Perfluoropolyether Intermediate Molds for Thermal Nanoimprint Lithography.

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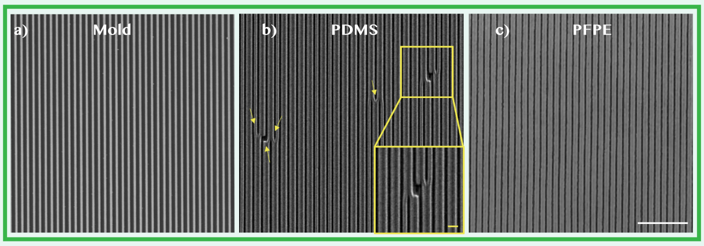
Abstract

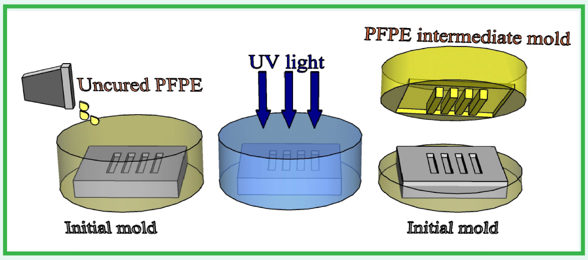
Among soft lithography techniques, Thermal Nanoimprint Lithography (**NIL**) is a high-throughput and low-cost process that can be applied to a broad range of thermoplastic materials. Usually, high-resolution and large-area NIL molds are difficult to fabricate and they are typically made of silicon or other hard materials for preserving their functionality [1] . Nonetheless, after a small number of imprinting cycles, they undergo degradation and become unusable. Our aim is to replace standard molds with elastomeric ones, which are generally very fast and easy to fabricate by using UV crosslinking or soft lithography processes. We introduce and characterize an innovative two-step NIL process based on the use of a perfluoropolyether (**PFPE**) intermediate mold to replicate sub-100 nm features from a silicon mold to thefinal thermoplastic material. We compare PFPE elastomeric molds with molds made of the standard polydimethylsiloxane(PDMS) elastomer, which demonstrates better resolution and fidelity of the replica process. By using PFPE intermediate molds, the nanostructured masters are preserved and the throughputof the process is significantly enhanced [2].

Step 1: PFPE intermediate mold fabrication and characterization.

We compared PFPE and PDMS using features of several hundreds of nm in close proximity and with high spatial density, which are challenging to be replicated over large areas in elastomeric materials.



Scanning electron microscope representative images of (**a**) the 600 nm-periodic nano-grating initial mold (duty cicle: 50%, depth: 300nm), (**b**) the PDMS replica, and (**c**) the PFPE replica. Scale bar: 5 μm. Yellow arrows highlight the presence of defects in the PDMS replica. Inset of (b) zoomed image of a representative area with defects, scale bar = 1 μm.



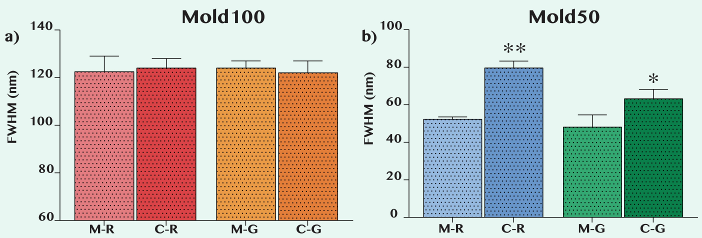
Schematic illustration of PFPE intermediate mold fabrication process.

PFPE resin was mixed with 3% w/w photoinitiator, poured on top of the mold surfaces, and crosslinked by UV light (356nm, 25 mW cm^{-2}). The samples were kept for 180 s in nitrogen atmosphere and then were kept for 60 s in air [3].

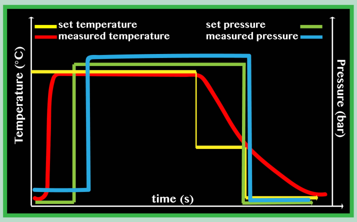
Even if PDMS could not successfully replicate nanograting profiles, PFPE replica shows perfect nanostructures over cm² areas without damages.

Step 2: Cyclic Olefin Copolymer (COC) Thermal NIL via PFPE Intermediate Molds.

We fabricated two types of arrays of isolated ridges and grooves: **Mold100**, with a nominal linewidth of **100 nm, aspect ratio (height/depth over width)=2** and **Mold50**, with a nominal linewidth of **50 nm aspect ratio=1**. This nanofeatures were transferred on COC by the use of PFPE intermediate mold.

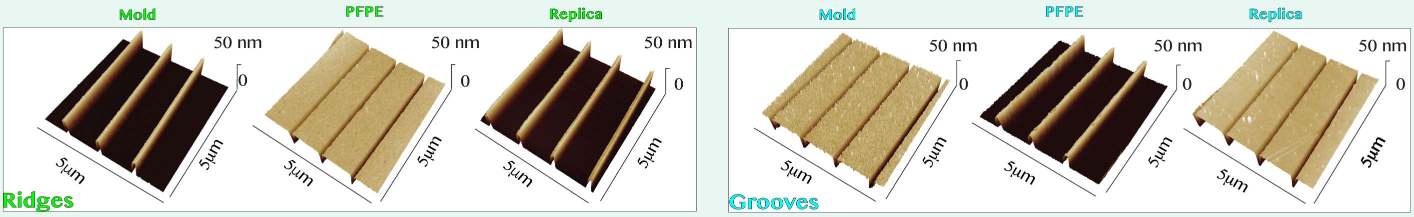


Atomic force microscopy measurements **Mold100**, **Mold50**, PFPE intermediate molds and COC final replicas. (**a**) FWHM of Mold100 ridges (**M-R**) and grooves (**M-G**), and respective COC replica ridges (**C-R**) and grooves (**C-G**). (**b**) FWHM of Mold50 ridges (**M-R**) and grooves (M-G) and respective COC replica ridges (C-R) and grooves (C-G). Data in a) and b) are mean ±SD, */**P < 0.05/0.01, unpaired t-test.



The thermal NIL fabrication principle is based on a nanopatterned mold employed to deform a thermoplastic polymer under controlled pressure and temperature.

COC process parameters
$T_{imprint}$ =150 °C (Tg_{COC} = 134 °C),
t = 300 s, P = 50 bar,
$T_{cool-down}$ = 80°C



Representative 3D AFM images for ridges and grooves of the **Mold100**, PFPE intermediate mold, and COC final replica.

PFPE intermediate mold allows to replicate nanofeatures of 100nm-width with high fidelity, while for sub-100nm the transfer process is impaired.

Conclusions

Mold ridges (**M-R**) and mold grooves (**M-G**) had similar FWHM values, demonstrating that process can successfully transfer isolated features with lateral dimension of the order of 100nm and aspect ratio=2. Sub-100 nm topographies as lines of lateral dimension of **80 nm (for ridges)** and **60 nm (for grooves)** and with an aspect ratio=1 can be considered as the **minimum feature size** allowed by our two-step replica process.

References
[1] Dell'Anna*, Masciullo* et al. 2017 RSC Advances "Multiscale structured germanium nanoripples as templates for bioactive surfaces."
[2] Masciullo et al. 2017 Nanoscale "Hierarchical thermoplastic rippled nanostructures regulate Schwann cell adhesion, morphology and spatial organization."
[3] Masciullo et al 2018 Nanomaterials "Perfluoropolyether (PFPE) Intermediate Molds for High-Resolution Thermal Nanoimprint Lithography."