Vilnius University
Faculty of Physics
Laser Research Center

Laboratory assignement No. MNFT-2

FAST REPLICATION OF MICROSTRUCTURES BY MOLDING

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

Vilnius 2017

1 The goal

The goal of this laboratory assignement is to familiarise yourself with rapid prototyping by microtransfer molding (µTM) technique and understand it's benefits and limitations.

2 Lab exercises

1. Make a PDMS transfer mold of microstructures created during the lab assignement No 1. Mold should include various types of structures: 2D, 2,5D, 3D structures for microtransfer molding, closed loop structure with membrane for membrane-assisted microtransfer molding.
2. Make replica structures from different resins provided (Autodesk Clear PR48, PEG-DA-700, SU-8 (depending on availability)).
3. Characterize master structures, molds and replica structures using scanning electrone microscope, analyse and discuss the changes of structure geometry in each stage. Does the geometry of replica depends on material used?
4. Discuss the advantages and limitations of the method. What was the finest feature size of structures replicated? Which prototyping resin showed the best performance?

3 Pre-lab questions

1. PDMS chemical and mechanical properties. Why it is preffered material for microtransfer molding?
2. Typical production throughputs via 3DLL (TPP) and µTM methods.
3. Master structure geometry limitations for µTM method.
4. Requirements for chemical and physical properties of prototyping resins.
5. The idea of membrane-assisted microtransfer molding.
6. The idea of hybrid aproach for 3DLL and replicating.

4 Materials and equipment

- Sylgard 184 Silicone elastomer base
- Sylgard 184 Silicone elastomer curing agent
- Ember Clear prototyping resin
- PEG-DA-700 + 1% IRG prepolymer
- UV Curing Optical Adhesive
- Glass substrate and molding form
- Laboratory dishes, scalpels and automatic pipettes
- Vacuum chamber
- Laboratory scales
- UV curing LED system
- Heating plate
- Scanning electrone microscope TM-1000
- Safety googles and gloves

5 Procedure

During this laboratory assignement you will work with toxic chemical materials and intense UV radiation. Use savety googles and glowes when required.

1. Preparation of PDMS prepolymer. For making 1 transfer mold 2 g of prepolymer is required. Add Sylgard 184 Silicone elastomer base and Sylgard 184 Silicone elastomer curing agent (ratio 1:10 (use laboratory scales)) into a assigned chemical glass and mix vogorously. Add resin in small portions (400 µl or less) in order not to contaminate automated pipette. Use disposable gloves!

2. Degasing the prepolymer. Place prepared prepolymer into the vacuum chamber and open the air valve. Switch on the vacuum pupm. Close the air valve and observe the prepolymer inside the chamber. Air bubbles inside the liquid will "inflate" and the volume of the mixture will increase. When the liquid level increases, open the air valve causing the explosion of air bubbles. Make sure not to spill prepolymer out of the glass. Repeat the procedure until no air bubbles remain (takes 20-30 minutes).

3. Stick the substrate with microstructures on to the thick (1 mm) glass plate. Use small droplet of optical adhesive and stack substrates together. Use UV lamp for curing adhesive (30 s for each side). Use safety googles!

4. Place a molding form on the substrate around the place microstructures are located. Pour prepared PDMS prepolymer into the form. Put the substrate on the hot plate and heat it for 60 min. at 100 °C temperature.

5. After curing is finished let the mold to cool down in the room temperature. Peel off the mold from the substrate gently. Use laboratory scalpels.

6. Making replica structures. Put a droplet of selected prototyping resin on the prepared mold. Place a clean 1 mm glass substrate on top and squeeze gently. Cure the resin under UV lamp (30 s for each side). Use safety googles! Peel off the substrate with replica structures from the mold gently.

7. Inspect master structures, molds and replica structures under the scanning electrone microscope.

6 Theoretical background

Replication of microstructures by molding

3DLL (or TPP lithography) enables truly 3D fabrication without any restrictions on the geometry of the part. TPP also offers impressive resolution with features <100 nm being frequently reported in the literature, thus making TPP comparable with 2D patterning techniques such as electron beam (e-beam) patterning or nanoimprint lithography. One criticism of 3D printing methods, including TPP, is the relatively long time it takes to create a device or a part. This slow speed is because the process is serial and one part must be finished before the next part can be started. Current microfabrication technologies, such as mask-based photolithography, are parallel and offer massive economies of scale. Inexpensive consumer electronics are made possible by these parallel fabrication methods as are countless other items from toys to disposable biomedical consumables. TPP is still some years away from being a technology capable of mass production and one of the key hurdles is its speed. However, there are several physical methods that may be able to create complex microstructures at speeds suitable for mass production. The strategy toward faster production of parts is to replicate microstructures fabricated by TPP. In this method, a 3D structure is first made by TPP, which is called the “master structure,” and the master is molded to make replicas by a faster process. One successful replication strategy is to employ microtransfer molding (µTM). µTM is a soft lithographic technique that uses a flexible elastomer PDMS to make transfer molds of the masters. The PDMS mold is then used to make replicas that are identical to the master structure [1].

PDMS is a commercially available chemical that is relatively inexpensive (∼\$100/kg). It has several ideal properties for nanofabrication, such as thermal stability, chemical resistance, optical transparency, and low Young's modulus. An important advantage of PDMS is its low surface free energy, which makes it easy to separate the mold from the master/replica. This low adhesion also ensures minimum deformation of the PDMS mold 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 deformation [2].

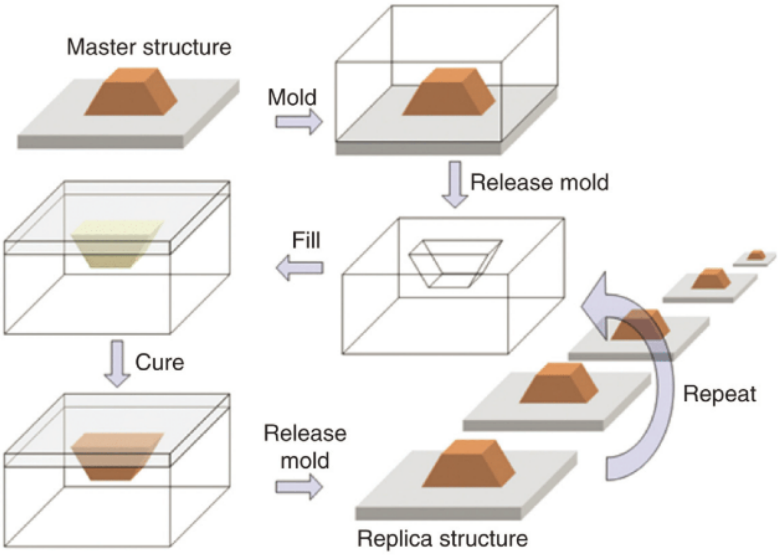

Fig. 1 Schematic of the µTM process starting from a master structure made by TPP, molding it in PDMS, and then casting a replica from the mold.

Figure 1 illustrates the process of the µTM using PDMS. The master is first made by TPP and then molded in PDMS. To facilitate the separation of the PDMS mold from the master, the master is usually coated with a fluorine-based anti-adhesion layer, such as perfluorooctyltrichlorosilane or perfluorodecyltris(dimethylamino)silane. The premixed PDMS prepolymer (Sylgard 184 base/curing agent = 10:1, w/w) is poured onto the master. PDMS premixing generates air bubbles and so it is necessary to degas the liquid PDMS in a vacuum chamber before or after applying it to a master. PDMS can cure at room temperature over 2 days, but it is usually cured at the elevated temperature (60°C) for a shorter curing time (3h). After fully cured, the mold can be easily separated from the master. The replication step is done by pouring monomers mixed with photoinitiator into the PDMS mold, followed by polymerization using UV exposure.

At present, the only mass production of 3D microstructures is done by µTM by a company called Liquidia. This company uses roll-to-roll processing to produce kilograms of microstructures out of a variety of materials from a perfluoropolyether mold [3]. Although their master structures are made using one-photon technology, it does let credence to the commercial viability of µTM for TPP-created masters.

Due to the flexible nature of PDMS, a variety 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) [4].

Methods have also been developed to successfully replicate master structures with closed loops. In traditional µTM, the mold would "lock" to itself when replicating structures with closed loop. This problem can be solved by a technique called membrane-assisted microtransfer molding (MA- µTM)[5]. In MA- µTM, a thin membrane is created in the center of each closed loop during master fabrication. This membrane stops PDMS to connect within the closed loop, allowing the mold to be released from the master. The PDMS in the region of the membrane is then induced to adhere to itself before the mold is filled, allowing closed-loop replicas to be created (Fig. 3). Using MA- µTM various geometries, including coils, tables, and tunnels, have been demonstrated. These examples show that molding may be used for a wide set of shapes and not only those that are topographically convenient.

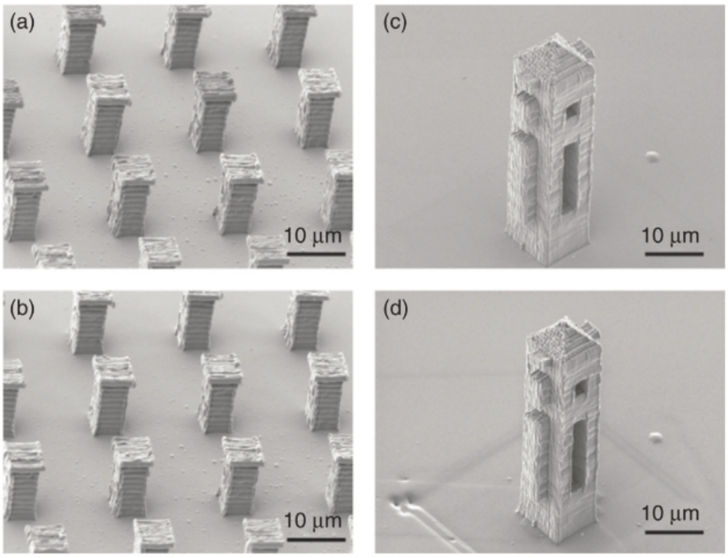

Fig. 2 Scanning electron micrographs of master structures made by TPP (a and c) having overhanging and undercut features can be faithfully replicated (b and d) by µTM [4].

Advantages of replicating by molding

The main benefit of µTM, or MA- µTM, is the time saved in reproduction versus fabrication. The time it takes to polymerize a replica is always the same, ∼1min, regardless of the size, density, and complexity of the microstructure. In this way, the mold takes the place of a mask in conventional lithography. High-resolution lithography masks are made using serial techniques such as direct laser writing or e-beam lithography and often take hours to create. However, once the mask is in hand, it can be used to quickly create patterns in a parallel way.

The same is true of the mold in µTM. The mold may contain many master structures that took hours to fabricate, but once the mold is made, it can be used to recreate many copies of the master in minutes.

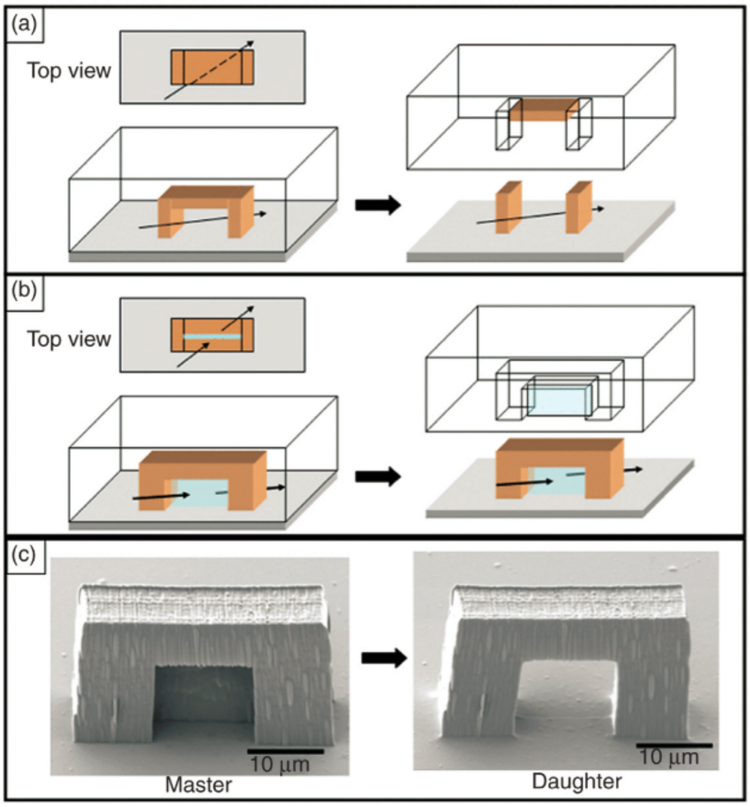

Fig. 3 (a) A schematic illustration of the issue of mold lock, where if a microstructure contains a closed loop, then the mold cannot be removed without destroying the structure. (b) A solution to the issue called membrane-assisted µTM where the closed loops are avoided by the creation of a thin membrane. After molding these masters, the mold can be removed without damaging the master and then gentle pressure can be applied to reversibly seal the mold in the region of the membrane. (c) Electron micrographs of a typical master and daughter structure [2].

Molding also offers another advantage, the diversification of materials. There are only a limited number of materials that can be patterned by TPP, but there are a much wider variety of materials that can be cast in molds. To our knowledge, only a couple of groups have reported replicating a microstructure from a different material than that of the master. This appears to be an area ripe for continued research [6, 7].

Method limitations

There are two important drawbacks of µTM: (1) the flash or scum layer and (2) the topographical restrictions. Flash refers to the residue material connected to the part of interest. In µTM the flash likely includes the substrate to which the structure is connected. Nanoimprint lithography is a relatively new method of patterning that removes flash by reactive ion etching (RIE) [8]. RIE has not yet been applied to the µTM of TPP structures, but should help to solve this issue. As fast as µTM is, it is still severely limited in the shapes that it can replicate. For example, the impressive chiral photonic crystals created by Wegener and coworkers that consist of an array of rigid vertical coils simply cannot be extracted from a mold. It may be possible, however, to significantly speed up fabrication of some structures using a hybrid approach of TPP and replication. For example, a simple 3D Cartesian lattice cannot be molded, because there are closed loops everywhere, but an array of 2D Cartesian lattices could be molded and replicated (Fig. 4). The replicas could then be quickly augmented with connecting lines to convert the 2D array into a 3D array. For the particular example shown in Fig. 4 much of the structure can be replicated in ∼1 min regardless of the size, and only one-third of the lines need to be written by TPP. This type of hybrid approach has not yet been reported in the literature, but seems feasible.

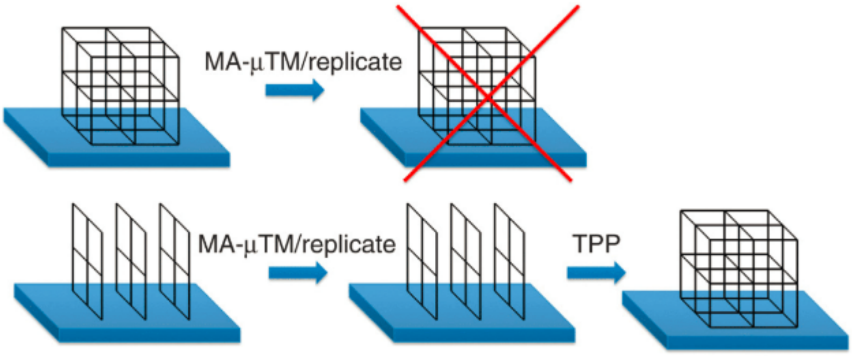

Fig. 4 At the top is shown that MA-mTM will not work for all geometries, but the hybrid approach, shown schematically at the bottom, may enable MA-mTM to be used in conjunction with TPP to speed up fabrication of complex geometries.

Annex.:

1. Autodesk Standard Clear Prototyping Resin (PR48) specs. sheet - 1 page
2. PEG-DA-700 (Sigma-Aldrich) specs. sheet - 1 page

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