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High Resolution Nanoimprinting with a Robust and Reusable Polymer Mold**

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High temperature nanoimprinting of viscous polymers which are glassy at room temperature is usually performed using brittle and expensive molds made of inorganic materials. As a replacement, soft molds made of plastics or elastomers have been used because of their low cost and ease of fabrication. However, the deformation of polymer molds under pressure remains a major issue which limits their resolution in high temperature nanoimprinting. Moreover, the replicated structures are often broken or lack definition due to sticking of the embossed polymer to the mold. We report a method for imprinting fine, densely packed nanostructures down to 12 nm into a wide range of technologically important polymers using a flexible and robust mold made from ethylene(tetrafluoroethylene) (ETFE). The high resolution achieved is due to the mold's mechanical stability and resistance to distortion at high pressures and high temperatures. The flexibility and low surface energy of ETFE provide a clean mold release without fracture or deformation of the embossed structures. Multiple imprinting and patterning on large areas is also made possible because of the good conformal contact and low-adhesion of the ETFE mold. Finally, this simple and inexpensive method allows reproduction of the stamps from one single master, thus providing an economical alternative to expensive and brittle inorganic materials.

1. Introduction

Imprint lithography techniques, such as nanoimprint lithography (NIL) or hot-embossing are a successful alternative to traditional optical lithography to produce micro- and nanostructures in a polymer film.[1,2] In NIL, the reproduction of the structures into a plastic material is performed by heating the polymer above its glass transition temperature (T_g) and applying a pressure to emboss (or imprint) patterns from a structured mold. Photodetectors, compact disks, magnetic disks and microfluidic channels have been successfully fabricated by NIL.[3–8] The accuracy of replication depends largely on the properties of the mold (or stamp) which needs to be mechanically, chemically, and thermally stable to resist pressures of several tens of bar at temperatures above 170 °C. Molds are often produced from silicon, fused silica (quartz) or nickel, materials in which small features can be obtained by well-established methods such as optical lithography, etching and electrodeposition processes. However, the processing of inorganic stamps requires large infrastructures and remains expensive. The need for an economical and reliable replication method is an incentive to find a replacement for silicon and other inorganic materials. Moreover, several technological applications demand ever smaller structures with a size approaching 10 nm. The mold therefore needs to provide a high accuracy of reproduction. While inorganic molds possess the mechanical stability necessary to imprint small patterns down to ~10 nm,[9] they also present a number of problems inherent to their physical properties, which limit their efficiency in imprint techniques. Because of their stiffness they tend to break easily when a pressure is applied and when they are separated from the substrate (Fig. 1a). Another drawback is that they often adhere to the polymer during embossing, resulting in the fracture of the polymer structures during demolding. To remedy this problem an anti-adhesive layer needs to be deposited onto the mold to lower its surface energy. However, the durability of these coatings is one factor that limits their efficiency.[10] A hydrophobic chlorinated-fluoroalkymethylsiloxane silicone coating deposited on quartz was shown to loose its anti-adhesive properties after several embossing steps as measured by the decrease in its water contact angle.[11] Both plasma deposited and ion sputtered Teflon layers have been shown to degrade during NIL.[12] Coatings obtained by silanization in the liquid or vapour phase also become less effective after a few imprints, which leads to

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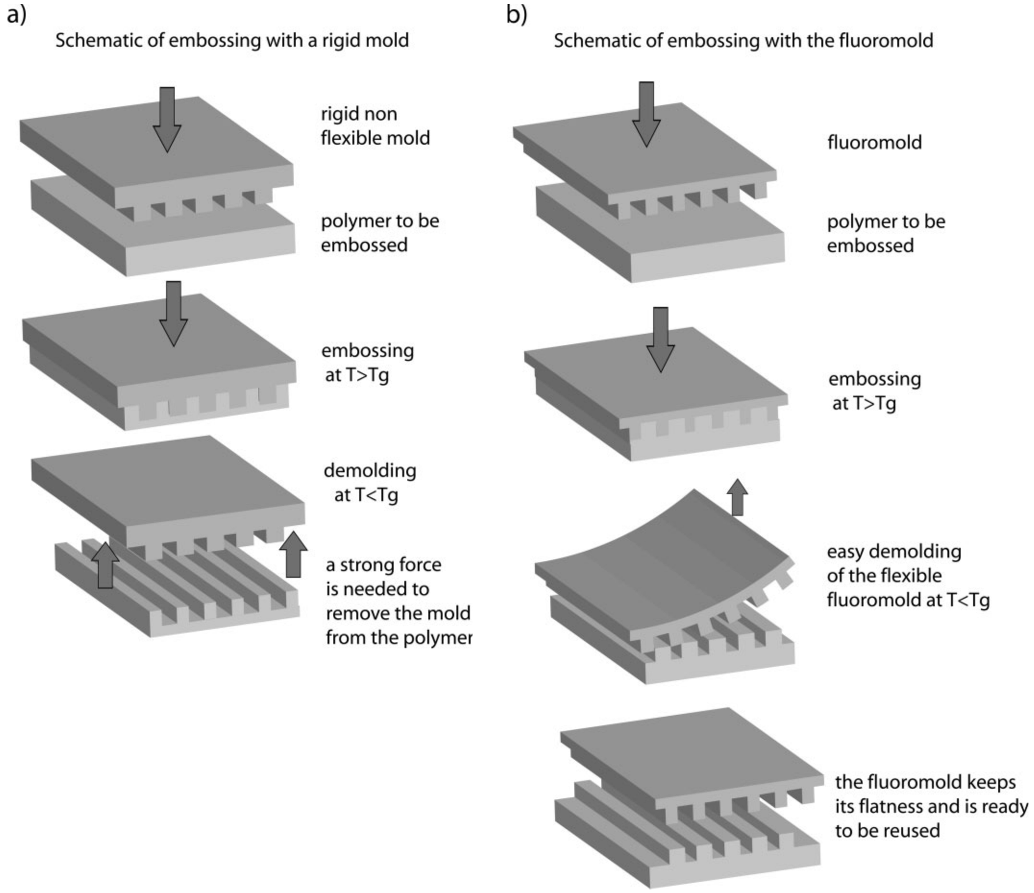

Figure 1. a) Schematic diagram of embossing using a rigid mold. The polymer and the structured rigid mold are heated above T_g while a pressure is applied to ensure flow of the polymer and to fill the cavities of the mold. Upon cooling below T_g, the entire surface of the mold in contact with the polymer must be separated at once. The relatively strong force required often leads to breaking of the stiff mold. b) Schematic diagram of embossing with a flexible fluoromold. During cooling and demolding, the fluoromold is bent and gradually separated from the substrate using only a low force since it doesn't adhere to the polymer. The fluoromold does not break or deform, and can therefore be reused several times.

adhesion of the polymer to the mold. X-ray Photoelectron Spectroscopy (XPS) measurements showed a 10 at % decrease in the fluorine concentration of silanized silicon stamps (with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane in vapor phase) after embossing once into nylon 6,6 at 160 °C.[13] The same result was found after embossing once at 170 °C into Poly(ethylene theraphthalate) (PET). Approximately 2 at % of fluorine were detected on both PET and nylon 6,6 after embossing, whereas no fluorine was detected before embossing.[13] Finally, the large difference in thermal expansion between a stiff inorganic mold and the polymer is another cause of deformation and fracture of the embossed structures during cooling and demolding. This is especially true when imprinting large aspect ratio features into thick films or into polymer sheets. A mold made from a polymeric material that is flexible and which has a low surface energy would reduce the high production cost of inorganic stamps and solve the problems of adhesion and fracture. Because it is less rigid, a flexible mold provides a better conformal contact with the substrate during imprinting. Moreover, once cooled down, it can be released more easily than a rigid stamp because it can be bent and gradually separated from the substrate.

To date a large number of soft and flexible molds have been used in imprinting techniques. However, their use is usually limited to imprint low viscosity polymers at room temperature and at low pressures. A slight increase in pressure results in the distortion of the mold and in the deformation of the patterns on its surface. For this reason, soft stamps suffer from a much lower resolution than that achieved by inorganic stamps in pressure assisted imprinting. Examples of materials used to make soft molds include a range of elastomeric materials such as poly(dimethylsiloxane) PDMS,[14–18] an ester type UV-curable prepolymer,[19] a fluorinated organic-inorganic hybrid sol-gel resin,[20] a photocurable perfluoropolyether (PFPE),[21] and the amorphous fluoropolymer Teflon AF.[22,23] Elastomers have a low elastic modulus (~2 to 4 MPa for PDMS) which causes them to deform when a pressure is applied. This limits the resolution of the replication process to ~100 nm. Low aspect ratios (<0.3), shallow structures and dense patterns are not stable and tend to collapse.[18,21,24–26] Stiffer polymers with superior mechanical properties are therefore required for a higher fidelity of pattern reproduction.[27,28] While low viscosity UV curing polymers can be imprinted at room temperature and at low pressure, patterning of higher viscosity thermoplastics often requires elevated temperatures and higher pressures. This is due to the fact that the resistance to flow increases with the viscosity of the polymer, and high temperature embossing provides a way to lower the viscosity. Moreover, it has been shown that the filling of the mold cavities is slowed down for high aspect ratio structures, as well as for small cavities where free flow is restricted.[29] Therefore, increasing the pressure facilitates filling of the mold cavities during NIL, and helps ensure full patterning.

Due to their high stiffness, high temperature resistance and unique anti-adhesive properties, fluorinated polymers are an obvious choice as a replacement for soft plastic molds and brittle inorganic materials. Until today, molds made of a fluoropolymer have been used only for low pressure imprinting of low viscosity photocurable polymers, and polymers mixed in a solvent at room temperature.[21,22] Khang et al. used a highly porous Teflon AF mold to reproduce ~80 nm patterns from a liquid solution at room temperature and at low pressure.[22] The high porosity of the mold, which is inherent to their method of production, is not desirable for fine nanopatterning and tends to lower the mechanical stability and strength of the mold. One attempt to imprint a polystyrene (PS) film at a higher temperature was performed with a solvent cast Teflon AF mold by a low pressure NIL process.[23] This approach also showed limitations due to the fragility of the mold, with stamps less than ~50 µm thick being prone to breakage during mold release. The mechanical properties of the mold were found to be dependent on its thickness, and imprinting with the Teflon AF mold was done only at low pressures (~2–3 bar) with a resolution limited to ~100 nm.

In order to provide a viable alternative to inorganic materials and to achieve high-resolution NIL with replication sizes close to 10 nm, the polymer mold needs to have a high mechanical stability and a high enough stiffness to prevent the pattern deformation or collapse encountered with soft elastomers. Good conformal contact with the surface of the substrate is also necessary to obtain a uniform and well-defined reproduction of small patterns. Sufficient pressure is therefore required to oppose the rigidity of the mold and to ensure an intimate contact with the substrate. However, increasing the pressure often leads to distortion and fracture of the stamp. This can be remedied using a tough material to prevent brittle failure. Therefore, a balance between stiffness, flexibility, and toughness is essential to allow a reproducible conformal contact, and to prevent deformation of the mold for high resolution patterning of small nanostructures.[30] In this paper, we demonstrate that molds made of ETFE effectively solve the problem of the low mechanical resistance often encountered with plastic stamps during NIL. These new molds also provide a high fidelity of reproduction with the added benefits of low-adhesion, flexibility and high temperature stability.

2. Results

Since most fluoropolymers are inert to virtually all solvents except a few perfluorokerosenes and perfluorinated oils, a thick and mechanically resistant layer of fluoropolymer cannot be easily prepared from a solution.[31,32] Instead, the present molds were produced by embossing of 100–200 µm thick ETFE sheets into a patterned silicon or quartz master. The fluoropolymer ETFE, which is a copolymer of ethylene and tetrafluoroethylene, possesses an exceptional toughness and flexibility, and a relatively high stiffness (elastic modulus ~1 GPa). In addition, ETFE also has a high melting point in the range of 255–280 °C, which confers the mold a high thermal stability.[33] The masters were processed by traditional lithography and etching, which yield a high definition of structures on the surface of the mold. The patterned ETFE sheet was then used as the mold to imprint a polymer substrate. The materials used for imprinting were either a thin polymer film deposited onto a rigid substrate (e.g., a silicon wafer), or a thicker free standing polymer sheet. Schematic drawings of the embossing process using the ETFE mold are shown in Figure 1b.

2.1. High Resolution Nanoimprinting of Sub-20-nm Features

Figure 2 shows the reproduction of dots and lines with feature sizes less than 20 nm into a ~100 nm thick polystyrene film of molecular weight 70 000 g mol^{-1}. The film was spin-coated onto a silicon substrate, heated to 170 °C, and embossed with an ETFE stamp for 200 seconds. The pressure was supplied from a compressed air system which uniformly applies an hydrostatic pressure on the back side of the stamp. The reported pressures are the effective pressures at the beginning of embossing, calculated from the actual surface of the stamp in contact with the substrate. The effective pressure is highest at the beginning of imprinting, decreasing to its lowest value when the entire surface of the mold is in contact with the embossed polymer. Due to the difference in area coverage of the various structures shown in Figure 2, the effective pressure was ~12.5 bar for the 70 nm dots, 24 bar for the ~45–50 nm dots and ~32.5 bar for the lines with feature sizes of ~14 nm. Once the patterns were fully formed, the pressure decreased to 6.5 bar for the lines and the 70 nm dots, and to 15.5 bar for the 45–50 nm dots. The size of the structures was similar to that on the original silicon master as measured by SEM (see Fig. 2c and d which show the structures imprinted into PMMA and the original structures on the silicon master). The 70 nm dots which form a very dense array with a period of ~90 nm (Fig. 2b) were also well defined. Remarkably, the walls of the ETFE mold which are as thin as ~12–18 nm, are strong enough to resist the pressure applied at high temperatures, forcing the polymer material to flow into the mold structures. No sticking of the polymer to the stamp was found and demolding of the structures was very easy and clean because of the flexibility of ETFE.

2.2. Imprinting of Microstructures

A variety of micron-size structures were imprinted into commercially available ~2 mm thick sheets of poly(methylmetacrylate) PMMA in the temperature range 135–160 °C. Because we wanted to investigate the effect of low pressures, a sample was heated on a heating plate and a low pressure of ~1 bar was

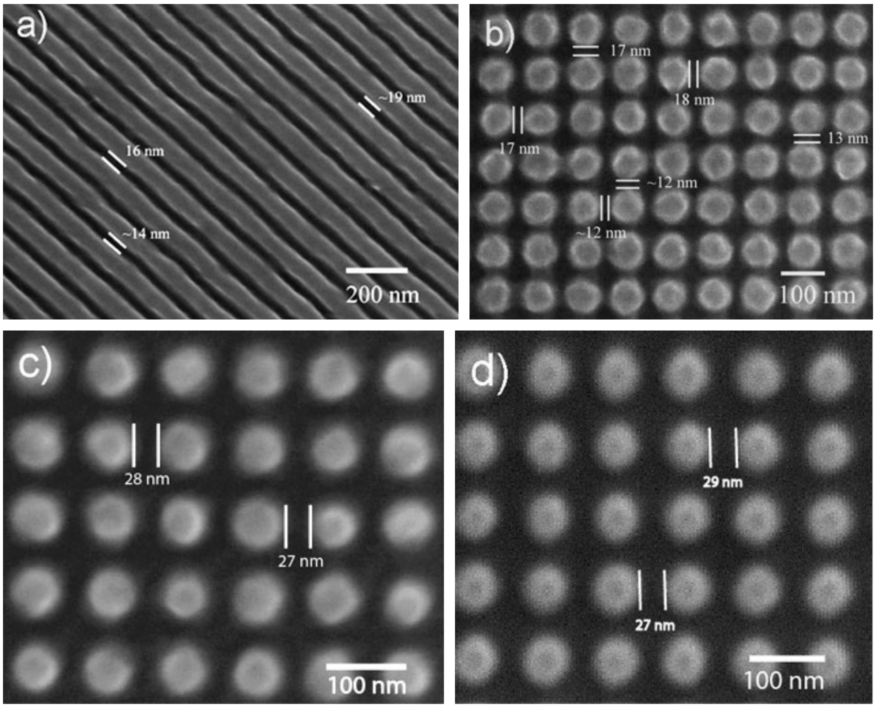

Figure 2. Scanning electron microscopy (SEM) images of fine structures embossed from an ETFE fluoromold. a) Channels as small as ~14 nm imprinted into PS at a pressure of 32.5 bar; b) densely packed ~70-nm pillars with a period of ~90 nm imprinted into PS at a pressure of 12.5 bar, showing a ~12 nm inter-pillar spacing. c) ~45–50 nm dots with a spacing of ~25 nm imprinted into PS at 24 bar; d) array of ~45–50 nm dots on the silicon master used to produce the ETFE mold that served to imprint the dots shown in (c).

applied from a small home-made mechanical press. Figure 3a and b show an example of 700 nm wide lines (with a 2 μm period and a height of 160 nm) imprinted into PMMA at 160 °C and 1 bar. The size of the structures was identical to that of the original master, as verified by SEM and Atomic Force Microscopy (AFM). Further experiments were performed with a higher pressure, which was applied from the hydrostatic press described in Section 2.1. Excellent replication of ~4 μm wide pillars was also achieved by imprinting into PMMA at 145 °C at various pressures. Figure 3c shows pillars that were obtained at 44 bar with a mold that was previously used 5 times. Again the replication is identical to the structures of the original master, and the tops of the pillars are flat which shows full polymer filling of the mold's cavities during embossing. Imprinting with the ETFE fluoromold was also performed at a pressure of ~17 bar into a ~1 mm thick carbon reinforced high density polyethylene (CRHDPE) sheet at 140 °C, and into a ~3 μm thick film of Teflon AF 1600 spin-coated onto a silicon substrate at ~175 °C. In both cases, the structures were very well defined and identical to that of the stamp. The embossed structures in Teflon AF are shown in Figure 3e, and the ETFE mold used to imprint the structures is shown in Figure 3f. The ETFE mold showed no deformation after embossing, which suggests that ETFE has superior mechanical properties compared to Teflon AF in pressure assisted imprinting at high temperatures.

Clearly, the ETFE fluoromold retains enough strength and stiffness for embossing of a large range of polymers, including Teflon AF, at temperatures up to at least 175 °C. Finally, to further test the versatility of ETFE molds for NIL, we imprinted 11 μm wide pillars into PMMA at 135 °C and 4.7 bar for 5 minutes. Figure 3d shows the resulting holes. The structures were very well defined on the entire embossed area, including near the edges of the sample. Imprinting large micron-scale features is often challenging because a large amount of material has to be displaced over a relatively large distance. Therefore, the mold has to resist distortion and deformation during the replication process. After imprinting, the pillars on the mold were intact and no deformation of the mold was observed. The depth of the holes, as measured by a scanning electron microscope (SEM) cross-section (not shown here) was identical to the height of the pillars on the surface of the mold (~11.5 μm).

2.3. Multiple Embossing and Large Area Imprinting with the ETFE Mold

Demolding structures from a stiff inorganic stamp often results in fracture of both the embossed structures and the stamp itself because of adhesion between the stamp and the substrate. Moreover, when using a rigid mold the entire embossed surface must be separated at the same time, requiring a large force which contributes to the mold fracture. In the set of experiments shown in Figure 4, we compare the surface of a silanized silicon mold with a fluoromold after 6 consecutive embossings into PMMA at 145–160 °C, and at a pressure of 7 bar for 3.5 minutes. No cleaning of the molds was performed between the different imprints. The silicon mold was silanized as described in the experimental section, resulting in an advancing water contact angle of ~115° on a smooth surface. In comparison, the advancing water contact angle on a smooth ETFE surface with a similar roughness as that of the silicon master was ~104°. Figure 4a shows PMMA adhering to the silicon mold after only 3 embossings, making it unusable for further imprints. On the other hand, the ETFE mold was clean after 6 embossings, and showed no trace of polymer adhering to its surface (Fig. 4b). The structures embossed by the fluoromold were still very well defined after the sixth imprint, suggesting that these ETFE stamps could be used many more times without being damaged. Multiple embossing of 700 nm lines was also performed at pressures as low as ~1 bar. After 6 embossings with the same mold at a temperature of 135–140 °C, no degradation of the mold or of the embossed patterns was observed. Varying the embossing temperature between 115 and 160 °C also

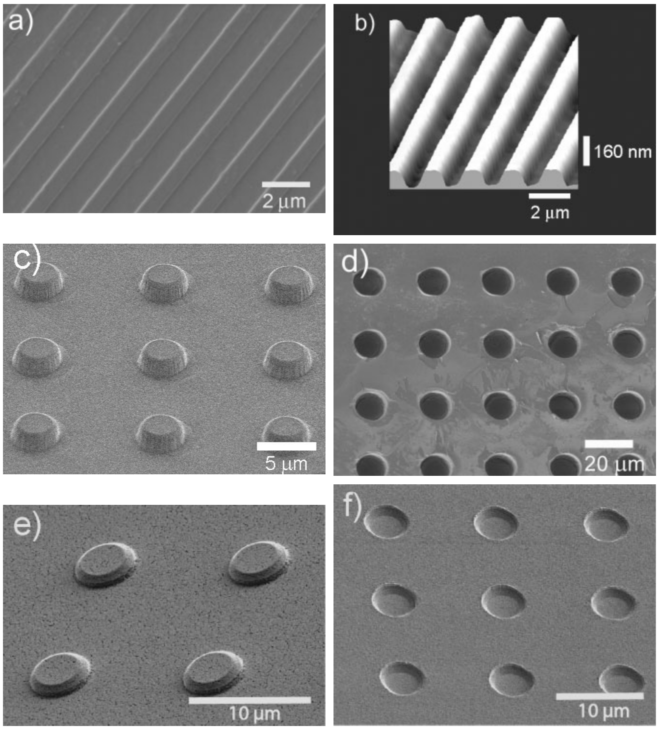

Figure 3. Scanning electron microscopy (SEM) images showing various microstructures embossed from an ETFE fluoromold. a) Image of 700 nm wide lines with a 2-µm period imprinted into PMMA at 160 °C and a pressure of 1 bar; b) AFM image of the structures in (a) showing a height of 160 nm which is identical to that of the original silicon master used to produce the ETFE fluoromold that served to emboss the lines. c) Example of ~4-µm pillars in PMMA that were embossed at 145 °C and 44 bar for 2 minutes with an ETFE fluoromold which was previously used 5 consecutive times. d) 11 µm wide and 11.5 µm deep holes embossed into PMMA at 135 °C, and 4.7 bar for 5 min. e) ~4-µm pillars in Teflon AF 1600 at ~175 °C, and ~17 bar. The graininess of the picture is due to the porosity on the surface of the Teflon AF. f) ETFE stamp after imprinting the structures shown in (e).

yielded similar results. The lateral dimensions and height of the embossed structures were identical to those of the original master as confirmed by both SEM and AFM.

Furthermore, embossing of large areas was performed into CRHDPE sheets at 140 °C with a ~50 mm × 40 mm ETFE mold which consisted of several regularly spaced regions of 8 mm × 8 mm with structures similar to the ones shown in Figure 3f. The total area covered by these 8 mm × 8 mm squares was approximately 20 % of the entire surface of the mold. The fluoromold showed no adhesion to the polymer substrate during embossing, and it was easily removed by sequential demolding thanks to the flexibility and low-adhesion of the stamp. The replication of the patterns occurred throughout the area of the mold which was covered by the structures, and the quality of the replicated patterns was the same as that shown in Figure 3.

2.4. High Pressure Embossing with the ETFE Mold

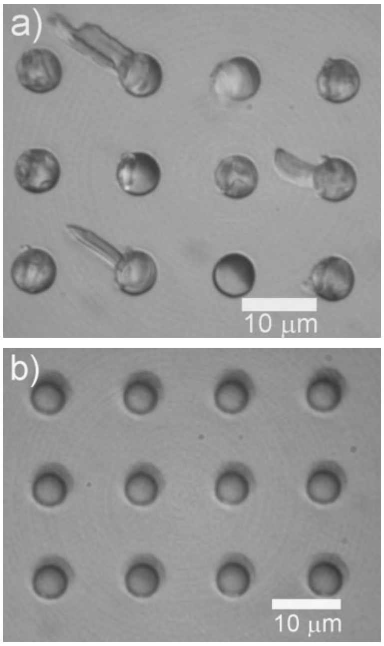

Figure 4. Optical microscopy images of the surface of a) a silanized silicon mold after 3 consecutive embossings, and b) an ETFE mold after 6 consecutive embossings. The experiments were performed at 145–160 °C, 7 bar and for 3.5 min. a) The embossed PMMA adheres to the inside of the holes on the silicon mold after 3 imprints, whereas the holes of the ETFE fluoromold (b) show no sign of adhered polymer after 6 imprints.

To further test the mechanical stability of the ETFE molds, we embossed PMMA with a fluoromold at 145 °C with a wide range of pressures. The pressure was maintained at the embossing temperature for 2 minutes. The lateral dimensions of the resulting structures were then measured using a SEM and compared to the original dimensions of the mold. Table 1 and Figure 5a show that perfect replication without deformation was obtained with the fluoromold with effective pressures ranging from ~2.2 to 55 bar. Embossing at higher pressures was not attempted, but this result suggests that the ETFE mold could withstand pressures greater than 55 bar. The same experiment was repeated with a PDMS stamp which was patterned by deposition of the liquid PDMS onto a structured silicon master and by curing for 24 h at 170 °C. These conditions provide an elastic modulus ~4 MPa. As can be seen in Table 2 and Figure 5b, the structures embossed with the PDMS stamp were strongly deformed even at low pressures, resulting in elongated and distorted patterns.

This result shows that the fluoromolds can be used for nanoimprinting at the higher pressures usually used with stiffer inorganic molds and that no deformation or loss of resolution is observed. Combined with the advantage of their low adhesion and flexibility, ETFE fluoromolds can therefore be used to replace brittle and expensive inorganic materials, as well as deformable elastomers and other plastic molds which lack strength when pressure is applied. The strength and robustness of ETFE stamps is essential for embossing large microstructures as well as small nanostructures with lateral dimensions approaching 10 nm.

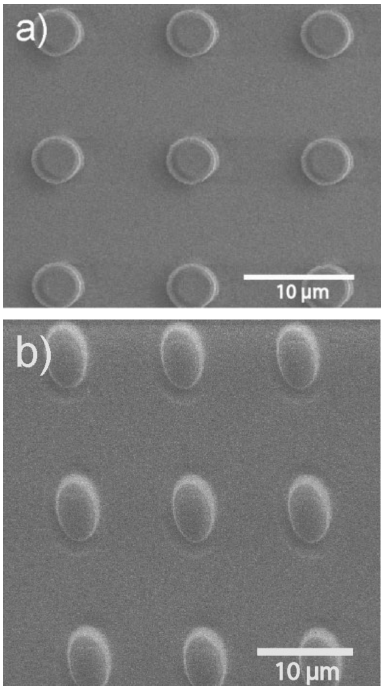

Figure 5. Scanning electron microscopy images showing the effect of pressure on the reproduction of the embossed patterns with a fluoromold and with a PDMS stamp. a) 4-μm pillars in PMMA that were embossed at 145 °C and ~55 bar for 2 min with an ETFE fluoromold. b) Deformed pillars embossed in PMMA with a PDMS stamps at 145 °C and ~33 bar for 2 min.

Table 1. Embossing of PMMA with an ETFE fluoromold at 145 °C, for 2 min at various pressures. The values are the averages of several measurements.

Sample	Diameter [μm]	Ratio to Mold	Period [μm]	Ratio to Mold
ETFE mold	4.37		11.80	
PMMA 2.2 bar	4.35	1.00	11.50	0.97
PMMA 16.5 bar	4.40	1.01	12.06	1.02
PMMA 22 bar	4.39	1.00	11.91	1.01
PMMA 33 bar	4.40	1.01	11.85	1.00
PMMA 55 bar	4.38	1.00	11.92	1.01

Table 2. Embossing of PMMA with a PDMS mold at 145 °C, for 2 min at various pressures. The values are the averages of several measurements.

Sample	Diameter [μm]	Ratio to Mold	Period [μm]	Ratio to Mold
PDMS mold	4.42		11.82	
PMMA 2.2 bar	6.32	1.43	13.81	1.17
PMMA 33 bar	7.88	1.78	15.48	1.31

2.5. Additional Properties of the ETFE Mold

We compared the performance of an ETFE mold with a mold made of the fully fluorinated poly(tetrafluoroethylene) (PTFE). We were able to successfully imprint 700 nm lines into PMMA with the PTFE mold. However, we found that PTFE is not as good a mold material as ETFE because of its high molecular weight and high melt viscosity ($>10^{11}$ Pa. s),[32] which makes it difficult to fill fine features on the surface of the master when manufacturing the mold. Additionally, PTFE is subject to cold flow and is softer than ETFE.[33] Experiments performed with ETFE fluoromolds showed the best combination of mechanical properties and thermal stability for imprinting at elevated temperatures and at high pressures. The unique properties of ETFE allow us to obtain non-porous and thick stamps (>100 μm) with the high mechanical strength that is required for the embossing process. We found that the ETFE fluoromold needs to have a minimal thickness of about 80 to 100 μm to achieve sufficient mechanical strength. A larger thickness was found to be beneficial for stability and resistance to distortion when higher pressures are needed, for example in the case of high-viscosity polymers. Thinner stamps were easily deformed and inadequate for embossing.

This improved mechanical strength is one key element for the accurate embossing of fine nanostructures. Another important parameter is the ease with which ETFE flows into the features of the master during production of the mold by NIL, providing an accurate negative replica of the master. As a result, the surface of the ETFE mold was always very smooth with a roughness similar to that of the silicon master. This property was important for the successful replication of fine nanofeatures. The fact that these ETFE molds are relatively thin (100–200 μm) also provides a good thermal conduction between the polymer and the heating plate, and fast heating and cooling rates of the embossed polymer. Moreover, since ETFE has a similar coefficient of thermal expansion than most thermoplastics, shrinkage and deformation of structures during cooling is small compared to stiff inorganic molds. Finally, because ETFE is transparent in the visible and in the UV spectrum (91–95 % transmittance in the 200–800 nm range for a 25 μm sheet),[33] it can be used to structure a photocurable polymer and to solidify it by irradiation with UV light at room temperature, providing a cheap alternative to quartz or other transparent inorganic mold materials.

3. Conclusion

We have shown the successful nanoimprinting of a variety of technologically important polymers such as PMMA, PS, CRHDPE and Teflon AF with a flexible fluoromold made from ETFE. We were able to replicate a wide range of structures without fracture or deformation of the mold and of the replicated structures. Using ETFE molds, high density arrays of nanostructures were embossed with feature sizes down to 12 nm. Because of the good mechanical properties and high temperature stability of the ETFE fluoromold, it is possible to perform NIL at the high temperatures and pressures that are typically reserved for inorganic molds. These stamps are sufficiently flexible to make good conformal contact with the substrate, but they are also stiff enough and mechanically stable to resist deformation when viscous polymers are imprinted. No prior surface treatment is needed since ETFE fluoromolds have a very low surface energy that confers them natural anti-adhesive properties. They may be reused several times without being torn or broken, which constitutes a considerable improvement over brittle inorganic materials. When imprinting large areas, ETFE molds show low adhesion, easy demolding, and a high fidelity of reproduction of the entire area that was embossed. Finally, fluoromolds can be replicated economically from one single master, and they have the potential for nanoimprinting of sub-10 nm features into viscous polymers.

4. Experimental

Fabrication of the Fluoromolds and PDMS Molds: Sheets of ETFE were cut into square pieces of the same dimensions as the master mold, cleaned with acetone, and dried in a nitrogen flow. The silicon and quartz masters were prepared by conventional optical lithography and electron beam nanolithography. For imprinting directly a non-fluorinated polymer, the masters were hydrophobized by silanization with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane diluted in purified benzene. The solution was inserted with the masters into a sealed glass container, and was allowed to slowly evaporate at room temperature and overnight to cover the surface of the inorganic molds with an anti-adhesive layer. Contact angle measurements were performed with a goniometer to confirm the change in surface chemistry. The fluoromolds were then prepared by embossing a clean piece of ETFE onto a structured silicon wafer, and heating the assembly to the desired temperature. In this case, the silicon mold did not have to be silanized because of the low surface energy of ETFE. Once a homogeneous temperature was obtained, a force was applied by a mechanical press (Interlaken Technology, USA; Obducat AB, Sweden) for a few minutes. The assembly was then cooled below the glass transition temperature of ETFE by an air cooling system mounted onto the press. The pressure was released and the structured fluoromold was demolded from the master mold. The time, applied force and temperature were monitored throughout the embossing procedure. PDMS molds were made using Sylgard 184 mixed with a curing agent in a 5:1 ratio that was deposited on the mold and put in a roughing vacuum for 5 to 10 min to allow bubbles to evaporate. It was then cured in an oven at 170 °C for 24 h to obtain a relatively high modulus of elasticity for PDMS (~ 4 MPa).

Structuring of the Polymers: Solutions of polystyrene (PS), and of Teflon AF, were obtained by dissolving PS powder (mol. weight = 70 kg mol^{-1}) in toluene, and Teflon AF 1600 granules in the fluorinated FC-75 solvent (3 M). The films were then produced by spin-coating a dilute polymer solution onto a clean silicon substrate. Commercially available poly(methylmetacrylate) (PMMA) and carbon reinforced high density polyethylene (CRHDPE) sheets were cut into pieces to fit the mold dimensions. The protective films on the sheets were removed immediately before embossing, and the surface was cleaned in a nitrogen flow to remove dust particles to ensure a good conformal contact between the mold and the polymer. For high pressure embossing, a similar procedure as for the fabrication of the fluoromolds described above was used, except that the master was replaced by the fluoromold. For the low pressure experiments, the force was applied using a small home-made press onto which a weight was loaded. The assembly, consisting of the mold and the polymer substrate, was heated on a heating stage and the temperature was monitored by a thermocouple connected to a digital temperature reader. Once the desired temperature was reached and kept constant for several minutes, the weight was applied to press the fluoromold into the polymer. The mold and the sample were then cooled in air and the mold was separated from the polymer substrate to reveal the replicated patterns.

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