

**High-Resolution Soft Lithography: Enabling Materials for Nanotechnologies\*\***

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The availability of commercially viable nanofabrication processes is key to realizing the potential of nanotechnologies, especially in the fields of photonics, electronics, and proteomics. The imprint lithographic (IL) technique is a case in point, an alternative to photolithography for manufacturing integrated circuits, nanofluidic and other devices with sub-100-nm features. However, it is becoming increasingly clear that new materials are needed to advance IL methods to their putative limits.<sup>[1-5]</sup> We recently reported the fabrication of organic-solvent resistant, microfluidic devices with features on the order of hundreds of microns made from photocurable perfluoropolyethers (PFPEs).<sup>[6]</sup> PFPE-based materials are liquids at room temperature and can be photochemically cross-linked to yield highly fluorinated, solvent resistant, chemically robust, durable, elastomers with a modulus of 4.0 MPa. Herein we report the successful use of PFPE-based materials in high-resolution imprint lithography.

Imprint lithography can be roughly broken into two areas: 1) so-called soft lithographic techniques,<sup>[1]</sup> such as solvent-assisted micro-molding (SAMIM), micro-molding in capillaries (MIMIC), and microcontact printing (MCP), and 2) rigid imprint techniques, such as nanocontact molding (NCM),<sup>[7]</sup> “step and flash” imprint lithography (S-FIL),<sup>[5]</sup> and nanoimprint lithography (NIL).<sup>[8]</sup> Polydimethylsiloxane (PDMS)

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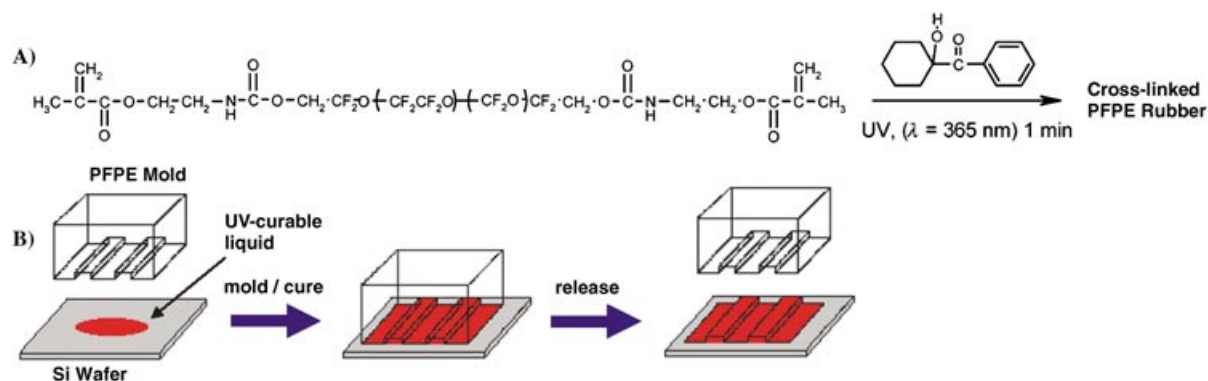
based networks have served as the material of choice for much of the work in soft lithography.<sup>[9,10]</sup> The use of soft, elastomeric materials, such as PDMS, offers numerous attractive properties in several lithographic techniques. PDMS is highly UV-transparent and has a very low Young's modulus which gives it the flexibility required for conformal contact, even over surface irregularities, without the risk of cracking.<sup>[11]</sup> Furthermore, flexibility in molds facilitates release from masters and replicates without cracking and allows the mold to endure multiple imprinting steps without damaging fragile features. While PDMS offers some advantages, there are a number of properties inherent to PDMS which severely limit its capabilities in soft lithography. First, PDMS-based elastomers swell significantly when exposed to most oil-soluble organic compounds.<sup>[12]</sup> With the exception of MCP,<sup>[1]</sup> resistance to swelling is critically important in nearly all soft lithographic techniques where a mold is brought into contact with a small amount of curable organic monomer or resin. Second, the surface energy of PDMS ( $\approx 22\text{--}25\text{ mN m}^{-1}$ ) is not low enough for procedures which require high fidelity. Thus, the patterned surface of PDMS-based molds is often fluorinated using a plasma treatment followed by vapor deposition of a fluoroalkyl trichlorosilane.<sup>[1]</sup> Third, the most commonly used commercially available form of the material (Dow Corning's Sylgard 184) has a modulus that is too low ( $\approx 1.5\text{ MPa}$ ) for many applications which results in collapse of features. Although elegant solutions to address this last problem have been developed,<sup>[13,14]</sup> the materials chosen still exhibit poor solvent resistance and require fluorination steps to allow for mold release.

Rigid materials, such as quartz glass and silicon, have also been utilized in imprint lithography.<sup>[1,3,5,7,8,15–23]</sup> Such materials are superior to PDMS in modulus and swelling resistance but lack flexibility and therefore conformal contact with the substrate. Another major drawback of such materials is the direct use of a valuable and difficult to fabricate hard mold which is typically made by using conventional photolithography or e-beam lithography.<sup>[7]</sup> Carter and co-workers<sup>[20]</sup> and Resnick et al.<sup>[21]</sup> have eliminated the requirement to repeatedly use expensive quartz glass or silicon molds in NCM processes by utilizing an acrylate-based mold generated from casting a photopolymerizable monomer mixture against a silicon master.<sup>[7]</sup> Despite such advances, there are other

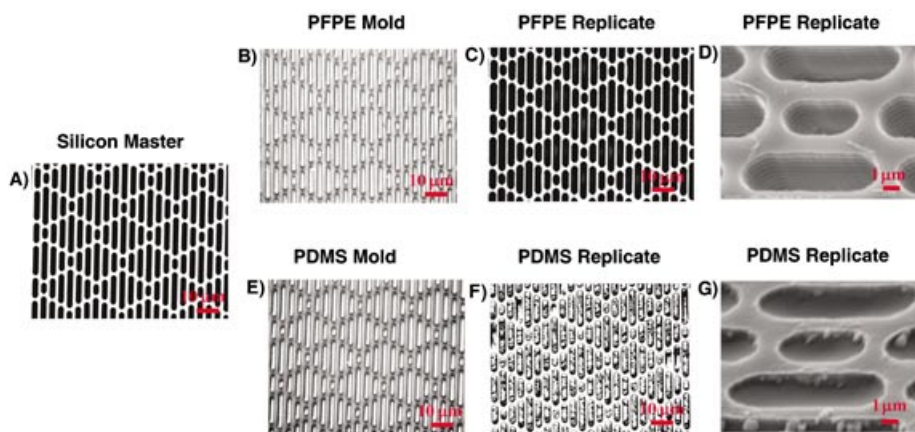
serious disadvantages of rigid materials used as molds which include the necessity to use fluorination steps, or thermoformed rigid fluoropolymers themselves<sup>[24]</sup> to lower the surface energy of the mold<sup>[3]</sup> and the inherent problem of releasing a rigid mold from a rigid substrate without breaking or damaging it.<sup>[3,10]</sup>

The photochemically curable fluoropolymer that we utilize herein is a  $\alpha,\omega$ -methacryloxy functionalized PFPE (PFPE-DMA) (Figure 1).<sup>[6]</sup> We have previously reported the synthesis of novel functionalized PFPEs.<sup>[24]</sup> However, herein we treated a commercially available hydroxy-terminated PFPE (Solvay Solexis,  $M_n = 3800\text{ g mol}^{-1}$ ) with isocyanato ethyl methacrylate (Aldrich) to yield a methacryloxy-functionalized polymer which is a pourable liquid of low viscosity (0.36 Pa s) at room temperature. A photoinitiator, 1-hydroxycyclohexyl phenyl ketone (1 wt %, Aldrich), was dissolved into the PFPE-DMA to make a photocurable liquid resin. A thermally curable polydimethylsiloxane-based material, Sylgard 184, (Dow Corning) was used for comparative controls.

Swelling is a commonplace issue with PDMS based molds since most organic liquids will swell PDMS, and it is organic liquids that are the materials most desirable to mold. To demonstrate the utility of a fluoroelastomer-based material in imprint lithography, we first generated replica molds made from both PDMS as well as from PFPE-DMA and used these to micromold an organic photopolymer resin, trimethylpropane triacrylate (TMPTA).<sup>[26]</sup> A patterned silicon-wafer master was used which had features with a width of  $2\text{ }\mu\text{m}$ , a depth of  $5\text{ }\mu\text{m}$ , and a spacing of  $2\text{ }\mu\text{m}$  (Figure 2A). The fluoroelastomer-based mold was made by pouring an approximately 1 mm thick liquid film of PFPE-DMA, which contained photoinitiator, onto the clean, patterned silicon wafer master. The material was then subjected to UV light ( $\lambda = 365\text{ nm}$ ,  $35\text{ mW cm}^{-2}$ ) for 1 min under a nitrogen purge. After curing, the approximately 1 mm thick mold was easily peeled from the master without employing a surface fluorination step. In an analogous fashion, PDMS molds were generated by first mixing the Sylgard 184 precursors (10:1 base:curing agent) and degassing under vacuum. An approximately 1 mm thick layer of the PDMS-based material was then poured onto the same clean, patterned silicon wafer master and was placed in a vacuum oven at  $80\text{ }^\circ\text{C}$  for about 15 h. For the PDMS molds, a vapor-deposition pretreatment



**Figure 1.** A) Formula of the UV curable PFPE liquid precursor used to generate high resolution stamps. B) Schematic representation of the imprint lithography process. First, a small drop of UV-curable liquid is placed on a silicon wafer. A patterned mold is then brought into contact with the drop and pressure is applied during UV exposure. The mold is then peeled from the wafer leaving the cured resin in the desired pattern.



**Figure 2.** Images of a silicon master with 2- $\mu\text{m}$  features (A), PFPE and PDMS molds made from this master (B, E), and replicate molds of TMPTA using the corresponding stamps (C, D, F, G). While both elastomers produced molds of high quality, the TMPTA replicate made with the PDMS mold contains residual PDMS that was ripped from the mold presumably because of adhesion (F, G). In contrast, the low surface-energy PFPE mold was easily released from the TMPTA replicate (D). The sub-micron striated features on the replicate in (D) are present on the silicon master and are a result of multiple etching steps used during its fabrication.

to the patterned silicon wafer using trichloro(1H,1H,2H,2H-perfluorooctyl) silane was applied to allow release of the mold. Replica molds of high quality with good feature fidelity were generated from both the PFPE-based elastomer (Figure 2B) as well as the PDMS-based elastomer (Figure 2E) when the feature sizes were this large.

Once both of the elastomeric molds were generated, they were each independently brought into contact with a small drop ( $\approx 2$  mm in diameter) of the uncured TMPTA which was first placed on a flat, unpatterned silicon wafer as illustrated in Figure 1B. A fixed pressure was exerted on the mold with a modified Instron to ensure conformal contact. UV light was then passed through the back of each mold for 1 min to fully cure the TMPTA while in contact with the mold. Each mold was then peeled from the wafer revealing the patterned TMPTA replicate.

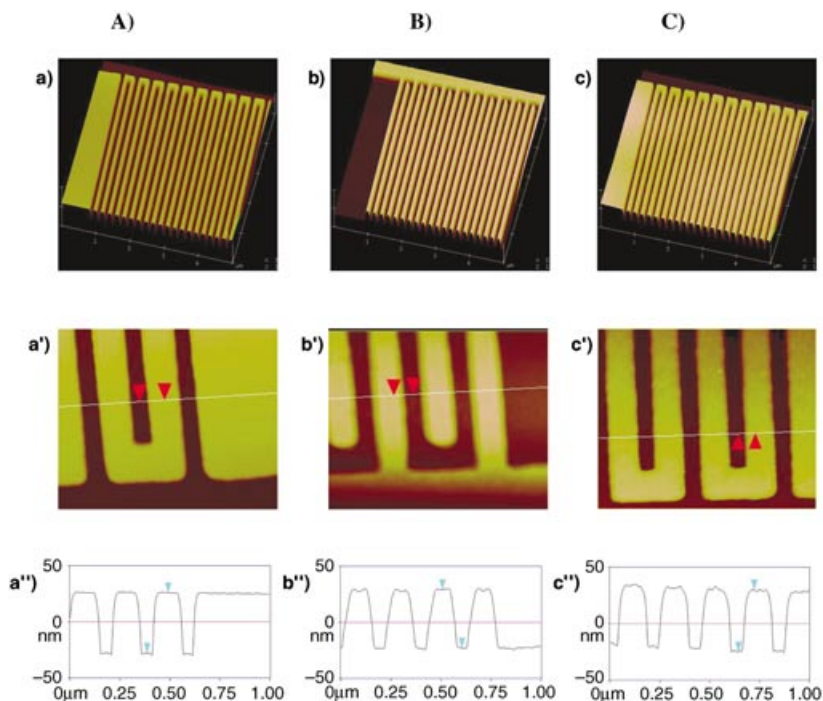
The TMPTA replicates generated from the PDMS molds were of very poor quality. SEM images (Figure 2F and G) of these replicates reveal pieces of the PDMS mold that were ripped out during the release as a result of swelling of the PDMS mold by the TMPTA prior to curing. In contrast, those replicates made from the PFPE-based mold look identical to the master with no tear out (Figure 2C and G) because it is not swollen by the organic-soluble TMPTA photopolymer resin. Additionally, the PFPE-based mold was extremely easy to peel away from the micromolded TMPTA, presumably because of the extremely low surface energy of the PFPE-based mold<sup>[24]</sup> and its elastomeric nature. The intrinsically oleophobic nature of this fluoropolymer-based mold material enables for the first time

imprint lithographic applications of commonplace organics using soft elastomeric mold materials.

In addition to the intrinsic swelling problems illustrated above for PDMS-based materials, previous attempts to perform 1:1 sub 1-micron patterning using PDMS-based elastomers, such as Sylgard 184, does not give replicas of high fidelity. Indeed, accurate replication of patterns using molds of features less than 1-micron in size with PDMS-based elastomers has had only limited success<sup>[1,4,10]</sup> even when using elaborate pre-treatment methods to reduce the interfacial adhesion between the object being molded and the PDMS-based replica.

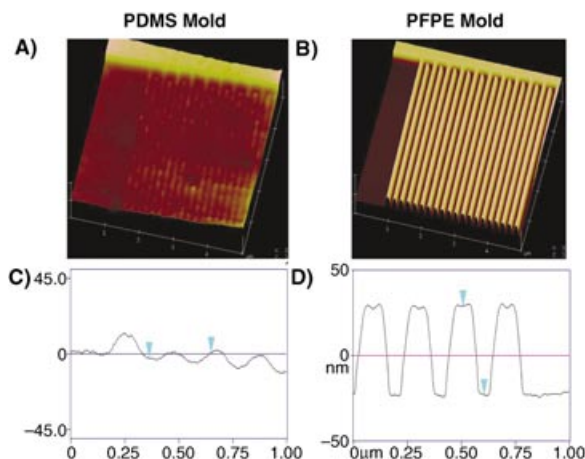
To test the viability of PFPE-based elastomers to perform accurate nanometer-scale molding we chose to fabricate replica molds from a patterned silicon-wafer master with features having a width

of 140 nm, a depth of approximately 50 nm, and a separation of 70 nm (Figure 3A). We found we could cast excellent molds using the PFPE-based fluoroelastomer materials with exact preservation of the nanoscale features of the patterned silicon-wafer master (Figure 3B). The features on the PFPE-based mold had an average height of 51 nm which was in excellent agreement with a measured height of 54 nm for the features in the silicon master. The widths of the features on the PFPE-based molds seem to vary from the top of the



**Figure 3.** High-resolution AFM images of A) a silicon master with lines of 140 nm width separated by 70 nm (a, a'), B) PFPE mold with 70-nm wide lines separated by 140 nm (b, b'), C) replicate made with PFPE mold with 140-nm wide lines separated by 70 nm (c, c'). Beneath each picture is a representative height profile (a'', b'', c'').

channel through to the bottom (Figure 3B). This is presumably due to some slight relaxation of the polymeric material upon release of its confinement from the patterned silicon wafer master. In contrast, attempts to fabricate PDMS-based molds from the same silicon master failed (Figure 4). The features on the PDMS molds are irregular, rounded, and only 5–10 nm in height.



**Figure 4.** High-resolution AFM image of a PDMS mold (A) and a PFPE mold (B) generated from the silicon master shown in Figure 3. Representative height profiles are shown underneath the respective images (C, D).

The ability of these soft elastomeric replica molds to be useful in the patterning of nanoscale features using NCM imprint lithographic techniques was explored (see Figure 3). The high-fidelity PFPE-based molds having 70-nm wide lines separated by 140-nm spaces (see Figure 3B) were used to contact mold the TMPTA photopolymer resin in a manner identical to that used above for imprinting micron-sized features. Remarkably, when using between 5 and 25 psi of pressure on the PFPE-based mold, we were able to easily imprint a drop of TMPTA photopolymer resin to generate patterns (Figure 3C) having nanometer-sized features that looked identical to the original patterned silicon wafer master (Figure 3A). In addition, the PFPE-based mold was easy to peel off of the nano-molded TMPTA replicates presumably because of the flexibility and low surface-energy of the PFPE-based elastomer and its oleophobic nature which prevented adsorption of the TMPTA into the mold. When using quartz molds, such release processes can take from tens of seconds to minutes and requires large separation forces that often result in delamination failures.

In summary, we have demonstrated the capabilities of PFPE-based elastomers to be used as ideal materials for advanced, high-performance imprint lithographic applications. Such highly fluorinated materials enable both soft lithographic techniques as well as more demanding sub-micron imprint techniques. They are easily fabricated, have the ability to make conformal contact, have a remarkably low surface energy, are resistant to swelling by small organic molecules, and endure multiple printing procedures. We have shown that while replica molds with 2- $\mu\text{m}$  features can be

generated from both PFPE-based and PDMS-based elastomers, only the PFPE-based materials could be used as molds to imprint and mold desirable organic-soluble materials because of the intrinsically oleophobic nature of such highly fluorinated materials. Furthermore, these PFPE-based materials were able to replicate sub-100-nm sized features with no indications of limits to going to even smaller in size. In addition, the low surface energy of the PFPE-based materials allows for unprecedented ease of release from both silicon masters as well as from patterned replicates-without the need for complex surface functionalization-making it good material to use in the routine fabrication of nanometer-scale structures and devices.

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