École Polytechnique
Fédérale de Lausanne

Reaserch Internship - Galatea Lab

Molding of 3D micro/nano scale glass structures with PDMS

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Abstract

This research investigates the PDMS molding of micro and nanostructures inscribed in glass using a femtosecond laser. The study aims to evaluate the limitations of the molding process and develop a protocol to address challenges such as adhesion between the mold and the polymer, and PDMS structural relaxation due to intrinsic stresses. Experiments were conducted on samples featuring various microstructures, ranging from large, soft micro-lenses to intricate, small-scale features like cracks and ablation lines/dots. The results highlight issues such as dimensional changes in the molded structures and the presence of PDMS residues on the glass molds. Additional techniques, including fluorescence microscopy and monolayer coatings, were explored to improve the de-molding process and reduce residue formation. The findings provide valuable insights into optimizing the molding of laser-inscribed glass structures with PDMS.

Acknowledgments

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Contents

1 Introduction

PDMS molding of in-glass laser inscribed micro and nano structures is an enabling technology both for its fabrication potential and for its capability as a characterization technique. However, a correct PDMS molding of glass comes with difficulties and limitation like the potentially strong adhesion between the mold and the polymer, and the PDMS structural relaxation due to intrinsic stresses.

The goal of this project is to test the limitation of PDMS molding of micro-structures in glass and to develop a protocol to overcome these issues. Eventually, the final goal will be to establish an approach for the repeatable molding of nano laser-inscribed structures in glass. An example of final application would be to produce highly motile PDMS nanoscale artificial cilia which will be useful for replicating and study the behavior of cilia found on human cells.

This project is very interesting to me as a microengineering student since it mixes microfabrication and bioengineering, both of which are directly related to my studies and potential outcomes. I am particularly excited about the interdisciplinary nature of the project, as it allows for the application of engineering principles to solve biological problems.

2 Methodology

2.1 Characterization step

Characterizing glass samples, which serve as molds, before the PDMS molding process is essential to ensure the quality and reliability of the final micro and nanostructures. This preliminary examination is crucial for several reasons: first, it helps detect any pre-existing defects or damage on the glass mold, which is important for distinguishing between issues that originate from the molding process and those already present on the mold. Moreover, during the molding process, residues of PDMS may adhere to the surface of the glass mold, potentially altering its properties and affecting the outcome of subsequent uses. Establishing a baseline through initial characterization allows for accurate detection and quantification of any changes or contamination resulting from the molding process. This characterization involves precise measurements of key features, such as the dimensions and surface quality of the glass mold, using tools like optical and confocal microscopes. These tools provide high-resolution images and detailed data necessary for assessing the impact of the molding process on the mold's integrity and for the comparison with the PDMS molding.

Selecting the appropriate characterization tools is therefore crucial, as each offers unique advantages for analyzing different aspects of the glass mold, such as surface morphology, structural details, and material properties. In the following subsections, the various tools utilized for characterizing the glass molds before and after PDMS molding will be introduced.

2.1.1 Olympus BX51M optical microscope

The Olympus BX51M optical microscope is equipped with an integrated camera system that enables the capture and storage of high-resolution images. This feature allows for detailed visualization and documentation of the sample's surface morphology and microstructural features, providing essential data for accurate analysis and comparison before and after the molding process.

2.1.2 Leica VMM 200 measuring microscope

The Leica VMM 200 measuring microscope is specifically designed to provide highly accurate and precise measurements of samples, surpassing the measurement capabilities of a standard optical microscope. This tool is essential for detailed metrology tasks, allowing for the exact quantification of microstructural features such as dimensions, spacing, and surface variations. Its enhanced accuracy ensures a more reliable evaluation of the sample's characteristics, which is particularly critical in applications where even minor deviations can significantly impact the molding process and the quality of the final product.

2.1.3 Keyence VK X-1000 laser confocal microscope

The Keyence VK X-1000 laser confocal microscope combines laser scanning with interferometry to provide high-resolution 2D and 3D images, enabling us to precisely measure micro and nanostructures on the glass molds. This tool allowed us to generate accurate topographical maps and quantify surface roughness, height, and other critical dimensions at the nanometer scale, which is crucial for understanding the impact of the PDMS molding process on the molds.

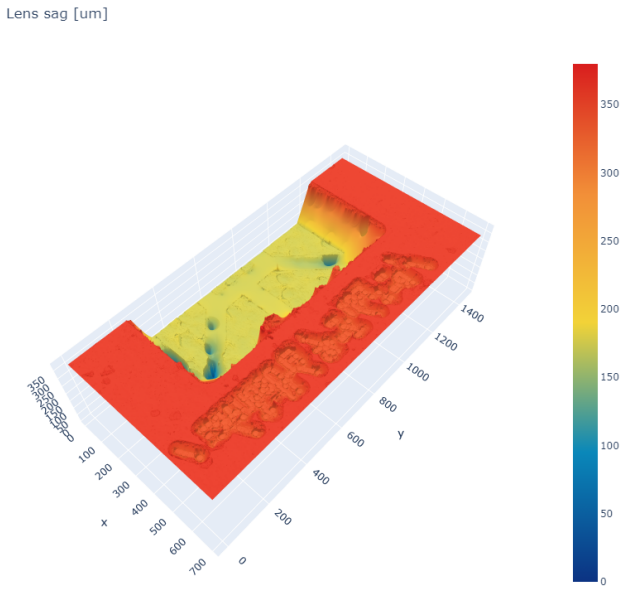


Figure 1: Example of 3D topographic image of glass microstructure captured with confocal microscopy, highlighting surface roughness and feature dimensions (in μm) critical for accurate PDMS molding

2.2 Molding step

The molding process consists of several critical steps to ensure the proper formation and quality of the final PDMS (polydimethylsiloxane) elastomer structure using the Sylgard 184 elastomer kit. The following steps outline the procedure in detail:

1. Prepare a Pool for the Sample: A suitable pool or containment area is created in which the sample will be placed during molding. This pool must be designed to fit the dimensions of the sample accurately, ensuring that the elastomer fully encapsulates the sample during curing. For samples that are 1 mm thick or less, a lasercutted 5 mm thick plexiglass structure can be used to provide adequate support and containment for the liquid PDMS mixture. Scotch tape (as shown in figure 2) can be used to secure the pool in a petri dish or on a microscope slide, while the sample can be fixed to the bottom using a droplet of DI (deionized) water, which adheres due to capillary forces.

Remark: Clean all supports (such as petri dishes, microscope slides, and pools) using acetone and isopropanol to remove any contaminants, and then dry them with nitrogen. This cleaning process should also be applied to the samples, and an ultrasonic bath may be used if the samples are particularly small or delicate to ensure thorough cleaning.

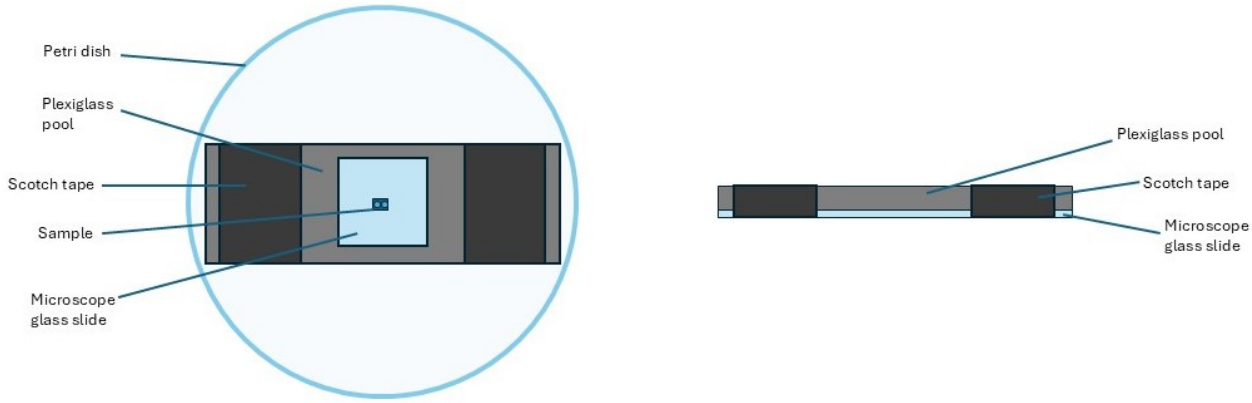


Figure 2: Pool setup for sample PDMS molding

2. Mix PDMS Base and Curing Agent: The PDMS base is mixed with the curing agent using a glass rod until the mixture is thoroughly combined and a significant amount of air bubbles are formed. The proportion of the curing agent is crucial and is usually chosen between 10% and 15%. It has been empirically proven that using a lower percentage (such as 10%) results in a more elastic final elastomer, whereas higher percentages may lead to a firmer material. This mixture preparation step is critical for achieving the desired mechanical properties in the final mold.

3. Cover the Sample with the Mixture: The prepared PDMS mixture is then carefully poured over the sample, filling about three-quarters of the pool's volume. This step ensures that the sample is completely covered and allows enough material for the mold to set properly. The uniformity of coverage is essential to avoid defects or irregularities in the final mold structure, which could impact its performance in subsequent applications.

4. Remove Air Bubbles by Vacuum: The pool containing the sample and PDMS mixture is placed under vacuum until all air bubbles are completely removed (at least 2-3 times). The vacuum process is vital to ensure that no trapped air remains in the mixture, which could cause voids or weaknesses in the final mold. Complete degassing is necessary to achieve a consistent and homogeneous elastomer structure.

5. Cure in the Oven: After degassing, the setup is covered with a petri dish lid to prevent contamination and is then placed in an oven set to 90 degrees Celsius for a minimum of two hours to allow the PDMS to cure fully. This curing step allows the PDMS to polymerize fully, forming a solid elastomer molding around the sample. The temperature and duration are carefully controlled to ensure that the curing process is uniform and that the desired mechanical properties of the mold are achieved.

6. Allow to Cool at Room Temperature: Once curing is complete, the mold is left to cool at room temperature for at least two hours before unmolding. This cooling period is crucial as it allows the elastomer to stabilize and reduces the risk of damage or deformation when the mold is removed from the sample. Ensuring adequate cooling time helps maintain the integrity and elasticity of the final PDMS mold.

2.3 Examination step

Once the PDMS moldings are obtained, they undergo the same charcterization as the glass samples to ensure that the molding step was successful. This examination step is crucial as it allows for a direct comparison between the molded structures and the original glass molds that were characterized prior to molding. By using the same characterization techniques, such as optical microscopy, confocal microscopy, or other relevant methods, we can assess the fidelity of the replication process, identify any defects or discrepancies, and determine how closely the molded PDMS structures match the intended designs inscribed in the glass molds.

Additionally, it may be beneficial to examine the glass molds after the molding process to detect any potential residues left behind by the PDMS. This analysis helps identify unwanted contamination that could affect subsequent moldings or reveal issues related to mold release and adhesion, guiding further refinement of the process for improved outcomes.

3 Experiences

3.1 Macro-molding

The initial tests on fused silica 3D samples were conducted using a set of micro-lenses (as shown in figure 3), selected specifically due to their relatively large size (100-300 μm features) and intersting patterns. These micro-lenses served as an ideal starting point to develop and refine the protocols for characterization, molding, and examination steps. By working with larger and more manageable structures, we aimed to gain a thorough understanding of the entire workflow, from initial characterization to final inspection, before progressing to more challenging, smaller-scale samples at the micrometric level. The choice of these larger, softer micro-lenses provided a practical foundation to ensure that all procedures were well understood and effectively executed, laying the groundwork for successful manipulation and examination of more delicate and complex structures in subsequent stages of the research.

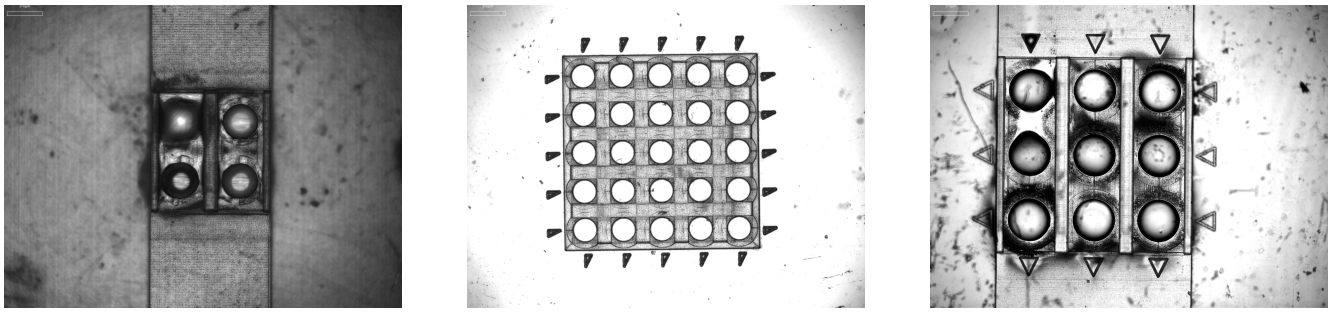


Figure 3: Optical microscope images of micro-lenses (150-300 μm diameter), showcasing examples of initial structures used for PDMS molding protocol development (316 μm scale bar, top left of each image)

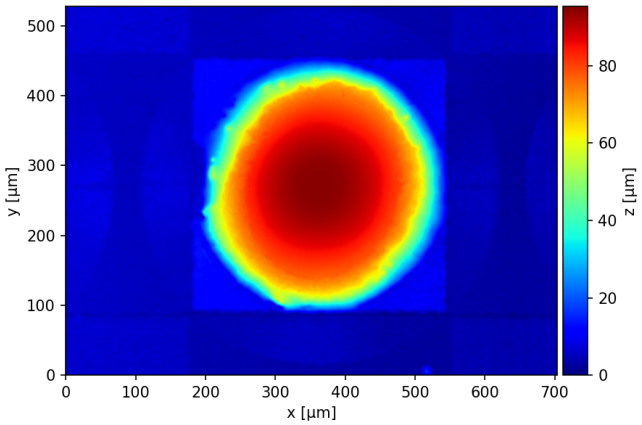
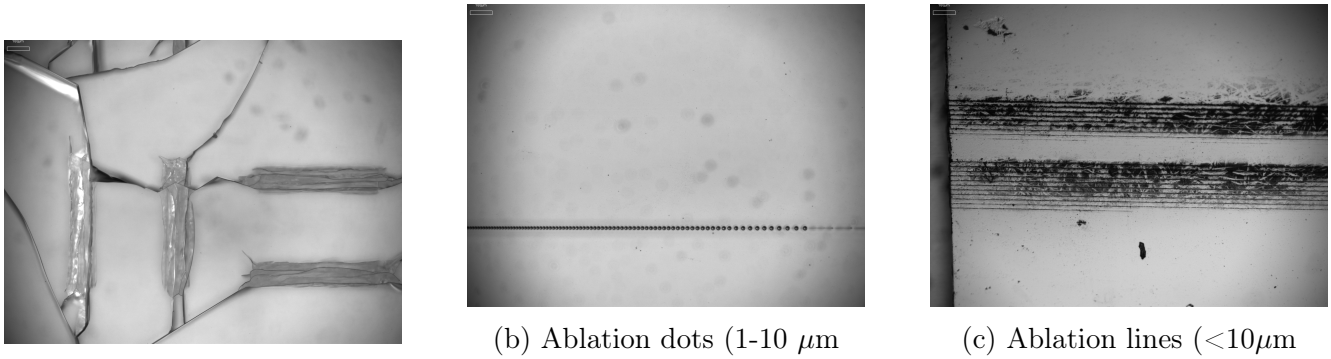


Figure 4: Detailed 3D reconstruction of a micro-lens obtained via confocal microscopy, demonstrating the accuracy and depth perception crucial for PDMS replication

3.2 Micro-molding

The second set of tests focused on samples with features ranging from 1 to 50 μm, such as cracks, micro-channels, and ablation patterns (as shown in figure 5). These samples were deliberately chosen to push the boundaries of the characterization and molding processes, allowing us to explore the limits of precision and resolution achievable with the current setup. By selecting samples with such fine, intricate features, we aimed to identify the challenges and potential failures that could arise when working at this smaller scale. This approach helped in assessing the capability of our techniques to accurately replicate and examine the microstructures, particularly in terms of maintaining fidelity to the original design, avoiding distortions, and preventing the loss of detail.



(a) Cracked sample

(b) Ablation dots (1-10 μm diameter)

(c) Ablation lines (<10μm thickness)

Figure 5: Optical microscope images of glass microstructures, including cracks, ablation lines, and dots, used to test the precision limits of PDMS molding (100 μm scale bar, top left of each image)

3.2.1 PDMS residues detection

Due to the rough nature of the samples, it was necessary to detect potential PDMS residues on the glass molds after the molding process. We employed a technique using Rhodamine B as a selective dye, which binds specifically to PDMS while leaving the fused silica surface of the mold unstained. After applying the dye to the molds, any residual PDMS areas are highlighted by the dye's fluorescent properties. The molds are then examined under a fluorescence microscope, where the dyed PDMS residues emit a bright fluorescence, enabling easy visualization and assessment of the residue distribution and quantity.

3.3 Monolayer coating

As described in [4], nanometer-thick, irreversibly physisorbed polydimethylsiloxane (PDMS) monolayers, known as pseudo-brushes, can be created on silica substrates using commercially available polydisperse PDMS melts (Gelest, Inc). The selected PDMS has an average molecular weight (Mw) of 139 kg/mol, reflecting a broad distribution of chain lengths. The purpose of this layer is to reduce the adhesion between the molding material and the mold, and perhaps more importantly, to minimize friction during the removal process, whether it is done manually or automatically. This step is crucial to ensure successful de-molding, especially for high-aspect ratio structures and when performing repeated moldings.

The monolayer coating process consists of several steps:

Deposition: Droplets of a highly concentrated PDMS solution in octane (VWR, 99+%) with a volume fraction of around 50% are quickly and evenly applied to freshly piranha-cleaned, nitrogen-dried fused silica substrates (0.5 to 1 mm thick) that contain femtosecond laser-written patterns.

Solvent Evaporation: The samples are left at ambient conditions (approximately 20°C and 1 bar) for 12 hours, covered by a clean glass dish, to allow the octane to evaporate slowly, leaving behind a thick, solvent-free PDMS film.

Incubation: The samples are then incubated in an oven at 110°C for 24 hours to complete the adsorption process and saturate the silica surface with PDMS chains.

Rinsing: Excess PDMS is removed by rinsing with toluene and then immersing the samples in a toluene bath for at least 2 hours, leaving a nanometer-thick PDMS monolayer on the substrate.

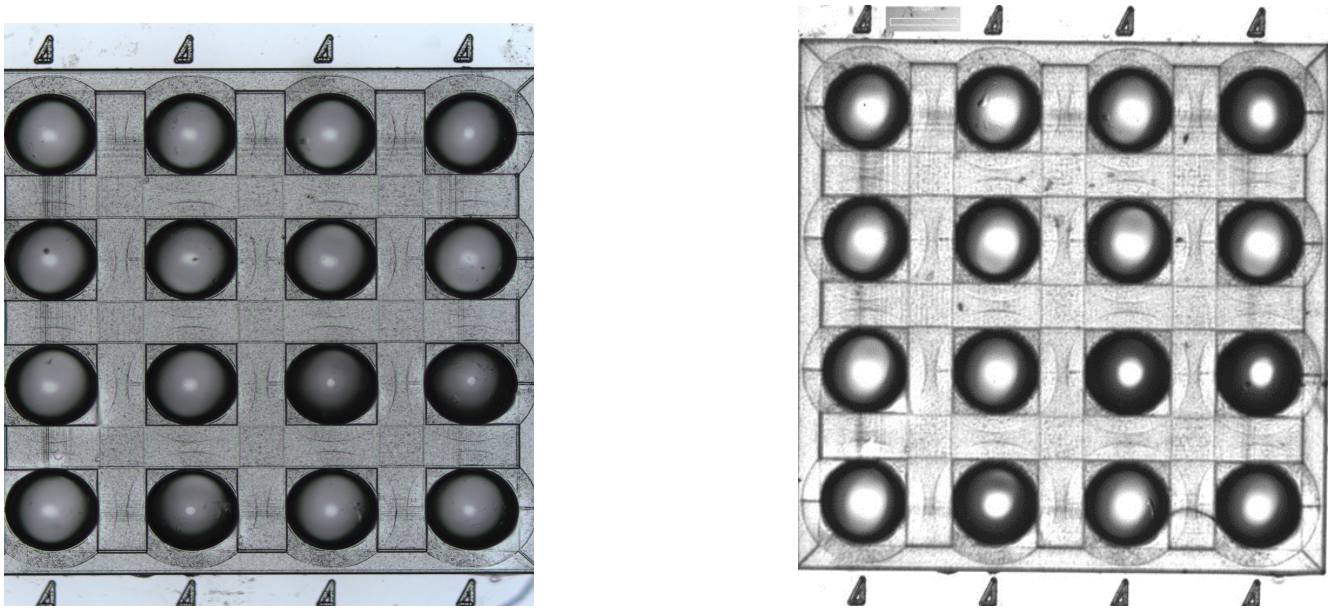
The tests conducted in this work followed the same steps, except that the piranha cleaning used to functionalize the surface of the samples during the deposition step was replaced with plasma cleaning, and the samples were placed on a heating plate in the fume hood instead of being incubated in an oven during the incubation step.

4 Results

The following section presents the results obtained from the experiments described earlier. This section focuses solely on the data and observations collected during the various tests, including measurements, visual assessments, and other relevant findings. The interpretation, significance, and implications of these results will be addressed in detail in the subsequent Discussion section. Here, the aim is to provide a clear and objective overview of the outcomes to serve as a foundation for the analysis that follows.

4.1 Macro-molding

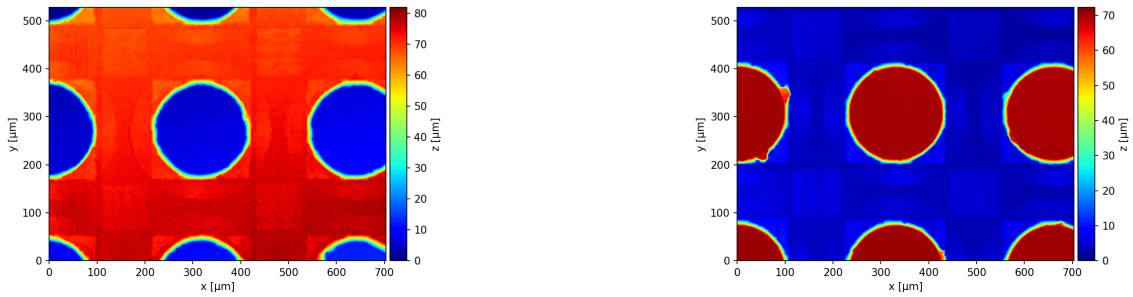
These results include optical images of both the lenses mold and the corresponding PDMS molding (figure 6), providing a visual comparison of the structural fidelity between the original mold and the replicated lenses surfaces. Additionally, topographic images (figure 7) and profile curves (figure 8) are presented to offer a more detailed assessment of the surface morphology and dimensional accuracy.



(a) PDMS molding (reversed image)

(b) Fused silica mold

Figure 6: Side-by-side comparison of optical microscope images: micro-lenses glass mold (right) and the corresponding PDMS molding (left), highlighting the fidelity of structural replication (316 μm scale bar, top left, mold image)



(a) PDMS molding (b) Fused silica mold

Figure 7: Side-by-side confocal microscopy topographic scans of micro-lenses glass mold and PDMS molding, highlighting the fidelity of structural replication

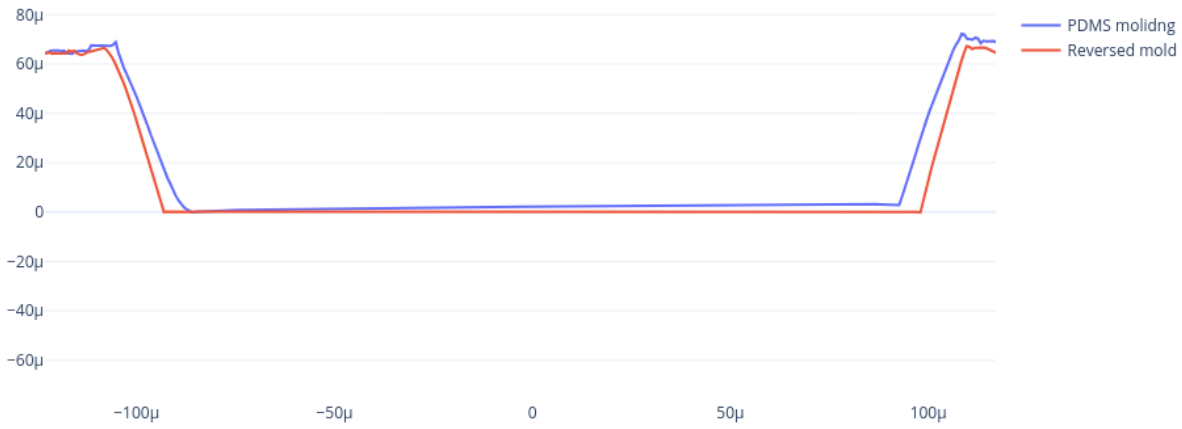
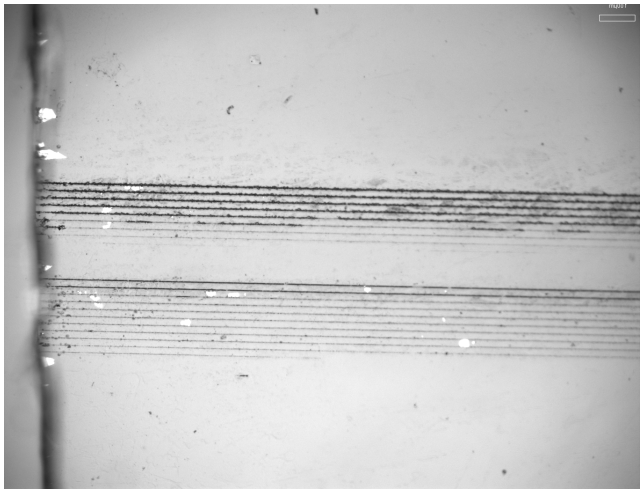


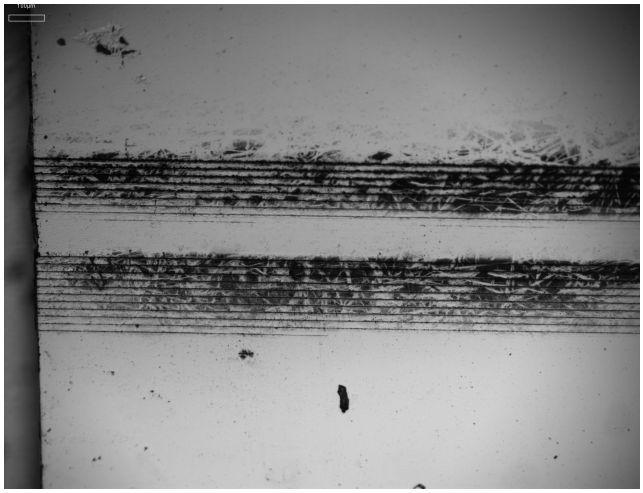
Figure 8: Quantitative profile comparison between glass mold and PDMS replica of a single micro-lens, demonstrating minor deviations in structure (in μm)

4.2 Micro-molding

These results include optical images (figures 9 and 10) of both the ablation dots/lines molds and the corresponding PDMS moldings. The cracked samples did not support the molding process, as they all broke during unmolding. Additionally, fluorescence microscopy was employed to detect any PDMS residues left on the glass molds after the molding process. The fluorescence images in figure 11 clearly reveal areas where residual PDMS is present, indicated by bright fluorescence signals.



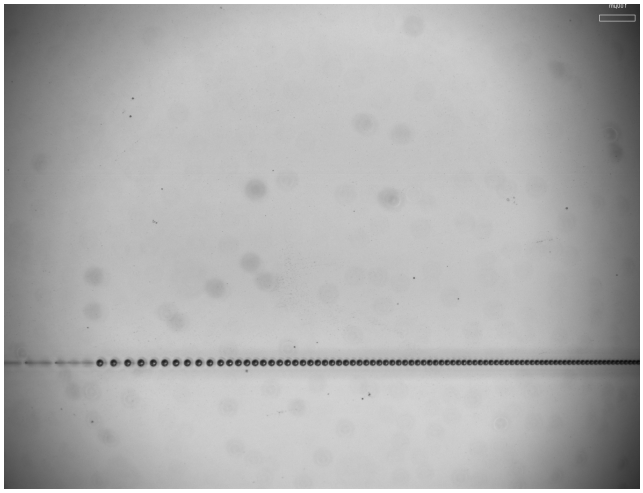
(a) PDMS molding (reversed image)



(b) Fused silica mold

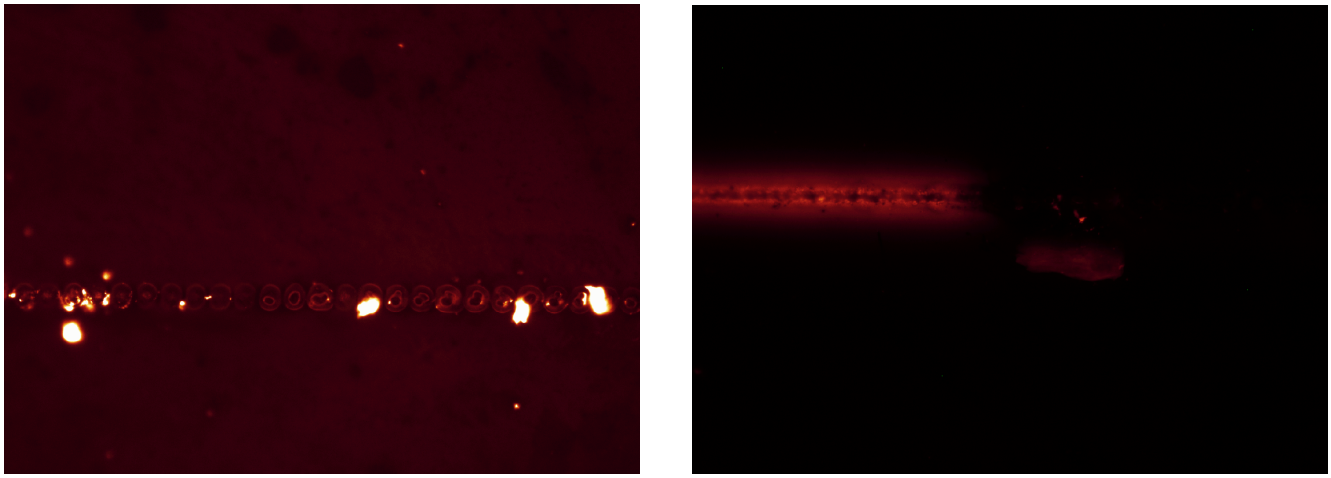
Figure 9: Side-by-side comparison of optical microscope images: laser inscribed ablation lines glass mold (right) and the corresponding PDMS molding (left), highlighting the fidelity of structural replication (100 μm scale bar, top right molding, top left mold)

(a) PDMS molding



(b) Fused silica mold (reversed image)

Figure 10: Side-by-side comparison of optical microscope images: laser inscribed ablation dots glass mold (right) and the corresponding PDMS molding (left), highlighting the fidelity of structural replication (100 μm scale bar, top left molding, top right mold)



(a) Ablation dots (b) Ablation lines

Figure 11: Fluorescence microscopy image showing Rhodamine B-stained PDMS residues on a glass mold, highlighting areas of polymer retention after demolding and the need for optimized residue reduction techniques

5 Discussion

This section examines the results of the experiments, highlighting key observations related to the molding accuracy, material behavior, and surface quality. The findings are discussed in the context of their implications for the replication process and potential improvements for future experiments.

5.1 PDMS structural relaxation

As seen in figure 8, the 3D images of the molded lenses reveal a slight elongation in the vertical dimension, with an increase of approximately 2-3% in the initial height. This elongation appears to be compensated by a slight reduction in the lens diameter, suggesting that the PDMS is undergoing structural relaxation. This deformation is likely a result of intrinsic stresses within the PDMS material, which arise during the curing process and subsequently cause the molded structures to relax into a slightly different shape. Additionally, this size change could also be attributed to the transition from a liquid to a solid state during the curing process, as the material undergoes volumetric shrinkage or rearrangement when solidifying.

To better understand and mitigate this relaxation, a mold should be designed in the future to specifically quantify these changes and minimize the effects of intrinsic stresses, ensuring more accurate replication of the intended dimensions.

5.2 PDMS residues

The molding process faces certain limitations when handling small and rough features, as these surfaces often promote the retention of PDMS residues. This is evident from the presence of fluorescent dots observed under fluorescence microscopy in figure 11, indicating areas where PDMS remains after the molding process. These residues can compromise the quality and fidelity of the molded structures, particularly in applications requiring high precision and cleanliness. One potential solution to this issue is the application of a monolayer coating on the mold surface, which can decrease the adherence of PDMS and reduce the likelihood of residue formation, thereby enhancing the accuracy and quality of the replication process.

5.3 Monolayer coating

The initial attempt to create a monolayer coating on the mold surface was not successful, or at least could not be definitively proven. The only method available to verify the presence of the monolayer was to scratch the coated sample and examine it using a Digital Holographic Microscope (DHM). However, this approach posed a challenge, as scratching could damage both the nanometer-thick monolayer and the underlying glass substrate, making it difficult to determine if the monolayer was actually formed. Given that only one test was performed, no conclusions can be drawn about the various steps involved in the monolayer creation process, as there is insufficient data to assess whether each step was executed correctly or contributed to the coating's formation.

6 Conclusion

This study demonstrates the challenges and limitations of PDMS molding for replicating micro and nanostructures inscribed in glass using a femtosecond laser. The findings indicate that intrinsic stresses in the PDMS can cause structural relaxation, resulting in dimensional changes in the molded structures. Additionally, the detection of PDMS residues on rough and small-scale features suggests a need for improved surface treatments or process modifications. Although the initial attempt to create a monolayer coating to reduce adhesion was inconclusive, further research with refined techniques may provide more definitive results. Overall, this work highlights the need for continued optimization of the molding process to enhance accuracy and fidelity in the replication of intricate glass microstructures. Future efforts should focus on developing more effective methods to control PDMS behavior and minimize residue formation to achieve reliable, high-quality moldings.

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A Annex A: Molding recipe

- Prepare a pool in which your sample fits
  - ▷ 5mm thick plexiglass can be used for 1mm or less thick samples
- Mix your PDMS base and the curing agent with a glass rod until you get a lot of bubbles
  - ▷ Choose the percentage of curing agent you want (usually between 10% and 15%); it was empirically proven by testing different ratios that the less curing agent you use (10%), the more elastic your final elastomer will be
- Cover completely your sample by filling 3/4 of your pool with the mix obtained in the previous step
- Vacuum until the air bubbles completely disappear
- Put in the oven at 90 degrees for at least 2 hours
- Leave at room temperature for 2 hours minimum before unmolding