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Fluorinated ethylene–propylene: a complementary alternative to PDMS for nanoimprint stamps

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Abstract

Polydimethylsiloxane (PDMS) is used by many for nanoimprint applications due to its affordability, ease of preparation, mechanical flexibility, compatibility with imprint resists and transparency to UV light. However PDMS is notoriously flexible, tacky and permeable to air. Here fluorinated ethylene–propylene (FEP) is considered as a viable and versatile alternative material for nanoimprint stamps. FEP possesses many of the desirable nanoimprint attributes associated with PDMS but crucially also features a range of complementary characteristics, including an order of magnitude more mechanical strength allowing it to handle higher loads than PDMS, an intrinsically non-stick surface and is compatible with oxygen sensitive resists. Unlike elastomeric polymers, FEP is glassy so patterning may be realised via hot embossing. Not only is this a facile and rapid means of physical structuring but it also facilitates combinatorial patterning, providing a versatility beyond that of traditional casting materials. Due to the intrinsically slow creep of FEP both micro- and nanopatterning are successfully performed sequentially. Feature sizes from 45 nm were successfully realised via the hot-embossing method. To further demonstrate the potential of the material, a modified computer numerical control machine is used. It is capable of photo-, nanoimprint- and laser lithography in conjunction with patterned FEP foils. The tool is used to perform pattern transfer into a developmental nanoimprint resist from Micro Resist Technology, mr-NIL210 XP, and Nano SU-8 3005 negative tone photo resist from MicroChem. Ultimately three-tier lithography is performed in unison and advantageous step-and-repeat performance is achieved with fabricated FEP imprint stamps as they demould more compliantly and resist pressure and contamination better than PDMS.

S Online supplementary data available from stacks.iop.org/NANO/27/155301/mmedia

Keywords: UV NIL, hierarchical, step-and-repeat, FEP, high aspect ratio, polydimethylsiloxane, Sylgard 184

(Some figures may appear in colour only in the online journal)

Introduction

Polydimethylsiloxane (PDMS) as a stamp material essentially defined soft nanoimprint lithography. Its affordability, simplistic processing, UV-transmission and physical flexibility are highly attractive assets for nanofabricators worldwide

[2, 14, 18, 20]. The most frequently used grade of PDMS in the field of microfabrication is Sylgard 184 from Dow Corning. Sylgard 184 possesses all of the abovementioned qualities, however it is not the perfect material for nanoimprint stamps. There are some applications where PDMS can struggle to perform; Sylgard 184 is intrinsically tacky and may be rapidly fouled by certain resists [7], it is absorbent of organic solvents which can hinder cleaning [15], it is permeable to oxygen which inhibits cross-linking of many resists in an air atmosphere [3] and above all is too flexible for high pressure applications or high aspect ratio protrusion stamping [11, 17]. These issues have been well documented by research groups and several attempts have been made to combat the hindrances [4, 6, 11, 17]. In this work the authors are not attempting to remedy PDMS, but rather combat the aforementioned issues by evaluating an alternative stamp material with complementary attributes to PDMS for soft nanoimprint lithography.

Fluoroplastics, such as Teflon® fluorinated ethylene–propylene (FEP), are well-known for their superior chemical inertness [5], which is why they have been utilised for a variety of applications requiring non-stick or chemically inert conditions [10]. Due to their intrinsic fluorination such plastics have very low surface energy. Which means they are hydrophobic and virtually non-stick to most materials by nature [8]. There are a variety of fluoroplastics which have been designed to be compatible with conventional forming methods such as moulding and extruding. The suitable candidates for flash-imprint are Teflon® AF (a PTFE (polytetrafluoroethylene) based polymer) [12, 13], Tefzel® (an ETFE (polyethene-co-tetrafluoroethene) based polymer) [1, 9], PFPE (perfluoropolyether) [16] and Teflon® FEP. Three of these four fluoropolymers have already been trialled as nanoimprint stamps with the results superior to PDMS in terms of compliant demoulding, cleaning and rigidity [1, 9, 12, 13, 16]. Teflon® AF and PFPE both possess high oxygen permeability similar to PDMS [16]. FEP and Tefzel® on the other hand possess low permeability to gas and moisture. Tefzel® is almost identical to FEP; they are both flexible, transparent polymers (FEP measured >99.9% transmittance/μm at 405 nm) with relatively low melt temperatures for fluoroplastics (250 °C–280 °C) and are resistant to most acids and solvents. These qualities make Tefzel® and FEP ideal materials for addressing the inadequacies of Sylgard 184 as a stamp material for soft nanoimprint lithography. Despite the similarities between Tefzel® and FEP, FEP is nearly twice as flexible (Young's modulus: 830 versus 480 MPa) and is rated for almost twice the service temperature range (maximum service temperature: 150 °C versus 205 °C). It is therefore anticipated that FEP foils will also perform effectively as nanoimprint stamps but curiously no evaluation has yet been documented. The greater flexibility FEP offers over Tefzel® will allow improved conformability across defects and compliance with three-dimensional patterning (supplementary section 1). Table 1 below documents the intrinsic material properties of FEP and compares them to those of Sylgard 184 PDMS. Table 1 shows that the material properties of both polymers are very much suitable for nanoimprint but complimentary to each other, thus each finds its merit in specific applications.

Table 1. Material properties for FEP and PDMS respectively. All data derived from manufacturer sources except contact angle which was measured by the authors.

Material property	FEP	PDMS
Approximate melting point (°C)	250–280	Not applicable
Glass transition temperature (°C)	80	−127
Young's modulus (MPa)	480	1.84
Tensile strength (MPa)	20.7	6.7
UV i-line transparent	Yes	Yes
Moisture absorption (%)	<0.01	0.03
CO_2 permeability (Barrer)	10.01 (25 °C)	1300.00 (28 °C)
Density (kg m^{-3})	2150	965
Sessile drop contact angle (°)	119 ± 3.2	107.5 ± 2.67

Here we present how to combinatorial master FEP imprint stamps. The fabrication process is outlined and ultimately the true ability for the fabricated stamps to function in soft micro- and nanoimprint lithography is demonstrated. Three level hierarchical patterning is documented using UV curing as the third macro layer above simultaneous micro and nanoimprinted layers. In order to illustrate the versatility of such hierarchical patterning, a multi-functional lithography tool was custom furnished from a computer numerical control (CNC) machine (full details of the custom build may be found in supplementary section 2). The tool is capable of performing nanoimprint stepping and laser lithography in addition to conventional mask-based photolithography. UV-laser lithography is performed through patterned FEP films and step-and-repeat processing is performed to demonstrate and evaluate the FEP material in industrial-style fabrication applications. The capacity of FEP as a nanoimprint stamp and its ability to supplement PDMS is discussed; namely resistance to deformity, compliance in demoulding of high aspect ratio structures and resistance to surface fouling.

Methods

In this work FEP foils manufactured by DuPont were obtained as 304 × 200 mm sheets with a thickness of 0.127 mm. The FEP was cut with domestic scissors into smaller samples (~25 × 25 mm) for the experiments. A hot plate was heated to above 80 °C (the T_g for FEP) in order to soften it upon a nano or micropatterned mould. Then a planar press plate (preferably quartz) may be used to compress the FEP with tweezers so as to ultimately hot emboss it. Quartz is a good choice for the press plate as it is transparent so air trapping may be monitored, and it is less likely to crack under the hot embossing conditions than glass [19]. The FEP is then immediately removed from the hot plate and once the temperature drops below T_g (80 °C) the mould may be released. This process can be completed comfortably within 5 min. Due

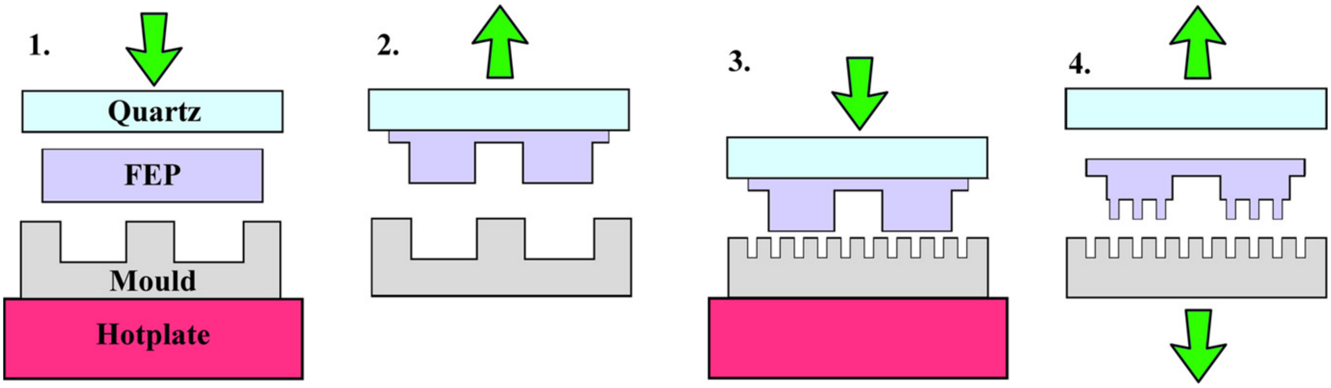

Figure 1. FEP mastering process schematic: 1—use a glass (ideally quartz) slide to press down a piece of FEP film onto a micropatterned mould upon a hotplate at 270 °C. 2—remove the sandwich from the hotplate and gently pry apart the glass and mould. 3—repeat step 1 with a nanopatterned mould. 4—repeat step 2 and peel the nano/micropatterned FEP film from the glass to realise a standalone two tier, flexible FEP imprint stamp.

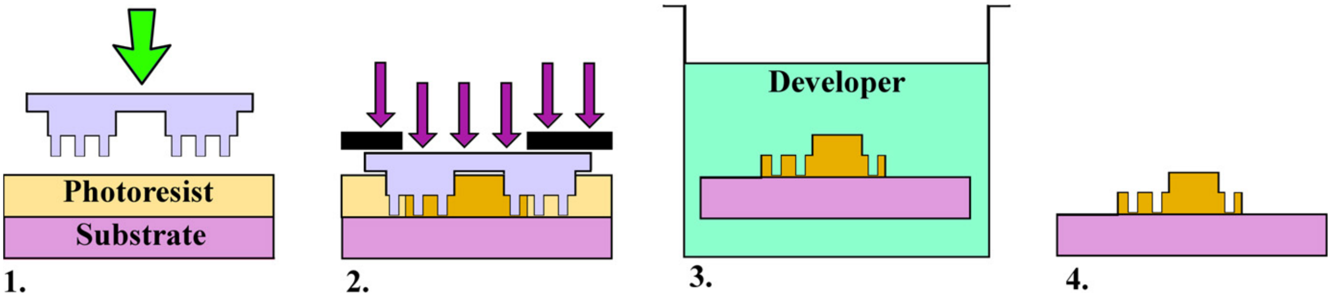

Figure 2. FEP stamp three-tier patterning process schematic. 1—imprint nano/micro stamp into a photoresist coated substrate. 2—perform UV-lithography using a photomask or laser source to cure the photoresist and retain the imprinted feature topography as well as realising a third macroscale geometry. 3—release the FEP stamp and develop the photo resist. 4—following chemical development a three-tier resist structure has been realised.

to the slow creep rate of FEP it may be sequentially patterned with different designs of topography. Figure 1 illustrates the facile FEP mastering process for two tier patterning. If alignment is required for the sequential patterning (step 3 of figure 1) then it is best to ensure that the FEP preferentially bonds to the press plate over the mould (in step 2) by considering surface chemistry. FEP may be purchased with an adhesive side, or surface treatments may be performed to the press plate and/or mould. Providing the FEP has preferential adhesion to the press plate then a microscope system may be used to align sequential embossing during the mastering process.

To demonstrate that the multi-tier FEP may itself be utilised as an imprint stamp a two-tier FEP stamp was imprinted into photoresist. Naturally photolithography is required to cure the photoresist. A typical process flow for such a procedure is displayed in figure 2. Nano SU-8 3005 dilution negative tone photoresist from MicroChem was spun at 3000 rpm for 1 min on silicon and during the resist soft-bake step at 95 °C a FEP film containing a combinatorial hexagonal micropattern (25 μm corner to corner with 5 μm wide perimeter trenches) and nanograting (300 nm 1:1 aspect ratio and 1 μm pitch) was placed on top. As figure 2 indicates, conventional photomasks may suffice for performing the third, macro, level of lithography. However by deploying a UV-laser to cure the resist additional patterning versatility may be achieved. A custom-built laser lithography tool was created by mounting a 405 nm, 1 mW laser pointer onto the X-Y-Z head of a CNC machine. A photograph and schematic of the custom built tool set-up may be found in supplementary section 2. Millimetre scale Y-channel mixer templates were written through the FEP film into the SU-8 resist. The entire structure was post baked at 95 °C for 2 min on a hot plate. The FEP film was released following this step and the SU-8 developed for 2 min in Microposit EC Solvent at room temperature.

Increased mastering efficiency can only be considered an advantageous quality and not an essential figure of merit for imprint stamps. The important characteristic is imprint performance. In the following comparative analysis Sylgard 184 is used as the PDMS standard in a 10:1 ratio of pre-polymer to curing agent and cured for 12 h in an oven at 70 °C.

Since FEP is stronger than PDMS it is better equipped to resist wear and tear during handling. Possessing a higher Young's modulus than PDMS, it is stiffer and more capable of withstanding high pressure which is beneficial for imprinting. To illustrate this fact nanopillars of the same dimensions (360 nm diameter with 1:1 aspect ratio) were fabricated from both materials and imprinted into a nanoimprint resist at a relatively high pressure of 180 kPa and the resultant imprint examined by scanning electron micrograph (SEM) for feature deformity. The nanoimprint resist utilised in this work is also novel, it is a new product from Micro Resist Technology known as mr-NIL210 XP and at the time of experiment was not commercially available. As far as the authors are aware this is the first documented evaluation of mr-NIL210 XP. The resist was pre-spun onto 4 inch (100 mm) Si wafers at 5000 rpm for 1 min and soft baked at 100 °C for 3 min on a hotplate, (however it is now known that 1 min is sufficient). The resist was found to be compatible in an air atmosphere and was partially cured within one second using a 365 nm source at 65 mJ cm^{-2}. In this work the exposure dose, at 365 nm, was 195 mJ cm^{-2}.

The hydrophobic nature of FEP is one of the main assets of the material. For serial imprinting it is important that the stamp is as resistant as possible to fouling. This is imperative for step-and-repeat machines. The same CNC machine which was tailored for laser-lithography has also been adapted to operate as a nanoimprint stepper. Full details on the construction of the custom-built lithography tool may be found in supplementary section 2. The true benefit of FEP as a stamp material over PDMS was contrasted by performing stepping with this tool into the aforementioned nanoimprint resist, mr-NIL210 XP. Three parameters were evaluated: demoulding compliance, quantity of iterations prior to imprint degradation and adhesion strength between the stamp and the resist. SEM analysis was used to evaluate demoulding compliance and stamp fouling. A Zwick Z250 compression machine with 5 N load cell was used to pull imprinted stamps from the cured resist in order to obtain force/displacement graphs to evaluate adhesion strength.

Results and discussion

FEP was successfully nanopatterned via the hot embossing method. The smallest features transferred to FEP in this study were 45 nm diameter pits. This is not considered to be the material limit, but it was the smallest features available to the authors at the time. Figure 3 displays SEMs of the 45 nm pits in the FEP film (for imaging purposes 10 nm of Au was evaporated onto the FEP surface).

Unlike elastomer casting, the FEP mastering process does not require the nano and micro pattern to be combined on one master template. Due to the intrinsic slow creep rate of FEP one may initially emboss a deep micropattern and thereafter emboss a shallow nanopattern from two seperate silicon masters. In addition the masters do not require fluorination treatment due to the chemical nature of FEP. Thus FEP mastering is efficient and rapid. Figure 4 exemplifies the results of combinatorial FEP mastering. It displays electron micrographs of FEP films following the initial micropatterning with a hexagonal design and after subsequent nanopatterning with two separate topographies (nanograting and nanopit).

Patterned FEP was utilised to provide three discrete layers of topographical patterning in photoresist. Nano-, micro- and macro-patterns were established in Nano SU-8 negitive tone photoresist. The laserlithography tool functioned effectively through the FEP film. The CNC speed was 0.05 mm s^{-1} and the intensity of the ~40 μm laser spot through the 0.127 mm thick FEP film was measured at 4.72 mW. Figure 5 displays exemplary photos and micrographs of three-tier Nano SU-8 patterning achieved by performing laserlithography through a two-tier patterned FEP film. The entire process of mastering, imprinting resist, performing laser-lithography and development was complete within 20 min.

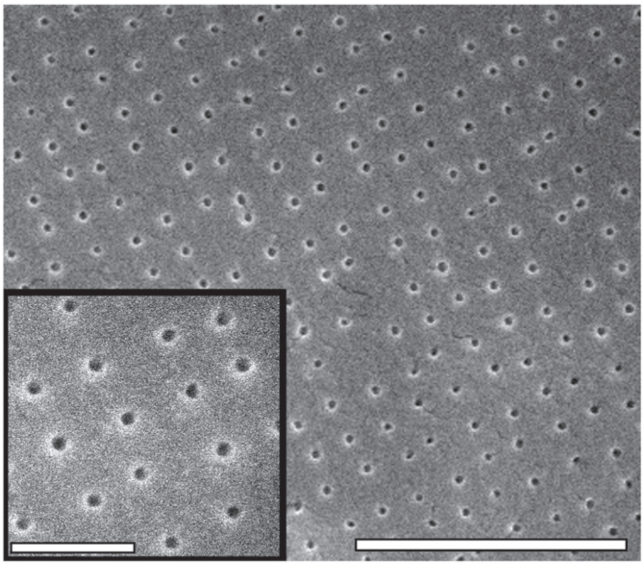
Figure 3. SEM of 45 nm diameter disordered pits in a FEP film transferred via hot embossing from Si, scale bar = 2 μm (inset: higher magnification, scale bar = 500 nm).

Of more importance than versatile and efficient mastering is the practical advantages FEP provides over PDMS for nanoimprint stamps. There are two main findings. Firstly, due to its mechanical properties, FEP may tolerate higher compressive forces than Sylgard 184 PDMS making it more robust and resistant to flexural deformation. To illustrate this point figures 6(a) and (b) display micrographs of imprints into mr-NIL210 XP nanoimprint resist using 360 nm diameter, 1:1 aspect ratio nanopillars, imprinted with the same pressure (180 kPa) but using the two different stamp materials (PDMS and FEP respectively). From examination of figure 6(a) one may observe that the PDMS pillars have collapsed during imprinting, resulting in the non-circular indents. Whereas the FEP counterpart shown in part (b) has produced bold, circular indents. Thus the FEP material has a distinct advantage over soft PDMS for high pressure or high aspect ratio nanoimprinting where features may be prone to flexural deformation.

The second imperative finding is that FEP is highly compliant in replicating 100 nm diameter high aspect ratio (>3:1) pillars in mr-NIL210 XP whereas Sylgard 184 PDMS was incapable of a single imprint. Although the resist manufactures have designed mr-NIL210 XP purposefully for compliance with PDMS, the integrity of the resist was found to fail for 100 nm diameter nanopillars with aspect ratios from 1:1. Up to fifty iterations of such high aspect ratio nanopillar imprinting is possible with FEP stamps before the nanopattern is compromised by stamp fouling. Figures 6(c)–(f) depicts

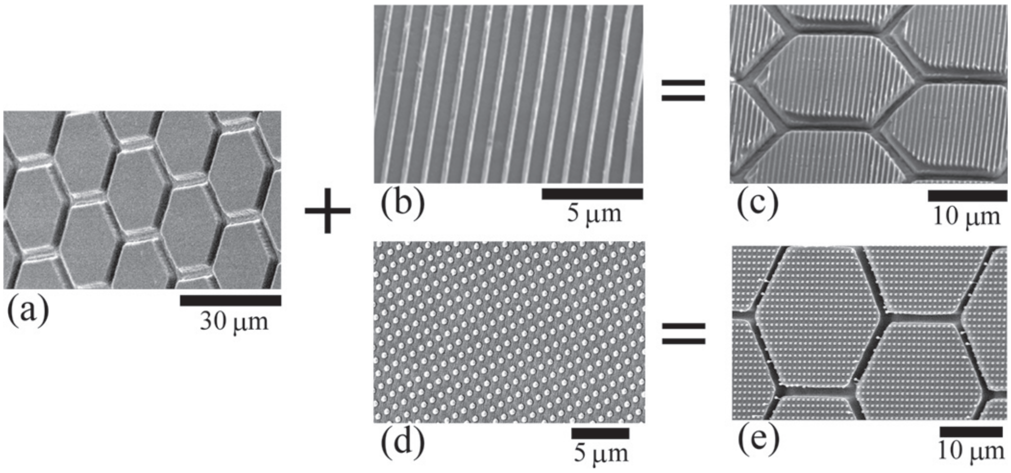

Figure 4. Exemplary SEMs of combinatorial patterning in FEP films: (a)—20 μm corner to corner hexagonal protrusions with 2 μm gaps (b)—300 nm grating at 1 μm pitch, (c)—resultant combination of embossing ‘(a)’ then ‘(b)’, (d)—500 nm diameter pillars, (e)—resultant combination of embossing ‘(a)’ then ‘(d)’.

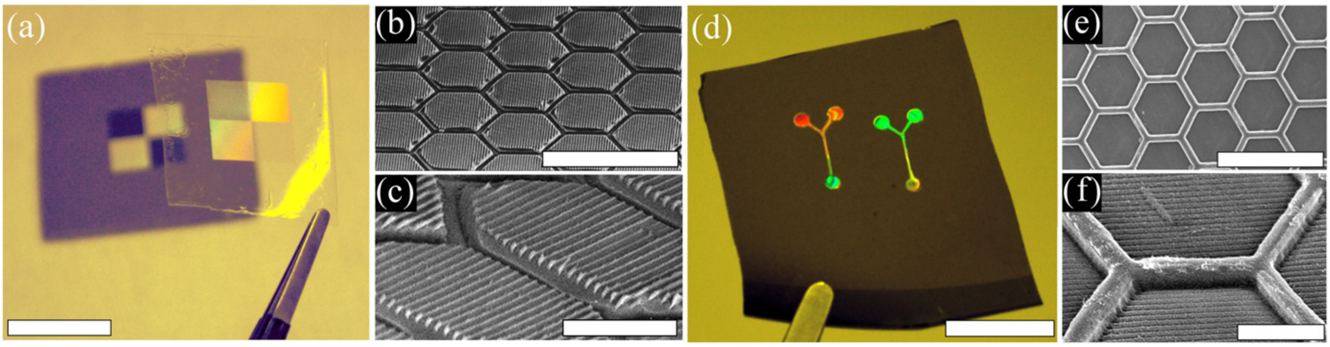

Figure 5. Overview of three-level patterning using FEP thin film stamps. (a) A photograph of a FEP film after embossing, scale bar = 8 mm. (b)–(c) Electron micrographs showcasing a two-tier FEP thin film stamp with a grating nanofeature and hexagonal protrusion microfeature, scale bars = 50 μm and 10 μm respectively. (d) Photograph of SU-8 3005 resist upon Ti-coated Si following patterning with FEP nano/micro stamp and curing using UV-laser lithography, scale bar = 4 mm. (e)–(f) Electron micrographs of photo-cured SU-8 3005 resist after patterning with the two-tier FEP thin film stamps shown in part ‘(b)’ and ‘(c)’, scale bar = 50 μm and 10 μm respectively.

top-down SEM micrographs of imprints into mr-NIL210 XP resist using the different stamp materials: 10:1 Sylgard 184 PDMS (with (e) and without (c) fluoro-silane termination) and FEP (d) and (f). It was found that during the initial imprint, 10:1 PDMS shaped nanopillars in the resist but then the integrity of the resist failed during demoulding, manifesting itself as a separation at the base of the nanopillars. Subsequent imprints did contain features but these were not as desired, they appeared globular and sporadic as a result of resist re-deposition. The issue was confirmed to be cross-link inhibition after comparing various stamp materials and treatments. Figure 6(c) displays one of the few textured defects found at the site of a 10:1 Sylgard 184 PDMS imprint attempt; 100 nm circular dents can be seen upon a hillock defect in the resist film indicating that pillars have been pulled from this site. Vapour coating fluoro-silane is a well established process for reducing surface adhesion. However the complication with fluoro-silane treatment upon PDMS is that the surface layer of PDMS can rapidly harden into a glass-like coating when the PDMS is pre-activated in oxygen plasma. Figure 6(e) shows an SEM depicting exactly this issue. The surface of the PDMS stamp has hardened into a thin glass-like film and cracked on impact with the resist leaving a micro-polygonal impression. On the contrary FEP, which does not require fluoro-silane treatment, produces near-perfect inverse replications of the stamp topography (figure 6(d) shows FEP imprint #1) and continues to do so for up to fifty imprints before pattern degradation (figure 6(f) shows FEP imprint #57 where peripheral defects become visible). The non-stick nature of FEP is responsible for the stamp longevity. Figures 6(g)–(h) highlights the sizeable difference in adhesion between the two stamp materials after curing mr-NIL210 XP. Part (g) displays a particularly adhesive PDMS stamp, but such results are not anomalous; PDMS is ductile and permeable to oxygen so the resist remains tacky and suction forces can often form under the stamp. Statistical analysis corroborates the result with an average force, beyond that required to lift the weight of a stamp, being 0.35 N for PDMS and 0.12 N for FEP with standard deviations from 3 measurements of 0.19 N and 0.11 N respectively.

The fidelity of the FEP nanoimprint reproduction is compared in figure 7. A minimum of four measurements were

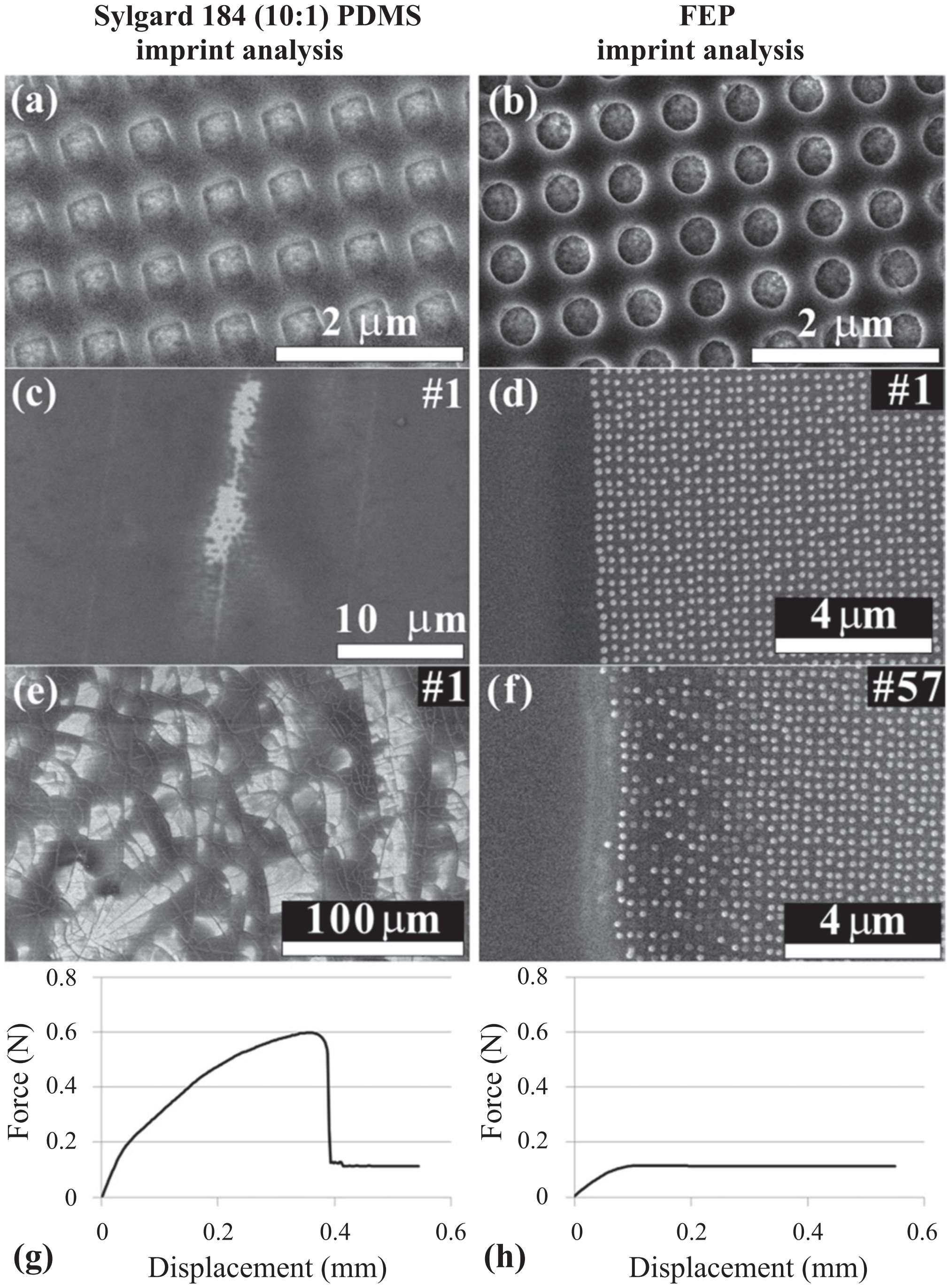

Figure 6. Imprint analysis into mr-NIL210 XP nanoimprint resist: comparative top-down SEM images between 10:1 Sylgard 184 PDMS and FEP for: (a)–(b) nanopillar stamp performance under loading at 180 kPa with the same geometry of nanofeatures; the PDMS features have evidently suffered flexural deformation unlike the FEP counterpart. (c)–(f) high aspect ratio (>3:1) nanopit stamp performance; (c) nanopillars have been pulled off with the PDMS stamp leaving only circular marks on film defects, (e) plasma induced fluoro-silane treatment of PDMS was performed but resulted in the PDMS surface hardening and smashing during imprinting, (d) the FEP equivalent shows well defined 100 nm diameter circular pillars left in the resist after the initial imprint, (f) FEP imprint #57 using the same stamp shown in part (d); here peripheral features are starting to lose contrast due to stamp fouling. (g)–(h) respective force/displacement curves for the withdrawal of PDMS and FEP nanopit (225 nm deep, 100 nm diameter, 300 nm pitch) stamps from mr-NIL210 XP.

made per sample. Anisotropy was measured at 96.0° ± 1.5° for the original master and 93.8° ± 1.8° for the imprints into mr-NIL210 XP. Feature circularity was retained but the diameter was reduced on average by 6.1%. Feature height was limited by the thickness of the resist film but from inspection of cross-section SEM images (c) and (d) it is evident that the feature tops were sharp and uniform in height (standard deviation 2.5 nm).

An additional benefit of FEP is its inertness and resistance to chemical agents. The mr-NIL210 XP resist is

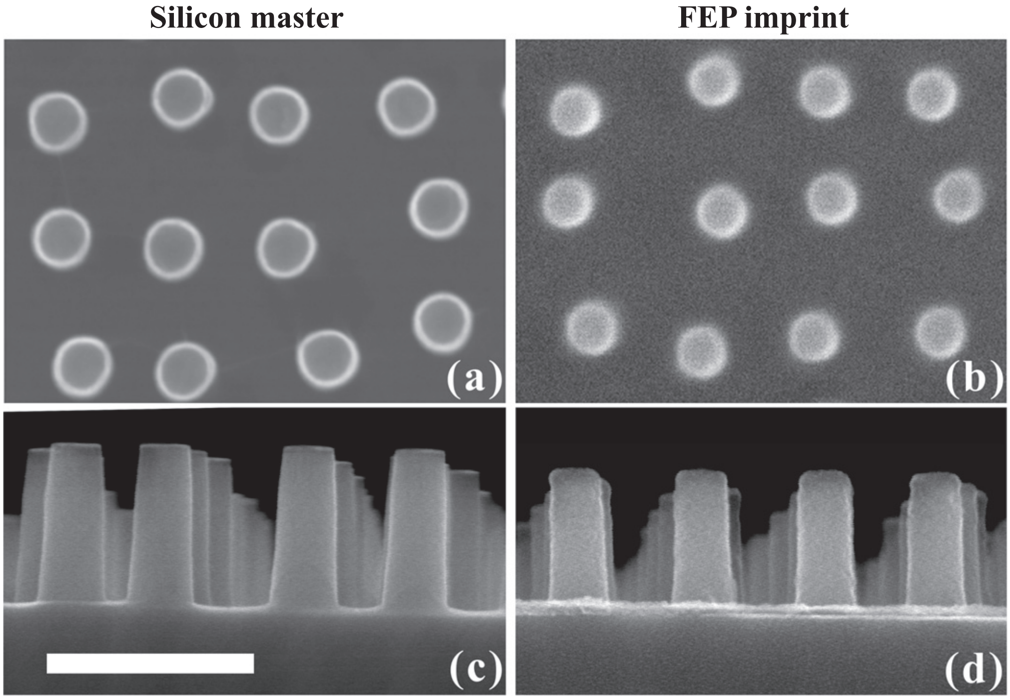

Figure 7. Top-down SEM images of (a) silicon master and (b) FEP imprint into mr-NIL210 XP resist. Cross-section SEM images of (c) silicon master and (d) imprint into mr-NIL210 XP resist. All images at the same magnification, scale bar shown in (c) =500 nm.

stubborn to remove from PDMS after curing. Acetone was ineffective and as previously discussed plasma treatment is detrimental to the PDMS surface. However either method may be used with FEP stamps. FEP is so highly fluorinated that it inhibits resist bonding and organic contaminants may be removed with traditional solvent cleaning in an ultrasonic bath. FEP is also inert to many acids, so acid may also be used if a more aggressive clean is required.

Limitations

FEP has so far been shown to be a viable complementary alternative to Sylgard 184 as a nanoimprint stamp, however it is not without its limitations. The stiffness of the material allows higher aspect ratio features to be imprinted without bending but on a broader scale the effect of contamination on the nanopattern is amplified. Radial planar areas form around any debris because the FEP is unable to deform around it as compliantly as elastomers like PDMS. That said contaminants are less likely to be transferred to subsequent imprints due to the non-stick nature of FEP. Both of these properties are illustrated in a photograph in the supplementary pages (figure S4). The second hindrance FEP suffers from is that it requires temperatures in excess of 250 °C to cast it, so the process of filling deep (mm scale) cavities is more stringent and hazardous than with PDMS which is cast at room temperature.

Conclusions

Here Teflon® FEP has been proposed as a material for soft-nanoimprint lithography. It features complementary properties to that of field forerunner PDMS. Here it has been demonstrated that FEP can be nanopatterned by hot embossing in a rapid and efficient manner with feature sizes demonstrated from 45 nm. FEP mastering can be completed in five minutes; an attractive property compared to the likes of elastomeric casting which can take the best part of a day. By taking advantage of the slow creep of FEP, two-tier hot embossing of micro and nanopatterns was realised. FEP, like PDMS, is transparent to ultraviolet making it useful as a UV-lithography stamp. Flood, photomask or laser writing may be performed through FEP films. It was demonstrated that three levels of lithography may be performed simultaneously using the aforementioned concepts. UV-laser-lithography was executed through a FEP two-tier stamp to create nano/micro patterned Y-channel templates which may be used for microfluidic processing. FEP is a relatively stiff polymer and was shown to be resistant to buckling and flexural deformation under loading. The most impressive result is that FEP is capable of imprinting 100 nm diameter high aspect ratio (>3:1) nanopillars into a developmental nanoimprint resist, mr-NIL210 XP, fifty times before pattern degradation whereas PDMS failed to generate a single imprint of the same design in the same resist. This was determined to be a result of gas permeation inhibiting resist curing. It was shown that on average the PDMS stamps require three times more force to be pulled from said resist than FEP alternatives. It was also discovered that there is no adverse effects upon the FEP material or surface features using solvent or acidic based cleaning agents.

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