

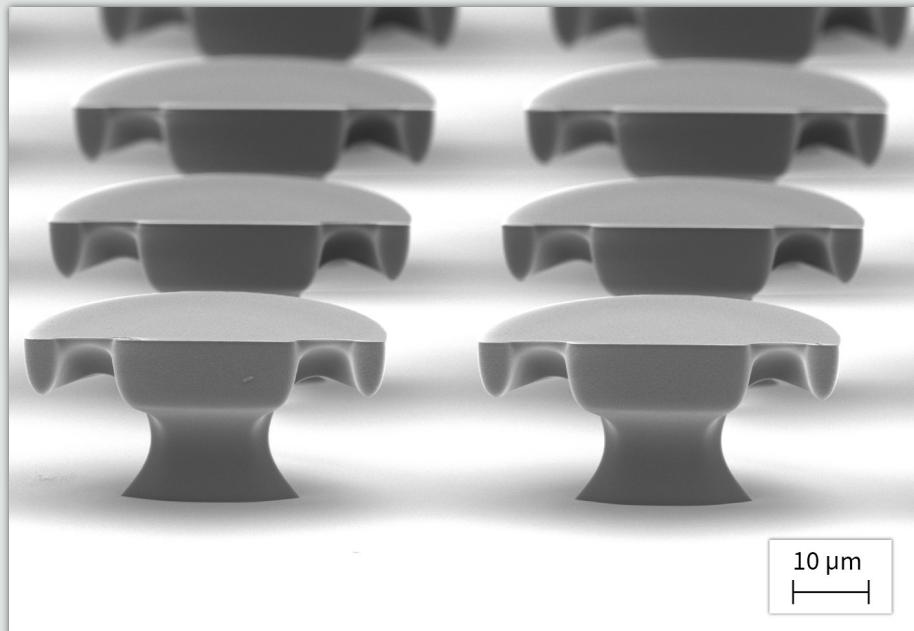
APPLICATION NOTE

SINGLE-STEP 3D PATTERNING OF NEGATIVE RESISTS VIA MASKLESS ALIGNER

by

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Negative resists are a class of photosensitive polymers that become less soluble upon exposure to radiation. By locally controlling the exposure dose, it is possible to create suspended microstructures with true 3D features in a single layer of resist, enabling the fabrication of complex designs. This application note describes the lithography process for achieving such 3D structures using the maskless aligner systems series (MLA) from Heidelberg Instruments Mikrotechnik GmbH. In this study two resists, mr-DWL 40 (from micro resist technology GmbH, Germany) and AZ nLoF 2070 (from Microchemicals GmbH, Germany), were used. However, the process can directly be transferred to other negative resists. This technique may find applications in biomedical scaffolds, microfluidic channels, micro-electro-mechanical systems (MEMS), and hydrophobic surfaces.



The core idea of maskless grayscale lithography is the precise control of photoresist curing depth by locally adjusting the exposure dose. This technique is widely used with positive tone resists to create complex, continuous surface topographies. By applying it to a negative-tone photoresist, however, it's possible to fabricate true 3D structures with suspended and overhanging features in a single lithography step.

As an example, we fabricated doubly reentrant surfaces for superhydrophobic applications using a specific three-dose grayscale lithography process (see e.g. Liu et al. *Science* 2014 for more information on the science behind the structure). This approach leverages the fact that the degree of cross-linking in a negative resist is directly proportional to the exposure dose. Higher doses result in greater cross-linking and a thicker cured layer, while lower doses result in less cross-linking and a thinner layer. The process is as follows (see Figure 1; detailed step by step recipes for mr-DWL 40 and AZ nLoF 2070 are described in the Appendix):

1. Negative photoresist is applied on a substrate using standard spin-coating procedures.
2. The substrate is then exposed to three distinct, patterned doses without being reloaded or realigned. The use of a single step, maskless processes, eliminates the need for complex alignment procedures.
 - a) The first and highest dose defines the base of the structure, or the **pillar**.
 - b) The second, lowest dose is used to create the **overhanging flat cap** (first reentrant part) at the top of the pillar.
 - c) The third, medium dose is applied to define the **vertical overhang** (second reentrant part), which extends downward from the cap.
3. The resist is developed, and the final structure is revealed.



Figure 1: Illustration of the multilayer exposure process used to create 3D structures via grayscale lithography.

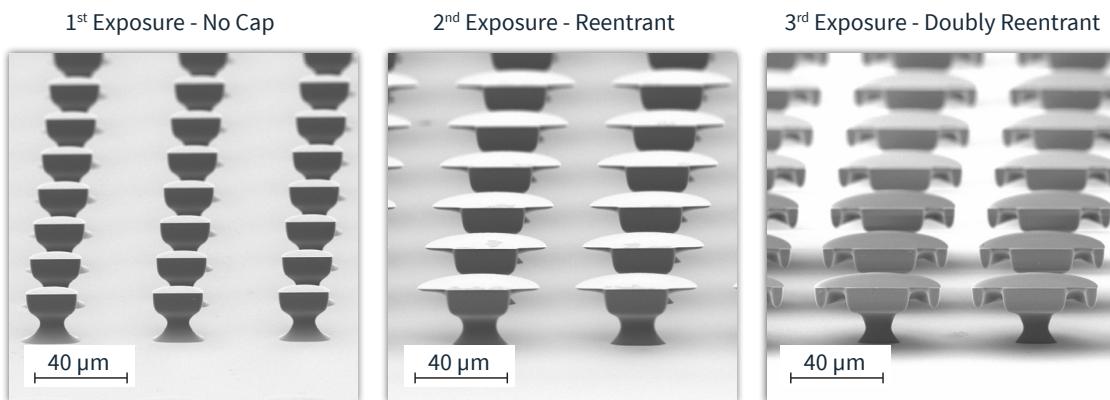


Figure 2: Realization of doubly reentrant structures using AZ nLoF 2070 after the first (left), second (middle) and third (right) exposure step .

This method allows for the independent control of the thickness and resolution of the flat cap and vertical overhang by simply adjusting the dose for each exposure step. The effect of the laser dose on the curing depth can be seen in Figure 3 for mr-DWL 40 exposed with at a wavelength of 405 nm.

Other examples are for example microfluidic channels or lattice structures with suspended lines. Those structures require only two exposure steps: a high dose to define the **pillars or channel walls**, and a lower dose to create bridges or **suspended roofs** that connect them.

For even more complex geometries, these elements can be stacked on top of each other using additional coating and exposure steps. This technique is not limited to a single photoresist system and can be applied to a variety of negative-tone resists, such as **SU-8, polyimides** or other **photopolymers**, depending on the required material properties for the target application.

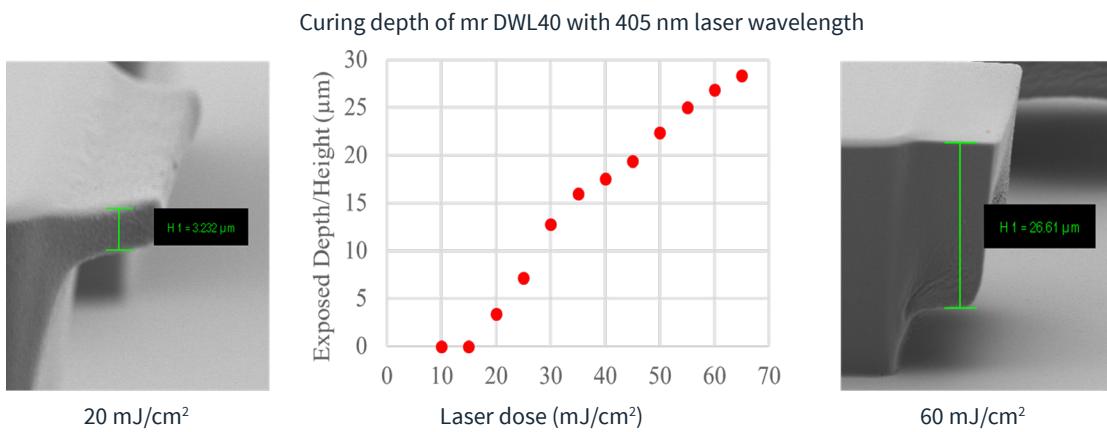


Figure 3: Curing depth of mr DWL40 in dependence of the laser dose at a wavelength of 405 nm using WMI of an MLA 150.

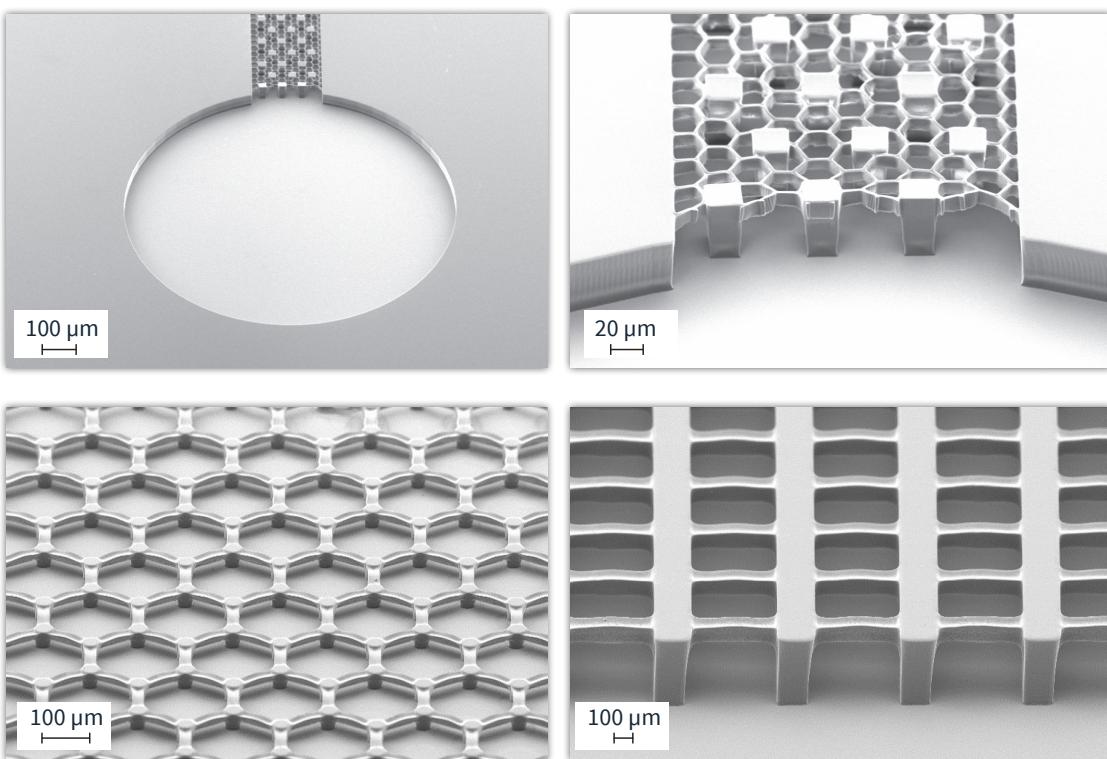


Figure 4: Microfluidic channels and lattice structures with suspended features fabricated in mr DWL40

APPENDIX: DETAILED DESCRIPTION OF PROCESSES

1. PROCESS OF FABRICATING DOUBLY REENTRANT STRUCTURES 1 USING AZ NLOF 2070

AZ nLoF 2070 is a standard I-line negative resist specifically designed for lift-off applications.

Spin Coating: Spin-coating of the AZ nLoF 2070 at 1000 rpm for 30 seconds on a wafer, resulting in a thickness of 16-18 μm.

Soft Bake: Pre-bake the resist at 110 °C for 2 min.

Exposure: The photoresist was exposed using an MLA300 at a wavelength of 375 nm three times without re-loading the substrate and without alignment using three different doses 500, 30 and 300 mJ/cm² and patterns. The first exposure

is to define the pillar, the second exposure to get the overhanging flat cap, and the third exposure is for the vertical overhang (second reentrant part) (Figure 2).

Post-Exposure Bake: Bake again at 110 °C for 2 min

Development: Develop using MIF 726 (from MicroChemicals GmbH, Germany) for around 5 min.

Remark: The development time affects the morphology of the final structure a lot as can be seen in the SEM images in Figure 5.

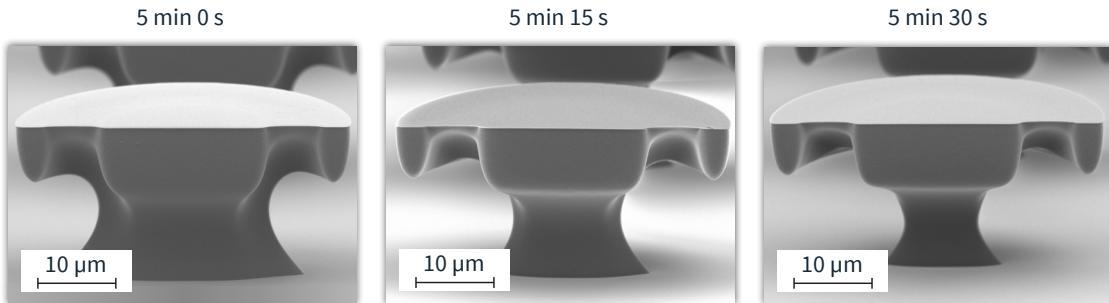


Figure 5: Effect of the development time of the doubly reentrant structures based on resist AZ nLoF 2070.

2. PROCESS OF FABRICATING DOUBLY REENTRANT STRUCTURES USING MR-DWL 40

The mr DWL40 is a negative-tone photoresist from micro resist technology GmbH which is specifically designed for direct laser writing and is suitable for 405 nm laser wavelength. It can be coated up to 100 μm in thickness and obtains high thermal and chemical stability and finds use in micro system technology applications.

Spin Coating: mr-DWL 40 is spin-coated on a wafer at 2000 rpm for 30 s. The film thickness was around 40 μm .

Soft Bake: Prebake the resist at 50 °C for 5 min and then 85 °C for 10 min

Exposure: The photoresist was exposed using an MLA 300 at a wavelength of 375 nm three times without re-loading the substrate and without alignment using three different doses 530, 25 and 25 mJ/cm^2 and patterns. The first exposure is to define the pillar, the second exposure to get the overhanging flat cap, and the third exposure is for the vertical overhang (second reentrant part).

Post-Exposure Bake: Post-bake the resist at 50 °C for 5 min and then 85 °C for 5 min.

Development: Develop the resist in mrDev600 (from micro resist technology GmbH, Germany) for 6 min. The results can be seen in Figure 6.

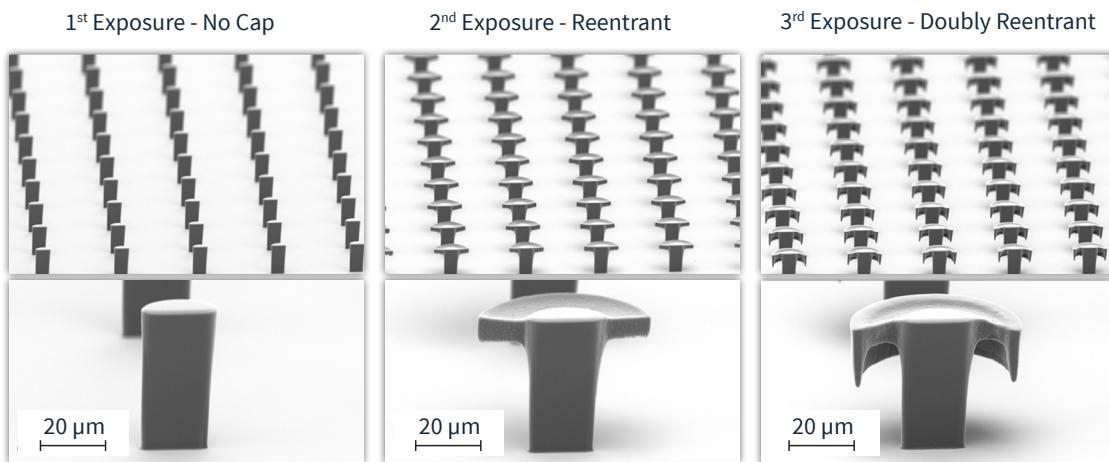


Figure 6: Scanning electron microscope images of the doubly reentrant structures fabricated in mr-DWL 40 after the first (left), second (middle) and third (right) exposure step.



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