Characterization of negative tone electron-beam resist mr-EBL 6000.1

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April 17, 2015

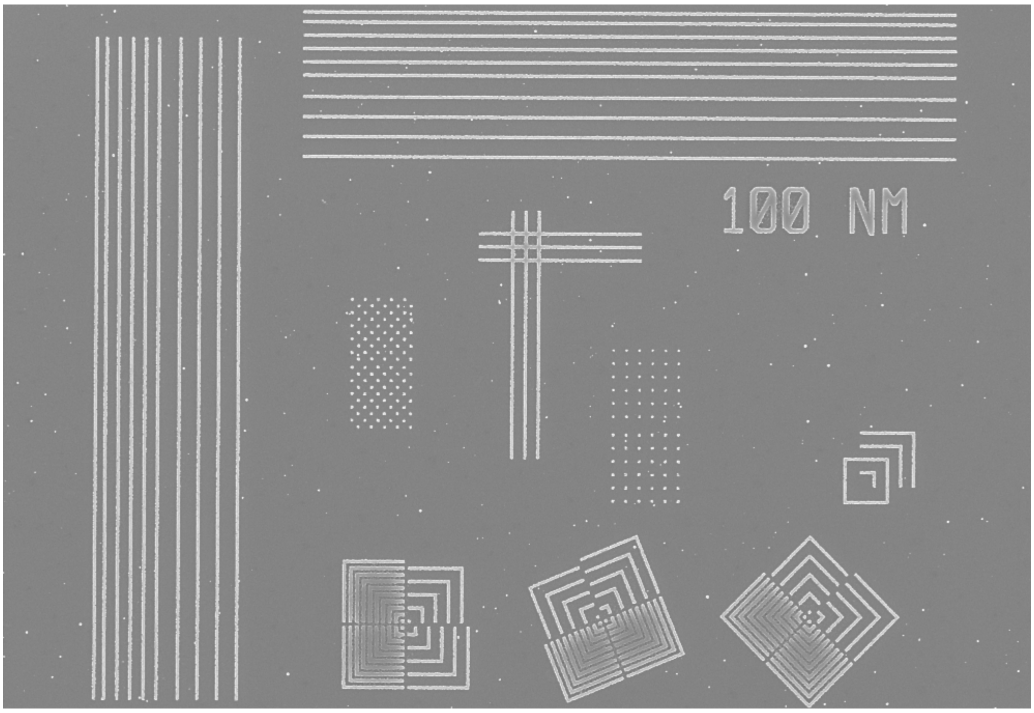

Figure 1: 100 nm wide lines and patterns, reproduced in mr-EBL 6000.1 and etched into silicon.

Contents

1 Introduction

This project took place in the framework of an electron beam lithography (EBL) related Ph.D., and was organized as a Special Course lasting 3 weeks, for a total workload of 5 ECTS. The ultimate goal was to investigate and characterize the process flow for a specific negative tone e-beam resist from *micro resist technology*, mr-EBL 6000.1.

This chemical is a chemically amplified negative tone e-beam photoresist. Its commercial dilution is based on anisole and its recommended developer (*micro resist* mr-Dev 600) is based on PGMEA. The supplier provides basic informations and few processing guidelines. Thicker dilutions are commercially available (mr-EBL 6000.3 and 6000.5) but are not considered of interest for our studies.

2 Process flow

The suggested process flow, developed during this project, can be found in Appendix B. The process has been tested but not properly optimized. If a user wishes to use this specific process flow, characterization results can be used to help determining optimal parameters.

3 Decant and Spin Curves

Decanting should be performed in a fume hood using clean glassware. Always keep spin solutions in brown bottles, to prevent exposure to white light. Similarly, spinning (and any process step up to development) should take place in yellow-light environment.

4-inch silicon wafers were used straight from a new cassette: no cleaning procedure was performed, but a 10 min bake-out at 200 °C to remove moisture was used. An approximate amount of 1.5 ml of solution per wafer is needed. Disposable pipettes were used for this project; no need for filtering arose although it may be a viable solution to comets appearing as a consequence of particle contamination in the solution.

Two different solutions and spin curves have been realized:

- **Resist as-is:** resist as poured from the bottle (*micro resist* mr-EBL 6000.1);
- **Diluted resist:** a 1:1 solution of resist and anisole (*AllResist* A-Thinner).

3 min at 110 °C were used to eliminate residual solvent after spinning. Data (Figure 2) was obtained with the VASE ellipsometer tool. See Tables 1 and 2 for the detailed data.

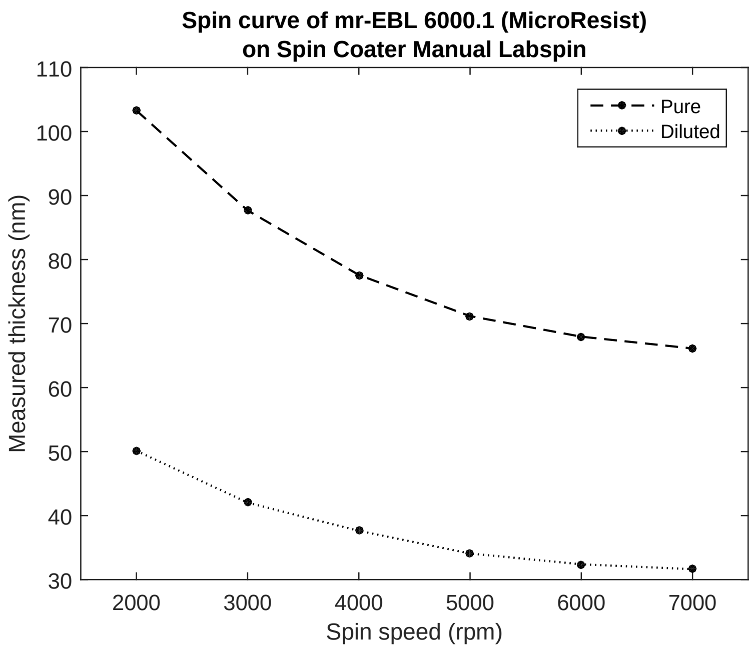

Figure 2: Spin curves for mr-EBL 6000.1 in pure and diluted form.

Spin Speed (rpm)	Thickness (nm)	St. Dev. (nm)
2000	103.28	0.5
3000	87.67	0.36
4000	77.59	0.4
5000	71.16	0.68
6000	67.95	0.52
7000	66.11	0.63

Table 1: Ellipsometry data for pure resist.

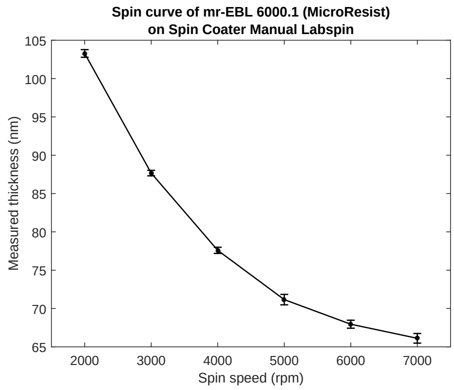

Figure 3: Spin curve for pure resist

Spin Speed (rpm)	Thickness (nm)	St. Dev. (nm)
2000	50.12	0.18
3000	42.03	0.28
4000	37.61	0.46
5000	34.08	0.32
6000	32.39	0.32
7000	31.63	0.31

Table 2: Ellipsometry data for diluted resist.

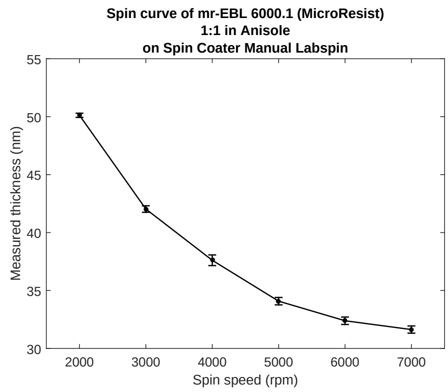

Figure 4: Spin curve for diluted resist.

4 Contrast Curves and Profiles

Exposure is performed on the JBX9500 E-beam Writer, using 0.2 nA beam current, aperture 5 (60 μm), doses in the 6-80 μC/cm^2 range, followed by 5 min post-exposure bake (PEB) at 110 ℃. The dose test focused on 100 and 500 nm wide lines. Development is performed using the supplier recommended developer, mr-Dev 600, with a 40 s dip followed by abundant rinsing with isopropanol for 1 min. Afterwards, the sample is dried with nitrogen gun and ready for characterization.

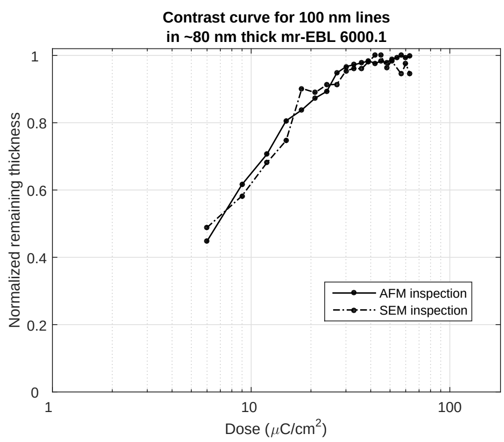

Figure 5: Contrast curves derived from AFM and SEM inspection.

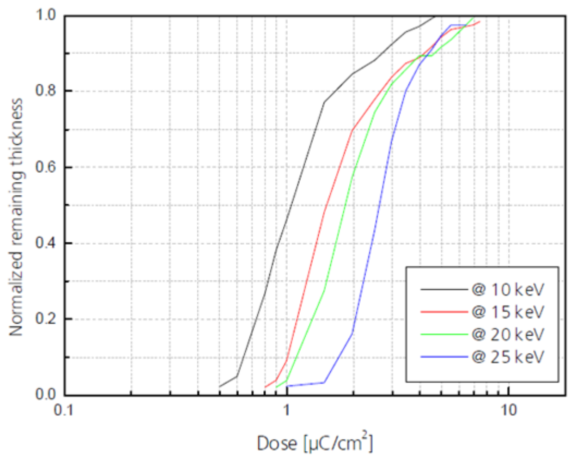

Figure 6: Contrast curves provided by micro resist.

Contrast curves (Figure 5) are provided for 100 nm lines in 80 nm resist with a 4 μm pitch. Measures were obtained with atomic force microscopy (AFM) inspection on the Icon AFM tool. A second set of measures is obtained via direct SEM inspection of a cross section of the lines (Figure 7). Clearance dose for 100 keV is higher than those at lower acceleration voltages provided by the supplier (Figure 6), as it should. Contrast appears fairly low with respect to curves provided in resist guidelines, which could be reconducted to the several necessarily different process conditions.

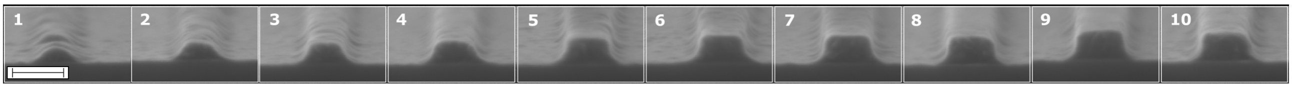

Figure 7: SEM pictures of lines used for the first 10 points of the contrast curves.

Preliminary tests showed strong proximity effects in this resist. As depicted in Figure 9, when progressively reducing the pitch between features these start to show asymmetry (indicating influence from the neighbouring line) when their spacing goes below 600 nm (inset B). For 100 nm lines proximity error correction (PEC) is thus required for patterns having width-to-pitch ratio above 1:6.

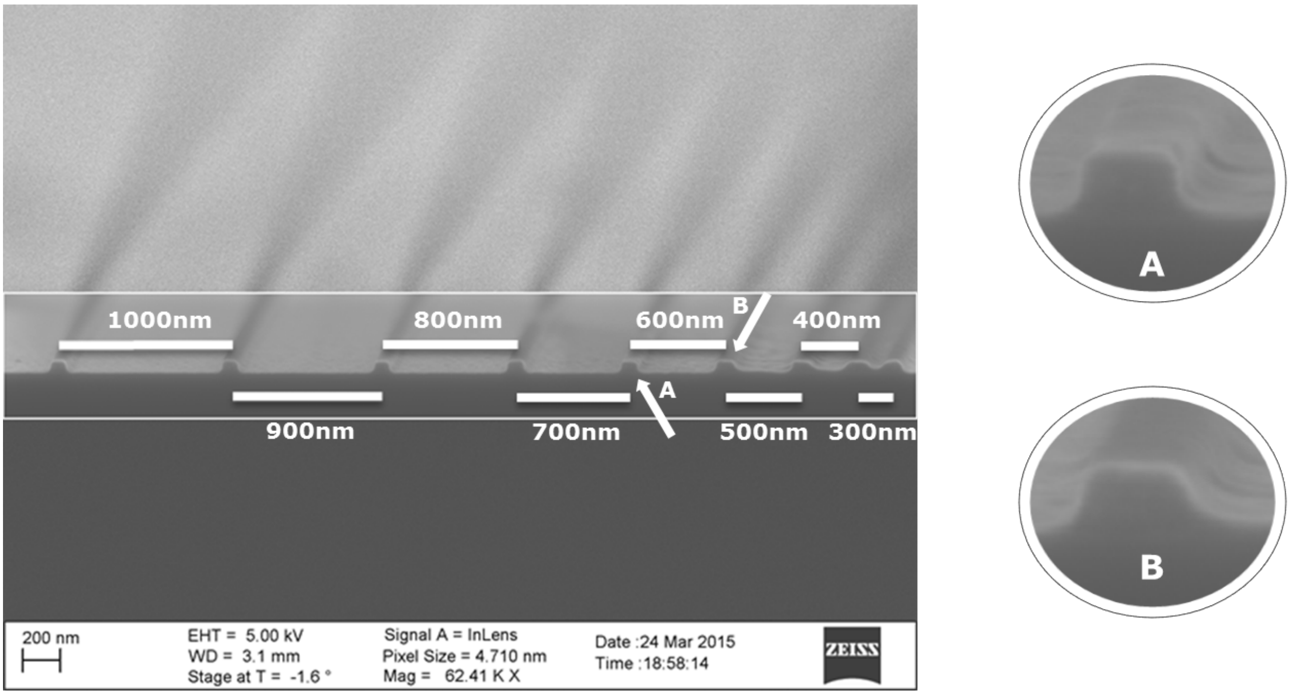

Figure 8: SEM pictures of test lines with progressively reduced pitch, with insets showing the first proximity induced asymmetry.

5 Dose Patterns

A dose test using a dedicated pattern was performed. The features used (Figure ??) include various checks for proximity issues, common geometries of interest such as lines and dots, and are repeated at different sizes to observe resolution limits. SEM inspection requires metal coating (platinum was used) otherwise high damage in the resist was observed. SEM inspection was performed on the Zeiss Supra 60 SEM tool.

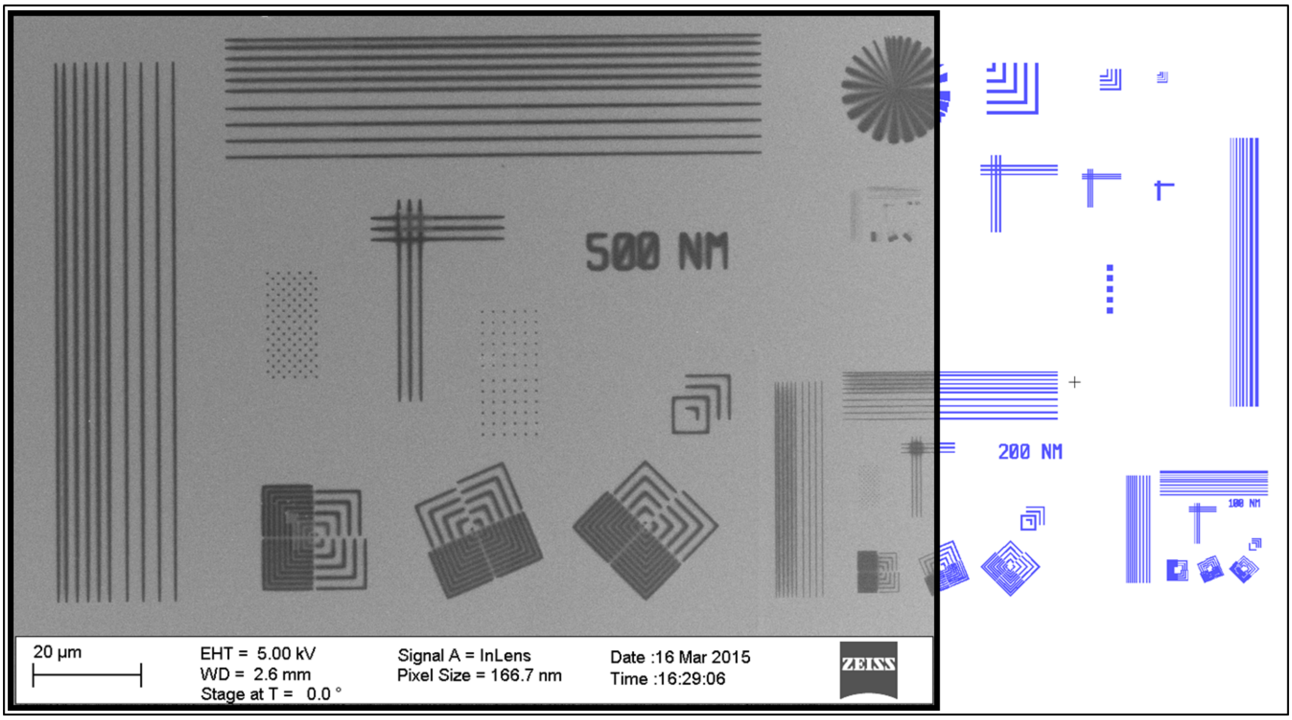

Figure 9: SEM pictures of a section of the dose pattern overlapping its full layout taken from L-Edit.

The pattern shows clearly the issues coming from proximity effects, which get enhanced with the increasing dose.

By observing under and overexposure, it's easy to see how the window for optimal dose is narrow (Figure 10), but smaller features require progressively higher doses (Figure 11). Dose modulation is thus recommended for patterns including different critical dimensions.

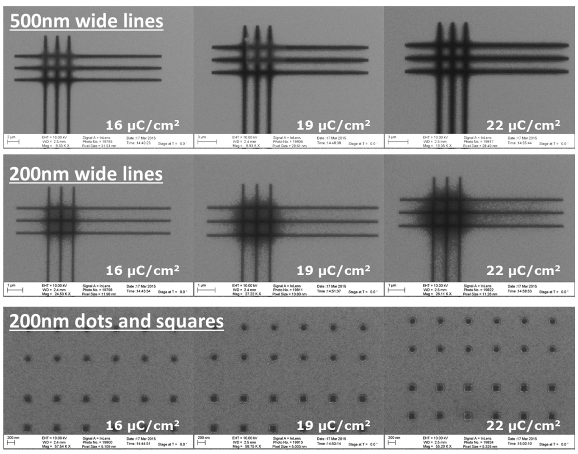

Figure 10: Images of various features at different exposure doses.

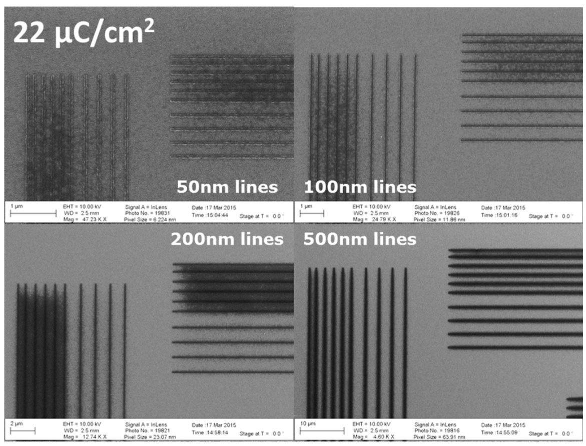

Figure 11: Images of the same geometry at constant dose and increasing size.

6 Pattern Transfer

Pattern transfer into the substrate was performed using reactive ion etching (RIE) with the DRIE: Pegasus tool. The "nano 1.42" recipe was used here, which among other things keeps the substrate at -20 ℃ during etch. A resist strip using a gentle oxygen plasma is performed afterwards to remove leftover resist. Some process parameters for the nano1.42 recipe can be found in Table 3.

Gas	C_4F_8 75 sccm, SF_6 38 sccm
Pressure	4 mTorr; strike 3 s 15 mTorr
Power	800 W CP, 40 W PP
Temperature	-20 ℃

Table 3: Process parameters of the nano1.42 DRIE: Pegasus recipe.

Etch selectivity was established using two test wafers with 90 nm of resist. The film thickness before and after 20 s of etch (Table 4) was measured as in Section 3 with ellipsometer inspection.

Sample ID	Initial Thickness (nm)	t_{etch} (s)	Final Thickness (nm)	Etch Rate (nm/min)
1.15	90.1± 0.7	20	77.72±0.6	37.2±2.4
1.16	92.2± 0.7	20	80.1±0.5	36.32±2.5
Si	(multiple observations)	(multiple observations)	(multiple observations)	150-180

Table 4: Results from calibration tests of mr-EBL 6000.1's etch resistance.

The resulting selectivity is 1:4÷1:5, which is better than the one reported for CSAR under the same recipe (∼1:2.5).

The lines patterned during the dose tests were successfully transferred using the same process parameters, with etch times ranging between 30 and 100 s. The etched sample in Figure 12 clearly shows how the proximity effects negatively affect further processing.

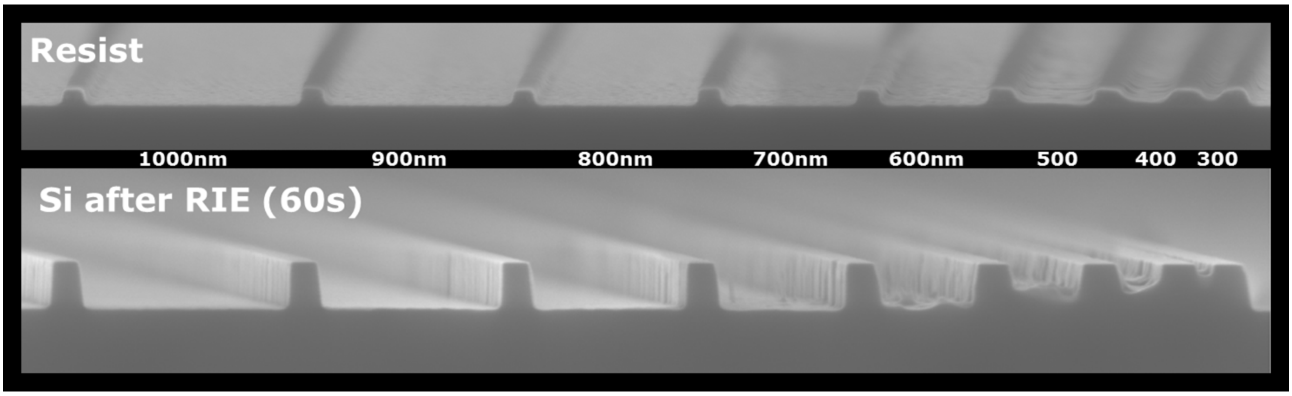

Figure 12: Pitch test pattern before and after the 60 s of RIE plus resist strip.

Dose patterns were processed as well with analogous results, with all the features tested (500 to 50 nm) successfully reproduced (Figure 13).

Note that a shallow etch (few tens of nm) can be used as an alternative to metal coating to overcome SEM inspection issues encountered with the bare resist.

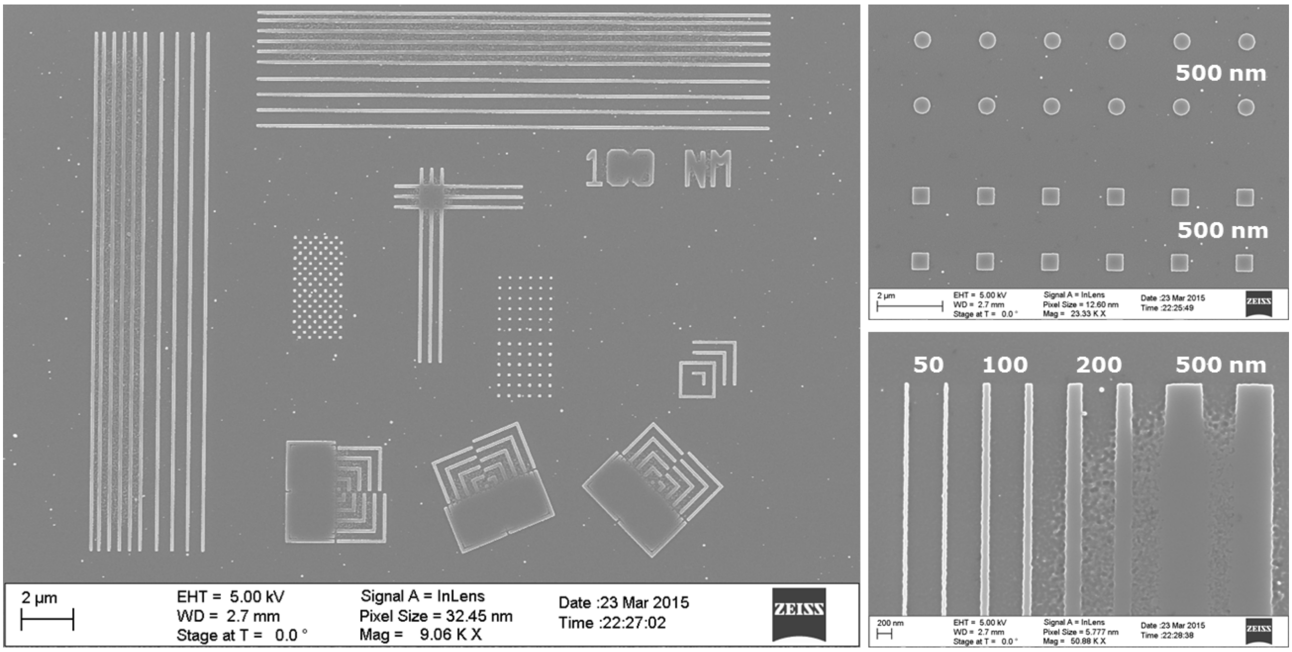

Figure 13: Results from calibration tests of mr-EBL 6000.1's etch resistance.

7 Conclusions

The results from this project should provide a solid base for future users interested in performing e-beam lithography on mr-EBL 6000.1 within Danchip's facilities. Spin curves, contrast curves, profiles, and several test patterns have been realized and characterized for future reference; the complete database of pictures acquired is available for consultation.

Minimum resolution achievable with the resist hasn't been determined, however results suggest higher doses than those tested would be needed to go below 50 nm. Thinner resist should also be considered when aiming for improved resolution. Lift-off protocol hasn't been tested but may be a viable option for pattern transfer.

The whole work is intended as a guideline: further optimization will be needed to tune the process to the pattern, process flow and overall performances desired. In particular, residues were initially observed after development: while a more thorough rinsing (including direct spraying from the squirt bottle to the sample) seemed to significantly improve the issue, a plasma descum step may be tested to remove unwanted leftover resist before proceeding to futher processing in order to improve pattern quality and avoid unwanted results (Figure 14). Similarly, significant roughness was observed in the resist sidewalls, which was then transferred in the etched profiles: optimization of exposure and development parameters may reduce this negative aspect producing smoother features and more straightforward lines.

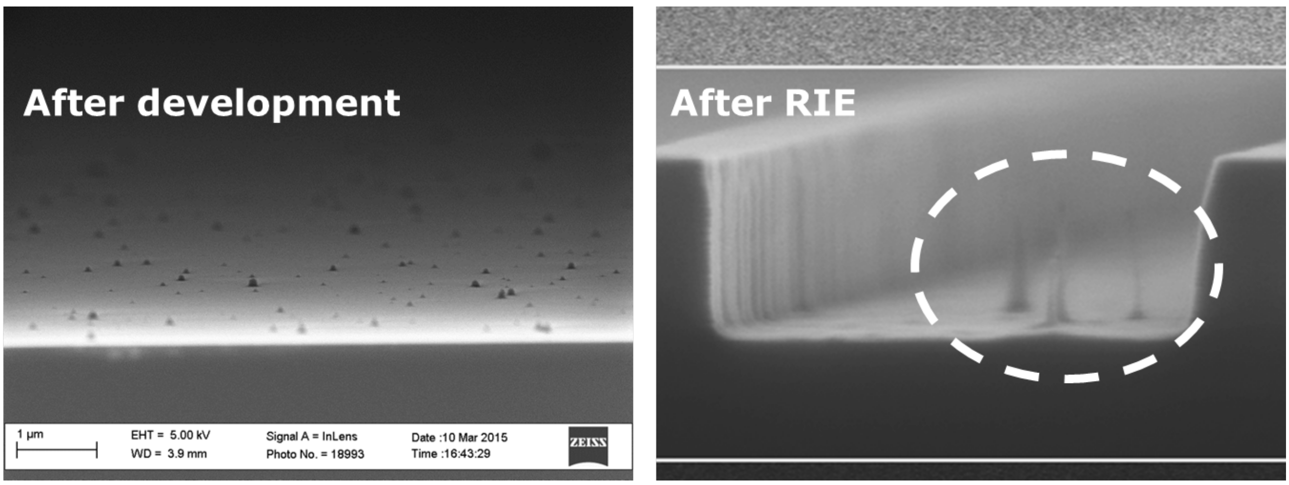

Figure 14: (left) Residual resist particles on the sample surface after development. (right) Resulting unwanted nanopillars after RIE caused by analogous residues.

Worth mentioning, PEC was tested on mr-EBL 6000.1 in a Ph.D. thesis by Gemma Rius Suñé, from Universitat Autònoma de Barcelona. This research managed to correctly identify the α, β and η parameters to include in the double gaussian approximation for the point-spread function of the beam, and demonstrate the validity of such a modelization by succesfully performing PEC on a series of patterns which were showing proximity issues. While process parameters (e.g. acceleration voltage) were different than those used here, this work may represent a good starting point for the user interested in exploring this path to achieve dense, high resolution patterns.

In conclusion, mr-EBL 6000.1 shows high potential as a negative tone e-beam resist. Its main limitations appear from the very low doses required to pattern it, which affects its performances due to proximity effects but also in terms of minimum beam spot pitch (due to the upper limit for beam speed). However, it seems suitable to pattern features in the 50 to 200 nm range with or without PEC, depending on the actual geometry. Some dedicated focus on the PEB and development step is recommended for further exploration of the process flow provided.

A List of Figures and Tables

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B Process Flow

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Process flow title **mr-EBL 6000.1**				Revision **1.02**
DTU Danchip National Center for Micro- and Nanofabrication	Contact email tigre@danchip.dtu.dk		Contact person Tine Greibe	Contact phone 4525 5701
	Labmanager group Lithography	Batch name Process template	Date of creation 2014/07/14	Date of revision 2015/04/12

Objective

Batch name: Process template

This process is a guideline on how to spin, e-beam expose develop and rinse mr-EBL 6000.1 on substrates as Si, SiO2 and SOI.
mr-EBL 6000.1 is a chemically amplified negative e-beam resist. The resist has been approved to carry into DTU Danchip cleanroom, the flow has been tested and partially characterized but not optimized.

Step Heading		Equipment		Comments
1	**Pretreatment**			
1.1	Surface treatment	Hotplate	Bake-out 10min @ 200 °C	
2	**Spin coat of resist**			
2.1	Coat wafers	Manual Spinner 1, or Spin coater LabSpin	**Resist:** mr-EBL 6000.1, pure or 1:1 anisole **Spin:** 60 sec @ 2000-7000 rpm, acc. 2000/s^2 **Softbake:** 3 min @ 110 °C Spin curves for 30-100nm available on LabAdviser.	Use syringe with filter or disposable pipette (cleaned by N2 gun). About 1,5ml x 4'' wafer. Keep coated wafers in yellow environments.
2.2	Measure thickness	VASE Ellipsometer	70deg, 9 points measure for whole wafers. 70deg, 1 point measure possible for chips.	Dedicated recipes available in VASE database. Use test wafers for characterization, to avoid exposure to white light
3	**E-beam exposure**			
3.1	E-beam exposure	E-beam writer	Dose: 10 - 50 µC/cm^2 at 100keV. An optimal dose of ~20 µC/cm^2 for was found for 100nm wide lines on Si. Proximity error correction is often necessary.	Dose depends strongly on substrate material, thickness of resist, critical dimension and load of pattern.
4	**Post exposure Bake**			
4.1	Post Exposure Bake	Hotplate	**bake:** 5 min @ 110 °C Bake immediately after e-beam exposure.	Exposed and PE-baked film has Cauchy coefficients of n0=1570, n1=104.9, n2=0
5	**Develop**			
5.1	Develop	E-beam Fumehood	**Developer:** 40±10s, mr-Dev 600, 20-25 °C. **Rinse:** IPA **Dry:** N2 gun	Rinse abundantly with direct jet of IPA before drying to avoid residues. If issues persist, consider a descum step.

6 Hardbake (optional)

6.1 Hardbake	Hotplate	**Bake:** 5 - 15 min @ 100 - 140 °C	Not tested

7.a RIE and Strip

7.a.1 Reactive Ion Etching	DRIE Pegasus	Recipe: 1-nano1.42, 20-100s 2-resist strip, 120s	Estimated etch rate: 37±3 nm/min Selectivity to Si 1:4÷1:5

7.b Lift-off and Strip

6.2 Lift-off	E-beam Fumehood	Mr-Rem 660 (NMP based) or Mr-Rem 500 (NMP free) Can be done at temperatures of 40 – 60 °C assisted by ultrasonics. Oxygen plasma also suitable.	Not tested