Vilnius University
Faculty of Physics
Laser Research Center

Laboratory assignment No. MNFT-2

FAST REPLICATION OF MICROSTRUCTURES BY MOLDING

For master students of Laser Physics and Optical Technologies and Laser Technology programmes

Vilnius 2026

1 Objectives

1. Become familiar with microtransfer molding (μTM) – a soft-lithography technique for the fast replication of microstructures fabricated by 3D laser lithography (3DLL).
2. Understand which master structure geometries can be replicated by μTM and what determines the fidelity of the replicas.
3. Gain practical experience in making polydimethylsiloxane (PDMS) molds and polymer replicas and in characterizing them by optical and scanning electron microscopy (SEM).

2 Tasks

1. Inspect the master structures fabricated in laboratory assignment MNFT-1 by optical microscopy and/or SEM. The sample should ideally contain 2D, 2.5D and 3D structures and closed-loop structures with a membrane for membrane-assisted μTM (MA-μTM).
2. Make a PDMS transfer mold of the master structures and inspect it with an optical microscope.
3. Make replicas of the master structures from at least two different prototyping resins (e.g., Ormocomp, SU-8 or others, depending on availability).
4. Characterize the master structures, the mold and the replicas by SEM.
5. Evaluate the advantages and limitations of the method.

3 Questions for the defence

1. Chemical and mechanical properties of PDMS. Why is it the preferred material for μTM?
2. Steps of PDMS mold preparation and the purpose of each step.
3. Typical production throughputs of 3DLL and μTM.
4. Limitations on the master structure geometry in μTM.
5. Requirements for the chemical and physical properties of prototyping resins.
6. The principle of MA-μTM.
7. The idea of the hybrid approach combining 3DLL and replication.
8. Why can the dimensions of the replica differ from those of the master?
9. Why can a PDMS mold be used only a limited number of times? What damages it?

4 Equipment and materials

The master structures are the microstructures fabricated by 3DLL on a cover glass in laboratory assignment MNFT-1.

Materials. PDMS kit Sylgard 184 (silicone elastomer base and curing agent); prototyping resins – Ormocomp, SU-8, etc., depending on availability; cover glasses as substrates for the replicas; isopropanol for cleaning the cover glasses or pipettes, if needed.

Molding equipment. Laboratory scales, vacuum chamber with a vacuum pump, hotplate, metal molding form, 1 mm thick glass slides and Kapton tape, ultraviolet (UV) lamp Superfire Z03 (365 nm, 12 W) with a curing chamber beneath it.

Characterization equipment. Optical microscope *Olympus* BX51 or *Olympus* IX73 and SEM (TM-1000, *Hitachi*).

Other laboratory supplies: disposable dishes for mixing, automatic pipettes with disposable tips, scalpels, tweezers, disposable gloves and UV safety goggles.

5 Workflow

During this laboratory assignment you will work with chemicals and intense UV radiation. Uncured PDMS and the prototyping resins can irritate the skin and eyes: wear disposable gloves whenever you handle them. Never look at the UV lamp while it is on – wear UV safety goggles or keep the curing chamber closed during exposure.

The workflow described below may be adjusted by the instructor depending on the situation in the laboratory. Take optical microscope and SEM images at the same magnification at every stage, so that the master, the mold and the replicas can be compared directly.

1. **Inspection of the master structures.** Before molding, the master structures are examined to document their initial shape and condition. Inspect the sample with the master structures under an optical microscope and/or SEM (SEM images taken in assignment MNFT-1 may be used, if available). Record images of every structure you are going to mold, and note any defects (collapsed, detached or distorted parts). These images are the reference for evaluating the mold and the replicas later.

2. **Preparation of the PDMS prepolymer.** Wear disposable gloves! The two components of the PDMS kit are weighed and mixed at a 10:1 mass ratio of base to curing agent. One mold requires about 2 g of prepolymer; calculate the required masses of the base and of the curing agent before you start. Place a clean disposable dish on the laboratory scales and tare them. Transfer the base into the dish with a pipette, then add the curing agent in the right proportion (use the scales, not the pipette volume, to set the ratio). The base is very viscous: before transferring it from the main bottle, cut off the narrow end of the disposable pipette tip, and

add it in small portions (400 μl or less) so that the pipette itself is not contaminated. Mix both components thoroughly with a clean disposable pipette tip for at least 2 min. Write down the masses of the base and of the curing agent that you actually added and calculate the resulting mixing ratio – you will need it for the report.

3. **Degassing of the prepolymer.** Mixing traps air bubbles in the prepolymer; they are removed in the vacuum chamber, otherwise they would end up as voids in the mold. Place the dish with the mixture into the vacuum chamber, open the air valve and switch on the vacuum pump. Then close the air valve and watch the prepolymer: the trapped bubbles expand and the level of the liquid rises. When the level gets close to the rim of the dish (before it overflows), open the air valve – the bubbles burst. Repeat this until no bubbles remain; it may take 20–30 min.

4. **Fixing the master sample.** The thin cover glass with the master structures should be fixed on a rigid support so that it does not move or bend during molding. Attach the cover glass to a 1 mm thick microscope slide with Kapton tape on all four sides, with the master structures facing up.

5. **Casting and curing of the PDMS.** Place the microscope slide onto the hotplate, then place the molding form on the cover glass so that the master structures are inside the form. Carefully pour the degassed PDMS into the form, making sure that the structures are fully covered and that no new bubbles are introduced. Switch on the hotplate, heat it up to 100 °C over about 5 min, and then cure the PDMS at this temperature for 35 min.

6. **Demolding.** After curing, take the slide off the hotplate with tweezers and let it cool to room temperature on the laboratory table. Careful: the metal molding form is very hot! When the mold can be handled with bare hands, cut through the PDMS around the form with a scalpel, then carefully slide the scalpel between the molding form and the glass (take care not to slide it under the cover glass) and slowly lift the form together with the mold off the substrate. Do not pull or twist the mold, as this can tear off or deform the master structures.

7. **Inspection of the mold.** The mold is checked under an optical microscope before it is used. Make sure that every master structure has left a cavity in the PDMS, and look for trapped bubbles, torn PDMS and pieces of the master structures that have been ripped off and stuck in the mold. Inspect the master sample again as well and note whether any structure has been damaged or detached during demolding. Record images of the mold and of the master.

8. **Making the replicas.** Place the mold with the cavities facing up and put a droplet of the selected prototyping resin on it. Cover it with a clean cover glass (if it looks dirty or dusty, clean it with isopropanol first), positioning it so that one of its edges lies close to the cavities: the replicas will then end up near the edge of the cover glass, where they are easier to view in the SEM. Press gently, so that the resin fills the cavities and the excess is squeezed out. Place the mold with the cover glass on top of it into the curing chamber, directly below the UV lamp, and cure

the resin for approximately 20 s for Ormocomp or 2.5 min for SU-8 (ask the instructor about the exposure time for other resins). Wear UV safety goggles or keep the chamber closed during the exposure! Then gently peel the mold off the cover glass – the replicas should remain on the cover glass.

9. **Inspection of the mold after replication.** The mold is checked once more for damage caused by the replication. Inspect it under the optical microscope for any visible changes: cured resin left in the cavities, replicas stuck in the mold, deformed or torn cavities. Inspect the replicas on the cover glass under the optical microscope as well.

10. **Replication with another resin.** Repeat steps 8 and 9 with another prototyping resin, using the same mold (several times, if time permits).

11. **Characterization by SEM.** The master structures, the mold and the replicas are compared at high resolution. Observe all samples at an angle of 45°, using the same magnifications for corresponding structures, and compare how the structures change at each stage.

12. **Report and conclusions.** In the report, include the optical microscope and SEM images of the master structures, the mold and the replicas. Describe what you observed at each stage (defects, changes in shape and size, differences between the resins) and write the conclusions of the assignment.

6 Theory

6.1 Replication of microstructures by molding

3DLL, also known as two-photon polymerization lithography, enables truly 3D fabrication with almost no restrictions on the geometry of the part. It also offers impressive resolution: features smaller than 100 nm are frequently reported in the literature, which makes 3DLL comparable to 2D patterning techniques such as electron beam (e-beam) lithography or nanoimprint lithography. A common criticism of 3D printing methods, including 3DLL, is the relatively long time it takes to fabricate a device or a part. The process is slow because it is serial: the structure is written voxel by voxel, and one part must be finished before the next one can be started. Depending on the size of the object, its filling factor and the level of detail, the fabrication of a single structure by 3DLL may take from several hours up to some days [1]. Established microfabrication technologies, such as mask-based photolithography, are parallel and offer massive economies of scale. They make inexpensive consumer electronics possible, as well as countless other items, from toys to disposable biomedical consumables. 3DLL is still some years away from being a mass-production technology, and its speed is one of the key hurdles.

Several physical methods, however, can produce complex microstructures at speeds suitable for mass production. One strategy is to replicate microstructures fabricated by 3DLL: a 3D structure, called the *master structure*, is first made by 3DLL and then molded, and the replicas are produced by a faster process. One successful replication strategy is μTM, a soft-lithography technique in which a flexible elastomer, PDMS, is used to make transfer molds of the masters. The PDMS mold is then used to make replicas that are identical to the master structure [2].

PDMS is a silicone elastomer. The Sylgard 184 kit is cured by a hydrosilylation reaction between vinyl (Si–CH=CH_2) groups and hydrosilane (Si–H) groups, which cross-links the liquid prepolymer into a solid elastomer [3]. PDMS is a commercially available and relatively inexpensive material ($\sim$\$100/kg). It has several properties that are ideal for microfabrication, such as thermal stability, chemical resistance, optical transparency and a low Young's modulus. An important advantage of PDMS is its low surface free energy, which makes the mold easy to separate from the master or the replica. This low adhesion also keeps the deformation of the PDMS mold to a minimum, even after multiple uses. One master structure can be used repeatedly to make dozens of PDMS molds, and each mold can be used to make approximately a dozen replicas before the material deforms [4].

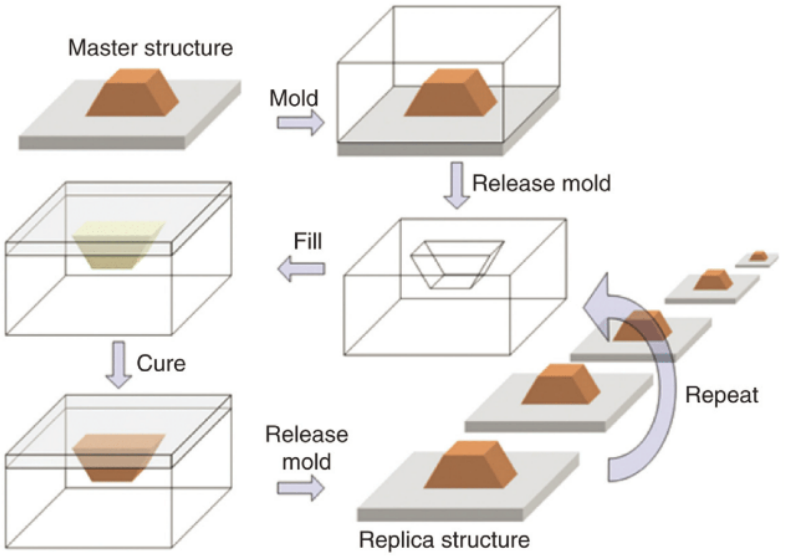


Fig. 1 Schematic of the μTM process: a master structure is made by 3DLL, molded in PDMS, and a replica is cast from the mold.

The μTM process is shown in Fig. 1. The master is first made by 3DLL and then molded in PDMS. To make the separation of the PDMS mold from the master easier, the master is often coated with a fluorine-based anti-adhesion layer, such as perfluorooctyltrichlorosilane or perfluorodecyltris(dimethylamino)silane. The premixed PDMS prepolymer (Sylgard 184 base and curing agent mixed at a 10:1 mass ratio) is poured onto the master. Mixing introduces air bubbles, so the liquid PDMS has to be degassed in a vacuum chamber before or after it is applied to the master. PDMS cures at room temperature in about 2 days, but curing is usually accelerated by heating: at 60 °C it

takes about 3 h, and at the higher temperature used in this assignment (100 °C) less than an hour. Once fully cured, the mold can be easily separated from the master. The replicas are made by filling the PDMS mold with a monomer mixed with a photoinitiator and polymerizing it with UV light.

An early example of μTM on an industrial scale is the PRINT (Particle Replication In Non-wetting Templates) technology of the company Liquidia, which uses roll-to-roll processing and perfluoropolyether molds to produce kilograms of shape-specific microparticles from a variety of materials [5]. Although its master structures are made by one-photon lithography, this example supports the commercial viability of μTM for 3DLL-made masters as well.

Due to the flexibility of PDMS, a wide range of structures can be replicated. Fourkas and coworkers have demonstrated that structures with high aspect ratios or large overhangs can be replicated with high fidelity (Fig. 2) [6].

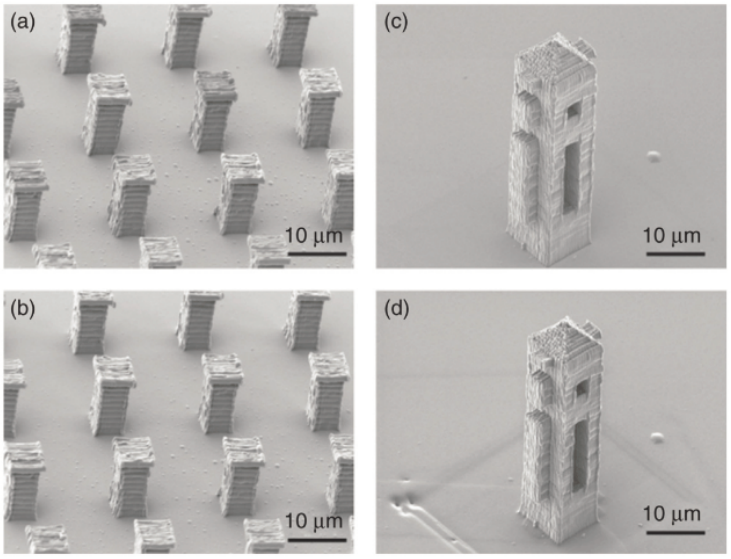


Fig. 2 SEM images of master structures made by 3DLL (a, c) with overhanging and undercut features and of their faithful replicas made by μTM (b, d) [6].

Methods have also been developed to replicate master structures that contain closed loops. In conventional μTM, the mold would "lock" onto such a structure: the PDMS passing through the loop cannot be pulled out without tearing the mold or the master. This problem is solved by MA-μTM [7]. In MA-μTM, a thin membrane is created in the centre of each closed loop during the fabrication of the master. The membrane prevents the PDMS from forming a continuous ring through the loop, so the mold can be released from the master. Before the mold is filled with resin, the PDMS walls on both sides of the membrane region are pressed together so that they adhere to each other, which makes it possible to cast closed-loop replicas (Fig. 3). Various geometries, including coils, tables and tunnels, have been replicated by MA-μTM. These examples show that molding can be used for a wide range of shapes and not only for those that are topographically convenient.

6.2 Advantages of replication by molding

The main benefit of μTM and MA-μTM is the time saved by replicating a structure instead of fabricating it again. Polymerizing a replica always takes about the same time, $\sim$1 min, regardless of the size, density and complexity of the microstructure. In this respect, the mold plays the role of the mask in conventional lithography. High-resolution lithography masks are made by serial techniques such as direct laser writing or e-beam lithography, which often take hours. Once the mask is ready, however, it can be used to create patterns quickly and in parallel. The same is true of the mold in μTM: it may contain many master structures that took hours to fabricate, but once the mold is made, it can produce many copies of the masters in minutes.

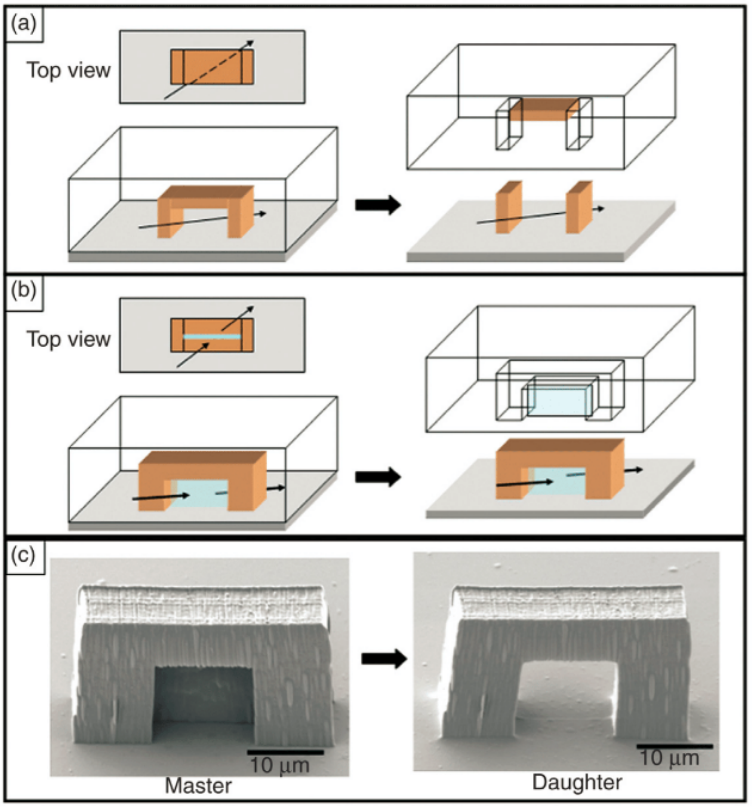


Fig. 3 (a) Mold lock: if a microstructure contains a closed loop, the mold cannot be removed without destroying the structure. (b) Membrane-assisted μTM: closed loops are avoided by creating a thin membrane. After molding, the mold can be removed without damaging the master, and gentle pressure then reversibly seals the mold in the region of the membrane. (c) SEM images of a typical master and its replica [4].

Molding offers another advantage: a wider choice of materials. Only a limited number of materials can be structured by 3DLL, while a much wider variety can be cast in molds. Replicating a 3DLL master in a different material has been demonstrated, for example to obtain ceramic or carbon microstructures by pyrolysis of the replicas [8, 9], and this remains an active area of research.

6.3 Limitations of the method

μTM has two important drawbacks: (1) the flash, or scum layer, and (2) the topographical restrictions. Flash is the residual layer of material connected to the part of interest; in μTM it usually includes the layer of resin that joins the structures to the substrate. In nanoimprint lithography the flash is removed by reactive ion etching (RIE) [10], and the same approach could help to solve this issue in μTM of 3DLL structures.

As fast as μTM is, the shapes it can replicate are still severely limited. For example, chiral photonic crystals made of polymer spirals by direct laser writing [11] cannot be extracted from a mold. Fabrication of some structures may nevertheless be sped up considerably by a hybrid approach that combines 3DLL and replication. A simple 3D Cartesian lattice cannot be molded, because it contains closed loops everywhere, but an array of 2D Cartesian lattices can be molded and replicated (Fig. 4). The replicas can then be quickly completed with connecting lines written by 3DLL, which turns the 2D array into a 3D lattice. For the example shown in Fig. 4, most of the structure can be replicated in $\sim$1 min regardless of its size, and only one third of the lines need to be written by 3DLL. Such a hybrid approach seems feasible, although it is not yet a routine method.

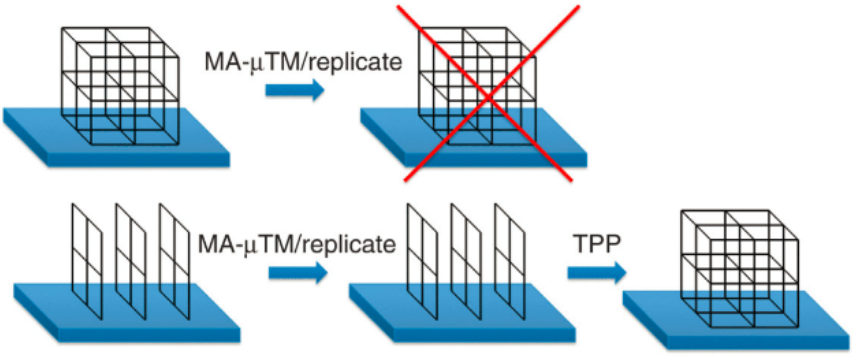


Fig. 4 Top: MA-μTM does not work for all geometries. Bottom: the hybrid approach, in which molding is combined with 3DLL, may make it possible to use MA-μTM to speed up the fabrication of complex geometries.

6.4 Requirements for prototyping resins

The resin used to cast the replicas has to meet several requirements:

1. *Low viscosity.* In μTM a thin layer of liquid prepolymer is applied to the patterned surface of the PDMS mold [3]. The resin must flow easily into all cavities, including narrow and deep ones, without trapping air; otherwise parts of the replica will be missing.

2. *Curing at the available wavelength.* The prepolymer is cured by illuminating the mold with UV

light [3]. The photoinitiator of the resin must therefore absorb the radiation of the light source used – in this assignment 365 nm.

3. *Low shrinkage.* Most resins shrink when they polymerize, and the replica becomes smaller than the cavity. UV-curable prepolymers used in soft lithography typically shrink by less than 3 % on curing [3].

4. *Compatibility with PDMS.* Cured PDMS swells in many nonpolar organic solvents, such as toluene and hexane [3, 12]. A resin containing such components can swell the mold and distort its cavities.

5. *Suitable adhesion.* The cured resin must adhere to the glass substrate more strongly than to the PDMS, so that the replicas stay on the glass when the mold is peeled off. The low surface free energy of PDMS helps here.

6. *Sufficient mechanical strength.* The cured replica has to withstand demolding without breaking or bending.

An important effect is related to oxygen. Resins that cure by free-radical polymerization, such as acrylates, are inhibited by oxygen. PDMS is highly permeable to oxygen, so oxygen diffusing through the mold can keep a thin layer of resin next to the PDMS walls unpolymerized [13]. In μTM this can lead to under-cured, tacky replica surfaces and to the loss of the finest features.

6.5 Why replica dimensions differ from the master

When comparing the master, the mold and the replica, keep in mind the following sources of dimensional change:

- *Shrinkage of PDMS.* PDMS shrinks by $\sim$1 % upon curing [3], and the shrinkage grows with the curing temperature: from 1.06 % at 65 °C to 1.94 % at 100 °C [14]. The master itself is not compressed: the PDMS solidifies at 100 °C around the master and, after the slide is taken off the hotplate, cools to room temperature while still held in place by the molding form and the glass. Only after demolding can the free mold contract, so its cavities are slightly smaller than the master.

- *Shrinkage of the resin* during polymerization (see above).

- *Deformation of the mold.* PDMS is soft. Relief features with a too high or too low aspect ratio can collapse or sag [3], and pressing the cover glass onto the mold can deform the cavities.

- *Incomplete filling and oxygen inhibition*, which lead to missing or rounded features.

- *Flash layer.* μTM on a flat surface usually leaves a thin film ($\sim$100 nm) of material between the raised features [3]. If the resin is not squeezed out well, this layer is thicker and increases the height of the replica.

6.6 What limits the lifetime of the mold

A PDMS mold can be reused, but only a limited number of times: each mold can produce approximately a dozen replicas before the material deforms [4]. The main causes of damage are:

- *Mechanical damage.* PDMS is soft, and every demolding stretches it. Thin walls of the mold can tear, especially around overhangs and undercuts, and relief features with a too high or too low aspect ratio can collapse or sag [3].

- *Residues.* Cured resin left in the cavities, or replicas that break off and stay in the mold, block the cavities during the next replication.

- *Swelling and absorption.* PDMS swells in many nonpolar organic solvents [3, 12] and absorbs small hydrophobic molecules [15]. Components of the resin that penetrate the mold can change the shape of the cavities and contaminate the next replicas.

References

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