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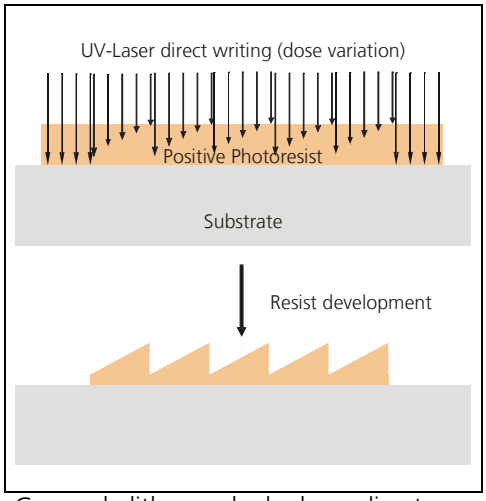
Greyscale Positive Tone Photoresist Series ma-P 1200G

Characteristics

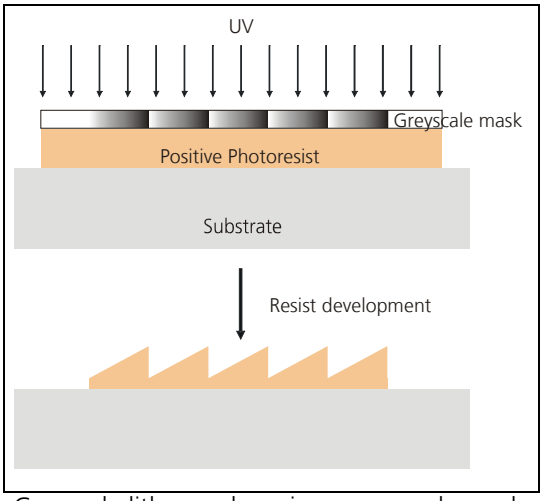
ma-P 1200G is a positive tone photoresist series specifically designed for the requirements of greyscale lithography. An application in standard binary lithography is also possible.

- Reduced contrast
- Film thickness up to 60 µm and higher
- 50-60 µm depth range of the patterns possible in greyscale lithography
- Spectral sensitivity 350…450 nm
- High intensity laser exposure possible without outgassing
- Aqueous alkaline development, for greyscale lithography with TMAH based developers, for standard binary lithography also with metal ion bearing developers
- Suitable for electroplating
- Suitable for dry etch processes e.g. with CHF_3, CF_4, SF_6
- Suitable for pattern reflow after standard binary lithography

Process flow



Greyscale lithography by laser direct writing



Greyscale lithography using a greyscale mask

Physical properties of the resist solutions

Properties		ma-P 1215G	ma-P 1225G	ma-P 1275G
Film Thickness [1]	[µm]	1.5 ± 0.1	2.5 ± 0.1	9.5 ± 0.3
Thickness range	[µm]			7 – 60 (with single coating)
Dynamic viscosity[1]	[mPas]	21 ± 1.5	51 ± 3	900 ± 80
Density[2]	[g cm^{-3}]	1.035 ± 0.003	1.049 ± 0.003	1.085 ± 0.003

[1] spin coated @ 3000 rpm, 30 s, [2] 25°C, 1000 s^{-1}, [3] 20 °C

Processing

Best patterning results are obtained at temperatures of 20 – 25 °C and a relative humidity of 40 – 46 %. The resist and unexposed resist films have to be processed under yellow light.
The guidelines relate to processing of resist films spin coated on silicon or silicon dioxide. The specific process parameters to be applied depend on equipment, substrate and resist film thickness.

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Processing Guidelines – ma-P 1200G

The exposure times/ spot stated for greyscale exposure in the following processing examples are presented by courtesy of Heidelberg Instruments Mikrotechnik GmbH where greyscale lithography was carried out using a Tabletop Maskless Aligner **µPG501** for direct writing.

Processing conditions for different film thicknessess of ma-P 1200G

Resist		**ma-P 1215G**	**ma-P 1225G**	**ma-P 1275G**	
Film thickness	[µm]	**1.5**	**2.5**	**9.5**	**15**
Substrate preparation		Oven: 30 min @ 200°C, HMDS for Si and SiO_2 substrates			
Spin coating	[rpm] [s]	3000 30	3000 30	3000 30	1500 30
Prebake (Hotplate)	[°C] [min]	100-105 1.5	100-105 2	100-105 10	100-105 15-20
Relaxation	[min] @ r.t.	—	—	10	20
Exposure times/ spot[1] (Direct Writing) → Greyscale exposure	[ms]	10…100 (for dose variation)		20…200 (for dose variation)	
Exposure dose[2] (Mask Aligner) → Binary exposure	[mJ cm^{-2}]	60 ± 10	90 ± 20	200 ± 50	450 ± 50
Development[3]	[s]				
mr-D 526/S → Greyscale (and binary) lithography		40 ± 10	50 ± 10	220 ± 30	340 ± 60
ma-D 331 → Standard binary lithography		35 ± 10	40 ± 10	140 ± 30	200 ± 60

[1] Exposure with 390 nm LED, initial power 10 W,
[2] Broadband exposure, intensity measured at λ=365 nm for dose calculation,
[3] Immersion development

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Processing conditions for thick films of ma-P 1275G

Film thickness	[µm]	**30** [1] (HIMT)	**30** [2] (mrt)	**60** [1] (HIMT)	**60** [2] (mrt)
Substrate preparation		Oven: 30 min @ 200°C, HMDS for Si and SiO_2 substrates			
Spin coating	[rpm] [s]	500 60	500 60	0 / 480 / 1500 10 / 60 / 2	1000 4
Prebake (Hotplate)	[°C, min]	20°C, 30min 60°C, 20min ↓ [20min] 100°C, 100min [switch off hotplate, cool down on hotplate] 20°C	100 °C, 30 min	20°C, 30min ↓ [10min] 100°C, 5min	25°C, 45min ↓ [15min] 50°C, 15min ↓ [15min] 90°C, 50min ↓ [10min] 100°C, 30min ↓ [1h] 50°C
Relaxation	[h] @ r.t.	12 - 24	1	0.5	12 - 24
2nd Spin coating	[rpm] [s]	—	—	0 / 480 / 1500 10 / 60 / 2	—
2nd Prebake (Hotplate)	[°C, min]	—	—	20°C, 30min 60°C, 20min ↓ [20min] 100°C, 100min [switch off hotplate, cool down on hotplate] 20°C	—
Relaxation	[h] @ r.t.	—	—	12 - 24	—
Pre-exposure bake (optional)	[°C] [min]				70 5
Exposure times/ spot[3] (Direct Writing) → Greyscale exposure	[ms]	50…350 (for dose variation)			
Exposure dose[4] (Mask Aligner) → Binary exposure	[mJ cm^{-2}]		800 ± 50		5000 ± 500
Development[5] ma-D 532/S, ma-D 526/S, MF 26A	[µm/ min]	~2 ~1 ~1			

[1] Spin coating and baking process by Heidelberg Instruments, [2] Spin coating and baking process by micro resist technology,
[3] Exposure with 390 nm LED, initial power 10 W,
[4] Broadband exposure, intensity measured at λ=365 nm for dose calculation,
[5] Immersion development, stirring at ~ 100 rpm

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Substrate preparation:

The substrates have to be free of impurities and moisture. They should be baked at 200 °C and cooled to room temperature immediately before coating. Alternatively, oxygen or ozone plasma cleaning is recommended. For improving resist film adhesion to Si and SiO_2 substrates it is advisable to apply an adhesion promoter such as HMDS.

Coating:

Uniform coatings are obtained by spin coating of the **ma-P 1200G** solutions in the thickness range indicated in the spin curves. Film thicknesses of 1 – 40…60 µm can be attained with a single coat. Please select the appropriate resist type and spin speed required for the desired film thickness and application. For higher film thicknesses a double coating can be beneficial, but it might implicate bubble formation during the second prebake step Also higher spin-speeds with a very short spin time result in a high film thickness with excellent homogeneity (cf. table above). The information refers to an open spin-coating system.

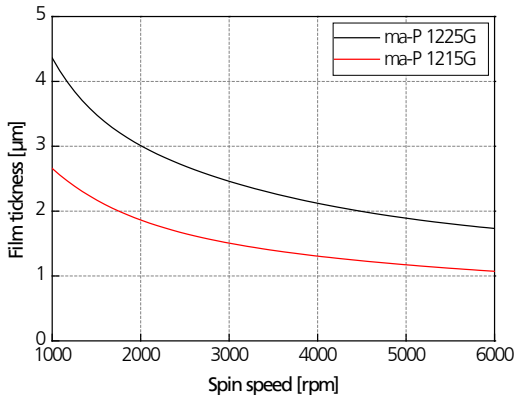

Fig. 1: Spin curves of ma-P 1215G and ma-P 1225G, 30 s spin time, SAWATEC spin-coater

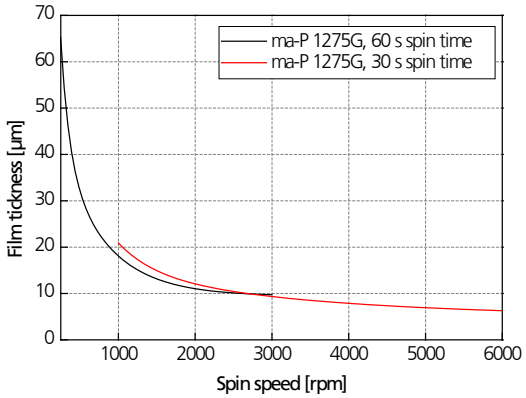

Fig. 2: Spin curve of ma-P 1275G, 60 s and 30 s spin time, SAWATEC spin-coater

The refractive index of the resist film depending on the wavelength and the Cauchy equation are given in Fig. 2. This information is needed for ellipsometric or other optical thickness measurement.

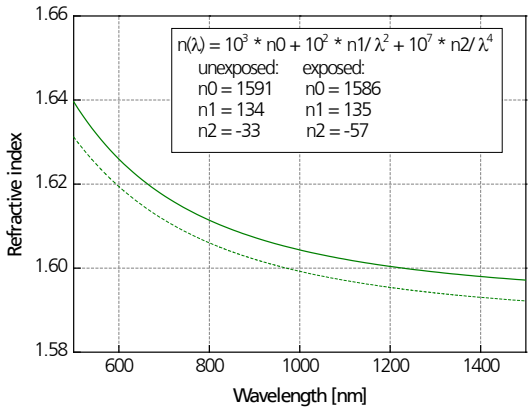

Fig. 3: Refractive index vs. wavelength, Cauchy coefficients of unexposed (——) and exposed (-----) ma-P 1200G

Processing Guidelines – ma-P 1200G

Prebake:

Resist films are baked on a hotplate at 100 – 105 °C.
The prebake conditions are crucial for the patterning results of very thick resist layers, and will have to be adapted to different requirements. In the examples given for 30 µm and 60 µm film thickness a 20…60…100 °C or a 25 °C…50 °C…90°C…100 °C temperature ramp were applied.

Relaxation of thick films:

Water is necessary for the desired photoreaction during resist exposure. Hence, a rehydration of the resist film is mandatory after the prebake, i.e. the diffusion of water from the ambient air into the film, in order to obtain a sufficiently high development rate, preferably consistent over the whole resist film. Therefore there has to be a relaxation time after the prebake in case of higher film thicknesses (from ~ 15…20 µm).

Pre Exposure Bake (optional):

A pre-exposure bake at 70 °C on a hotplate for 5 min, followed by a relaxation time at r.t. (off the hotplate) of 15 min, is recommended if coated substrates of ≥10 µm film thickness have been stored for a longer time (≥ 24 hours). This will stimulate a slightly more homogenous water distribution in the resist film, and avoid bubble formation during exposure.

Exposure:

The resist is effective for exposure wavelengths of 310…450 nm.

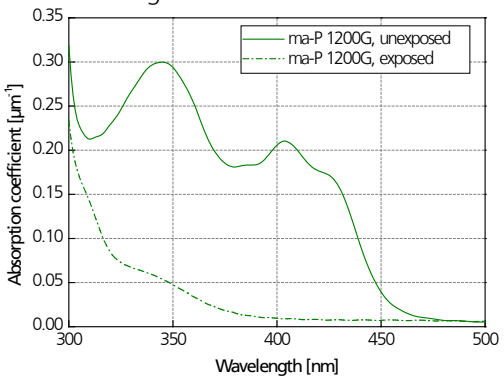

Fig. 4: UV/vis absorption of **ma-P 1200G**

The achievable pattern depth depends on a number of parameters.

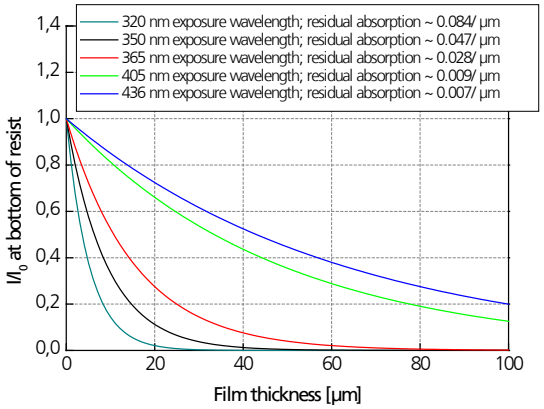

Fig. 5: Light attenuation in **ma-P 1200G** films

During exposure the resist bleaches, i.e. its absorption decreases to a low, wavelength-dependent residual absorbance (Fig. 4). This attenuates the exposure light intensity with increasing depth in the resist film. The intensity reduction is bigger for lower exposure wavelengths, due to higher residual absorption. Hence, higher wavelengths of monochromatic laser or LED exposure (within the sensitivity range of the photoresist) allow deeper patterning in very thick resist films (Fig. 5).

Too high intensity with laser exposure results in a lower pattern depth.

Furthermore, the prebake should not be too strong. A very dry resist film will give a lower pattern depth.

Develop:

In **greyscale lithography** only metal ion free developers should be applied. Good results are obtained with **mr-D 526/S**. 0.26 N (2.38 %) TMAH developers from other suppliers, such as MF 26A from DOW Electronic Materials, can also be applied. **ma-D 532/S** is recommended as developer for thicker films if a somewhat higher dissolution rate is required.
For **standard binary lithography** the metal ion bearing developer **ma-D 331** (NaOH based) is suitable.
The temperature of the developer should be 20 – 25 °C. The developed resist films are thoroughly rinsed with deionized water and then dried.

Post Development Bake in greyscale lithography (optional):

A post development bake, preferably in an oven, can be beneficial if a very smooth resist surface is required. Careful annealing with a temperature ramp is recommended to minimize undesirable reflow effects extending a smoothed surface. The maximum temperature (~ 90…95 °C) depends on the preceding processing steps, especially on the prebake conditions.

Removal:

Ready-to-use removers **mr-Rem 500** (free of N-methylpyrrolidon (NMP)), **mr-Rem 700** (free of NMP and of N-ethylpyrrolidon (NEP)) and **ma-R 404/S** (strongly alkaline) are recommended. Acetone, 1-methoxy-2-propyl acetate (PGMEA), or oxygen plasma is also suitable for the residue free removal of the resist.

Storage

Storage at temperatures of 18 – 25 °C is recommended. Do not store **ma-P 1200G** in a refrigerator. Keep the bottle closed when not in use. Under these conditions a shelf life of 12 months from the date of manufacture is ensured.
Resist and unprocessed resist films have to be stored under yellow light.
A shelf life of 12 months is ensured for developers and removers.

Disposal

Unexposed resist and solvent based remover: dispose of as halogen free solvent
Exposed resist: dispose of as resist/ old resist
Developer and aqueous-alkaline remover: dispose of as weak alkaline aqueous solution

Environmental and health protection

ma-P 1200G resist contains "safe solvents". Ensure that there is adequate ventilation while processing the resist. Avoid contact of the resist with skin and eyes and breathing solvent vapours. Wear suitable protective clothing, safety goggles and gloves.
Please, review the current product safety data sheet before using the materials.

Equipment

ma-P 1200G is compatible with most commercially available photoresist processing equipment, and with equipment specifically for greyscale exposure.

The data given in these guidelines were obtained using:

- Sawatec spin coater without cover (micro resist technology GmbH) or Convac spin coater without cover (Heidelberg Instruments)
- Contact hotplate
- Exposure:
  Heidelberg Instruments: Tabletop Maskless Aligner **µPG501** for direct writing, LED with 390 nm wavelength as light source, Initial power = 10 W; light intensity at photoresist surface depending on optical components, ~ 1 µm light spot diameter (greyscale lithography), or **DWL66+** direct write lithography system with a 405 nm laser

  micro resist technology GmbH: Suss MA 56 and MA 6 mask aligner (standard binary lithography)
- Immersion development, ~100 rpm stirring for thick resist films
- Convection oven for post development bake

Patterning examples

Exposure with µPG501 (390 nm LED) at Heidelberg Instruments:

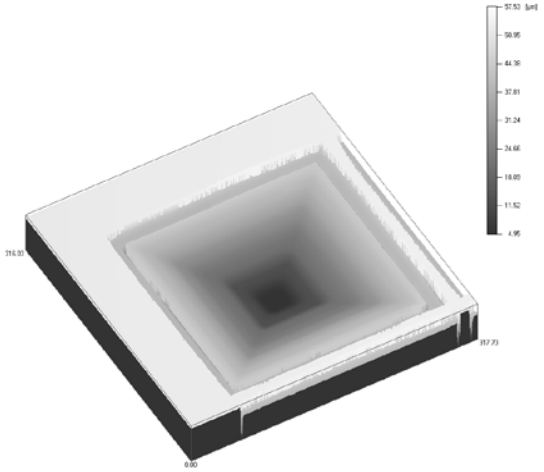

Fig. 6: 53 µm deep pyramid hole in 58 µm thick ma-P 1275G (confocal microscopy);
by courtesy of Heidelberg Instruments

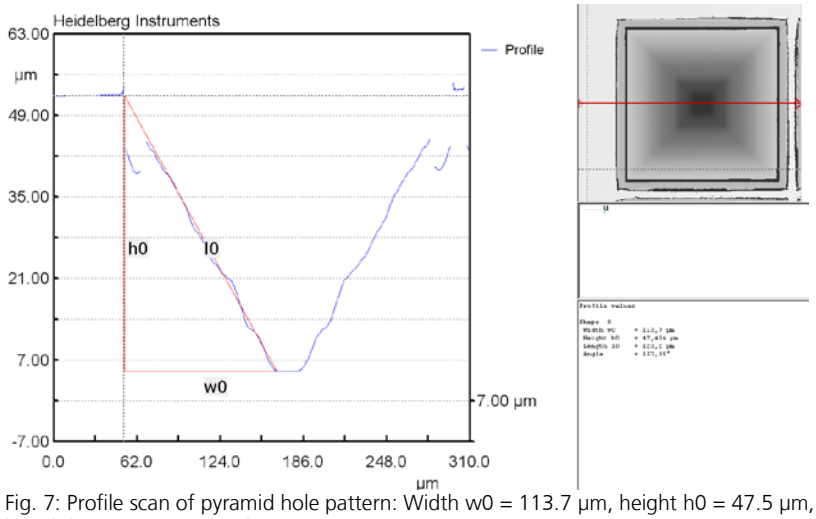

Fig. 7: Profile scan of pyramid hole pattern: Width w0 = 113.7 µm, height h0 = 47.5 µm, length l0 = 123.2 µm, angle = 157.4 °;
by courtesy of Heidelberg Instruments

Exposure of ma-P 1275G with DWL66+ (405 nm Laser) at Heidelberg Instruments (Fig. 8 - Fig. 10), and with VPG 400 (355 nm laser) at IMS CHIPS (Fig. 11):

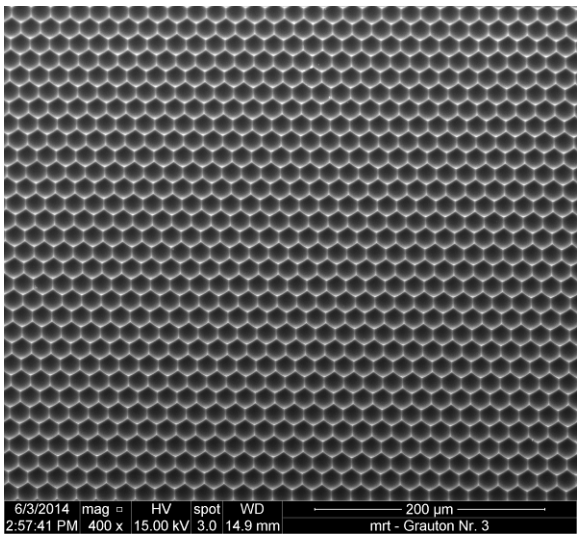

Fig. 8: Hexagonal concave lenses, ~ 17 µm width

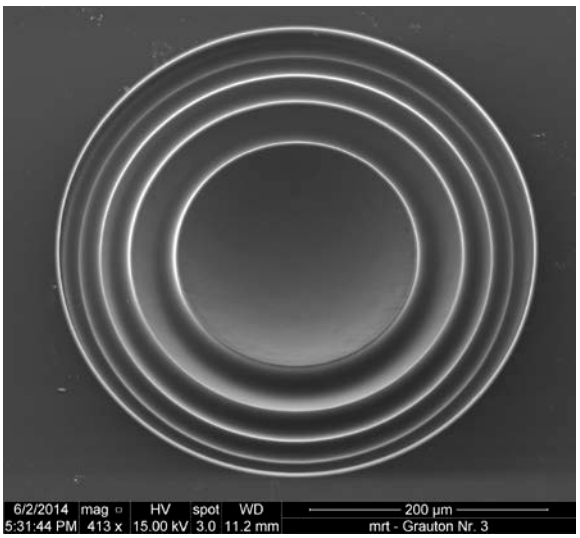

Fig. 9: Fresnel lens

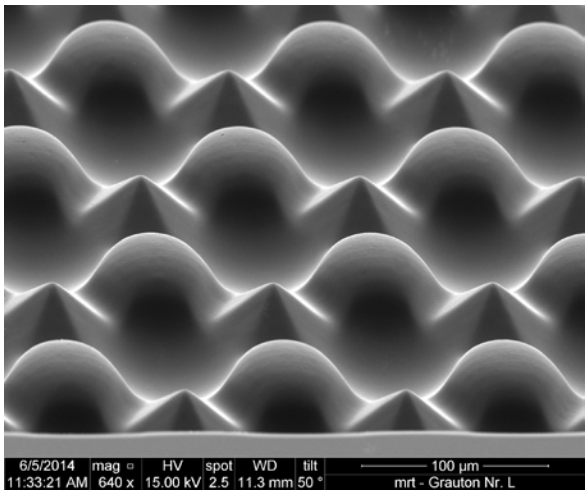

Fig. 10: Convex lenses, concave lenses and hexagonal pyramids in a honeycomb arrangement, hexagon diameter = 80 µm

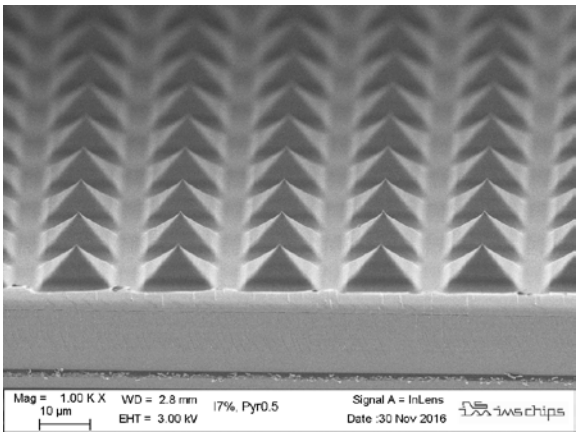

Fig. 11: Pyramid structure, base of pyramid = 10 µm, height = 5 µm, angle = 45 °; by courtesy of IMS CHIPS

Processing Guidelines – ma-P 1200G

Exposure of ma-P 1275G with mask aligner broadband exposure:

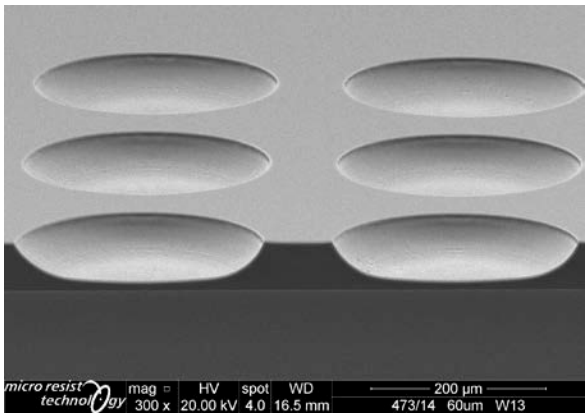

Fig. 12: Exposure through greyscale mask + post development bake, 48 µm, pattern depth

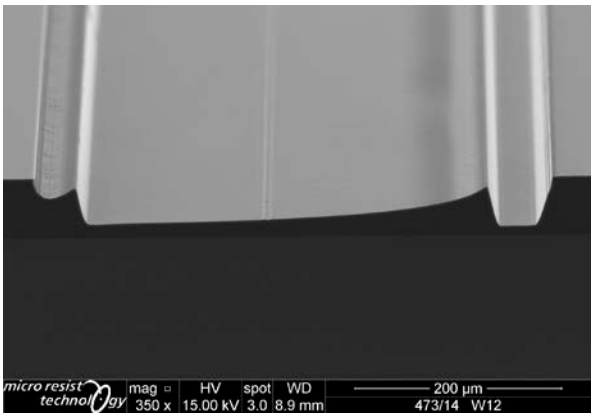

Fig. 13: Exposure through greyscale mask + post development bake, 47 µm, pattern depth

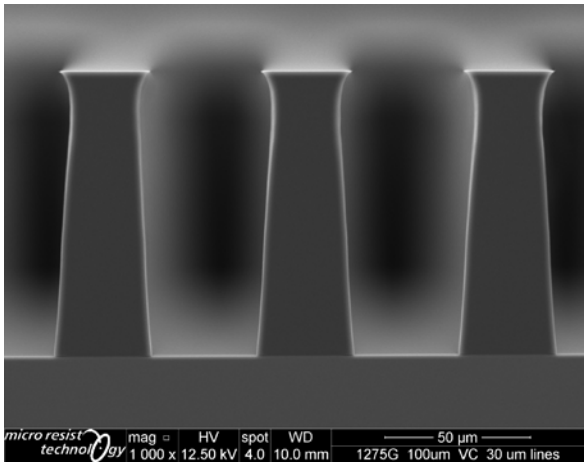

Fig. 14: Binary standard lithography, 100 µm film thickness