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D7.9

Development of NIL replication using polymer and sol-gel resists

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DELIVERABLE DESCRIPTION

The current deliverable is focused on demonstration of replication of sub-10 nm features in polymers and in sol-gel resists using UV-nanoimprint. High-resolution intermediate polymer stamps made from OrmoStamp material, were used for replications experiments. Imprints with feature sizes as small as 5.6 nm demonstrated in TU-7 polymer resist, while an optimised alumina-based sol-gel resist, developed for electron and ion beam exposure, was proved capable of replication 10-11 nm features.

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Executive Summary

In the present deliverable, we report on sub-10 nm replication in both polymeric and sol-gel resists. Intermediate polymer stamp made of OrmoStamp material was used for the UV nanoimprint replication experiments in TU7 polymer and alumina-based sol-gel inorganic resist. The sol-gel resist viscosity has been optimised in order to demonstrate the 10 nm resolution. High etch stability of the AlOx mask is very promising for development of high-resolution pattern transfer using e.g. reactive ion etching, but a descum process to remove the alumina residual layer after imprint is to be developed.

1. Approach

In the present experiments, we used the nanoimprint technique developed during the earlier phases of the NFFA-Europe project to demonstrate high-resolution replication in polymers and sol-gel resists. The approach is based on the use of a soft intermediate polymer stamp (IPS), which is made by a UV-enhanced replication from a master Si stamp. The IPS is used for imprints in both organic (polymers) and inorganic (sol-gel) resists with high resolution. Our previous reports, the Deliverable D7.1, *Investigation of optimum NIL stamp fabrication method to copy sub-10 nm BCP features* [1] and the Milestone MS10, *Nanoimprint-based replication of sub-10 nm features into resists* [2], give a detailed description of the methods used in our experiments, so only a short overview of the approach will be provided in this section.

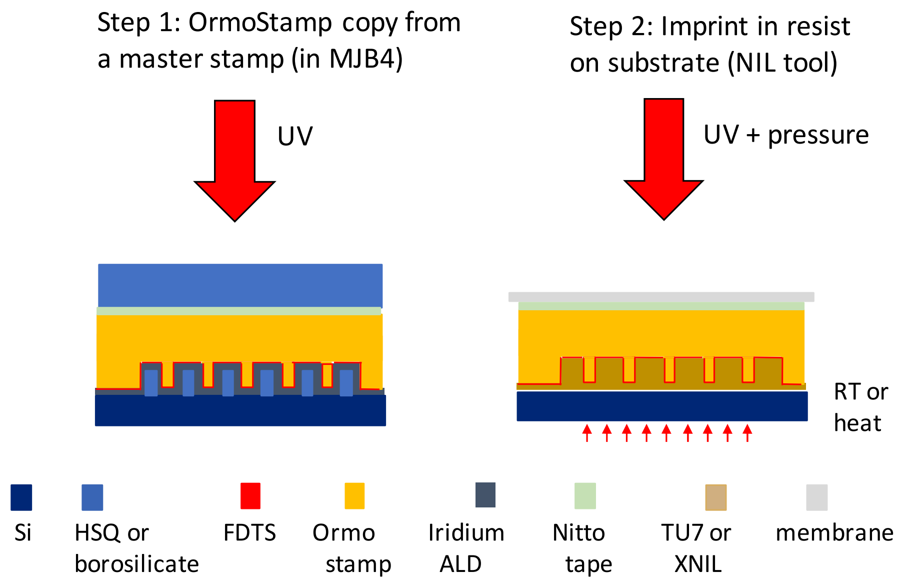

Figure 1: Schematic illustration of the two main process steps used: (1) fabrication of the intermediate polymer stamp (IPS) in the Ormostamp material from Si master and (2) nanoimprint of a polymer (e.g. TU7 resist) or another resist (e.g. sol-gel).

Figure 1 shows a simplified drawing of the imprint experiments, which included two main steps, formation of an OrmoStamp copy from Si-master stamp (IPS) and imprint in polymer or sol-gel resists using a single-use IPS. The Si-master stamps, which determine the final resolution of the method can be fabricated by electron beam lithography, ion beam or block-copolymer patterning combined with reactive ion etching for pattern transfer. Atomic layer deposition of Ir can be used to further reduce lateral features to sub-10 nm range, as reported in Deliverable D7.1 [1] and published recently [3]. The formation of the OrmoStamp copy is taking place using UV-irradiation at room temperature, which prevents unwanted pattern distortions due to difference in thermal expansion of Si and OrmoStamp. Features as small as 5.6 nm have been obtained in the OrmoStamp material and successfully imprinted in TU7 polymer resist [2, 3] as illustrated in the second step of Figure 1. The same approach was used for demonstration of high-resolution imprint in a newly developed sol-gel resist, see Section 3 below.

2. Replication in polymers

Previously, we have already reported replication in polymers with sub-10 nm resolution [2, 3] using the process described in Figure 1. The OrmoStamp material was proved to be of sufficiently high resolution with demonstrated feature sizes below 10 nm after replication from Si-master [3]. As a result, we used this material for nanoimprint replication in different resists. Table 1 below shows a short summary of the replication experiments.

Table 1: A summary of the nanoimprint replications in different polymer resists

#	Replication from:	Replication to:	Replication conditions	Achieved resolution, nm
1	Si-master	PMMA	T-NIL	≈50
2	Si-master	OrmoStamp	UV-process	5.6
3	IPS (OrmoStamp)	OrmoStamp	UV-process	≈20
4	IPS (OrmoStamp)	TU7 resist	UV-process	5.6
5	IPS (OrmoStamp)	XNIL26 resist	UV-process	Not successful

The imprint in PMMA using a thermal NIL, was not optimised in terms of resolution, due to the fact that we decided to use UV-based IPS process with OrmoStamp as the material for the intermediate stamp. Replication experiments in XNIL26 resist did not show equally good performance compared to imprints in TU7 resist due to large variations of resist thickness and damages after separation of the stamp from substrate [2].

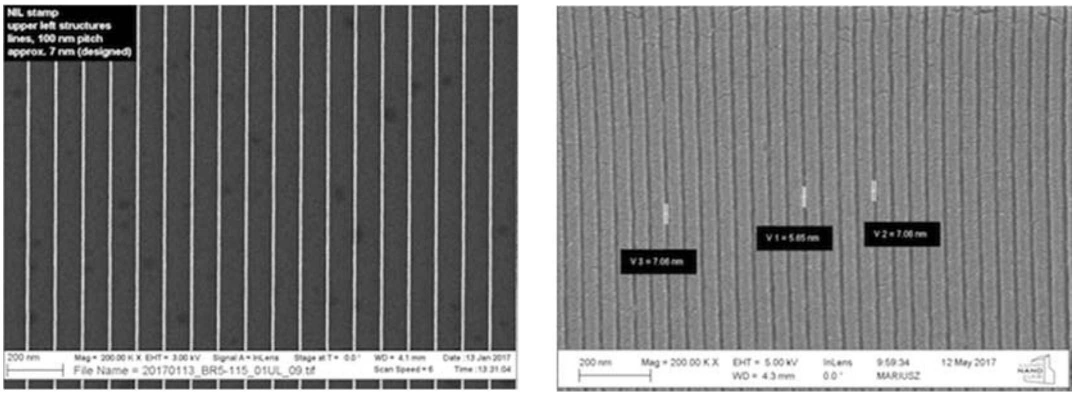

Figure 2: Example of replication of sub-10 nm features from the Si-master stamp (left) to TU7 polymer resist (right). The imprint was performed using Obducat's 6" nanoimprint machine with a pressure of 10 bar, temperature of 75°C and UV-irradiation. Lines with width as small as 5.6 nm were successfully transferred to TU7 resist.

Figure 2 illustrates the results of the replication process by showing sub-10 nm imprints in TU7 resist, and more experimental data about the high-resolution replication in polymer materials can be found in the Milestone MS10 report [2].

3. Replication in sol-gel resist

According to the objectives proposed for the subtask 7.2.2 ("Replication of nanostructures on the sub-10 nm level" - LUND, CNRS, PSI), we focused our efforts to demonstrate NIL replication of regular sub-10 nm features into inorganic resist synthesized by sol-gel method. Compared to conventional polymeric resists, the choice to work on inorganic resist was dictated by a potentially superior etching resistance when used as a mask for dry etching processes, a fundamental requirement for pattern transfer at such high resolution.
Following the successful results obtained in subtask 7.1.1 "Novel resist materials and processing" for which we demonstrated sub-10 nm electron and helium ion beam lithography using a recently developed alumina resist [4], and considering the exceptional etching selectivity of this alumina resist to fluorine-based processes for silicon, we decided to focus our efforts to develop a suitable NIL process for such an alumina resist.
In its original formulation, the alumina resist features a relatively high viscosity. Previously reported attempts to emboss the resist at room temperature were only successful applying a relatively high pressure (500 bar) for 5 min resulting in 200 nm width lines and residual layer as low as 30 nm [5].

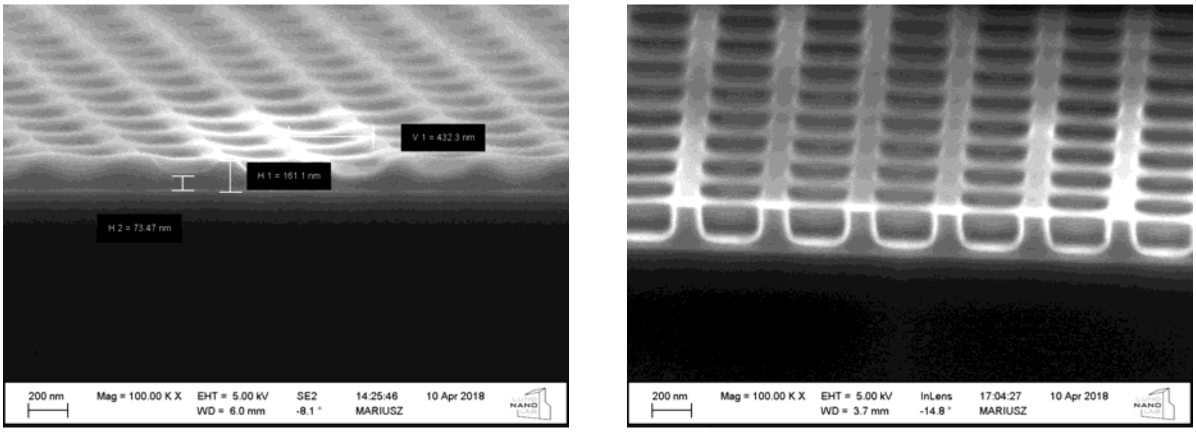

Figure 3. SEM images of embossed alumina resist at 40 bars using a standard (left) and modified (right) alumina resist formulation. The residual reists layer thickness is 25 nm, height = 198 nm and contrast = 173 nm

Therefore, we modify the original sol-gel solution to modify the spin-coated resist rheology thus reducing the imprint pressure. We start with the "mother" solution synthesized stirring (1 h at 70°C) aluminum-tri-sec-butoxide in a solution of methoxyethanol and acetic acid in the molar ratio of 1:21:4.3. After 1 h the triethoxyphenylsilane was added in a molar ratio of 0.25 and the solution stirred for another hour at 70°C. We then modified the formulation adding a combination of two solvents: ethanol to dilute the sol-gel solution and calibrate the resist thickness and a small amount of ethylene glycol (low vapour pressure solvent) to modify the rheology of the resist. The rationale is based on the fact that, after spin-coating the ethanol will be essentially evaporated while the ethylene glycol remains in the film thus lowering its viscosity.
Figure 3 shows a comparison between the standard alumina resist (left) and the modified alumina resist (right) after embossing using a OrmoStamp stamp (treated with FDTS), with a pressure of 40 bars applied for 1 min and stabilized at 130°C for 4 min before demolding.

In the first case, we obtained a residual layer of 74 nm, and a contrast of 87 nm while in the second case a residual layer of 25 nm and a contrast of 173 nm (essentially the contrast present in the original OrmoStamp stamp).
The choice to replace the original solvent (methoxyethanol) with ethanol for the dilution of the "mother" solution, stems from the fact that the first solvent is highly hygroscopic and an excess of water would accelerate the aluminium tri-sec-butoxide hydrolysis thus increasing the resist viscosity (speculation supported by evidence). It should be noted that, at the time of the experiments, the "mother" solution was not methoxyethanol-free and we expect a further reduction of the sol-gel viscosity if ethanol is used instead of methoxyethanol for the "mother" solution preparation (experiments in progress).
Higher resolution embossing was demonstrated using a master with dimers rods structures. Figure 4 shows SEM images of top view (left and center) and cross-section (right) embossed alumina resist. We demonstrated the replication of features as small as 10-11 nm. Nevertheless, it should be noted that embossed dimers are deformed as compared to the original dimers patterned in the silicon master mold used to replicate the Ormostamp stamp (dashed lined in Figure 4, left). For example, in the silicon master the bridge (distance between the two dimers) is 30 nm while in the embossed alumina resist is 11 nm. We suspect an asymmetrical deformation of the Ormostamp rods with a "lateral nanoimprint" that squeezes the resist between the two rods. Remarkably, the bridges are intact after demolding, with the same height as the resist surface (Figure 4, right). We suspect an elastic behaviour of the Ormostamp rods so that, after releasing the pressure, the deformed rods first detach laterally from the alumina bridge thus ensuring the preservation of an intact bridge.

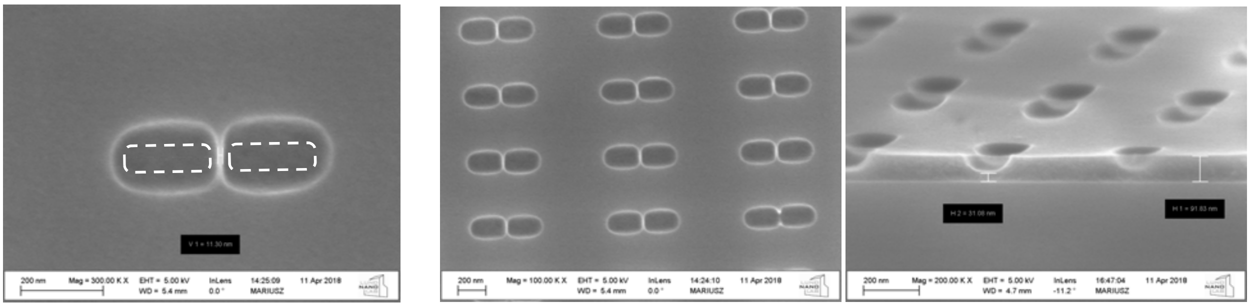

Figure 4. SEM images of high resolution embossing at 40 bars in modified alumina resist. Dashed lines (left) represent the original dimension of the dimer inside the Silicon master used to replicate the OrmoStamp stamp used for the NIL process.

The embossed structures feature a residual layer of 31 nm and a contrast of 60 nm (original contrast of the silicon master mold being 90 nm). Further attempts to reduce the residual layer by reducing the original sol-gel thickness resulted in a reduced residual layer (12 nm, not shown) but a reduced thickness contrast (56 nm, in progress). We expect to further improve these results by further lowering the sol-gel viscosity using a methoxyethanol-free sol-gel solution as previously mentioned. Currently a descum process based on CHF_3 plasma [6] for the removal of the alumina resist residual layer is under development.

4. Conclusions

In the current deliverable, we have successfully demonstrated sub-10 nm replication in polymer and sol-gel resists. The replication process in polymers is implemented by both hard Si-master stamps (replication in OrmoStamp) and by OrmoStamp IPS (replication in TU7), while a newly developed alumina-based sol-gel inorganic resist has been imprinted using the OrmoStamp IPS with feature sizes of about 10 nm. One of possible applications of the sol-gel imprint is high-resolution pattern transfer using AlOx as an efficient etch mask. The experiments are underway to develop a suitable etch recipe to remove the AlOx residual layer after imprint.

References

[1] NFFA-Europe Deliverable D7.1, Investigation of optimum NIL stamp fabrication method to copy sub-10 nm BCP features, February 2017

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