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3	IMEC	**IMEC**	RES	Belgium
4	Mikrosistemi Ltd	**µS**	SME; End-User	Bulgaria
5	Universität Bayreuth	**UBT**	HER	Germany
6	Technische Universiteit Delft	**TUD**	HER	Netherlands
7	Spanish National Research Council	**CSIC**	RES	Spain
8	IBM Research GmbH	**IBM**	IND; End-user	Switzerland
9	École polytechnique fédérale de Lausanne	**EPFL**	HER	Switzerland
10	SwissLitho AG	**SL**	SME; End-User	Switzerland
11	Oxford Instruments Nanotechnology Tools Ltd	**OINT**	IND; End-user	UK
12	Imperial College London	**IMPERIAL**	HER	UK
13	The Open University	**OU**	HER	UK
14	Oxford Scientific Consultants Ltd	**OSC**	SME	UK
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SNM

Work Package WP1

Deliverable: D1.6

“Evaluation report on SPL-patterning of hybrid molecular resist (h-MR) films”

Lead beneficiary number	1	**Nature**	R	**Dissemination level**	PU
Estimated Person-months	12,5				
Person-months by partner for the Deliverable	TUIL 12,5				
Estimated Delivery Date	04/2016	**Delivery Date**	30/04/2016		
Author	• Marcus Kaestner, Yana Krivoshapkina, Ivo W. Rangelow				
Reviewed by:	• WP1-Leader: Marcus Kaestner • WPG1-Leader: Armin Knoll • Coordinator: Ivo W. Rangelow				

Criteria and Achieved Results	**Criteria**	**Achieved result**
	Patterning of inorganic 2D MoS_2 nanoribbons	Resist-less patterning of MoS_2 nanoribbons with 15 nm width achieved –> highest value up to now.
	Patterning of organic resist material: functionalized fullerene resist IM-HM-01	90 nm resolution in negative tone mode and 13 nm in positive tone mode demonstrated. Low sensitivities and development-related problems inhibit further application.
	Patterning of two component molecular glass resist hybrid mixtures (UBT8+UBT14, UBT8+C60)	High resolution patterning in UBT8+C60 hybrid mixture resist demonstrated: 10 nm half pitch (hp) dense line/space.
	Patterning of organic/inorganic hybrid resist materials	Organic/inorganic hybrid resist material PMMA+ ZrO_2 mixture: Organic matrix

		material (PMMA) ablated, whereas metallic ZrO_2 particles were left behind → Directed assembly of inorganic materials demonstrated
Description of the Deliverable	TUIL investigated, together with the SNM partners UBT, OSC & EPFL, the patterning of organic, hybrid and organic/inorganic resist material systems. In particular, the following tests were done: (a) Direct (resist-less) patterning of 2D MoS_2 for nanoribbon based devices; (b) Patterning of organic resist IM-HM-01 (functionalized fullerene resist); (c) High-resolution patterning of two-component molecular glass resist mixtures (UBT8+UBT14, UBT8+C60); (d) ZrO_2 + PMAA mixture as a hybrid organic / inorganic resist material; (e) Patterning tests on amorphous carbon based resist materials. Hereinafter, the results obtained are summarized: **(a) Direct (resist-less) patterning of 2D MoS_2 for nanoribbon based devices (Collaboration of WP1 – WP9; TUIL-EPFL):** TUIL has patterned nanoribbon structures into $\mathrm{MoS_2}$ layers by application of (positive tone) FN-SPL. The lithographic capability of WP1 SPL technology platform for patterning of $\mathrm{MoS_2}$ mono- and multilayers was evaluated. $\mathrm{MoS_2}$ samples were prepared by exfoliation technique on highly doped Si substrate. FN-SPL is used for exposure, whereby a bias voltage was applied between sample and tip causing Fowler-Nordheim emission current of low energy electrons. The $\mathrm{MoS_2}$ samples were exposed at bias voltage of 35 V. The line dose was varied between 1.5 and 650.0 nC/cm (10-60 pA) at a temperature T=29…30 C and a relative humidity of RH=28…30%. Direct oxidation of $\mathrm{MoS_2}$ was possible without the need of a resist material. The exposure mechanism is assumed to follow the same reaction as for oxidative SPL (o-SPL), described in [F. M. Espinosa, et al., Appl. Phys. Lett., 106 (2015) 103503]: $\mathrm{2MoS_2 + 9O_2 + 4H_2O \rightarrow 2MoO_3 + 4H_2SO_4}$. To confirm this, the samples were developed by rinse in distilled water for 5 s. The written structures were directly etched, which confirms molybdenum oxide formation during exposure. At doses >150 nC/cm large pattern widening was observed. Exposure tests at low doses (<4 nC/cm line dose) reveal that no $\mathrm{MoS_2}$ oxidation was possible. The achieved line edge roughness (LER) after development (water rinse) is not yet optimized and will be studied in collaboration with EPFL in more detail. Sub-50 nm wide lines with depth 1.5 nm were obtained with direct writing. Minimum features sizes of 15 nm wide $\mathrm{MoS_2}$ nanoribbons with height of 1.0 nm were left after water rinse, shown in Fig. 1 (measurement of full width half maximum width value).	

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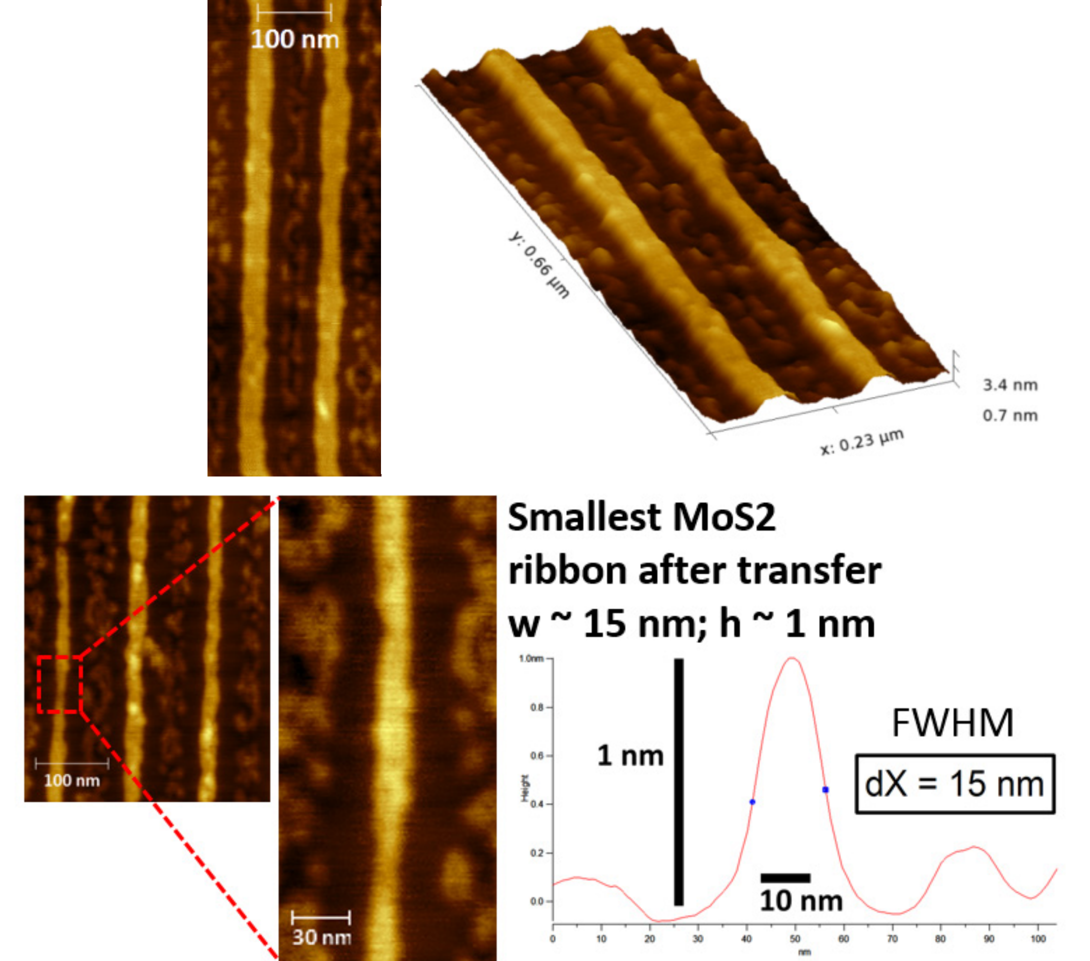


Figure 1. Smallest MoS_2 ribbon left standing after water rinse – 15 nm (width measured at full width half maximum (FWHM)).

(b) Evaluation of functionalized fullerene resist materials for patterning with FN-SPL (Collaboration of WP1-WP4; TUIL-OSC)

Samples with 20 and 30 nm thick spin-coated IM-HM-01 fullerene-based resist were prepared by OSC and sent to TUIL for evaluation in FN-SPL. IM-HM-01 is a negative tone electron beam lithography resist based on functionalized fullerenes. Ultrathin silicon-on-isolator (SOI) chips (15x15 mm) were used as substrate.

Evaluation of direct removal: 20 nm thick films were prepared via spin-coating with subsequent pre-bake step. Films with good surface quality were obtained (Rms =0.27 nm). First exposure dose test was performed via applying 32 V bias voltage and doses in range of 7-700 nC/cm (5-60 pA) (Fig. 2). Sensitivity of the resist in self-development mode was low compared to other molecular glass resist materials reported in D1.3: only 5 nm deep lines written at 700 nC/cm were achieved. Best 14 nm lines are achievable. However, the line depth is comparable to the surface roughness as seen in Figure 3.

In summary, direct removal (without a development step) was inefficient due to the high

stability of the fullerene molecules (Figure 4).

Figure 2. Exposure dose test on IM-HM-01 sample with film thickness 20 nm.

Figure 3. Direct-removal mode patterning on IM-HM-01 with corresponding cross section.

Figure 4. a) Normalized thickness and b) feature width vs. line dose (nC/cm) for IM-HM-01 after patterning (black squares) and after wet development (red circles).

Evaluation of negative tone mode (with subsequent wet development step): In negative tone mode wet development (WD) was performed via stirring in ultrasound bath for 5 min in cyclohexanone. Sensitivity of the material in negative tone is 120 nC/cm as shown in Figure 4-a. In Figure 4b) at an exposure dose of around 200 nC/cm the tone switching from negative (low doses) to positive tone (high doses) is visible. Feature widths increase in negative tone mode rapidly since the resist crosslinking is accompanied with a swelling

behaviour. However, features with good vertical sidewalls were obtained (Figures 5-b & 6-a). The lowest feature width achieved for negative tone is 90 nm. Concluded from Figure 4-b, negative tone lines with width ≤35 nm can be achieved if optimized wet development procedure would be found.

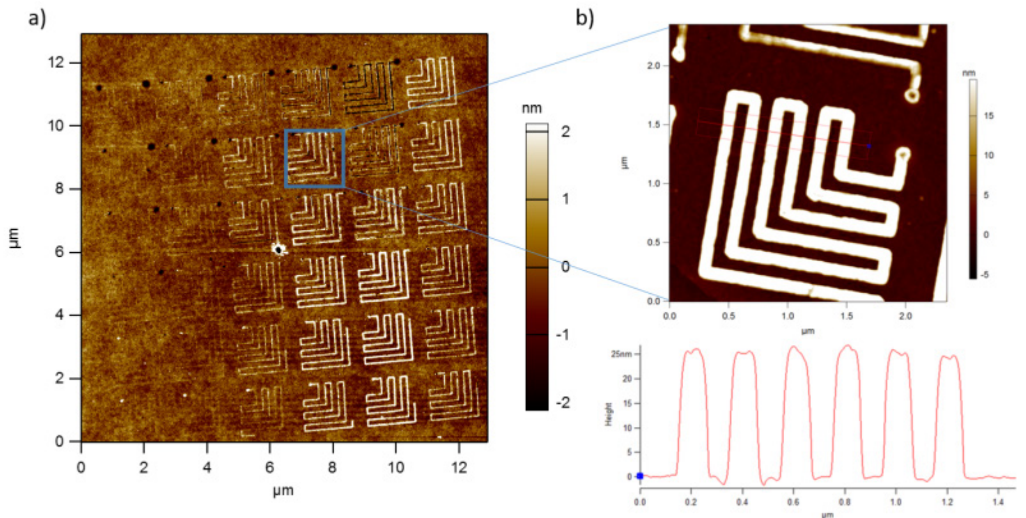


Figure 5. a) Exposure dose test performed on IM-HM01, measured by AFM directly after lithography. Swelling of the resist as function of exposure dose is visible. b) Zoom in into a feature written at 450 nC/cm after wet development.

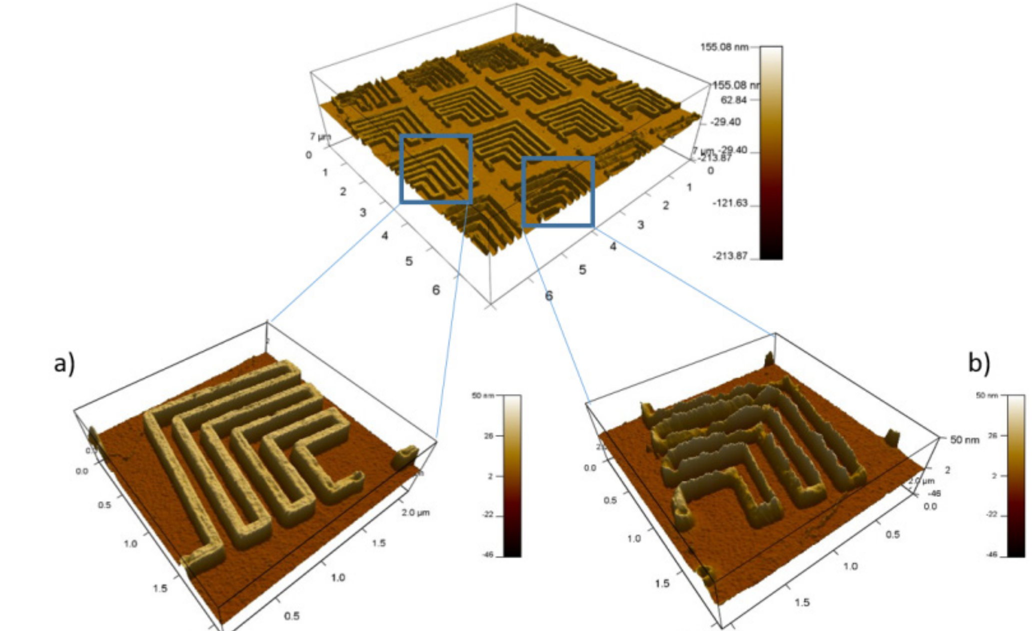


Figure 6. AFM topographic 3D image of exposed IM-HM-01 after wet development step. Exposure doses applied: a) 400 nC/cm, b) 200 nC/cm.

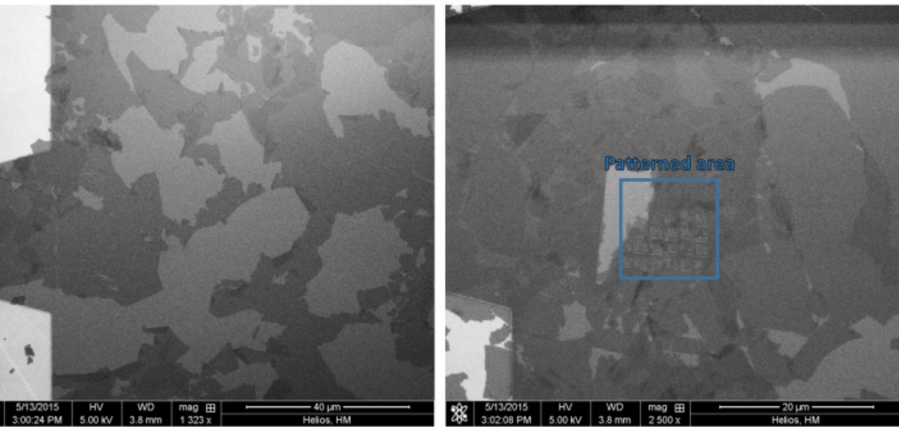


Figure 7. IM-HM-01 sample after wet development: resist leftovers (flakes) all over the sample

However, due to an ineffective crosslinking process, features written with doses between 150 and 300 nC/cm exhibit uneven heights as shown in Figure 6b). Additionally, the WD process produces resist leftovers which were observed all over the sample (Figure 7).

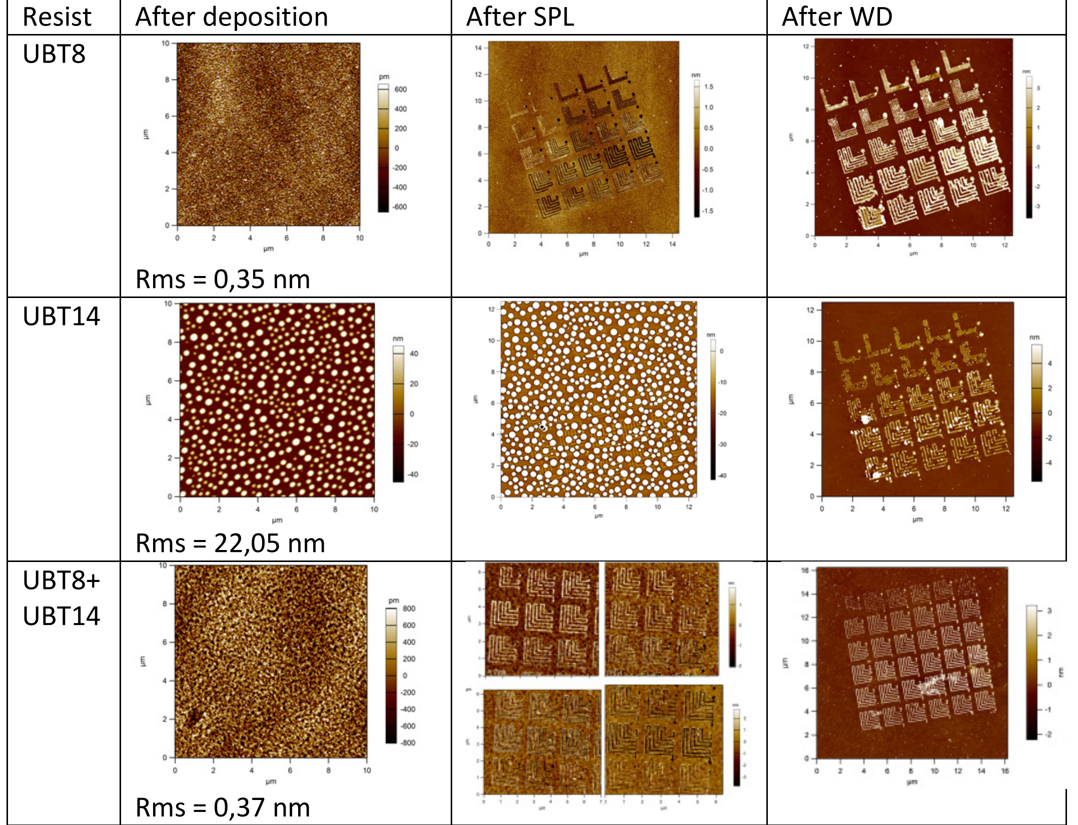
In summary, IM-HM-01 is not suitable for patterning in direct-removal mode due to low sensitivity of the resist compared to other molecular glass resist materials (ref. D1.3). The weak conformity of the achieved negative tone features and the resist leftovers causes that the resist IM-HM-01 is not considered further for high resolution negative tone patterning.

(c) Two component molecular glass resist hybrid mixtures

As result of task T-1-2, the single component resist UBT8 is usable in direct removal mode of FN-SPL. However, the high resolution capability is limited since very thin films seem to soften the resist film which yield bridges of separated SPL lines and blurred AFM images (see 2nd periodic report). The opportunity of co-evaporation of two materials given due to the use of physical vapor deposition (PVD) yield to the studies with several resist mixtures. We found that a hybrid mixture of UBT8 with another resist significantly improves the resolution capability of UBT8. First attempts were made by co-evaporation UBT8 with UBT14 resist, summarized in Figure 8.

Examining UBT8 and UBT14 as single materials has given following results (see Figure 8):

- Evaporated film of UBT14 has very high surface roughness (Rms > 20 nm)
- Good quality films were obtained for UBT8 (Rms = 0,35 nm);
- Due to high crystallinity of UBT14 film no reliable lithography results were obtainable. Pattern visible after wet development belongs to oxidation of the silicon substrate;
- UBT8 was suitable for direct-removal process and appeared as a low contrast negative tone resist. However, line edge roughness of negative tone pattern was high.



Resist	After deposition	After SPL	After WD
UBT8	Rms = 0,35 nm		
UBT14	Rms = 22,05 nm		
UBT8+ UBT14	Rms = 0,37 nm		

Figure 8. AFM images of UBT8, UBT14 and UBT8+UBT14 after deposition, patterning and wet development, all films were prepared via physical vapor deposition and had specified thickness of 10 nm.

In order to overcome the issue of crystallinity of UBT14 and to obtain good quality films, it was mixed with UBT8. The mixture of UBT8+UBT14 materials demonstrates surface roughness as good as for pure UBT8 (Figure 8). After evaluation of SPL-pattern before and after wet development it was seen, that impact of UBT14 into lithographic behaviour of the UBT8+UBT14 mixture is not sufficient (Figure 9).

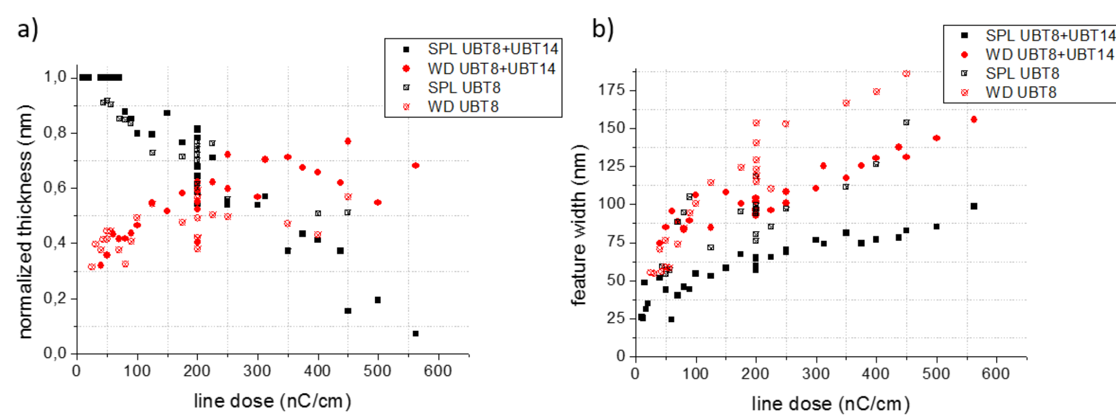


Figure 9. a) Normalized thickness vs. line dose (nC/cm) and b) feature width vs. line dose for UBT8+UBT14 (filled squares and dots) and UBT8 (intersected squares and dots) after patterning (black) and after wet development (red).

Concerning negative tone, the height of developed structures is slightly higher for UBT8+UBT14 than for UBT8 when applying doses >200 nC/cm, which gives a bit better contrast of UBT8+UBT14 system compared to UBT8. However, developed structures exhibit high line edge roughness for both. Addition of UBT14 did not affect direct removal behaviour of UBT8 (see the black symbols in Figure 9a) because the depth of the SPL pattern in UBT8+UBT14 coincides with that of UBT8. Nevertheless, single line with width of 25 nm was achieved on UBT8+UBT14 (full width at half maximum). Compared to pure UBT8 the addition of UBT14 decreases the line width significantly (20-50 nm lower depending on the dose). However, no dense line patterning was possible due to refilling of the written patterns with non-crosslinked resist.

To overcome this particular problem we have mixed UBT 8 with an even tougher material to form a hybrid material: the Buckminsterfullerene C60. Mixture of molecular glass UBT8 and fullerene materials gives evaporated films with good quality (Rms = 0.31 nm) with a thickness of 10 nm. Similar to the pure UBT8, the co-evaporated UBT8+C60 reveal a direct removal patterning behavior. No differences in line dose exposure requirements between pure UBT8 and UBT+C60 co-evaporated resist were determined. The resolution capability was improved towards 10 nm hp stable dense line/space patterning, summarized in Figure 10. Furthermore, the outstanding etch performance of UBT8/C60 mixture in N2/H2 etch gas (summarized in WP5/WP6 summary) opens the possibility to use very thin resist film thickness of 5 nm or even below in future.

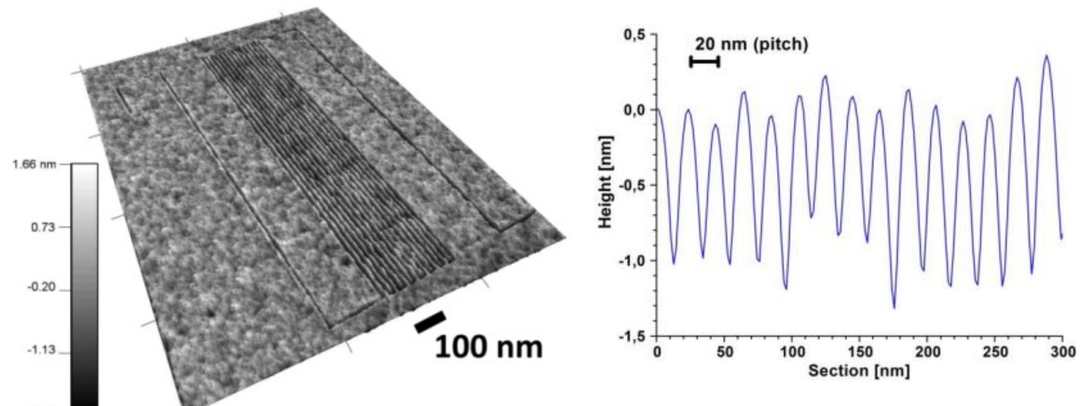


Figure 10. High resolution AFM topography image of 10 nm hp dense line/space feature patterned into co-evaporated UBT8+C60 resist thin film. The estimation of the patterning

(d) Hybrid organic / inorganic resist materials based on PMMA + ZrO_2 (polymer resist with incorporated metal oxide nanoparticles)

The idea behind this mixture was to write a self-developed pattern via removing soft organic material, while hard nanoparticles will resume under the pattern creating a film of ZrO_2. Samples with 10 nm films of PMMA+ZrO_2 mixture were prepared by UBT via spin-coating, resulting film had Rms = 0.26 nm. An ultrathin SOI chip was used as substrate. The received

samples had 10 nm film thicknesses.

Samples were exposed using FN-SPL at a bias voltage of 35 V. The line dose was varied from 10 to 880 nC/cm (10-60 pA) (see Figure 11). The direct removal process of the PMMA starts at doses above 10 nC/cm. When applying doses above 500 nC/cm ZrO_2 crystals appear within the written lines (Figure 11-d, e). Due to the formation of ZrO_2 aggregates (crystals) no closed films within the cleared resist regions are defined. In order to enable a functionality of the novel patterning method further basic investigations are required, which are beyond the scope of this project. However, an interesting novel patterning approach is enabled showing the directed assembly of inorganic materials by utilizing the FN-SPL scheme.

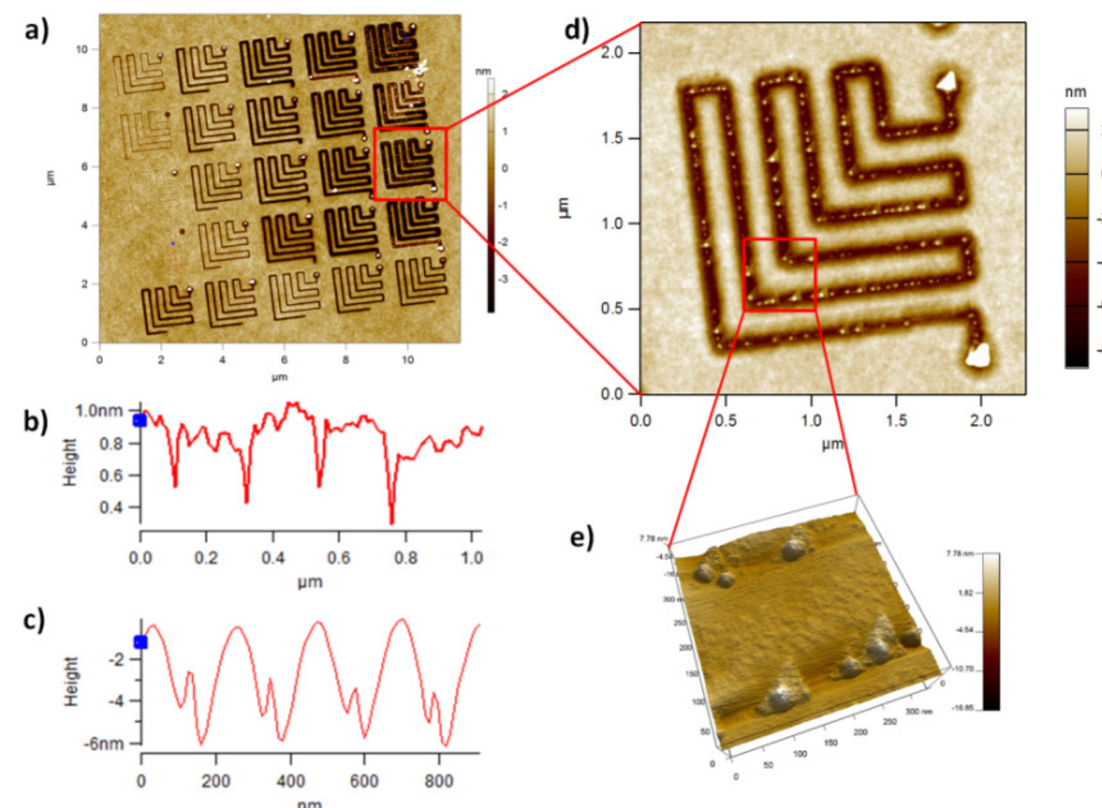


Figure 11. a) AFM scan of exposure test field, doses in range of 10-880 nC/cm were applied, direct removal process starts directly at the lowest dose applied; b) cross-section of feature written with 10 nC/cm, line depth ca. 0.5 nm; c) cross-section of feature written with 880 nC/cm, line depth ca. 10 nm; d) AFM scan of zoomed feature; e) ZrO_2 crystals within SPL-written line.

(e) Patterning tests on amorphous carbon based resist material (AZ Barli 200):

To improve the quality, in particular the linewidth, of the transfer of the SPL written patterns into the silicon, a different resist was tested. Therefore 7 nm thick layers of the resist AZ Barli 200 (MicroResist Berlin) were prepared on SOI samples by spin-coating and prebaking. Different types of patterns were written with different doses to obtain information about the minimum of the linewidth and the pitch values. The samples were afterwards etched by SF_6 at cryogenic temperature (ref. D1.3). AFM and SEM measurements

were performed after etching and subsequent resist stripping.

Figure 12 shows a representative result for corner features written with different line doses resulting in different line widths after SPL and etching. Thereby, the line dose increases from left to right due to increasing current of the electron beam and decreases from front to back due to increasing writing speed. A variation of line width is observed which is shown for two examples in figure 13. Minimal line widths of 30-35nm were observed for etched patterns with the carbon resist. In Figure 14 we show a pitch test structure, which is used to determine the minimal possible distance between two (or more) lines after etching. It was possible to obtain a 50 nm pitch, whereby the lines were etched 15 nm in deep. Wider lines could be etched up to 50 nm deep. Thus the carbon resist AZ Barli shows slightly better etching results than TUIL's standard calixarene resist. However, the lithographic resolution seems to be limited.

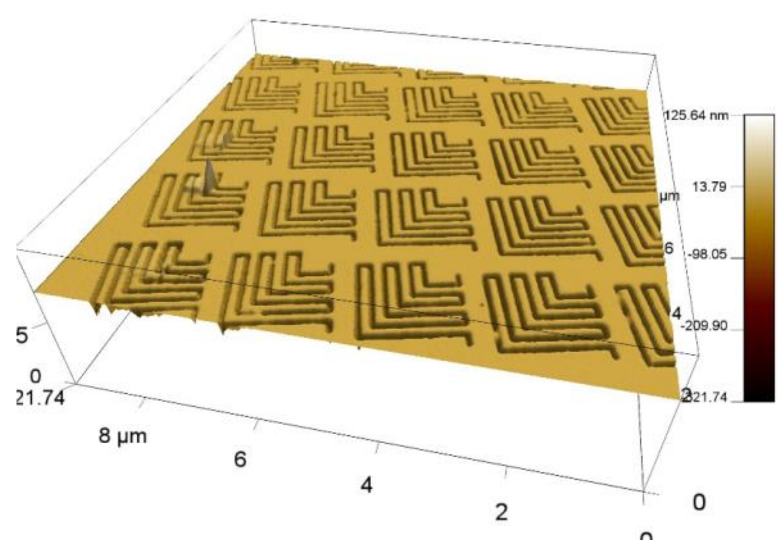


Figure 12.
Corner features written with different line dose. Line dose is increasing from left to right (increasing Litho current) and decreasing from front to back (increasing litho speed).

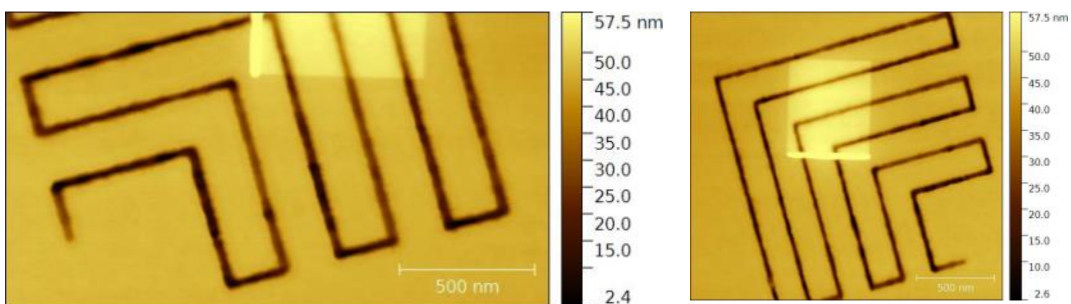
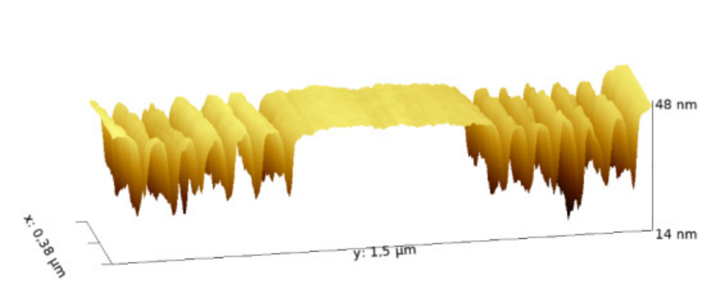


Figure 13. AFM images taken after etching and resist stripping of corner features with different linewidths due to different line doses during SPL. Left: linewidth is 35 - 40 nm and right: line width is equal to 45-50 nm.

	 **Figure 14.** 3D representation of AFM image taken after etching and resist stripping of pitch test structures. Clearly separated lines are etched into the silicon with a depth of 15 - 20 nm. **Summary and Conclusion** In summary, TUIL has investigated together with SNM partners UBT, OSC & EPFL the patterning capability beyond the single component calixarene molecular glass resist (ref. D1.3). Herein, novel hybrid resist materials as well as the direct resist-less patterning of MoS_2 for nanoribbon based devices were evaluated. In this terms the direct MoS_2 patterning (15 nm wide nanoribbons are created) as well as two component molecular glass resists prepared by co-evaporation (10 nm hp resolution demonstrated) has proven as promising approaches. Furthermore, the organic/inorganic resist material concept using a directed assembly of nano-features shows good initial results. However, further work concerning the organic/inorganic hybrids is required in order to form directly usable inorganic nano-structures.
Explanation of Differences between Estimation and Realization	
Metrology comments	AFM metrology applied. The system performance of WP1 tool was validated via the VSL metrology benchmarking test sample (ref. WP7).

Material	Coating*	AFM – fresh sample	AFM – fresh sample Zoom	AFM – stored sample (3-11 months)	AFM – stored sample Zoom	Rms fresh, [nm]	Rms stored, [nm]	Applic-able for SPL
SOI chip without resist, standard cleaned	/			n/a	n/a	0,230		-
Cmc4ra	PVD					0,265	0,233	Yes
4m1ac68a	SC		n/a			0,250	0,274	Yes

* SC – spin-coating; PVD – physical vapour deposition

** On which criteria the material does not match

Material	Coating	AFM – fresh sample	AFM – fresh sample Zoom	AFM – stored sample (3-11 months)	AFM – stored sample Zoom	Rms fresh, [nm]	Rms stored, [nm]	Applic-able for SPL
UBT3	PVD		n/a	n/a	n/a	10,976		No
UBT4	PVD			n/a	n/a	4,956		No
UBT5	PVD			n/a	n/a	2,960		No

Material	Coating	AFM – fresh sample	AFM – fresh sample Zoom	AFM – stored sample (3-11 months)	AFM – stored sample Zoom	Rms fresh, [nm]	Rms stored, [nm]	Applic-able for SPL
UBT7	PVD				n/a	0,345	0,331	Yes
UBT8	PVD					0,333	0,361	Yes
UBT9	PVD					0,402	0,385	No

Material	Coating	AFM – fresh sample	AFM – fresh sample Zoom	AFM – stored sample (3-11 months)	AFM – stored sample Zoom	Rms fresh, [nm]	Rms stored, [nm]	Applic-able for SPL
UBT12	PVD					0,564	2,478	No
UBT14	PVD			n/a	n/a	22,038		No
UBT8/C60	PVD					0,260	0,283	Yes

Material	Coating	AFM – fresh sample	AFM – fresh sample Zoom	AFM – stored sample (3-11 months)	AFM – stored sample Zoom	Rms fresh, [nm]	Rms stored, [nm]	Applic-able for SPL
UBT8/UBT14	PVD					0,269	0,244	Yes
C60	VPD			n/a	n/a	11,583		No
MoO3	PVD					0,274	0,245	Yes
IM-HM-01	SC		n/a			0,274	0,313	Yes

Material	Coating	AFM – fresh sample	AFM – fresh sample Zoom	AFM – stored sample (3-11 months)	AFM – stored sample Zoom	Rms fresh, [nm]	Rms stored, [nm]	Applic-able for SPL
C4a	PVD			n/a	n/a	33,500		No
4tbc4a	PVD			n/a	n/a	10,850		No
4tbtc4a	PVD			n/a	n/a	9,750		No