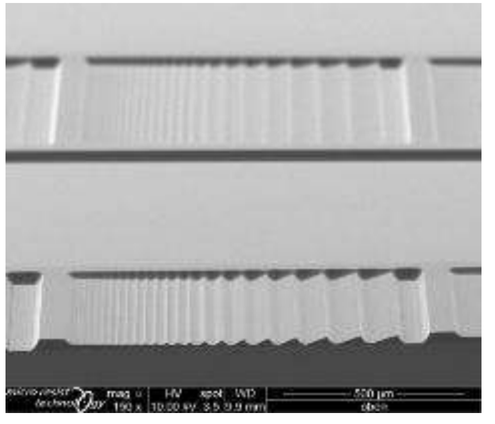
GenISys





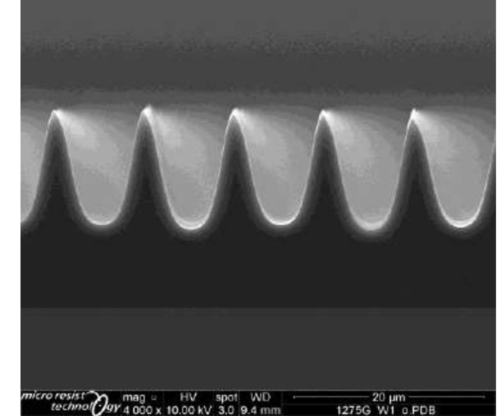
DWL66+, FT: 40 – 100 µm

Mask based greyscale litho (MA)



HEBS (high energy beam sensitive glass) mask: tinted glass substrates, grey values tuned by the optical density of the glass

CANYON MATERIALS, INC.



Pixelated mask, FT resist: 30 µm

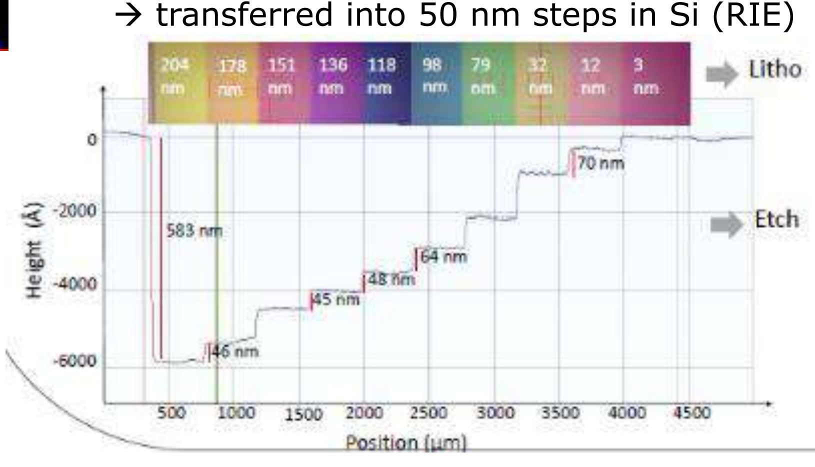
Benchmark TECHNOLOGIES

Reticle based greyscale litho (i-line stepper)

FT resist: 1,5 µm/ 7,5 µm

S. Schermer et al https://doi.org/10.1117/12.3008954, EIPBN 2024; MNE 2024

FT: 500 nm, tool: µPG 101,
→ 20 nm high steps,
→ transferred into 50 nm steps in Si (RIE)



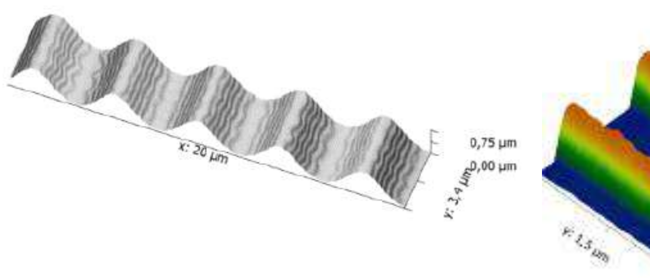
N. Gerges et al DOI 10.1116/6.0001273

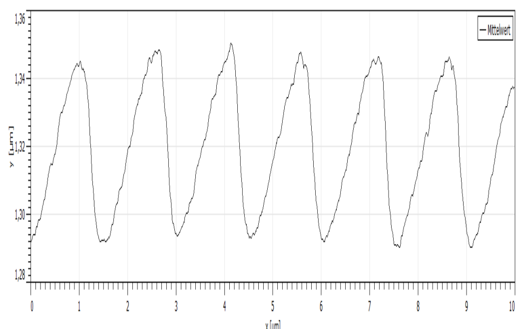
Positive resists – for gray scale lithography

ma-P 1200G/LIL

LIL @ 405 nm

FT range: 100 nm – 1





Manufacture of
- laminar gratings as well as
- saw tooth patterns

as master for etching

WHITE PAPER

Advancing greyscale lithography and pattern transfer of 2.5D structures using ma-P 1200G resist series

Christine Schuster, Marina Heinrich, Martin Herder, Susanne Grützner, Anja Voigt, Arne Schleunitz, Gabi Grützner

micro resist technology GmbH, Köpenicker Str. 325, 12555 Berlin, Germany
E-mail: c.schuster@microresist.de | Web: https://www.microresist.com

Keywords: greyscale lithography, positive photoresist, DNQ, novolak, hybrid polymers

ABSTRACT

Greyscale lithography is applied to manufacture complex 2.5D and freeform microstructures in photoresists. The thus obtained structures serve as master or template for different methods of pattern transfer into materials for final, permanent applications. Here, we describe the chemical background and processing fundamentals of typical positive photoresists used for this purpose as well as the characteristics of the ma-P 1200G resist series developed by us specifically for enabling greyscale lithography. Different resist patterning examples are presented as well as a method to transfer such 2.5D resist patterns by UV moulding into hybrid polymers to be used permanently.

INTRODUCTION

In greyscale lithography a photoresist layer is exposed with UV light of spatially modulated intensity, thereby controlling the amount of photons absorbed within the resist layer. The photoresist is chemically altered to different degrees depending on the exposure dose, inducing a gradual change of dissolution rates. During a wet development step this exposure dose and dissolution rate gradient is transferred into a film-thickness gradient of the photoresist layer remaining on the substrate. This way, complex 2.5D topographies with discrete or continuous height levels can be generated, which are highly relevant for the fabrication of diffractive, refractive and freeform microoptical elements, MEMS and MOEMS as well as microfluidics.

Particularly, greyscale lithography is applied when standard binary photolithography processes, including thermal reflow of binary structures to generate rounded patterns, does not suffice due to the complexity of the desired topography (Figure 1). This is the case for:
- Applications with high structure density, such as high fill-factor microlens arrays, where reflow patterns would merge
- Complex structures such as concave and convex lenses
- Combination of patterns at different length scales and hierarchical structures
- Microlenses or discrete diffractive patterns with different heights next to each other
- Any freeform microtopography used for e.g. beam-shaping and -steering in optical applications

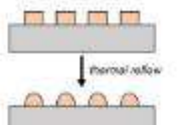


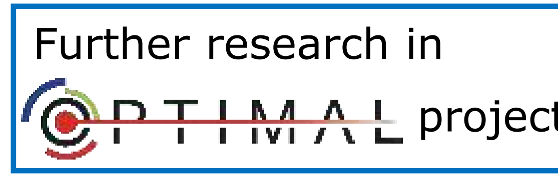
Fig. 1. Exemplary resist patterns manufactured with binary standard photolithography and thermal reflow, compared to greyscale lithography.

A general process scheme for greyscale lithography using a positive photoresist is shown in Figure 2. Individual steps are very similar to standard binary UV lithography comprising:
- Coating of the substrate with resist
- Softbake
- Relaxation and re-hydration of the photoresist film. The re-hydration time required increases exponentially with the film thickness, from seconds in thin films

© micro resist technology GmbH | 01/2022

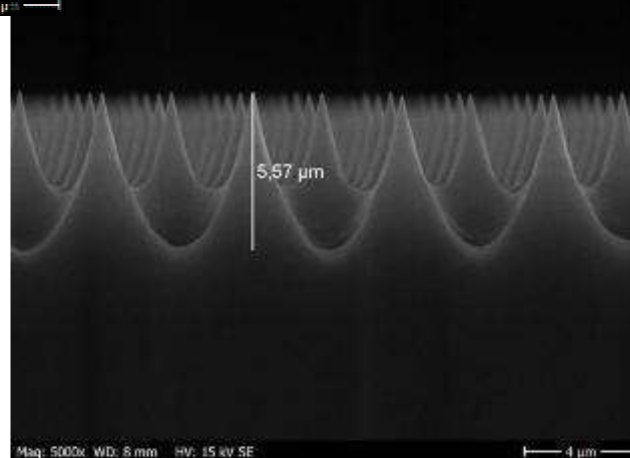
LIL @ 351 nm

FT range: 3 µm – 10 µm



µm

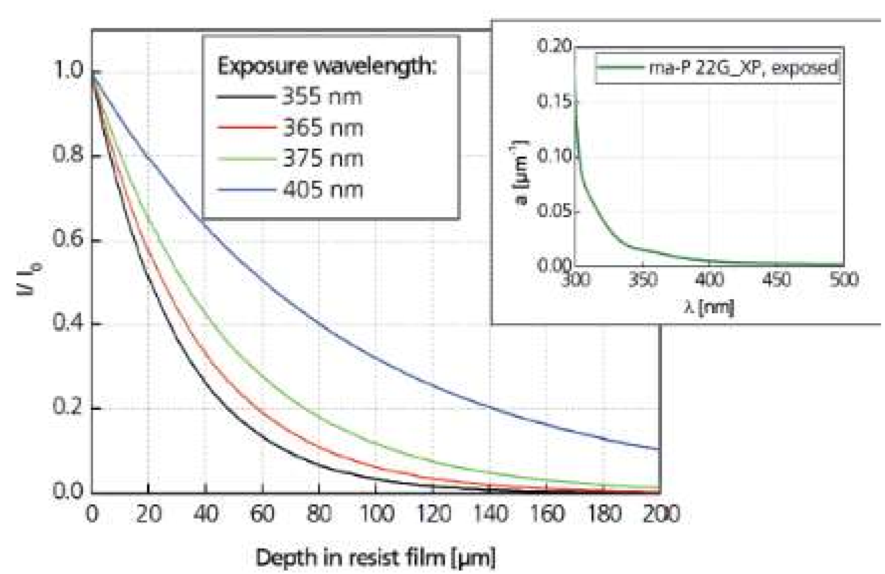
as well as
rns
roplating



Positive resists – for gray scale lithography

mr-P 22G_XP

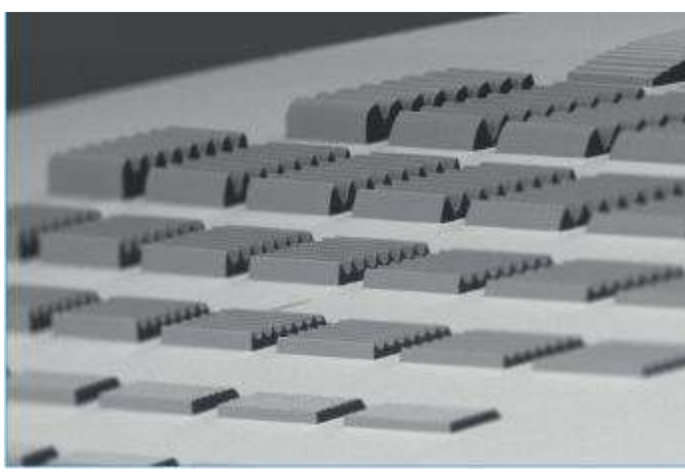
- Up to 120 µm (single), 200 µm (double) film thickness
- Further reduced bubble formation during exposure,
- max. grayscale exposure depth of 160 µm successfully demonstrated with LDW @ 405 nm
- Smooth surface after development in TMAH



Residual absorption after exposure and resulting light attenuation in the resist film

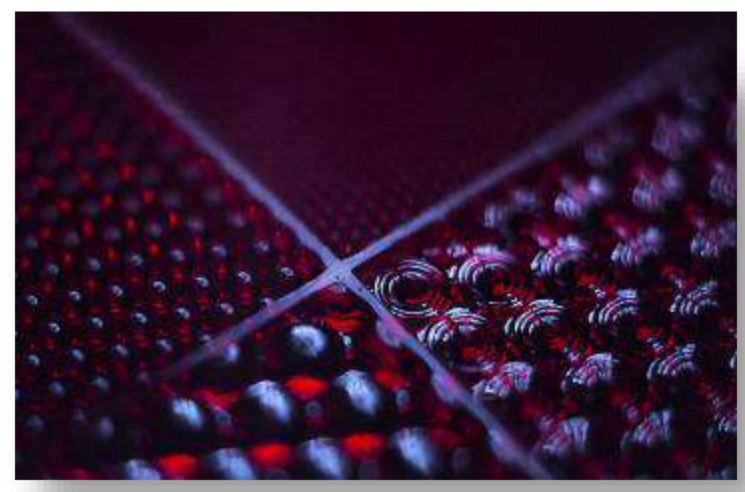
Lower residual absorption after exposure gives less attenuation of exposure light in the resist film, and allows deeper patterns

(MA) UV-lithography with HEBS greyscale mask



Max. 70 µm pattern height, saw tooth pattern in different heights & pitches

Laser direct writing @ 405 nm
PICOMASTER XF 200



125 µm high lenses, 125/ 250/500 µm diameter, Fresnel lenses 500 µm diameter

Raith Laser Systems B.V.

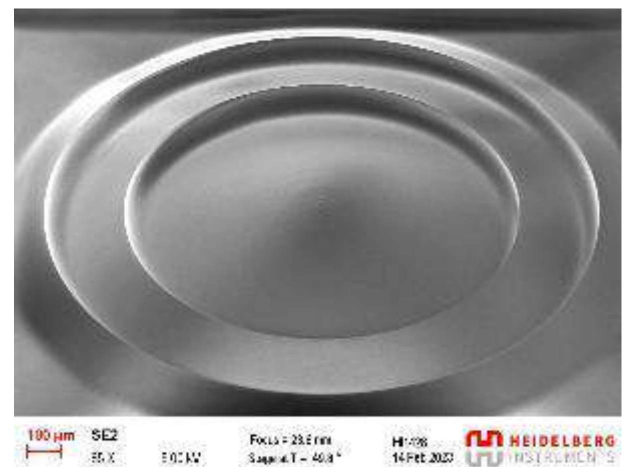
Acknowledgement:
Dr. Kahraman Keskinbora

mr-P 22G_XP

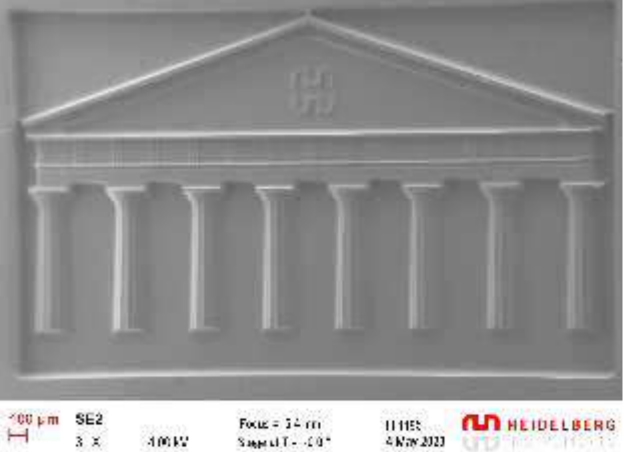
HEIDELBERG INSTRUMENTS

Laser Direct Writing - with DWL66+ @ 405 nm at HIMT

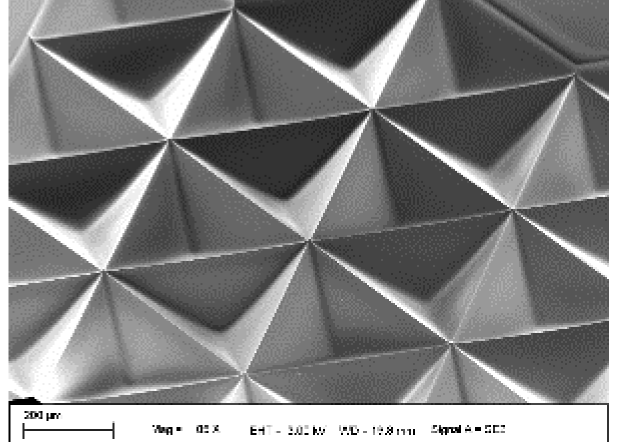
Variation of laser power (max. 300 Watt), filters, writing heads, mode and number of overlapping exposures, and developing; gray value distribution (GVD 1024) adjusted to contrast curves



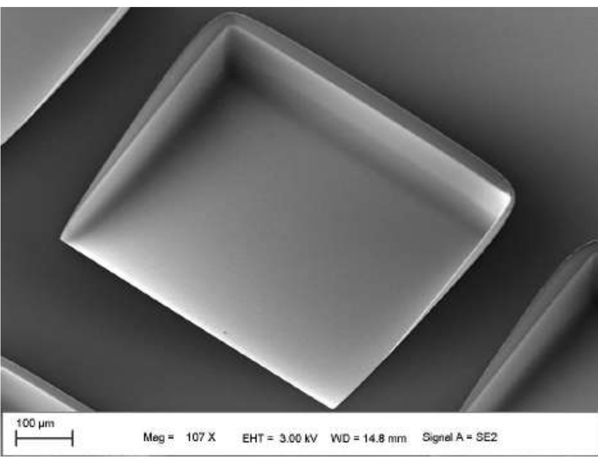
Fresnel lens, **103 µm** deep, 2 mm ∅, FT~120 µm (single coat; 4 mm writing head, CI-Over 20, 1.5 h develop)



Temple, **120 µm** deep, FT~180 µm (double coat; 10 mm writing head, CI-Over 40, 2 h develop)



Pyramids, **155 µm** deep, FT~200 µm (double coat; 10 mm writing head, CI-Over 40, 2h develop)



167 µm deep ramp structure, FT~200 µm (double coat; CI-Over 40, 2h develop)

G. Schuster, G. Ekindorf, A. Voigt et al:
a) SPIE AL+P 2023 https://doi.org/10.1117/12.2661526
b) MNE 2023
c) SPIE AL+P 2024 https://doi.org/10.1117/12.3010852

Positive resists – for gray scale lithography

Methods for **pattern transfer**

Resist pattern

→ DRIE etching
(works for << 15 µm thick films)

Favourite
(non-destructive)

Resist pattern

→ Thermal moulding with PDMS

→ UV-moulding with hybrid polymers (e.g. OrmoComp®, OrmoClear®FX, or OrmoStamp®FF)

Resist pattern

→ UV-moulding with hybrid polymers

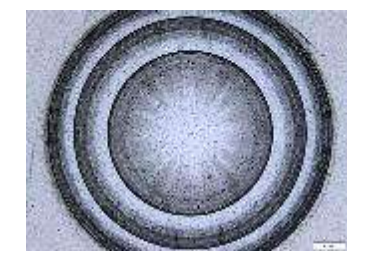
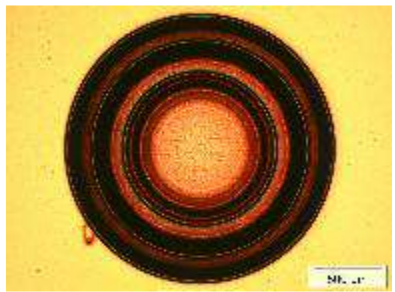
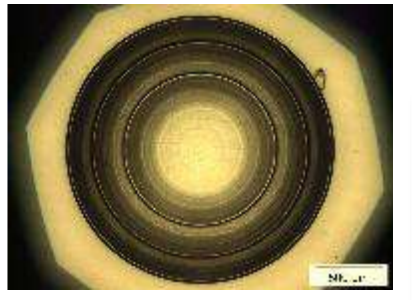
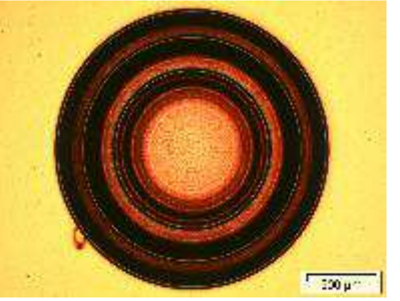
Resist pattern

→ Metallisation

→ Electroplating

→ UV-moulding with OrmoComp®

Resist

Challenges with thick resist films

Remaining DNQ reactivity in generated resist master

- thermal stability & “light” stability?

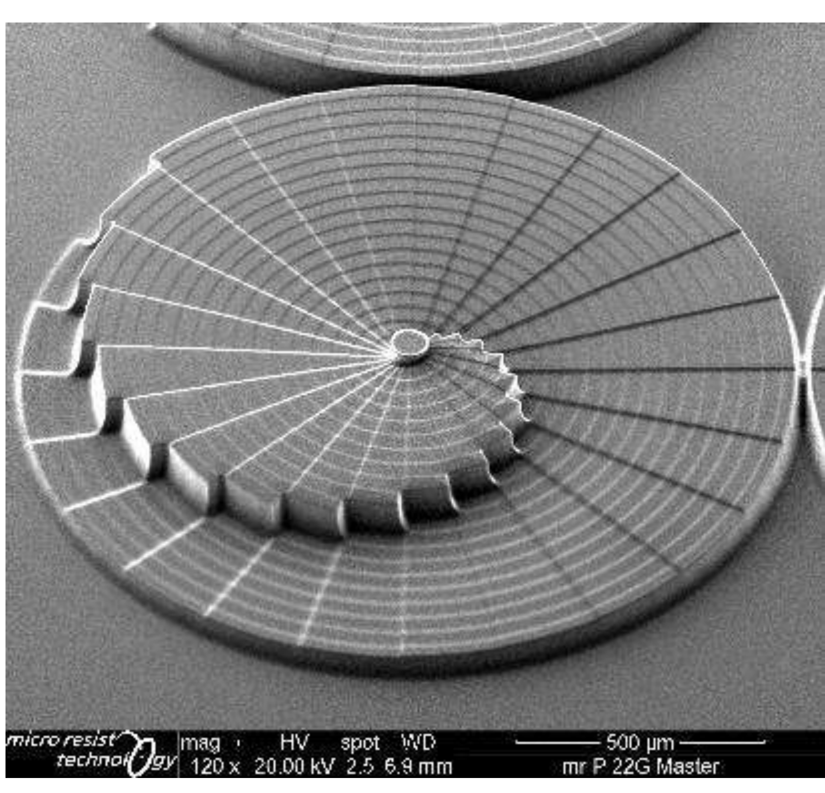
⇒ Resist pattern distortion possible

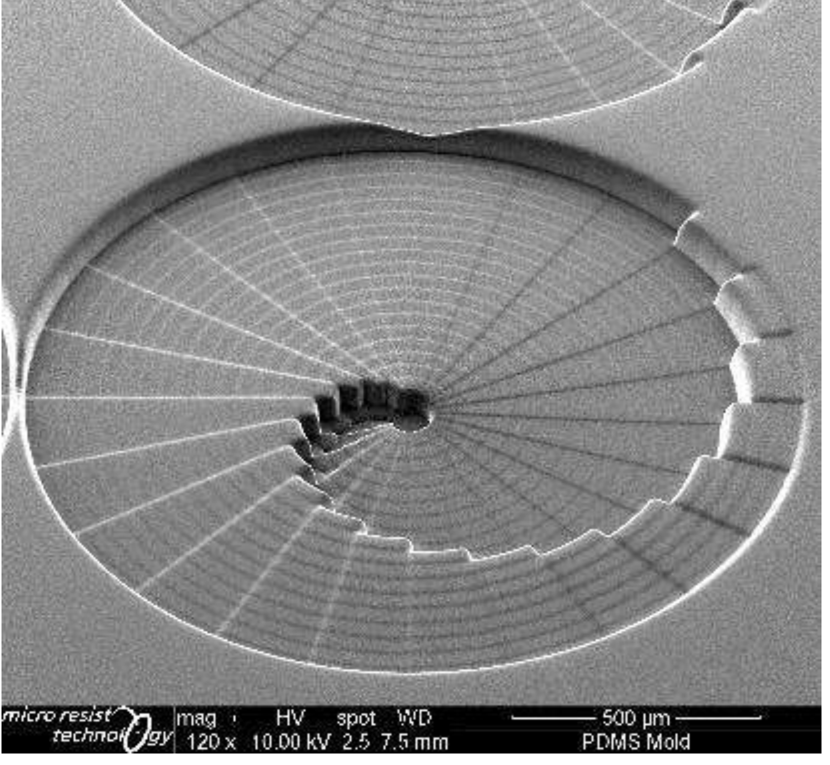
OrmoComp®, OrmoClear®FX, OrmoStamp®FF
- Inorganic-organic hybrid polymer
- Suitable for optical applications

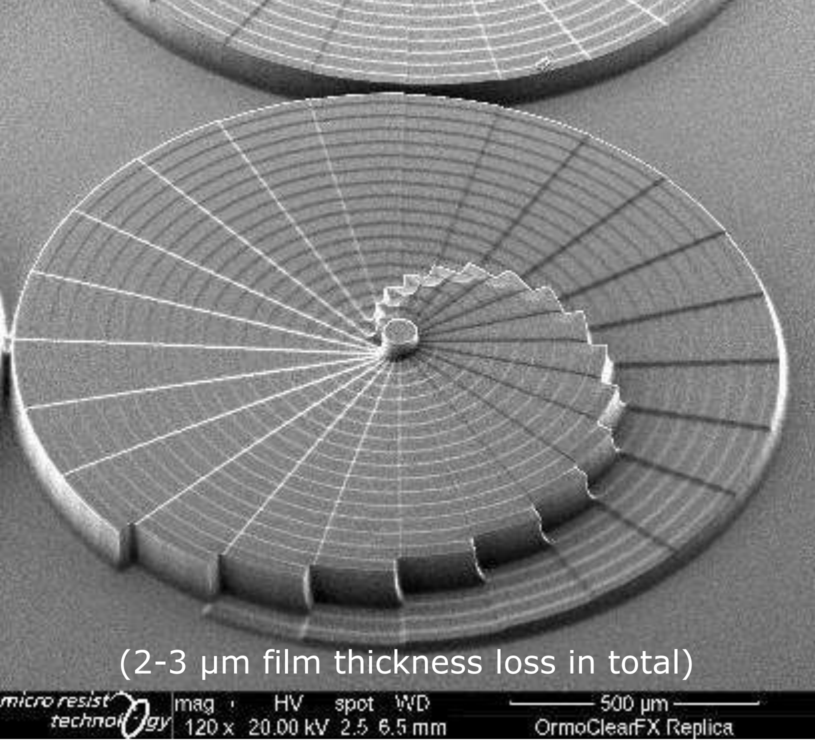
mr-P 22G_XP

Favourite method (non-destructive for resist pattern): **Replication with PDMS** & **Hybrid polymer**

Resist pattern	→ Thermal moulding with PDMS	→ UV-moulding with OrmoClear®FX
130 µm deep, DWL @ HIMT	48h @ 35°C	2J/ cm² (MA6) → bake @130°C >10min



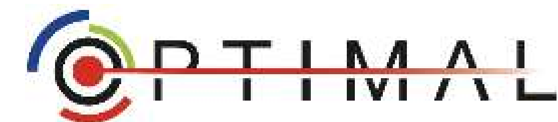




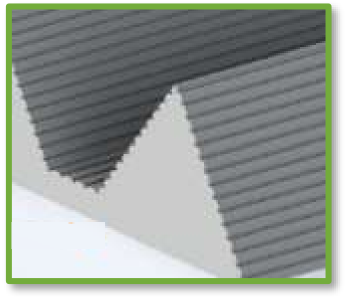
Positive resists – for a Mix & Match approach

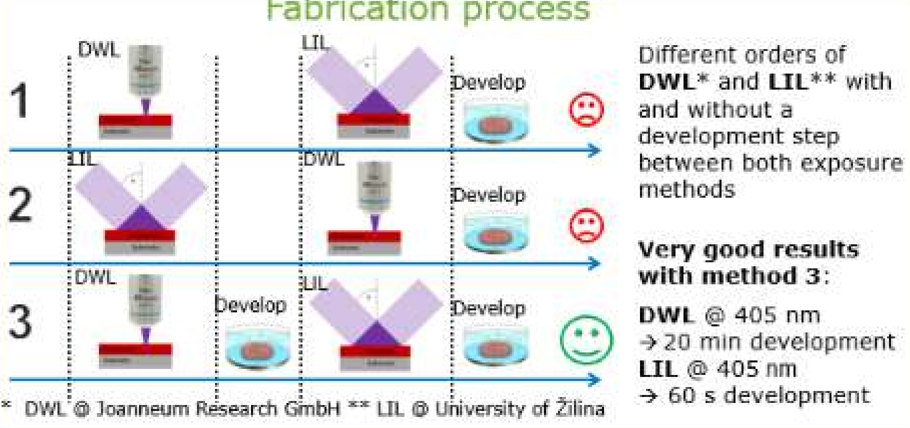
ma-P 1200G & mr-P 22G_XP

Generation of hierarchical riblet structures by combining LDW & LIL



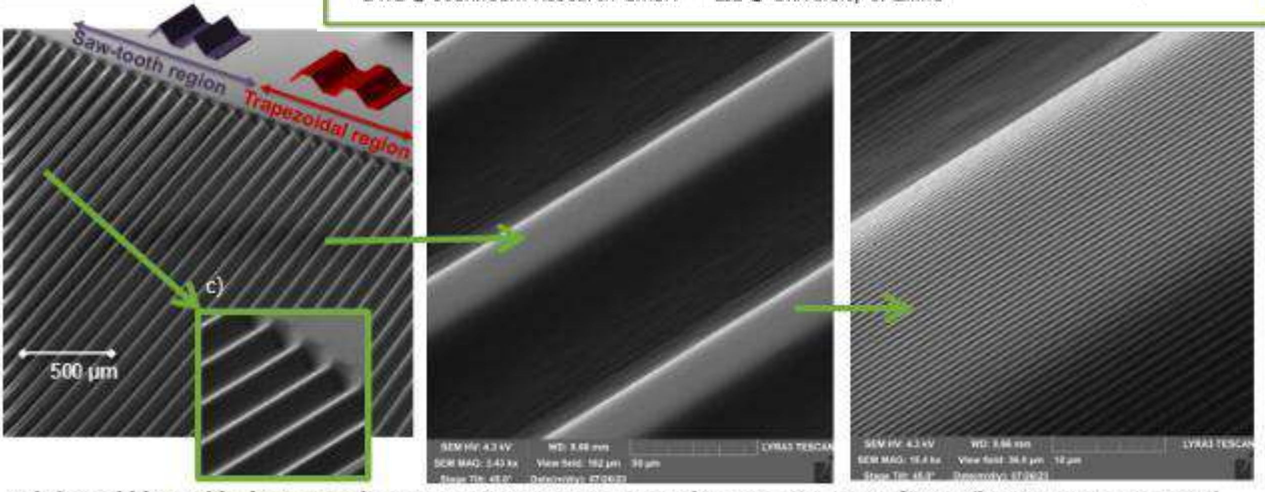
(Automated Maskless Laser Lithography Platform for First Time Right Mixed Scale Patterning)



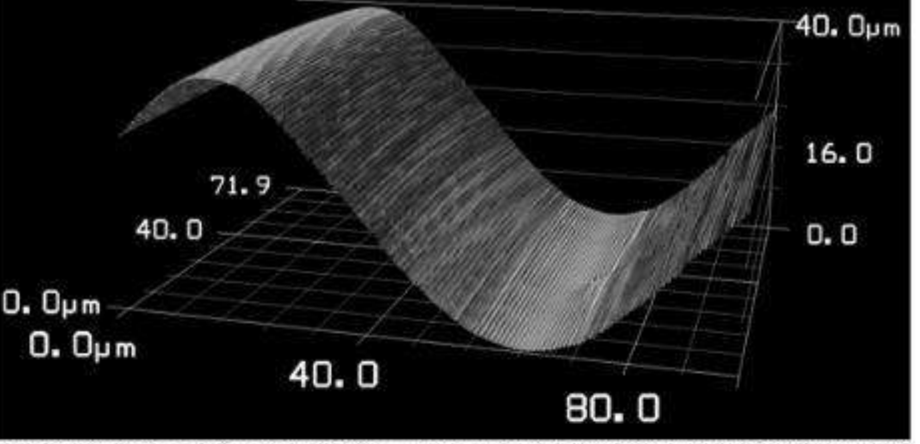


DWL @ JOR
Joanneum Research
Forschungsgesellschaft mbH
Austria

LIL @ UZA
University of Žilina
Slovakia



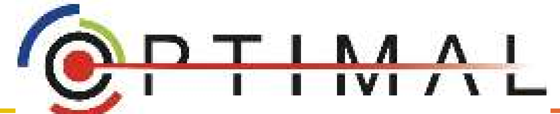
***Fabricated hierarchical patterns in ma-P 1275G:** Large structure (405nm - **DWL** manufactured): 100 µm grating period, 40 µm depth; small structure (405nm - **LIL** manufactured): 690 nm grating period, ~ 400 nm depth*



***Optical pattern assessment:** 405nm - **LIL** manufactured surface gratings on different parts of the 405nm - **DWL** fabricated greyscale wave pattern in **ma-P1275G**, grating on the slopes slightly tilted due to the oblique incidence of light*

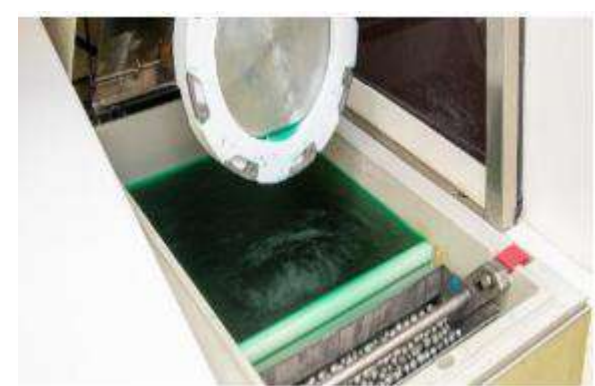
Application: Generic riblet structures of micro & nano scale used to reduce frictional resistance on surfaces in turbulent flow
→ beneficial for surfaces of any means of transport to reduce fuel consumption and increase speed + mitigation of ice formation risk

Photoresists – for a Mix & Match approach



The **OPTIMAL** “all-in-one” laser lithography platform will be validated through the manufacturing of master tools for **4** different use cases:

1. Full-polymer **micro lenses** for industrial optics.
2. **Hierarchical multifunctional** drag reduction **riblet** structures.
3. **Free-form lens arrays** for high-end virtual reality displays.
4. **Microfluidic** structures for lab on chip medical devices.



Use case 1

Use case 2

Use case 3

Use case 4

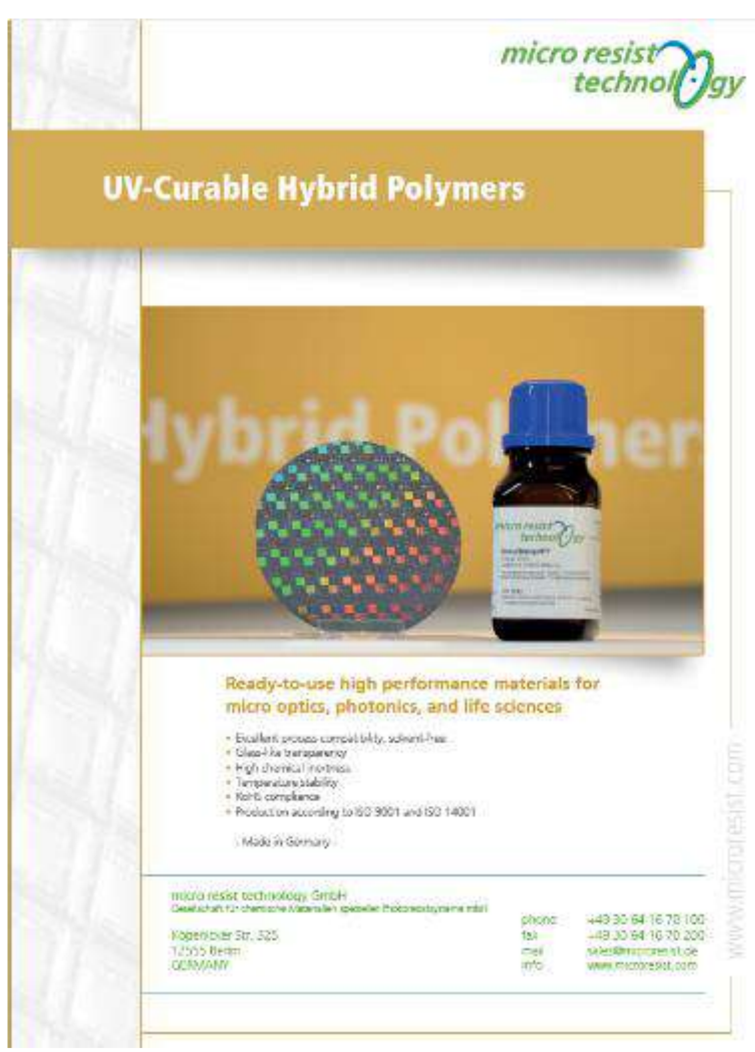
Positive resists for laser based gray scale litho via 1PL & LIL

ma-P 1200G, mr-P 22G_XP, …

Negative resists for laser based lithography via 1PL & 2PP

mr-DWL series

Hybrid polymers

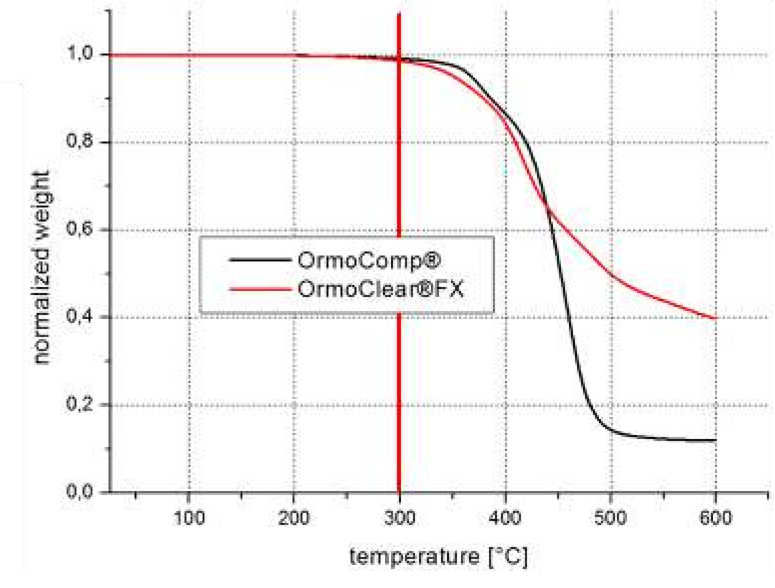


- UV curable, highly transparent materials for (permanent) micro-optical applications

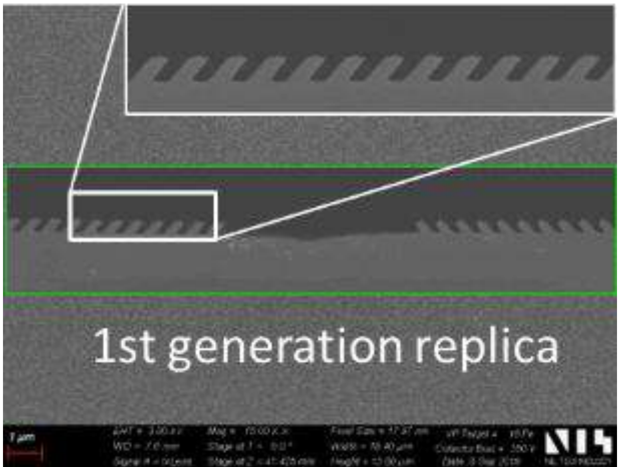
Hybrid polymers

Materials for non-sacrificial applications – hybrid polymers

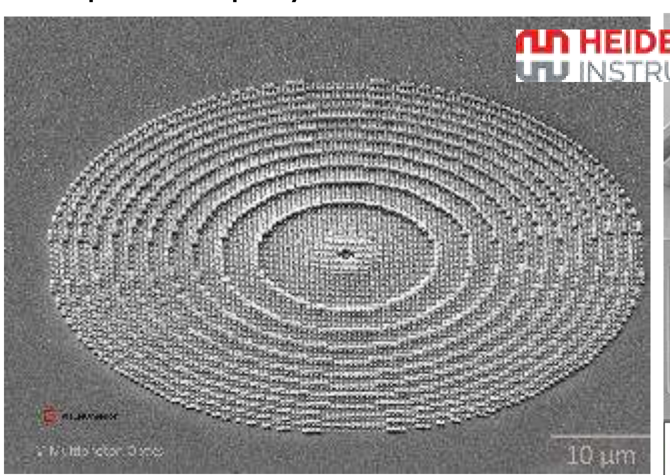
- High optical transparency
- High thermal stability (300°C)
- Sub-100nm resolution with high AR
- Large customer base (diverse patterning)



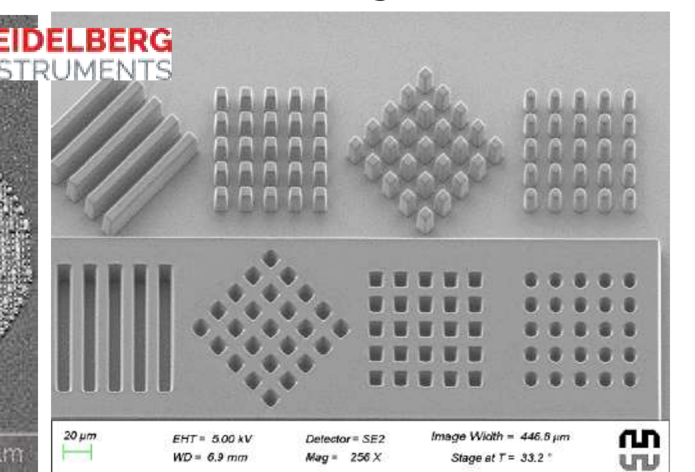
Direct imprint



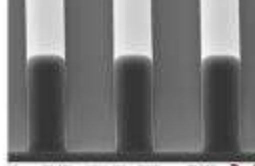
2-photon polymerization

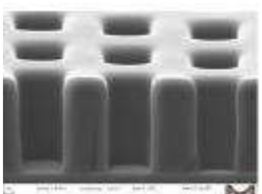


Direct laser writing

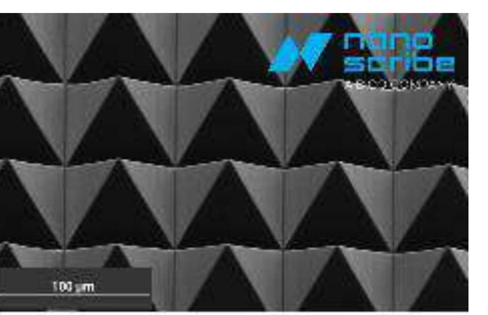


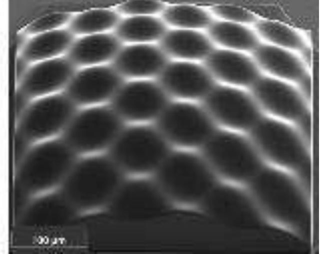
photolithgraphy



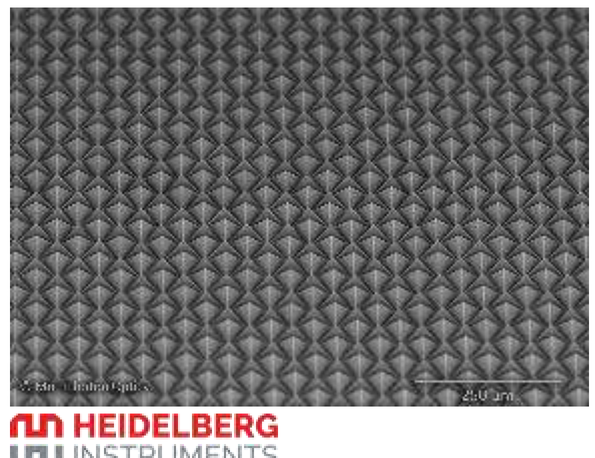


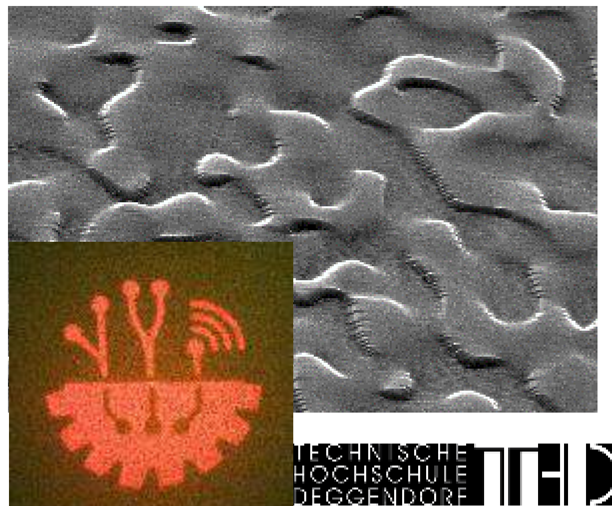
Hybrid polymers

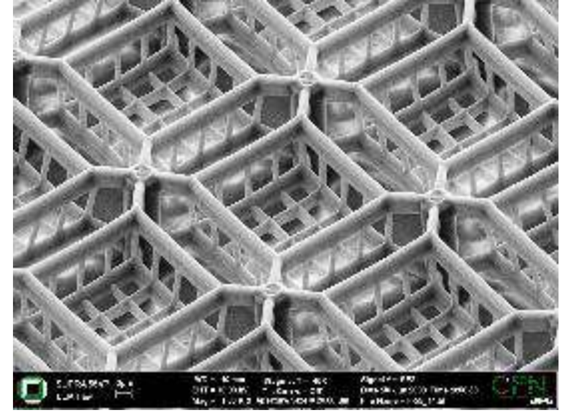




- Rapid prototyping & design testing of optical structures
- Suitable products: OrmoComp®, OrmoCore, OrmoClear®, OrmoClear®FX
- Compatibility to various 2PP-machines (Nanoscribe, Heidelberg Instruments,…)

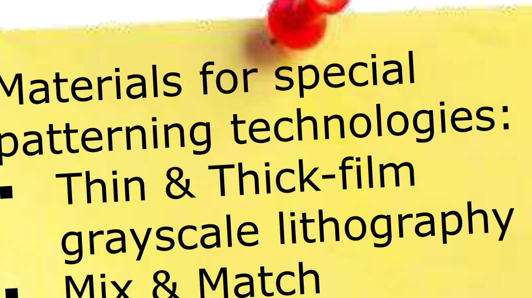






HEIDELBERG
INSTRUMENTS

Materials for E-beam, standard UV & laser based lithography – for conventional pattern transfer processes and fast and contactless prototyping



Materials for special patterning technologies:
- Thin & Thick-film grayscale lithography
- Mix & Match techniques
- 1PL & LIL (Pos.PR)
  1PL & 2PP (Neg.PR)
  1PL (UV) + e-beam (Neg.PR)

OPTIMAL

Thank you for Your Attention!