Photoresists, their chemistry and application examples

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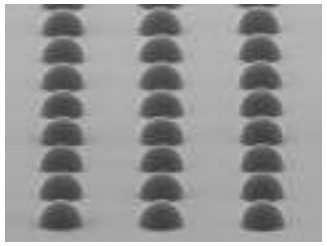
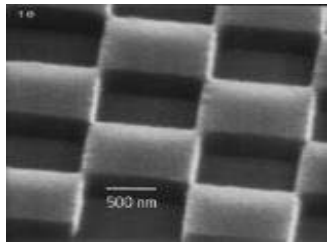
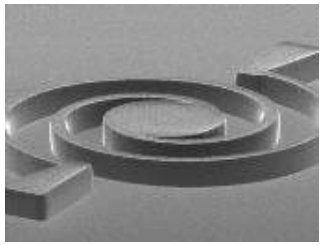




OPTIMAL Online Seminar

September 11, 2024



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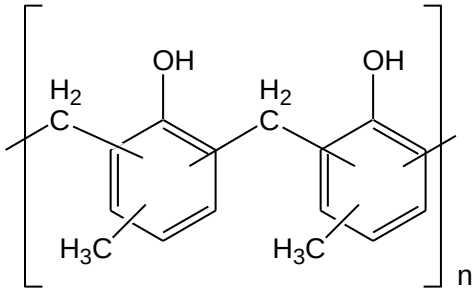
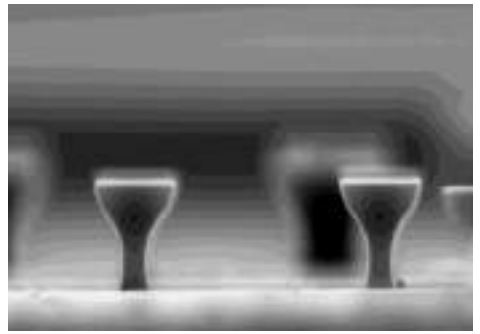
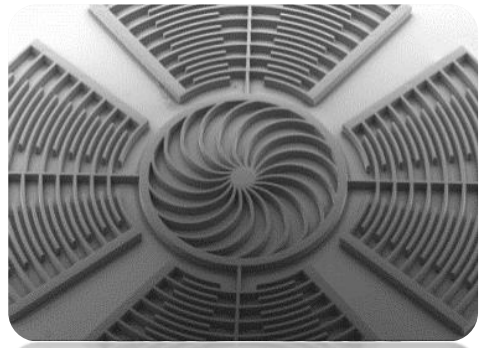
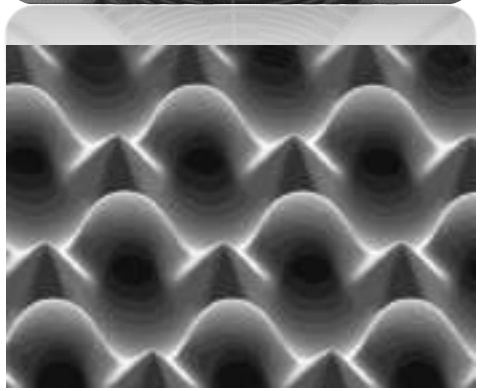
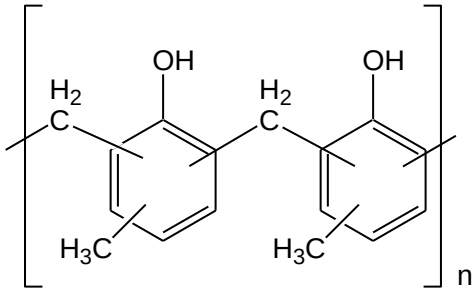
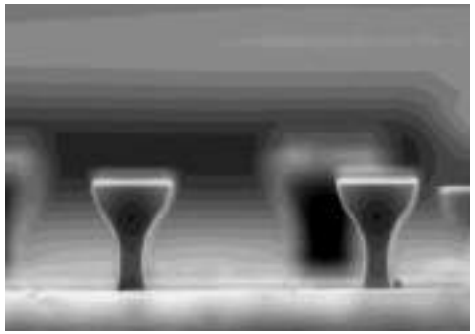


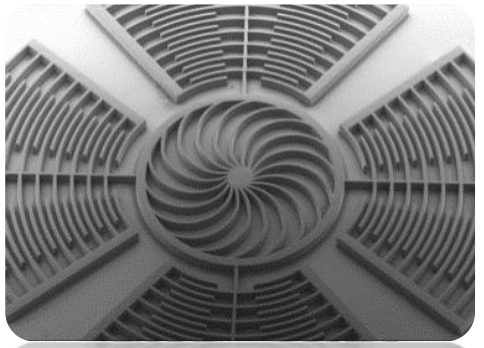


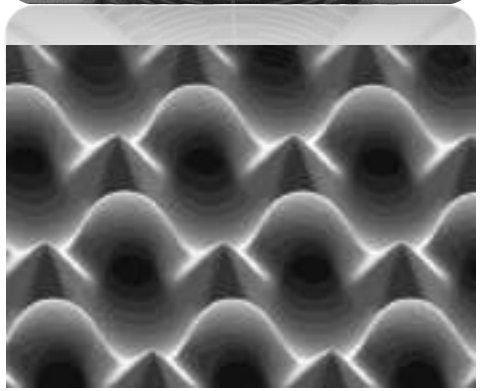










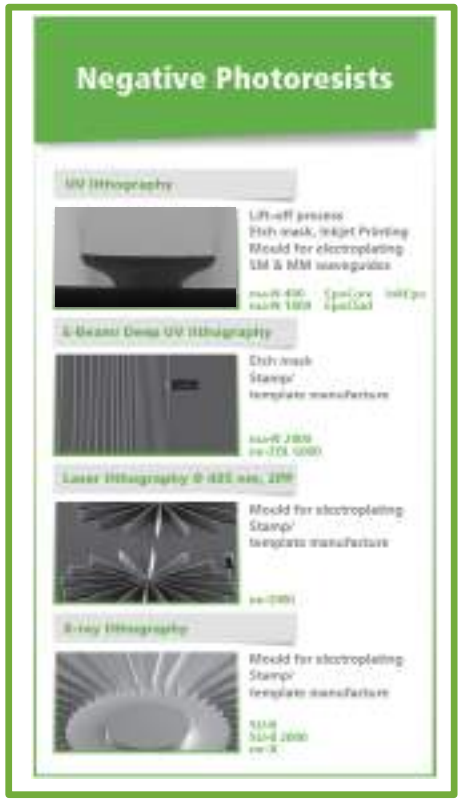


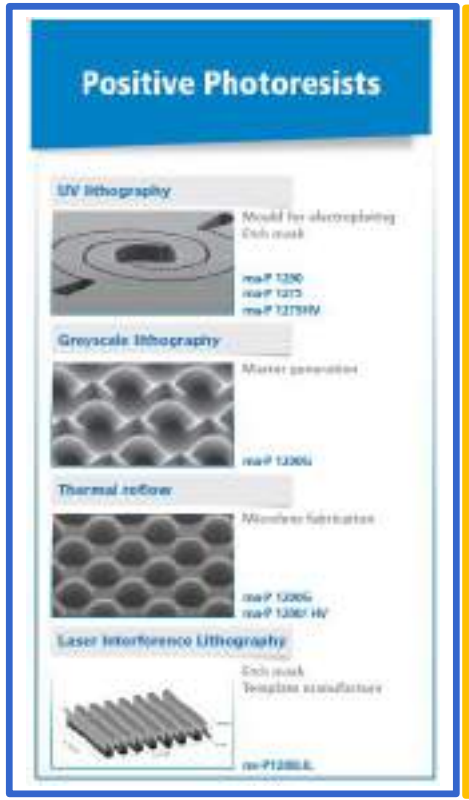
Specialized in providing **innovative resists, polymers, photopolymers and ancillaries**,
we support our high-tech customers with high performance materials, technologies and process solutions.

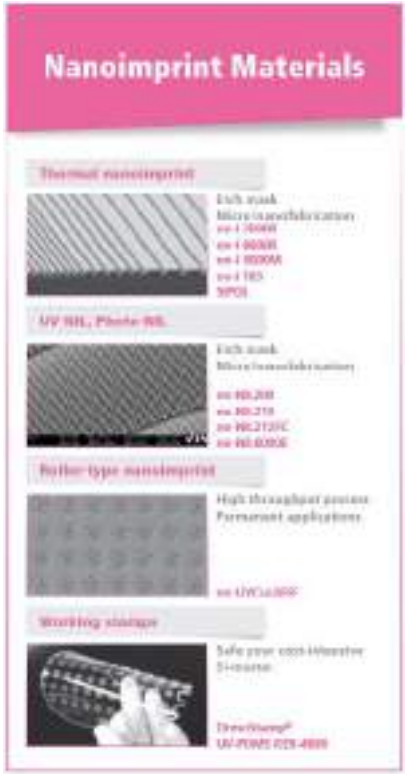
- *Established:* 1993
- *Employees:* ~50 (2024)
- *Location:* Berlin, Germany
  (Corporate office, logistics and manufacturing)
- *Facility*: 3.450 m^2 incl. clean room (300 m^2)
- *Certifications:*
  ISO 9001:2015
  ISO 14001:2015

- *Fields of business activities:*

– Manufacturing: formulation / synthesis
– Distributorship (products of partner companies)
– Researching advanced materials and processes
– Lithographic Services

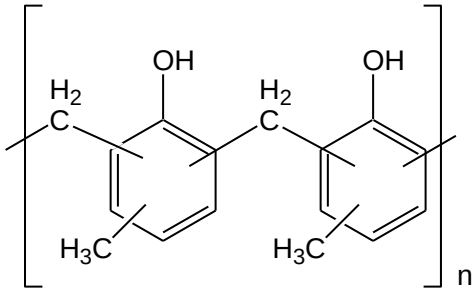


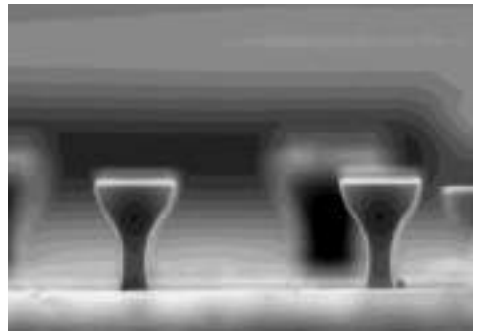


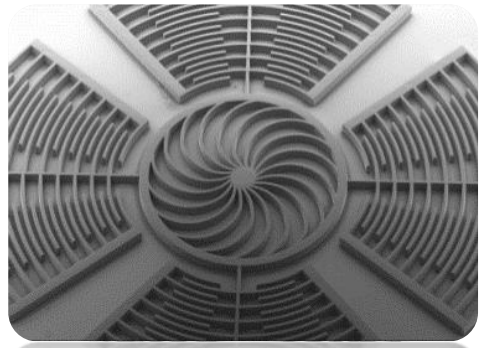


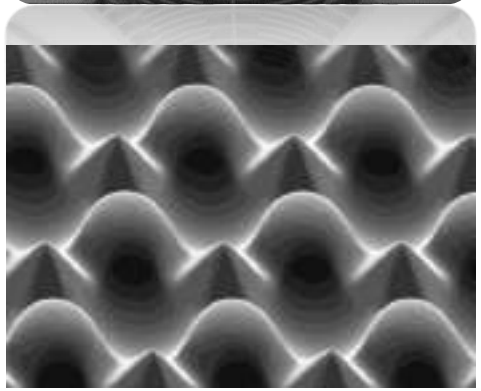
Strategic Distributorship in Europe:
DuPont (electronic materials, WLP, dry film),
Kayaku Advanced Materials (SU 8/2000/3000, PMGI, PMMA),
DJ Microlaminates (Dry film sheets), **ShinEtsu** (Photo-curable PDMS), etc.

Content



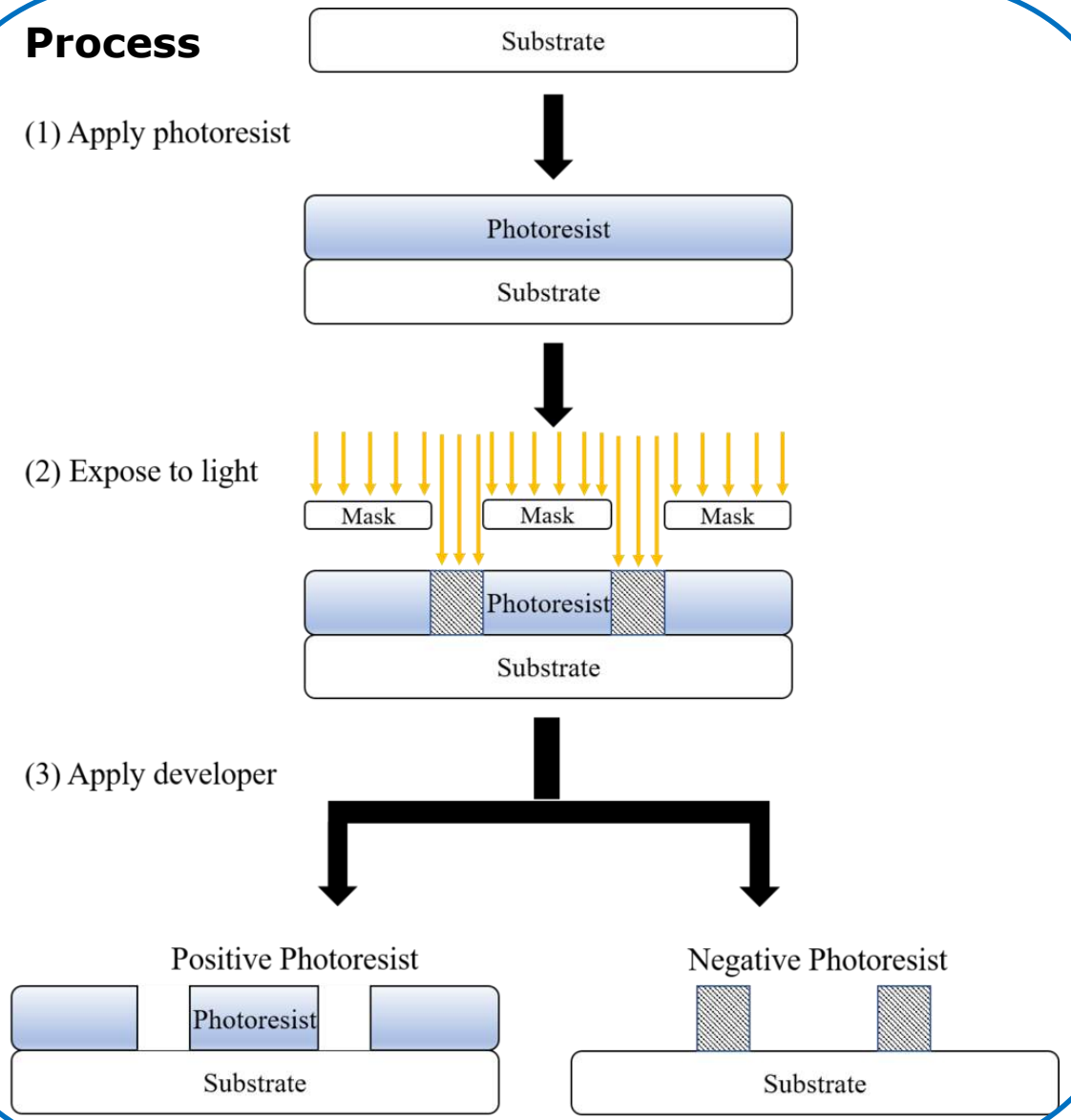




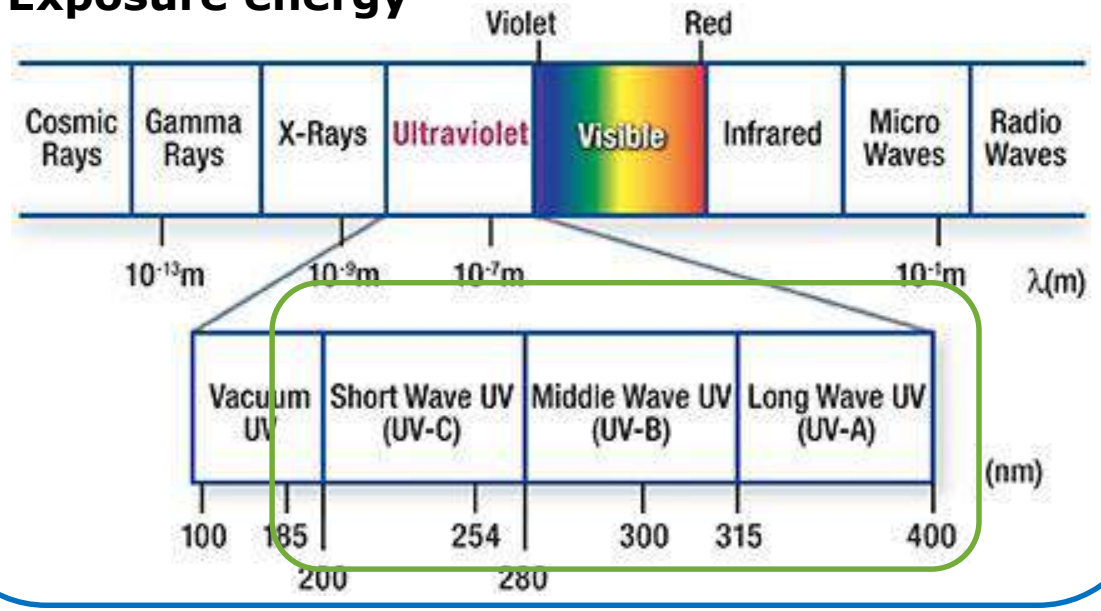


Photolithography – General aspects

Process



Exposure energy



Resist sensitive @:

- UV broadband 300 – 450 nm: mask aligner/ mercury lamp/ LED
- UV: i-line/ 365 nm – Stepper/ LED
- UV: 365 nm, 405 nm (excimer/ diode) laser – direct writing & interference lithography
- DeepUV (248 nm, 266 nm)
- E-beam
- UV-molding, imprint (T, UV)

Photolithography – General aspects

Photoresist is a light-sensitive material

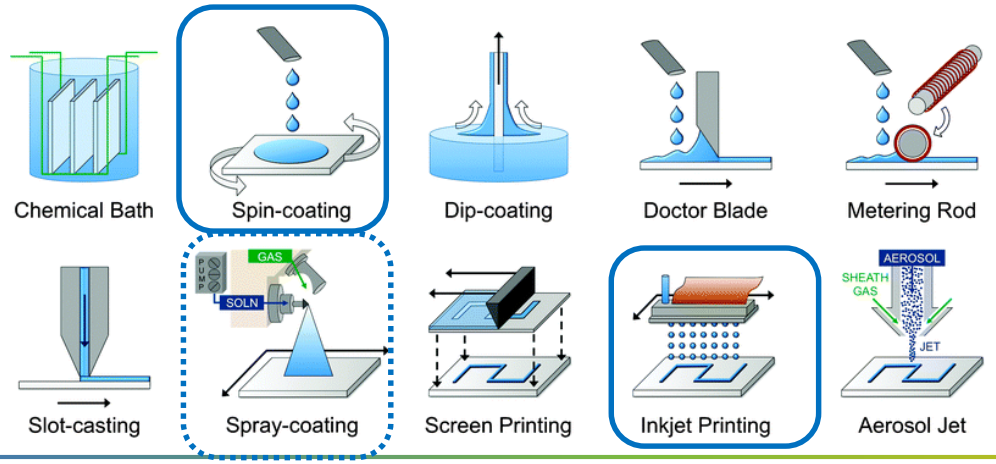
Polymer binder / resin

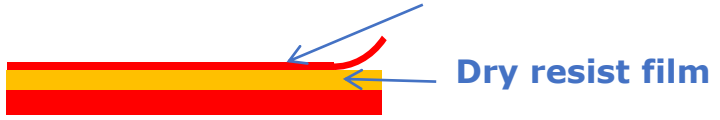
Photoactive Component (PAC)

Solvent (mixture)

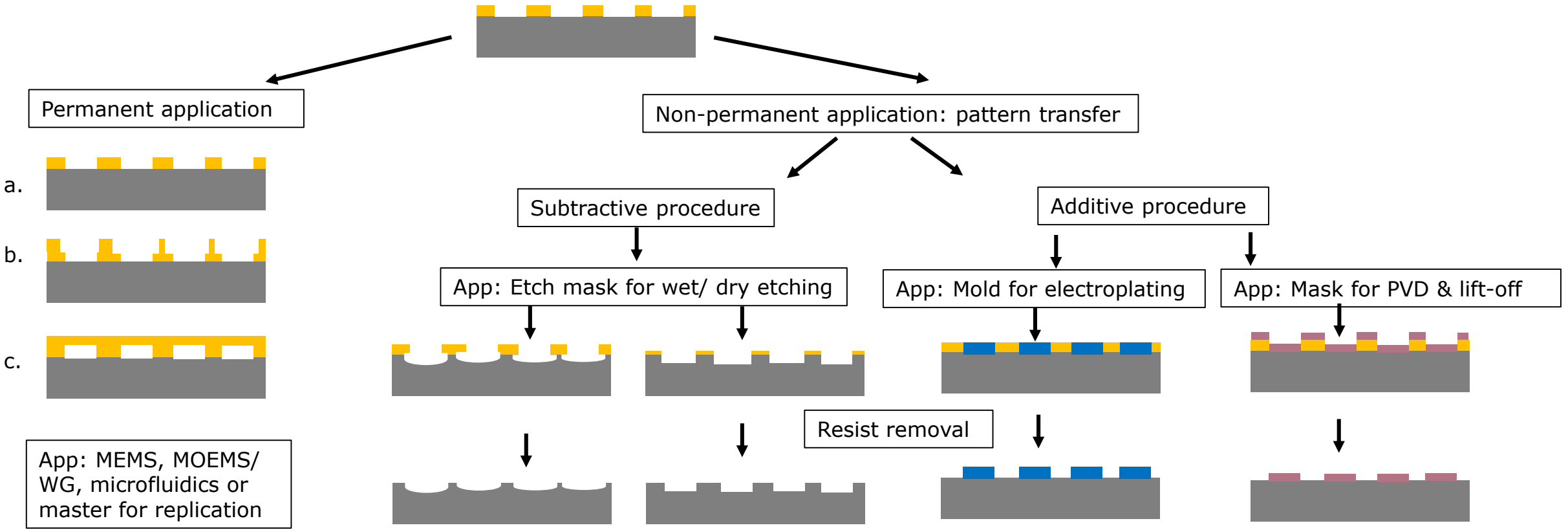
Additives (leveling agents, adhesion promoter, surfactant, etc.)

Photoresist layer preparation





Application of generated resist patterns

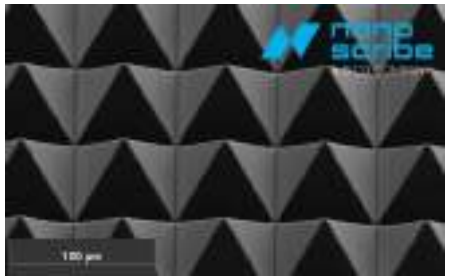


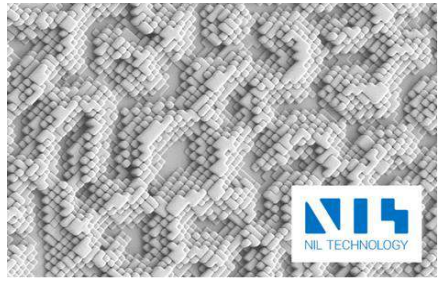
Use of negative resists

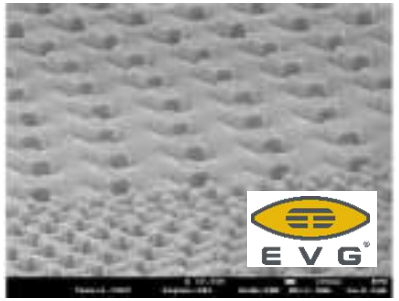
Use of (preferably) positive resists, use of negative resist

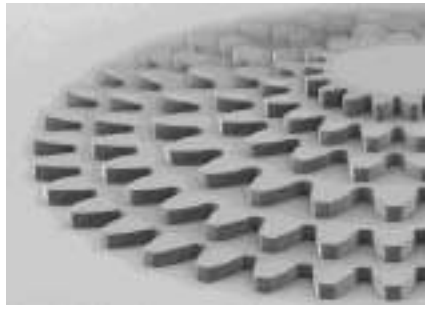
Application examples

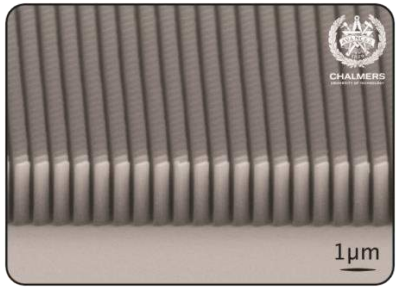
1 mm	100 µm	10 µm	1 µm	100 nm	10 nm
(freeform) Micro lenses Micro prisms	MEMS, metal parts MOEMS, lens arrays Masters	Contact pads Metal mirrors Diffractive grating Waveguides	Diffractive beam shaper	AR coatings photonic crystals Meta-lenses & surfaces	











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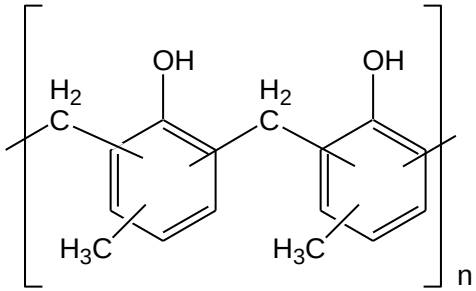
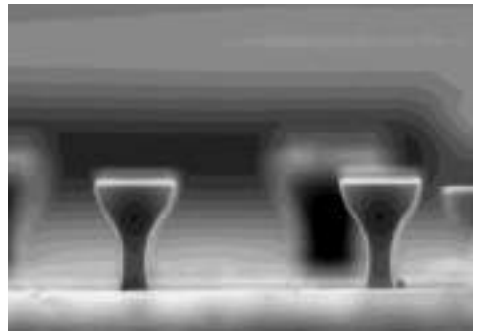
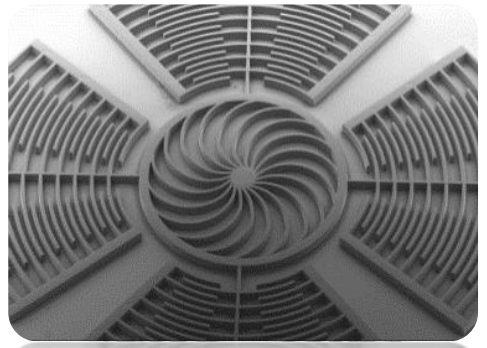
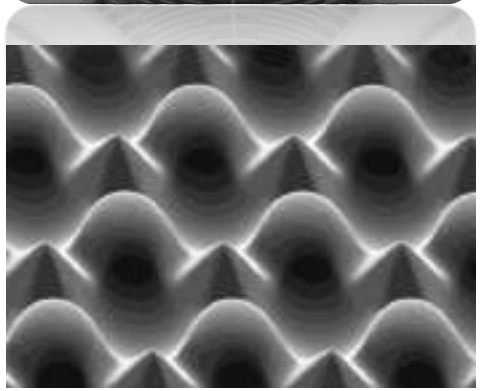
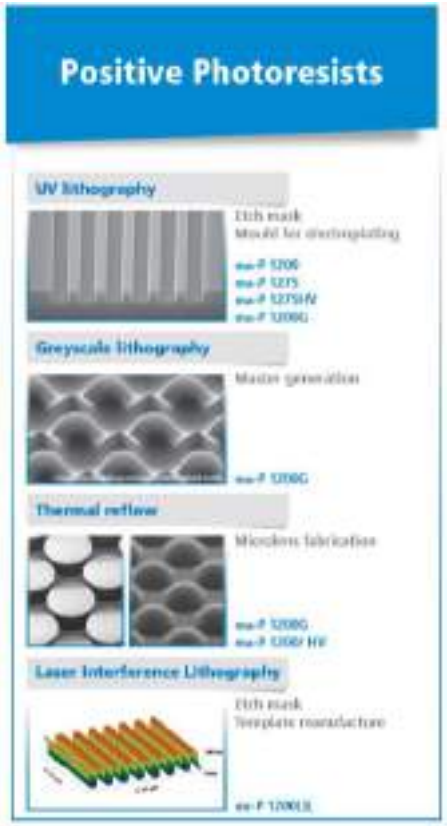








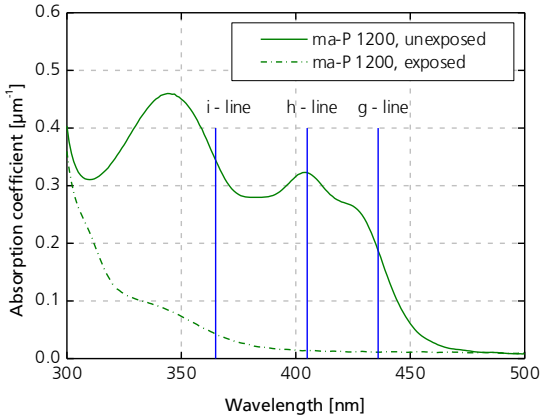
Positive photoresists

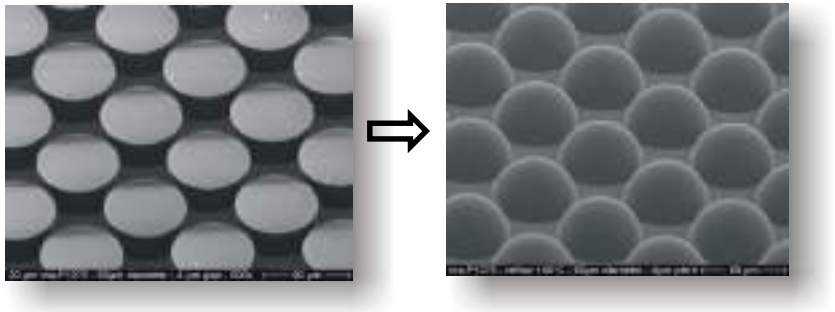


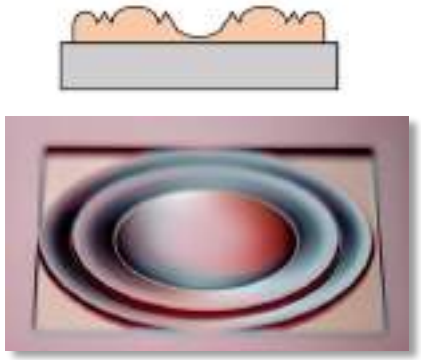
- For – thin (< 1µm) & thick (>100 µm) – binary and gray scale lithography
- **ma-P 1200/ HV, mr-P 1200LIL, ma-P 1200G** & **mr-P 22G_XP**

Applications:

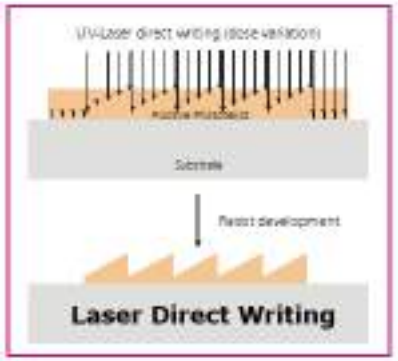
- Etch mask for semiconductors (e.g. Si), SiO_2, metals
- Mask for ion implantation
- Mould for electroplating & for UV molding

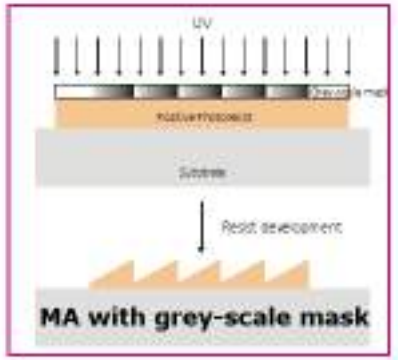




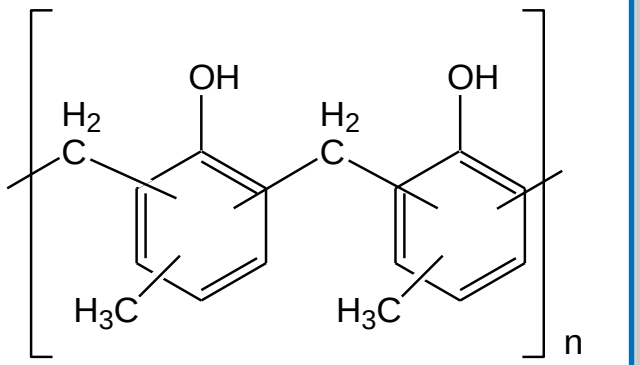


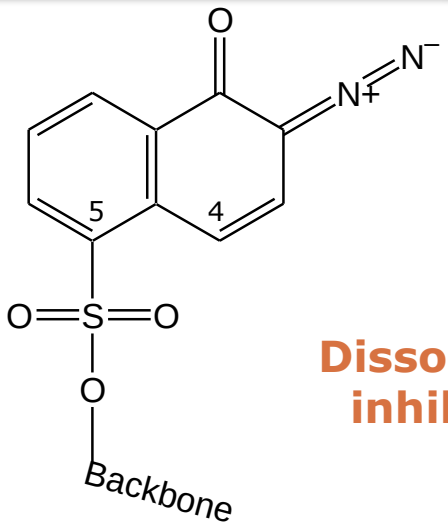
Methods to create an exposure gradient





Composition





Dissolution inhibitor

Resin: Novolak

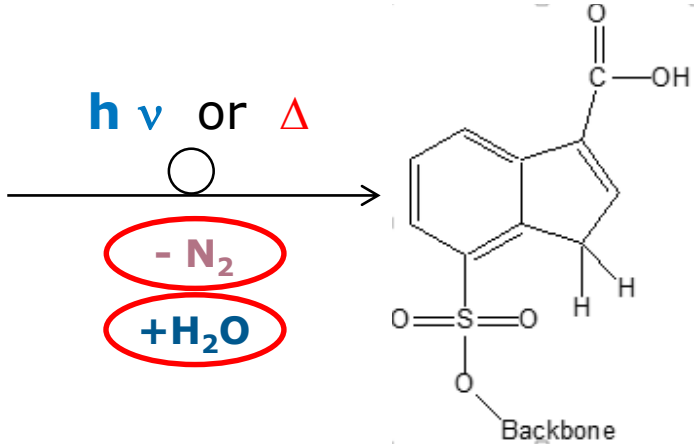
Photo**a**ctive **c**ompound (PAC):
Diazo**n**aphtho**q**uinone (**DNQ**)

Usually several DNQ chromophores attached to a backbone molecule

Solvents Additives

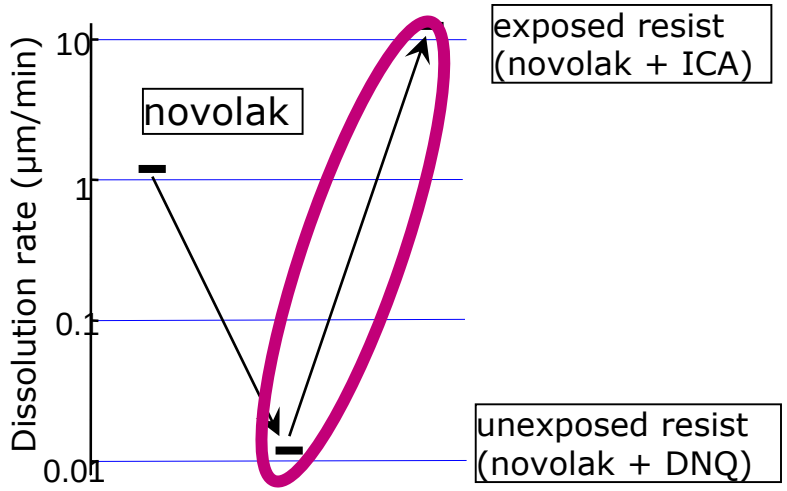
- **non-CAR**
- **Aqueous alkaline development**

Photoreaction and resist function



Indenecarboxylic acid (**ICA**)

Dissolution promoter



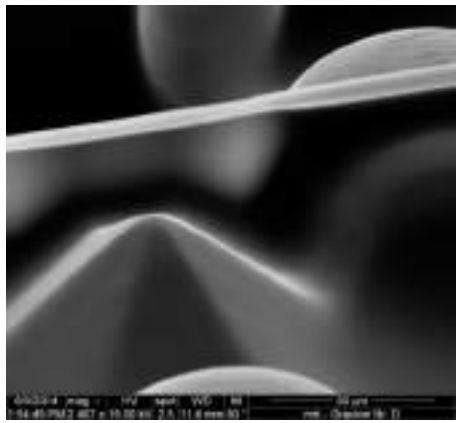
Positive photoresists

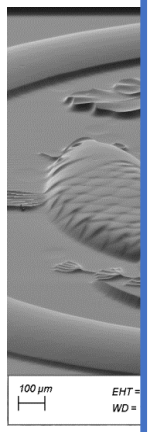
ma-P 1200G

micro resist technology

HEIDELBERG INSTRUMENTS **Laser direct writ**

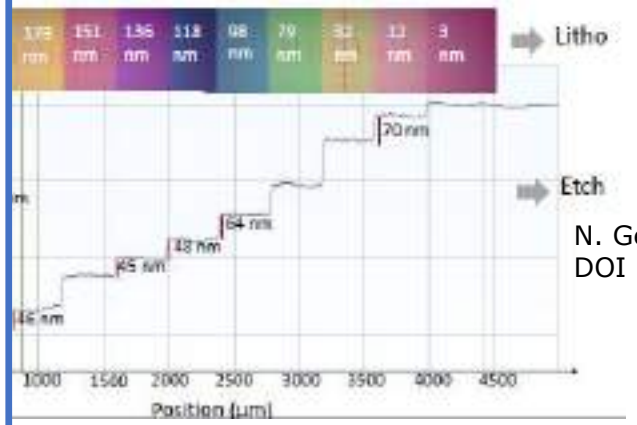
GenISys





DWL

ool: µPG 101,
steps, → transferred into 50 nm steps in Si (RIE)



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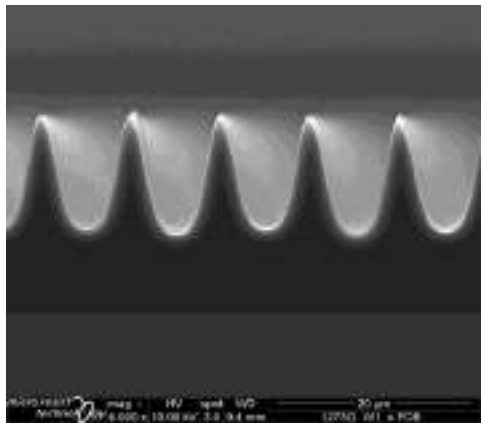
DOI 10.1116/6.0001273

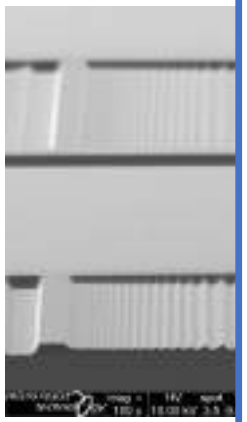
Mask based greyscale litho (

litho

LIL @ 351 nm

FT range: 3 µm – 10 µm



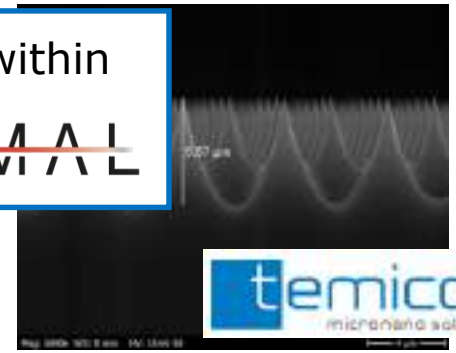


Pixelated mask,
FT resist: 30 µm

HEBS (high energy bea
tinted glass substrates,
optical density of the gl

Benchmark TECHNOLOGIES

CANYON MA



Further research within OPTIMAL

temicon micro nano solutions

Manufacture of
- laminar gratings as well as
- moth eyes patterns

as master for electroplating

2.3008954

WHITE PAPER

micro resist technology

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

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Keywords: greyscale lithography, positive photoresist, DWL, 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 dependent 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 round-shaped 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

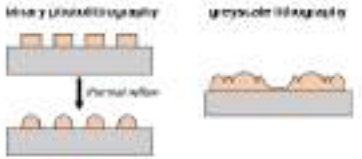


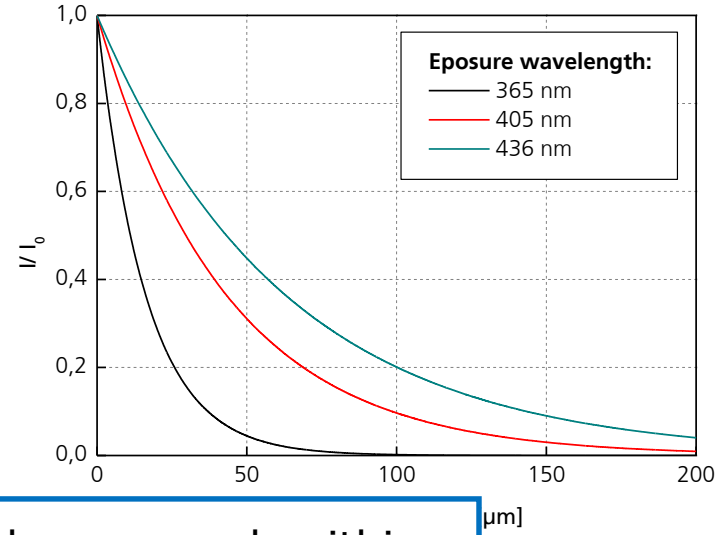
Fig. 1: Exemplary resist patterns manufactured with binary standard photolithography and thermal reflow, compared to greyscale lithography.

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:

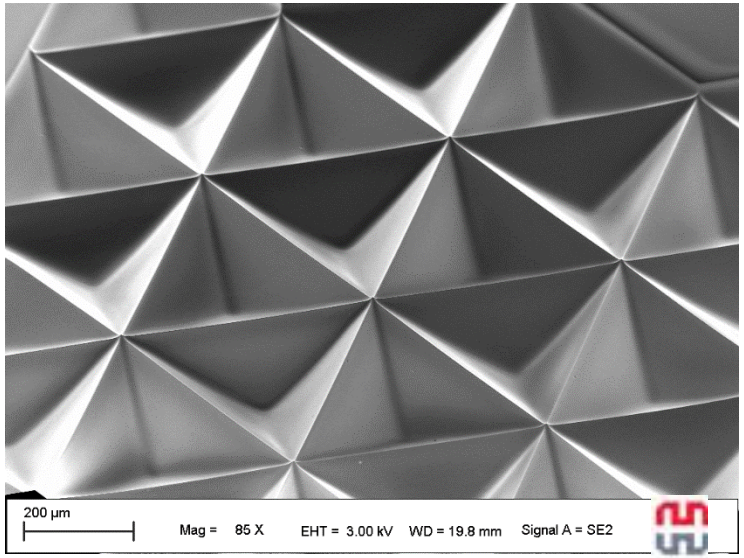
- Coating of the substrate with resist
- Softbake
- Exposure
- Relaxation and re-hydration of the photoresist film. The re-hydration time required increases exponentially with the film thickness, from seconds in thin film

mr-P 22G_XP

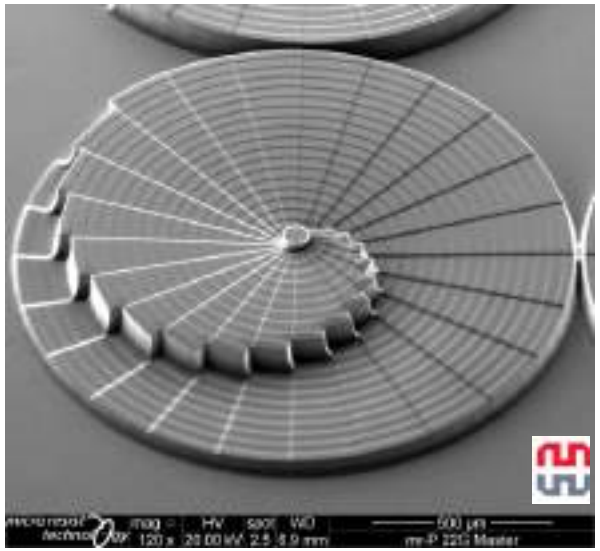
- Up to 130 µm (single), 200 µm (double) film thickness
- Lower residual absorption after exposure gives less attenuation of exposure light in resist film, and allows deeper patterns
- greyscale exposure depth 160 µm with LDW @ 405 nm successfully demonstrated
- Smooth pattern surface with DWL: roughness on top and in patterns < 10 nm



Laser direct writing @ 405 nm



FT: 200 µm,
Pyramid patterns, 155 µm deep



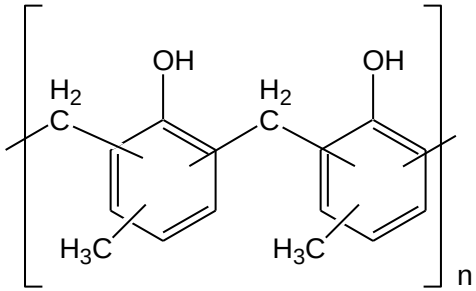
130 µm deep, DWL @ HIMT

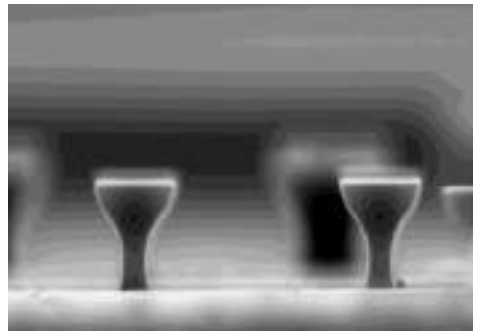
Further research within OPTIMAL

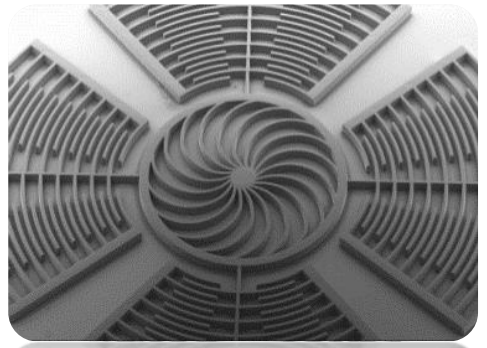
a) SPIE AL+P 2023 https://doi.org/10.1117/12.2661526
b) MNE 2023
c) SPIE AL + P doi: 10.1117/12.3010852

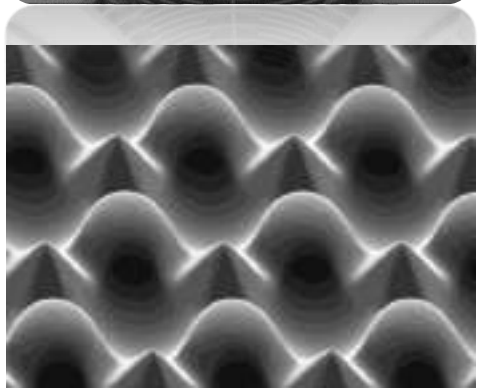
Pattern transfer methods:
a) via PDMS & optical polymer, b) direct moulding with an optical polymer or c) replication via electroplating

Content

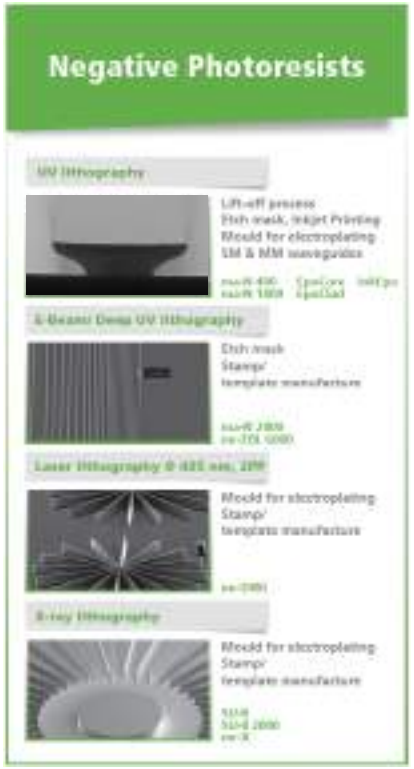




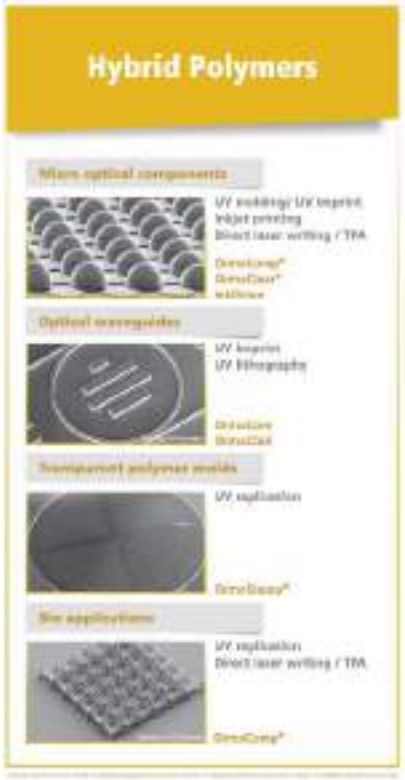




Negative photoresists



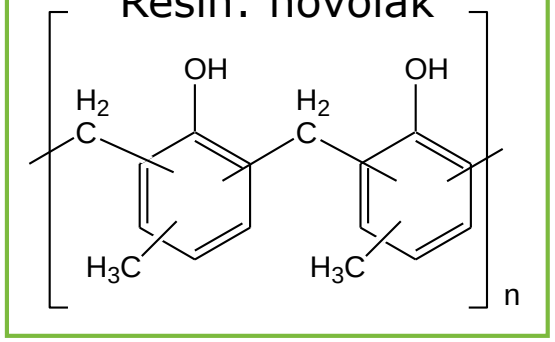
- For – thin (< 1µm) & thick (>100 µm) binary lithography
- **ma-N** novolac resin based
- Epoxy resin based (**EpoCore, Clad, mr-DWL**)

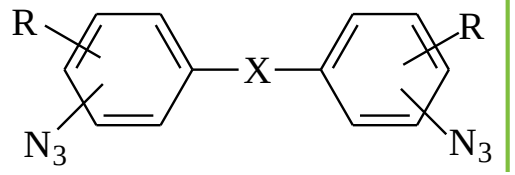


- UV curable materials for micro-optical applications
- Broad thickness range

Composition

Resin: novolak





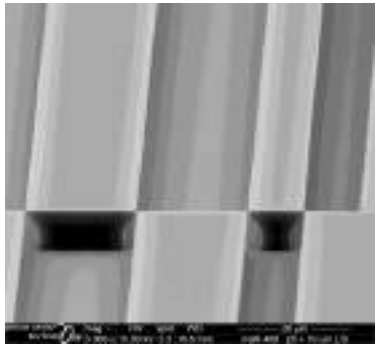
PAC:
aromatic bisazide,
different for all ma-N

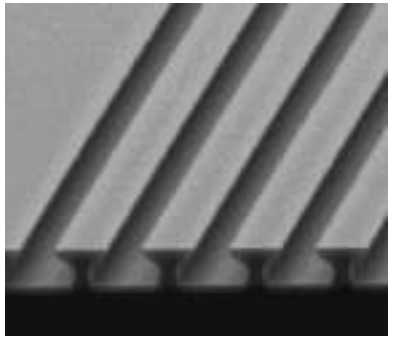
Solvents Additives

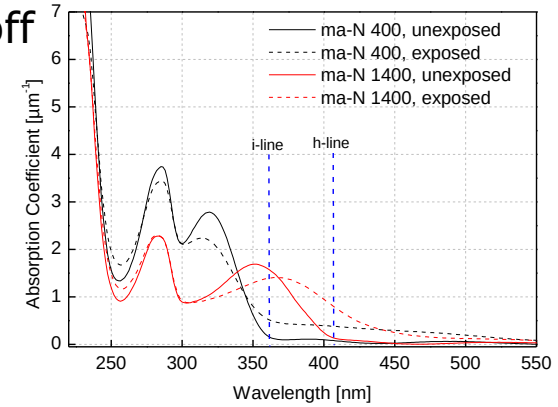
- **non-CAR**
- **Aqueous alkaline development**

Features & Application:

UV sensitive; pattern transfer via PVD & Lift-off

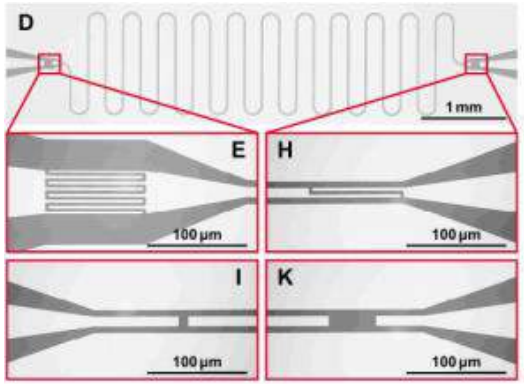




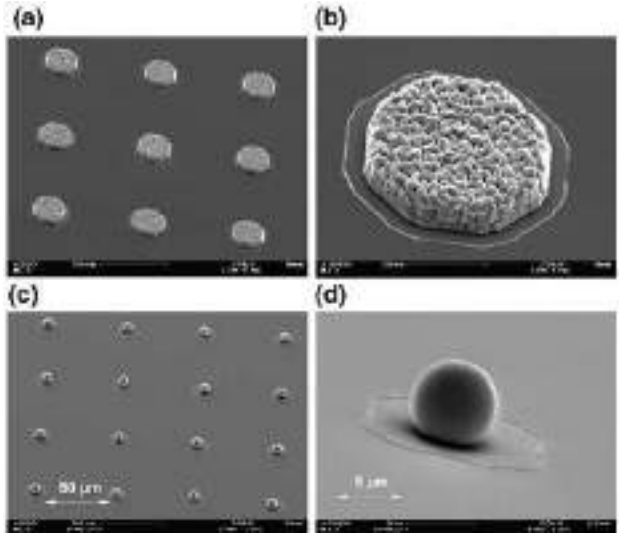


SEM: Sn/ Au sandwich layer on TiW pad,
reflowed sperical bump (∅ 7.5 µm)

Al resonator



Goeppl et al J. Appl. Phys. 104, 113904 (2008)

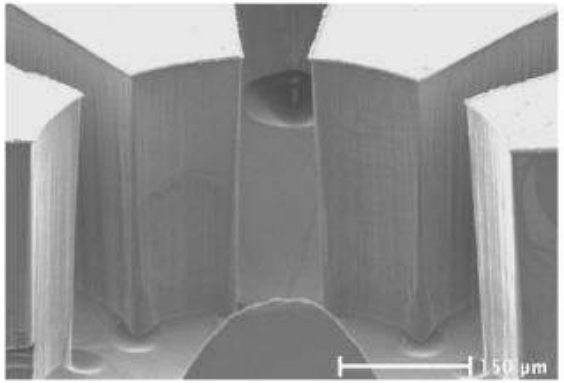


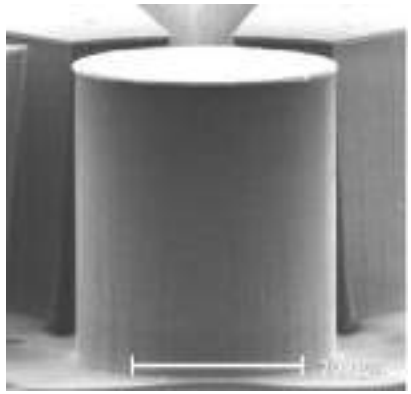
Voigt et al, Microelec. Eng. 78-79 (2005) 503

ma-N 2400

Features & Application:
e-beam sensitive; pattern transfer via dry etching

Pattern transfer via RIE





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

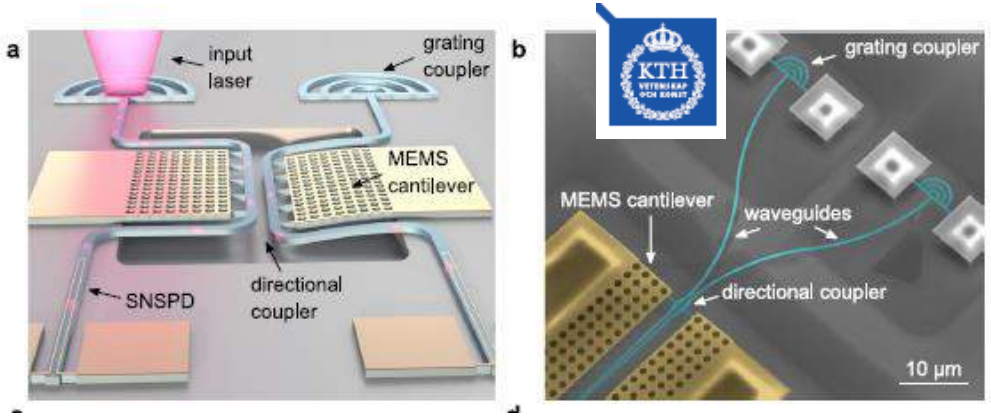
Blideran et al Microelectron. Eng. 86 (2009) 769 – 772
Schuster et al AnalBioanalChem (2008)

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. Yousefi et 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

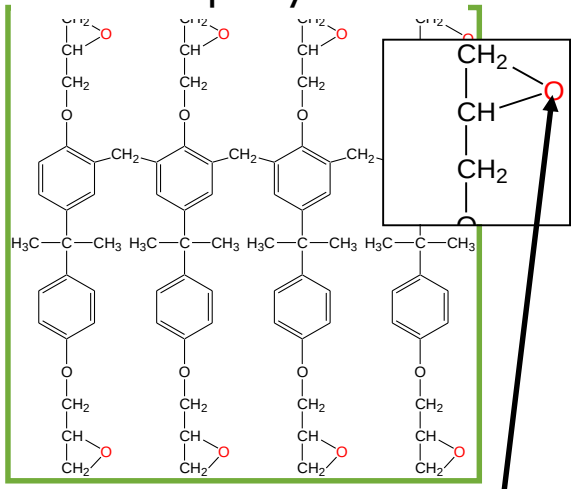
High AR patterns on Si, glass or PET,
FT: 1.9 µm;
400µC/cm² (EPRG200, 100 keV)

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

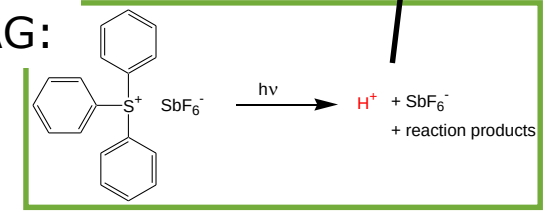
EpoCore& EpoClad

Composition

Resin: Epoxy resin



PAG:

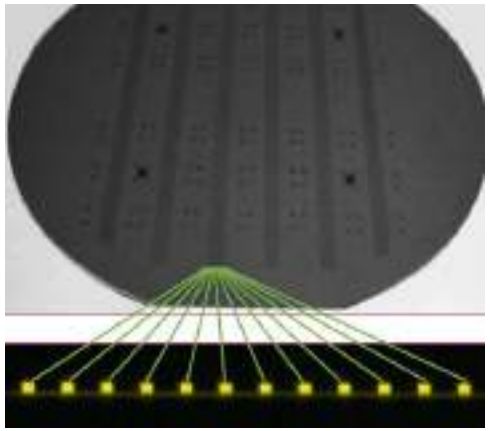


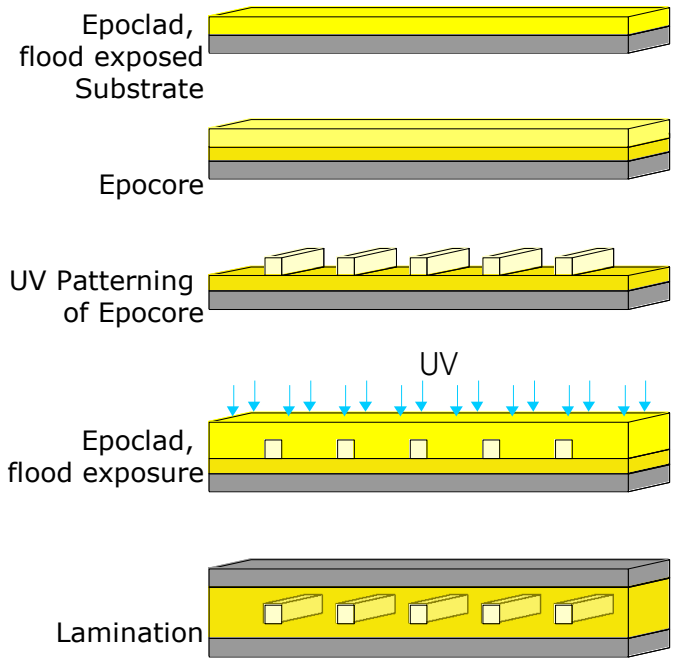
Solvents Additives

- **CAR**
- **Solvent based development**

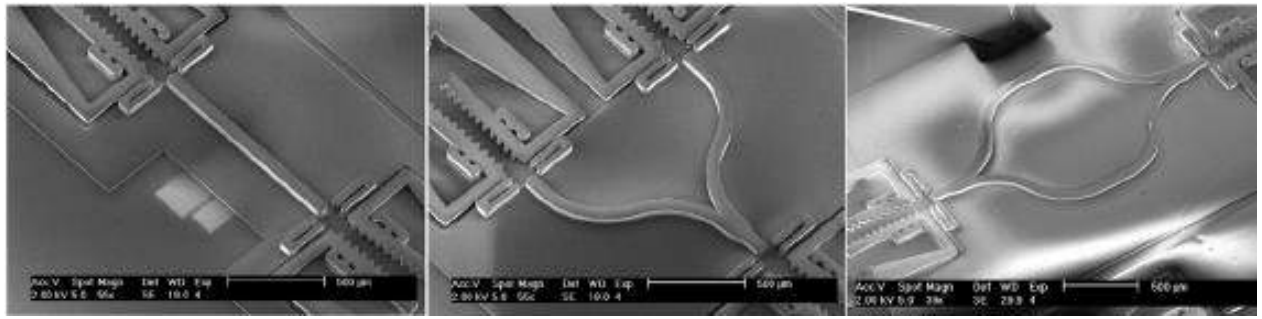
Features & Application:

UV sensitive; manufacture of polymer based optical MM&SM waveguides





WG configuration based on EpoCore/ EpoClad

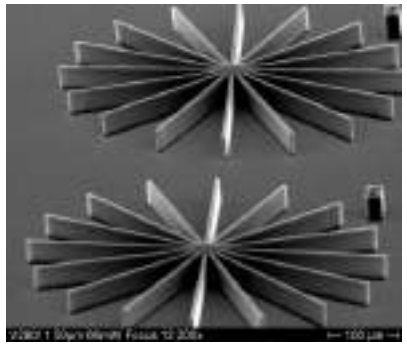


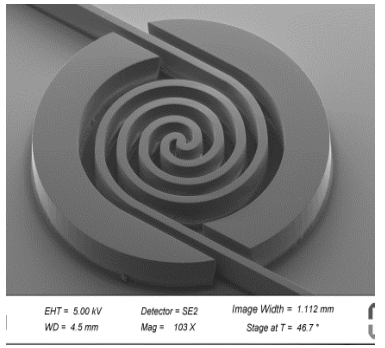
Straight-type Y junction Guan et al JMicromechMicroeng_2013 Mach-Zehnder

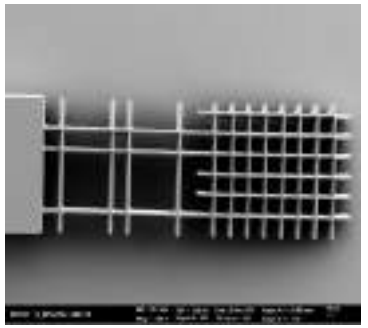
Features & Applications:

- Fast and contactless prototyping with DWL @ 405 nm
- Optical applications in micro system technology
- Mould for electroplating and stamp fabrication

HEIDELBERG INSTRUMENTS



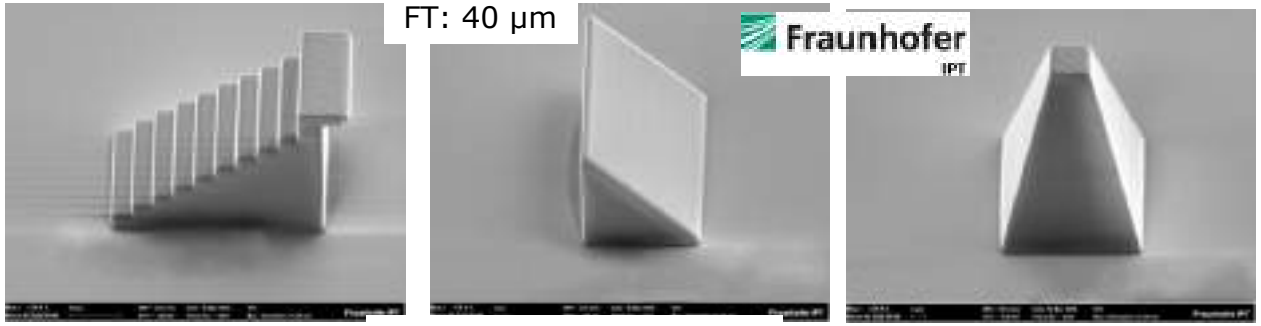




FT: 50 µm, AR: 10 FT: 80 µm FT: 150 µm

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

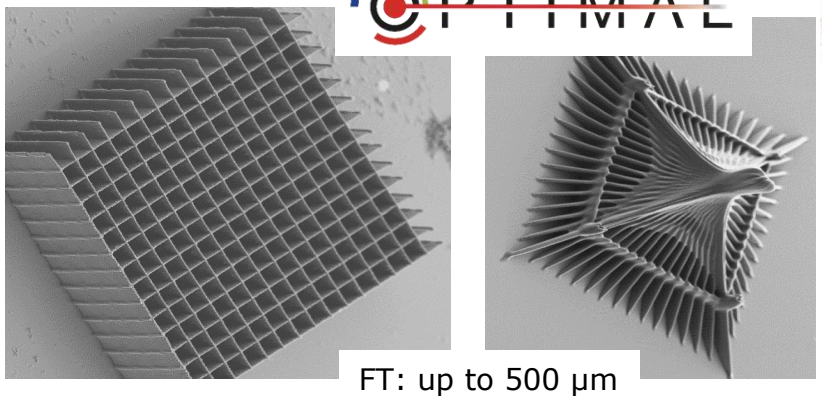
2 Photon Polymerization (2PP)



FT: 40 µm

Fraunhofer IPT

OPTIMAL



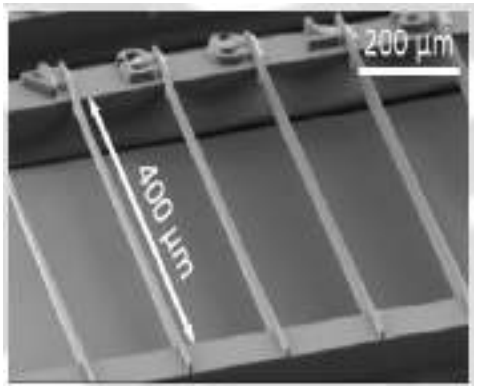
FT: up to 500 µm

Further research within OPTIMAL

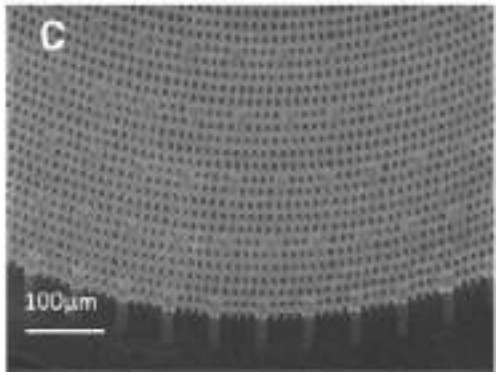
2 Layer litho with 2 laser emission wavelengths

(one developing step)

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



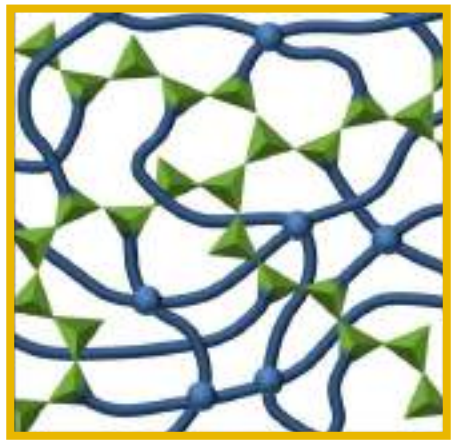
V. Cadarso Poster EIBPN 2012



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

Hybrid polymers

Composition



inorganic building block

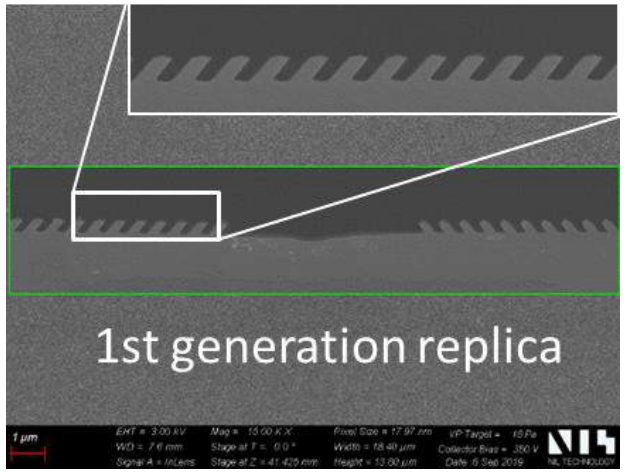
organic polymer chain

- **CAR**
- **Solvent based development**

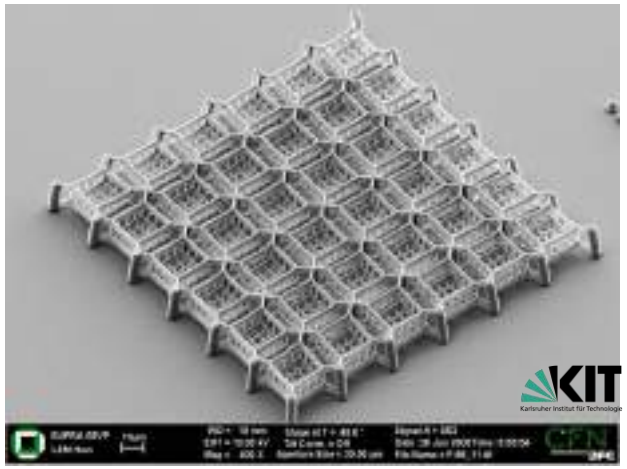
Features & Application:

- UV sensitive
- High optical transparency
- High thermal stability (300°C)
- Sub-100nm resolution with high AR
- Permanent optical application

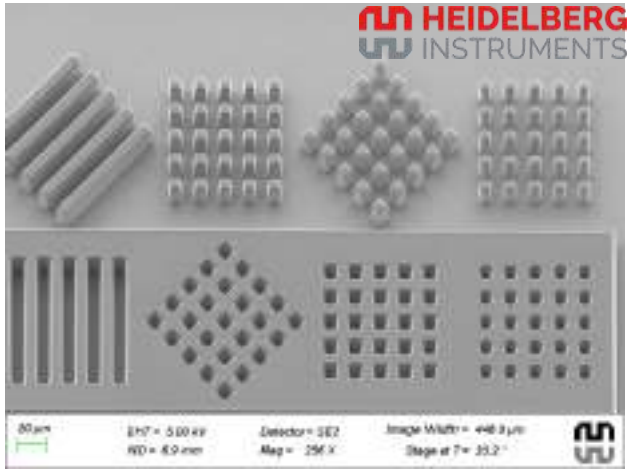
Direct imprint



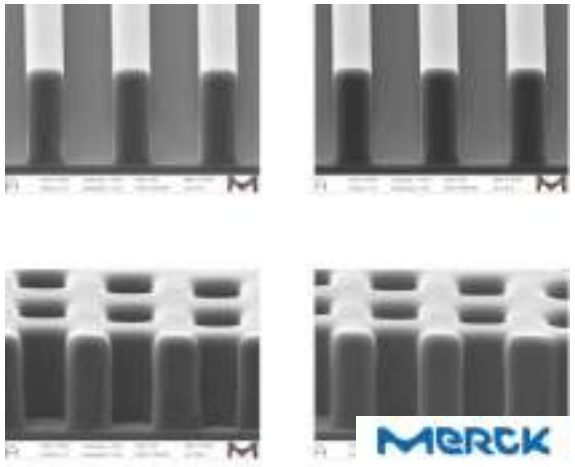
2-photon polymerization



Direct laser writing

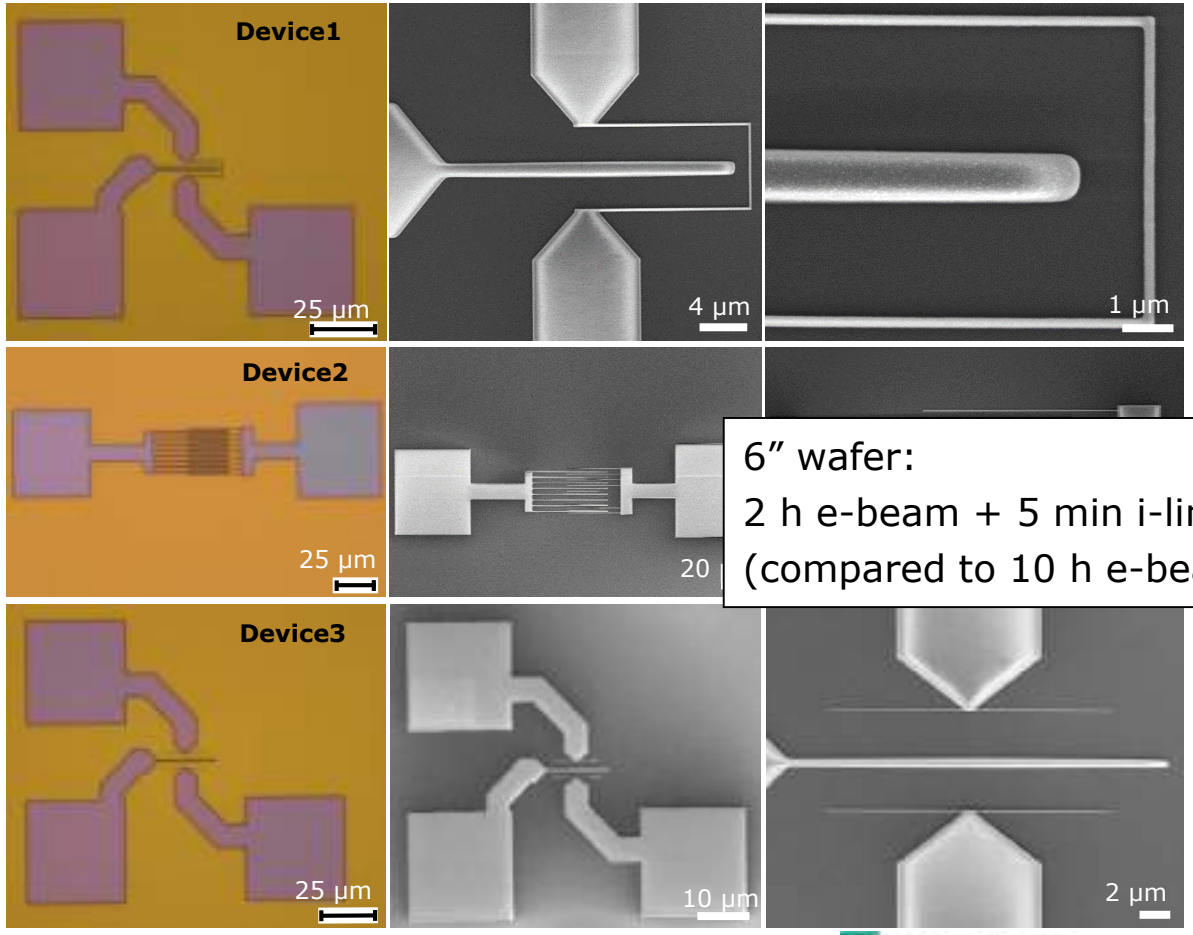


Photolithgraphy



Application for a Mix & Match approach

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



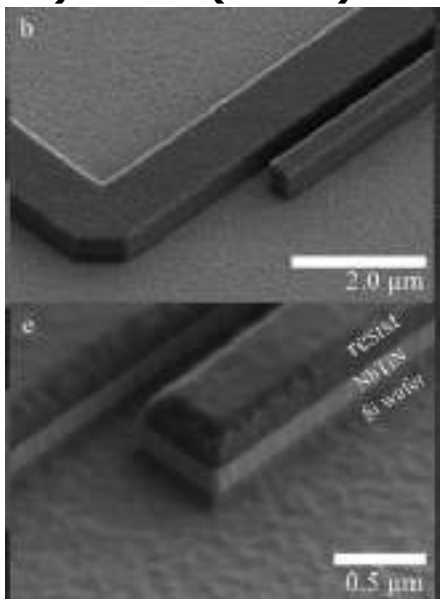
6” wafer:
2 h e-beam + 5 min i-line
(compared to 10 h e-beam only)

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

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

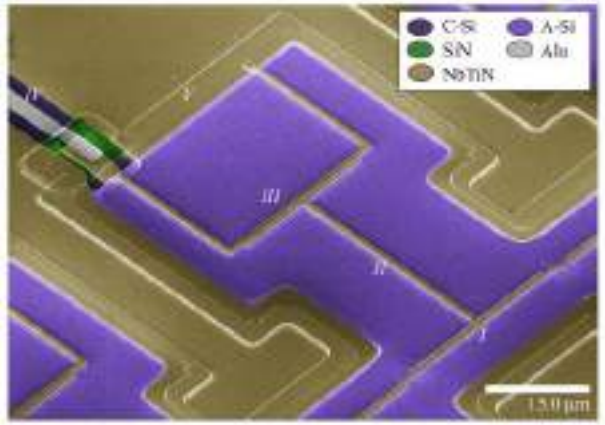
500 nm thick ma-N 1400,
Pattern dimensions:
1 µm + 0.45 µm, gap 300 nm

(smallest resolution
by EBL: 100 nm L)



Further research within OPTIMAL

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) C. H. 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

Summary

A variety of different materials are available for:

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 greyscale lithography
- Mix & Match techniques
- 1PL & LIL (Pos.PR)
  1 PL & 2PP (Neg.PR)

OPTIMAL

Hybrid polymers for direct fabrication of micro-optical components & devices

Thank you for Your Attention!

CERT

micro resist technology

Gesellschaft für chemische Materialien spezieller Photoresistsysteme mbH

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