Optical contact lithography using positive and negative tone resist

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Abstract

In this report we investigate the effects of using AZ 5214 E as both positive and negative tone resist for creating microstructures using optical contact lithography. We varied several parameters of the existing recipes to get optimal results with a MJB-3 mask aligner. Optimal exposure times for positive tone resist were found to be around 2 min. For the negative tone resist an initial exposure of around 0.4 min. and a flood exposure for 4 min were found to be optimal.

Introduction

Optical lithography is a process used to transfer patterns from a photomask to a photosensitive resist. Optical lithography is widely used in academia and industry to fabricate structures on a micrometer or nanometer scale. In this report the effects of using a positive or negative tone resist and the differences between the two were studied.

Lithographic system

The basic working of optical contact lithography is illustrated in figure 1.

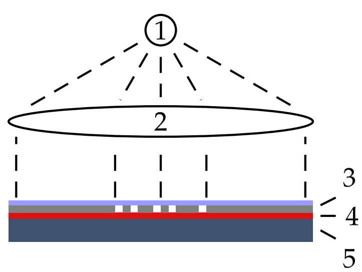


Figure 1: *Simplified working of contact lithography, with 1. light source, 2. condenser lens(es), 3. glass/quartz plate with mask, 4. photographic resist, 5. substrate. Dashed lines indicate light ray paths.*

Light emitted from a source is collimated using a condenser lens (or an array of lenses). The collimated light travels through the transparent parts of the mask and illuminates the resist areas directly below these areas. For this experiment an MJB-3 mask aligner from Karl Suss Microtec with a mercury-vapor lamp was used. However, this particular model is designed for deep ultraviolet (DUV) while the used resist is designed for exposure to the I-line and H-line (365.4 nm and 404.7 nm respectively) of the Hg lamp or near ultraviolet (NUV). To prevent the DUV light from exposing the resist and damaging it, the mask is clamped to a glass plate which blocks light with $\lambda \lesssim 300$ nm. The minimal feature size (MFS) is given by

$$\mathrm{MFS} = k\sqrt{\lambda \frac{z}{2}},$$

where k is the process constant ($\sim$1.5), λ the wavelength of the light source and z the resist thickness. Assuming a resist thickness of 1.6 μm and that only the I-line has a significant contribution, MFS = 0.81 μm.

Substrate and resist

Patterns were written on a series of square cut silicon substrates of approximately 15 mm by 15 mm. For both the negative and positive tone samples, AZ 5214 E[1] is used as photoresist. Since the optics of the MJB-3 is designed for DUV light, much intensity of the NUV is absorbed. Thus the exposure times of standard recipes

[1] AZ 5214 E is a high resolution image reversal resist produced by MicroChemicals

designed by the Kavli Nanolab facility are not sufficient. The recipes are modified to accommodate the decrease in light intensity. Some initial guessing was needed and different exposure times are investigated.

Positive resist

As a positive tone resist, AZ 5214 E is used. To promote adhesion to the Si substrate, HMDS (hexamethyldisilazane) is applied first as a primer. The primer is deposited by hand on top of a silicon wafer and spun at 4000 RPM, it is then baked on a hot plate at 200° C for two minutes. The resist is spun at the same speed as the primer, which should result in a layer thickness of 1.40 μm. The resist is baked on a hot plate at 90 °C for one minute.

After the resist is deposited, the sample is positioned in the mask aligner for an exposure time τ of 1, 2, 2.5, 3, 3.5, or 4 minutes. After exposure the sample is developed for 60 seconds in MF-321[2] after which development is stopped by rinsing the sample another 60 seconds in purified water.

Negative resist

AZ 5214 E contains a special cross-linking agent which becomes active at temperatures above 110° C where the resist has been exposed. The cross-linking agent causes the individual molecules to bond, creating an almost insoluble, non-photoreactive substance. This allows the AZ 5214 E to also be used as a negative resist.

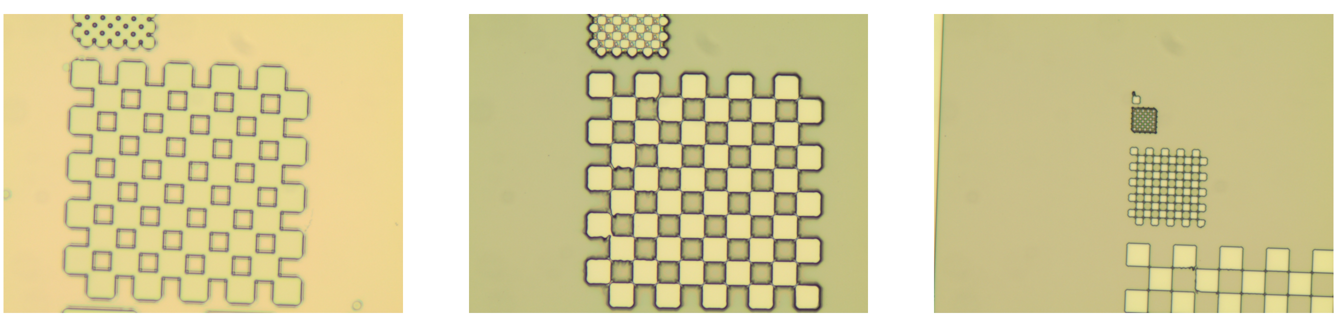
Using the same mask as for the positive exposure, the sample is illuminated for a period τ_1 of 0.1, 0.2, 0.3, 0.5, 1 and 1.5 minutes. After this first illumination the sample is baked in an oven at 120 °C for 42 seconds. During this time cross-links are formed in the areas of the resist that were exposed during the first illumination. During baking the sample lies on an aluminium slab inside the oven, which prevents large temperature drops when the oven door is opened and ensures good heat transfer to the sample. After baking, the entire sample is exposed a second time (flood exposure) for a period τ_2 of either 3 or 4 minutes. During this time the areas of the resist that are not cross-linked are cut up into smaller chains. When the sample is submerged in the MF-321 (again for 60 seconds), these smaller chains are dissolved. After development, the sample is rinsed with purified water as was done with the positive resist samples [1].

Results and discussion

The mask was made with a variety of shapes in different sizes, including but not limited to, checkerboards, outward radiating lines and shapes with optical proximity correction (OPC). The complete design is shown in figure 6. In this section only the checkerboard shapes are discussed as the other shapes did not contribute to more insight. A more complete overview of microscope images of the designed shapes can be found in appendix B.

To find the optimal exposure time τ, the checker-

[2] MF-321 developer is mainly composed of water and tetramethylammonium hydroxide and is produced by Microposit.

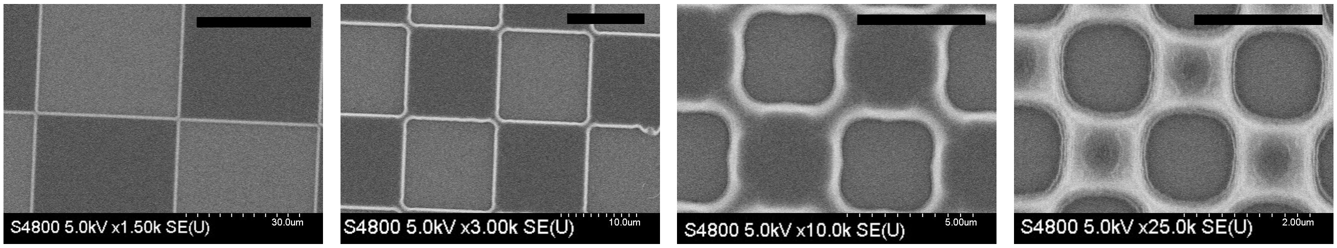


(a) $\tau = 1$ *min. Significant underexposure visible.*

(b) $\tau = 2.5$ *min. Slight overexposure.*

(c) $\tau = 2$ *min. The checkerboard pattern in the lower-right corner is of the same size as the one in sub figure a.*

Figure 2: *Positive tone resist with different exposure times.*



(a) *Largest checkerboard. Black scale bar is 30.0 µm wide.*

(b) *Slight overexposure can be seen at the vertices of the squares. Black scale bar is 10.0 µm wide.*

(c) *The effects of overexposure become pronounced here. Black scale bar is 5.00 µm wide.*

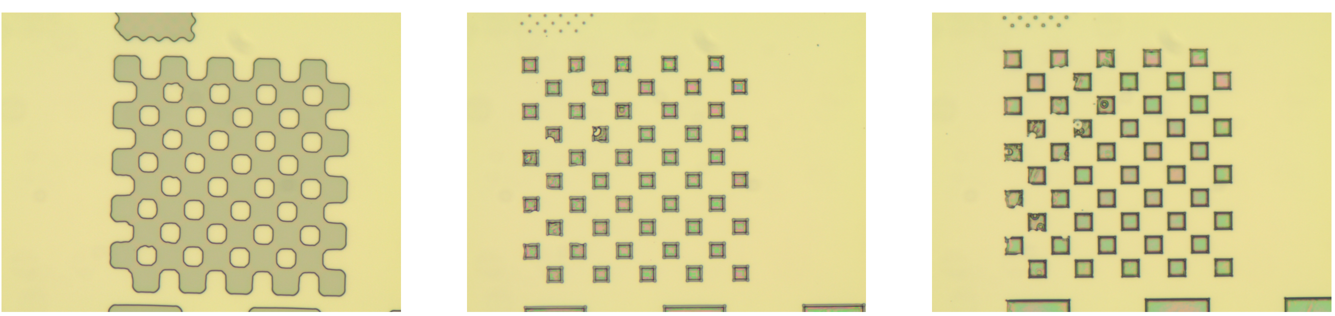
(d) *The patterns starts become unrecognizable. Black scale bar is 2.00 µm wide.*

Figure 3: *SEM images of the checkerboard patterns in order of decreasing size on the positive tone sample.* $\tau = 2$ *min.*

board pattern of each sample is inspected under an optical microscope. With a positive tone resist, underexposure results in not enough resist being dissolved in the development solution (figure 2a). Of the exposed areas, the molecules near the boundary do not reach the dose threshold, while the molecules in the center do. This is because the molecules in the center receive much scattered light from neighbouring molecules, while molecules near the boundary do not nearly have as many neighbours. When the resist is exposed for too long, boundary areas underneath the opaque parts of the mask also reach the dose threshold (figure 2c). With the limited amount of developed samples, an exposure time of 2 minutes was found to be optimal (figure 2b). The "shadows" seen at the edges of the patterns are caused by overcut and undercut. The light diffracts from these areas, which causes the light to not hit the lens.

Images of the checkerboard patterns on the positive tone sample with an exposure time of 2 minutes were taken with a Hitachi S4800 scanning electron microscope. On the largest checkerboard (figure 3a) the exposure time appears to be just right. When looking at the smaller checkerboards however, the effects of overexposure become apparent (figure 3b-d). The bright areas around the pattern boundaries is due to the "edge effect", which is a phenomenon where more secondary electrons can escape the sample if the electrons hit the pattern under an angle, which increases the contrast.

The negative tone has two exposure times that are varied, the initial exposure τ_1 for the cross-linking and the flood exposure τ_2. The first three samples were done with $\tau_2 = 3$ minutes. During the analysis of these samples it was found that the quality of the samples fluctuated, and that longer exposure times were required, thus $\tau_2 = 4$ minutes was used for the remaining samples.

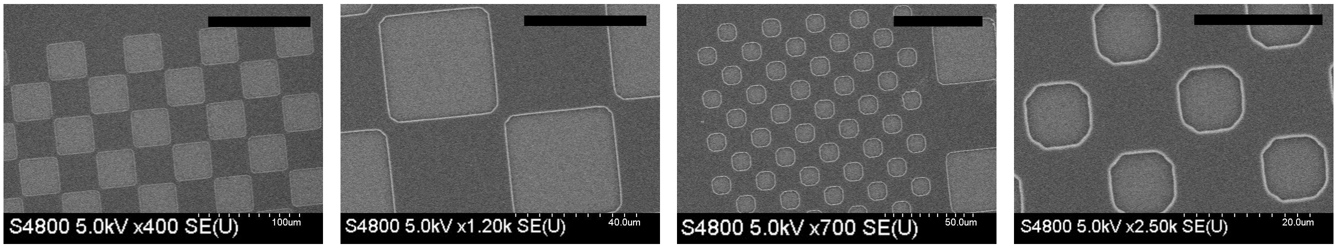


(a) $\tau_1 = 0.5$ *min. and* $\tau_2 = 4$ *min. Too much resist is cross-linked (grey areas) as a result of overexposure.*

(b) $\tau_1 = 0.2$ *min. and* $\tau_2 = 4$ *min. Too little resist is cross-linked as a result of underexposure.*

(c) $\tau_1 = 0.3$ *min. and* $\tau_2 = 4$ *min. The sample is again underexposed, but not as much as in subfigure b.*

Figure 4: *Optical microscope images of the third largest checkerboard on the negative tone resist with different exposure times.*



(a) *Largest checkerboard. Scale bar is 100 μm*

(b) *Largest checkerboard. Scale bar is 40 μm*

(c) *Second largest checkerboard. Scale bar is 50 μm*

(d) *Second largest checkerboard. Scale bar is 20 μm*

Figure 5: *SEM images of the two largest checkerboard patterns on the negative tone sample (inverse version of the patterns shown in figure 4).* $\tau_1 = 0.5$ *min,* $\tau_2 = 4$ *min.*

It was found that for the negative tone resist an exposure time of 0.1 min. resulted in no pattern creation at all, while exposure times of 0.5 minutes and longer resulted in overexposure (figure 4a). While an exposure time of 0.2 or 0.3 min. resulted in underexposure (figure 4b and c respectively). Thus an exposure time of around 0.4 minutes probably would have been optimal, but was not done due to lack of time.

The coloration in the exposed areas (4b and c) are also an indication of underexposure. Incident light travels through the remaining resist and gets reflected at the resist-primer interface. Depending on the thickness of the remaining resist layer, certain wavelenghts interfere contructively or destructively, resulting in colored areas.

The negative tone sample where $\tau = 0.5$ min. was inspected in the SEM (figure 5). The mask appeared to contain the pattern as designed and an inverse version. As a result, the SEM image are from the inverted design as opossed to the optical microscope images (figure 4). From at the largest checkerboard (figure 5a and b) the overexposure is already apparent and becomes even more pronounced at the second and third largest checkerboards (figure 5c and d). The squares of the smaller versions merged together into a single square (not shown).

The thickness of the resist layers is analyzed using a profilometer. A straight line was traced such that the probe scanned both exposed areas as well as unexposed areas. The difference in height between the removed and untouched resist Δh was determined from two scans at different locations on a sample. From table 1 it is clear that $\tau = 1$ min. is too short to completly remove the resist. From the longer exposure times, the thickness of the resist was measured at around 1.6 μm, which is thicker than the expected 1.4 μm for AZ 5214 E at 4000 rpm.

Table 1: *Positive tone resist height difference between exposed and unexposed areas.*

τ (min)	Δh (μm)
1.0	0.3175(3)
2.5	1.6286(4)
3.0	1.5932(2)
3.5	1.5920(3)
4.0	1.6696(3)

For the negative samples (table 2) $\tau_1 \leq 0.3$ min. is too short for the cross-linking to reach the full height of the resist. For $\tau_1 = 0.1$ min. no patterns were visible at all and no significant height difference was measured. The height difference for longer τ_1 is smaller than for the positive resist, although still larger than expected. There are several possible causes for this. Coating a substrate influences the ambient solvent saturation in the spin-coater, this in turn has an effect on the resist thickness of resist on substrates coated afterwards. The airflow conditions in the spin-coater influence the evaporation rate of the solvent in the resist, thus also influencing the attained resist thickness. Another influence on the resist thickness, is the concentration of solvent in the resist. If the bottle of resist is opened frequently, the solvent concentration gradually drops. It is unclear if any or some of these factors are responsible for the higher than expected resist thickness, since the order in which the substrates were coated was not documented, the airflow conditions were not measured and the actual solvent concentration of the resist is unknown.

Table 2: *Negative tone resist height difference between cross-linked and areas without cross-links.*

τ_1 (min)	τ_2 (min)	Δh (μm)
0.5	3.0	1.3845(2)
1.0	3.0	1.4822(2)
1.5	3.0	1.6816(2)
0.1	4.0	0.0450(4)
0.2	4.0	0.5664(2)
0.3	4.0	0.8637(2)
0.5	4.0	1.5371(2)
1.0	4.0	1.5552(3)
1.5	4.0	1.5381(2)

Other parameters of the recipe also influence the obtainable resolution. However, unless the parameters deviate significantly from standard values, the obtainable resolution will depend primarily on the exposure time. Some samples turned out to be of inferior quality because they were created on recycled substrates. This combined with the limited time available resulted in not accurately finding good parameters for a recipe for both the positive and – especially – the negative tone resist. Possible further experiments could be done to narrow down the optimal exposure time and to analyze the required development time.

Conclusion

In this report we presented the effects of using AZ 5214 E as both positive and negative tone resist for creating microstructures using a MJB-3 mask aligner. Several different exposure times were used to approach optimal times. For positive tone resist, the best exposure time was estimated to be 2 min, resulting in a MFS of 2-10 μm. For negative tone resist, the optimal exposure time was estimated to be around 0.4 min, although there were no samples made to confirm this. The MFS of the negative tone sample with an initial exposure 0.5 min. and a flood exposure time of 4 min., was found to be 20-40 μm, which is well above the diffraction limited optimum (MFS = 0.81 μm).This shows that 2.0 min. for the positive tone resist is close to optimal, while 0.5 min. for negative tone resist is far from optimal.

The edges of both the positive and negative patterns suffer from over- and undercut, respectively. This can be seen near the edges of the patterns by the increased contrast in the SEM images and the dark areas in the microscope images. While some undercut is expected for the negative tone, the amount of overcut for the positive tone is higher than desired. The overcut is typical of low dosages, so it is expected that higher resolutions will be attainable with higher dosages.

References

[1] MicroChemicals. (2015) AZ 5214 E product data sheet. [Online]. Available: http://www.microchemicals.com/micro/az_5214e.pdf

A. Mask design

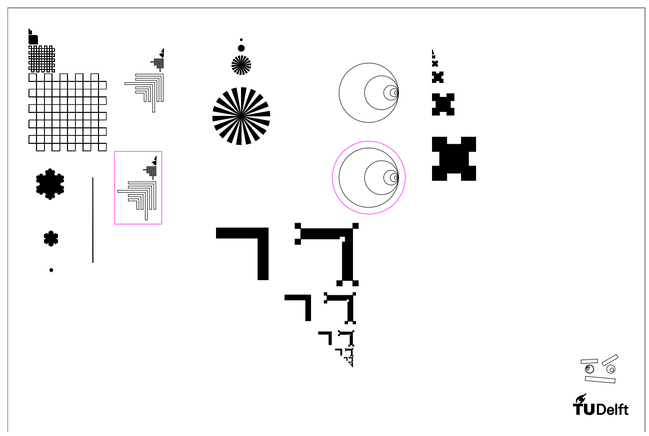


Figure 6: *Used lithography design*

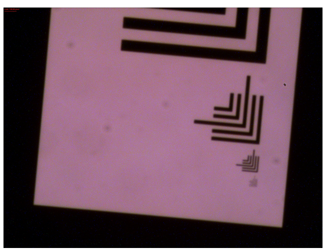
The design for the mask was made to enable easy detection of the attained resolution with certain patterns. This was done by taking patterns specifically designed to test the resolution and/or by taking patterns that are common in the semiconductor industry. Starting from the top left and moving clockwise,

- Checkerboard
- Single line surround by multiple lines
- Outward radiating lines
- Internally touching circles
- Shapes with OPC
- Slightly non-parallel lines

- Koch snowflake

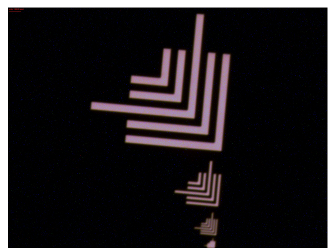
The checkerboard pattern is a widely used pattern in micro- and nanofabrication checkerboard pattern, allowing easy detection of over- and underexposure. The next pattern is a much seen pattern in nanofabrication, and is important for analyzing the effect of interference when multiple lines are close together. The outward radiating lines have the feature that the distance between the lines becomes smaller towards the center, making it possible to see at what length scale the lines are still separable. This principle also holds for the internally touching circles. In the top right there is a square with an (approximate) optical proximity correction (OPC) pattern. The Koch snowflake has (in the idealized case) infinite detail, allowing the comparison between the different length scales of the snowflake to see where the resolution becomes too low to see the details. Note that this version has only five iterations, since infinite detail would be unpractical.

B. Inspection images

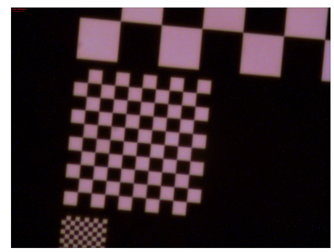


(a) *Single line surrounded by multiple lines pattern at several length scales.*

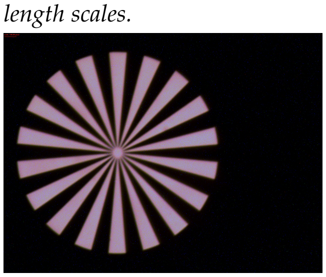
(b) *Inverse of the previous pattern.*



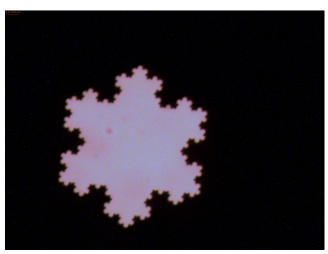
(c) *Zoom in on the previous image.*



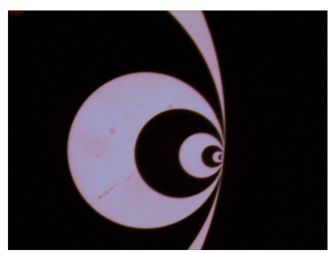
(d) *Checkerboard pattern at several length scales.*



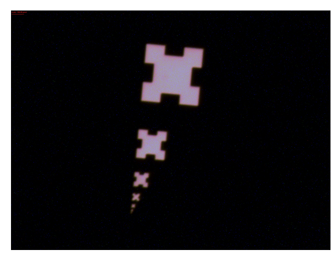
(e) *Outward radiating lines*



(f) *Koch snowflake.*

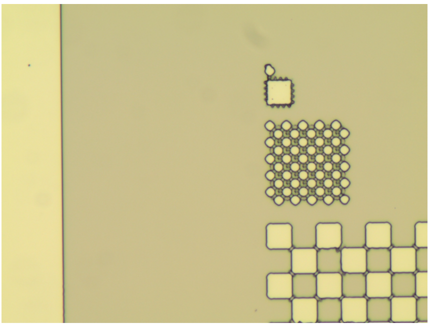


(g) *Internally touching circles.*

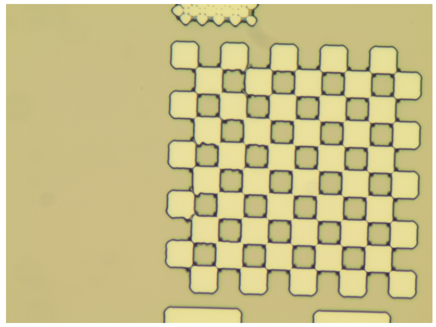


(h) *Squares with OPC patterns.*

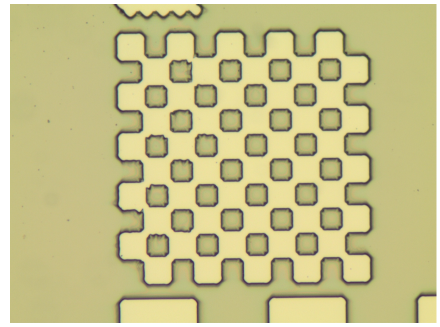
Figure 7: *Optical microscope images of some parts of the photomask. Images were taken in transmission mode.*



(a) *Exposure time of 3.0 minutes*

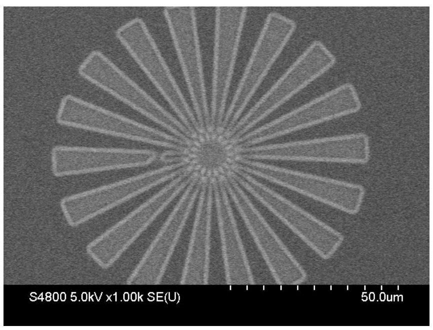


(b) *Exposure time of 3.5 minutes*

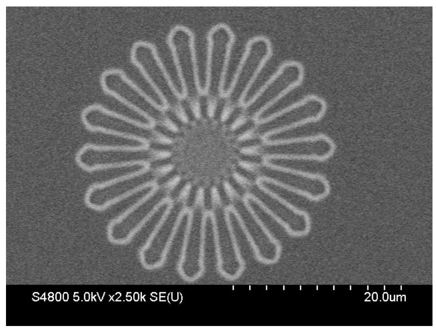


(c) *Exposure time of 4.0 minutes*

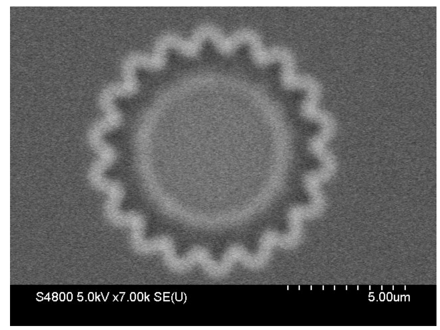
Figure 8: *Optical microscope images of the positive tone samples for several exposure times. Images were taken in reflection mode.*



(a) *Feature size of* $\sim$*6 μm. There is a small defect in the line pattern on the left side, which was most likely caused by improper handling of the sample.*

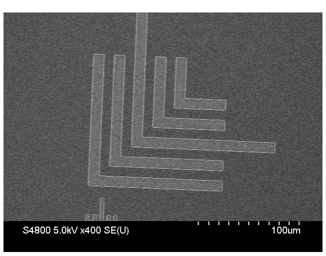


(b) *Feature size of* $\sim$*2 μm. The pattern loses its features near the center due to interference effects.*

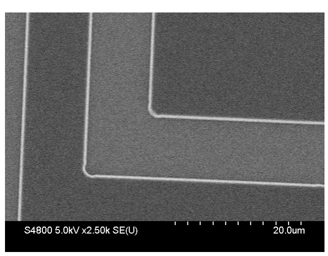


(c) *Feature size of* $\sim$*1 μm. Almost the whole pattern is dominated by interference at these length scales.*

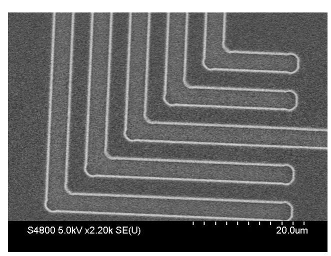
Figure 9: *SEM images of outward radiating lines pattern on the positive tone sample with* $\tau = 2$ *min. For the feature size the width of the line at the edge of the pattern is taken as guideline.*



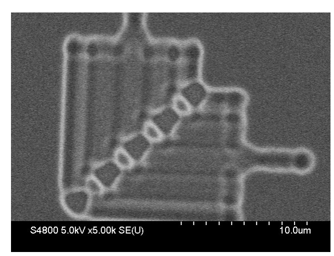
(a) *Structure size of* $\sim$*12 μm.*



(b) *Zoom of the previous picture. Rounding off the corners can be seen. These could in principle be corrected by using OPC.*

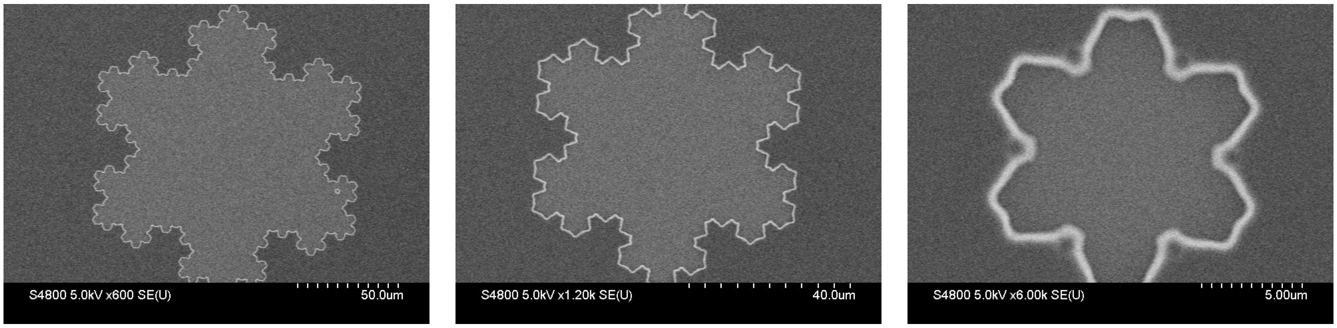


(c) *Structure size of* $\sim$*1.5 μm. The rounding of the corners has become more pronounced.*



(d) *Severe interference effects start to occur at the bends for feature sizes* $\sim$*1μm.*

Figure 10: *SEM images of a single line surrounded by multiple lines on the positive tone sample with* $\tau = 2$ *min. For the feature size the width of the line is taken as guideline.*

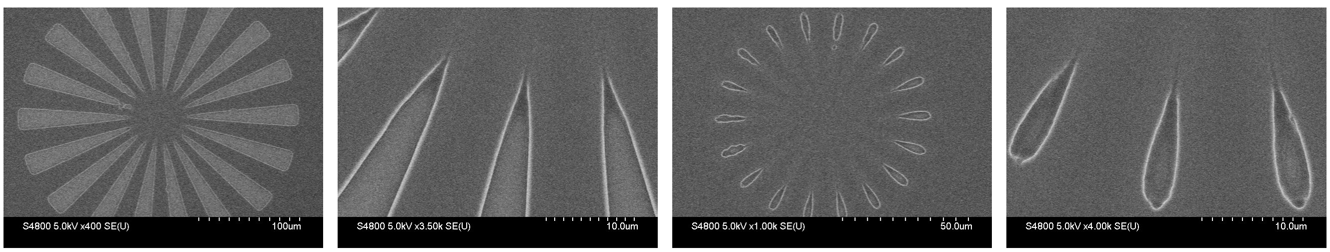


(a) *Structure size of ∼50 μm.*

(b) *Structure size of ∼30 μm. In comparison with the previous image, a significant drop in detail can be seen at the eges.*

(c) *Structure size of ∼4 μm. All fine details have been lost.*

Figure 11: *SEM images of Koch snowflake on the positive tone $\tau = 2$ min. For the feature size the width of one of the bulbs is taken as guideline.*



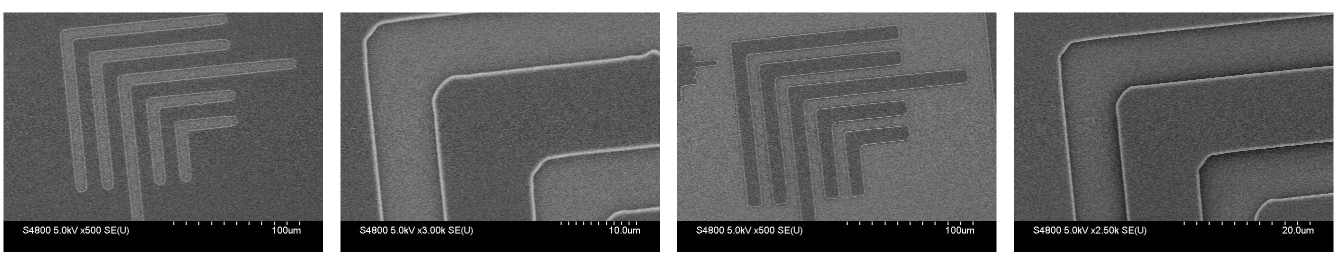
(a) *Structure size of ∼20 μm. Already at these length scales rounding of the corners can be seen. The pattern disappears in the center due to the overexposure.*

(b) *Zoom in of the previous picture, to display how the pattern tapers of due to overexposure.*

(c) *Structure size of ∼5 μm. The pattern is almost completely gone. Even after the tapering of the pattern, the photoactivation of the resist is still visible.*

(d) *Zoom in on the previous picture.*

Figure 12: *SEM images of outward radiating lines pattern on the negative tone sample with $\tau_1 = 0.5$ min. For the feature size the width of the line at the edge of the pattern is taken as guideline.*



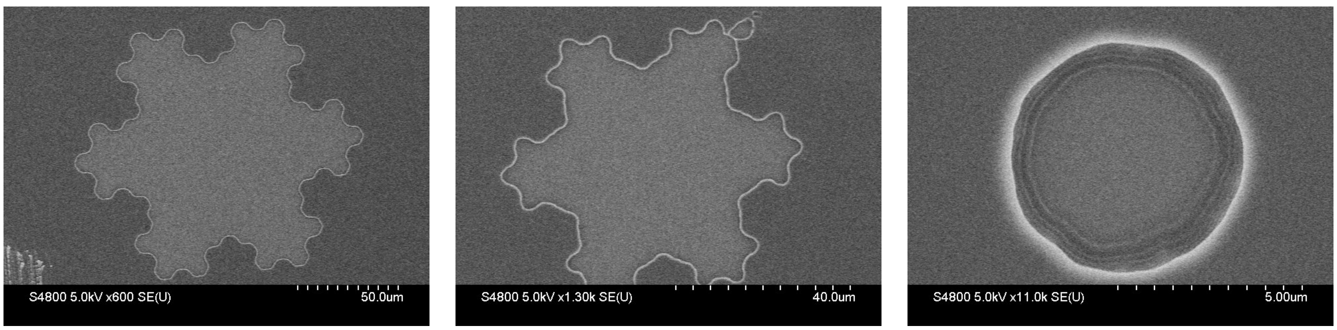
(a) *Structure size of ∼10 μm.*

(b) *Zoom in of the previous image. Rounding of the corners can be seen.*

(c) *Inverse of the two previous images.*

(d) *No significant differences can be seen between the inverses of the pattern.*

Figure 13: *SEM images of single line surrounded by multiple lines on the negative tone sample with $\tau_1 = 0.5$ min. For the feature size the width of the line is taken as guideline. For feature sizes smaller than ∼10μm the pattern loses all detail.*



(a) *Structure size of* $\sim$*20μm. There is already significant loss of detail at these feature sizes.*

(b) *Structure size of* $\sim$*10μm. All fine detail is lost.*

(c) *Complete loss of detail for feature size* $\sim$*1μm.*

Figure 14: *SEM images of Koch snowflakes on the negative tone sample with* $\tau_1 = 0.5$ *min. For the feature size the width of one of the bulbs is taken as guideline.*