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Decal Transfer Microlithography: A New Soft-Lithographic Patterning Method

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Abstract: A new soft-lithographic method for micropatterning polymeric resists, Decal Transfer Microlithography (DTM), is described. This technique is based on the transfer of elastomeric decal patterns via the engineered adhesion and release properties of a compliant poly(dimethylsiloxane) (PDMS) patterning tool. An important feature of the DTM method is the exceptionally broad spectrum of design rules that it embraces. This procedure is capable of transferring micron to submicron-sized features with high fidelity over large substrate areas and potentially simplifies to a significant degree the requirements for effecting multiple levels of registration. The DTM method offers some potential advantages over other soft-lithographic patterning methods in that it is amenable to transferring resist patterns with both open and closed forms, negative and positive image contrasts, and does so for a wide variety of aspect ratios and a significant range of pattern pitches that can be accommodated without degradation due to mechanical distortions of the pattern transfer tool. The most significant advance embodied in the DTM method, however, is that it offers useful new capabilities for the design and fabrication of advanced planar and 3D microfluidic assemblies and microreactors.

Introduction

The ability to pattern materials in thin-film form is a central competency in the manufacturing methods used for a diverse range of technologies, ones with vast economic impacts.[1] High performance microelectronic devices provide the best and most explicit examples of the technological importance of such manufacturing methods and the microstructures they produce. A state-of-the-art integrated circuit, for example, can contain as many as 100 million transistors and several billion discrete electrical connections integrated into a complex multilevel architecture. These devices certainly qualify as being among the most complex objects made by human hands. The manufacturing processes used to construct these devices rely heavily on photolithography as a key patterning method. This process has been engineered to exceptional levels of performance and is capable of developing the submicron-sized, polymeric patterned features (resist structures) that serve to template the etching and deposition of other functional thin-film and bulk materials that are used to construct the chip's integrated devices.[2,3] The enormous sophistication of this process, its resolution along with its extensive optimization as a method capable of achieving high fidelity in multiple levels of registration, is attended also by the fact that it is an exceptionally capital-intensive fabrication method.[1] As a result, it is not easily applied to low-cost applications. Because of its reliance on projection optics, it is also a method that possesses only limited utility for patterning materials in 3-D or nonplanar geometries.[4] The reliance of photolithography on projection optics also makes it difficult to integrate devices onto large area substrates in a low-cost, easily manufacturable way. This method is also sensitive to the limitations that result from the availability of secondary patterning methods (e.g., the etching processes) that are used to transfer the latent image of the resist into a thin-film or other material structure. These latter processes are well developed for the materials that are commonly encountered in electronics manufacturing but remain limited in significant ways for emerging areas of interest that include the diverse challenges encountered in integrated optics,[5] microelectromechanical systems (MEMS),[6−9] microfluidic systems,[10−15] and architectures that incorporate biological materials or cells.[13,16−18]

For these reasons, there has been increasing attention given in research to the development of new patterning methods, ones that lift constraints intrinsic to processes based on photolithography. Very significant advances have been made in this regard, most notably in the development of the suite of new methods of microfabrication often referred to as soft lithography.[17,19,20] Soft lithography defines a complementary set of patterning tools

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that are based on the use of elastomeric polymers, primarily poly(dimethylsiloxane) (PDMS), as a vehicle for transferring patterns via the replication of a master. Many soft lithography methods use printing,[21] embossing,[22] or molding[23] as the means of effecting this pattern transfer. The power of this technology lies in its versatility because the materials patterned can range from proteins,[17,24-26] cells,[17,25,27,28] metals,[29-31] polymers[32-36] and ceramics,[37-39] to self-assembled molecules (SAMs)[21,39-42] and more conventional thin-film materials. In addition to patterning nontraditional materials via additive lithography, the chemically robust patterns formed by soft lithographic methods can also serve as etch resists.[41-44] This unique suite of lithography techniques has enabled the microfabrication of a diverse range of structures and device architectures that includes MOSFETs[45] and TFT arrays,[46,47] on-chip microfluidics for bioassays and microreactors,[48-50] Schottky diodes,[51,52] 3-D microstructures for MEMS,[53,54] optical components,[55-58] and electrodes and back planes for organic electronics.[59-63]

Despite these notable achievements and the progress they portend, the engineering bases of soft-lithography remain incompletely developed and, thus, warrant further attention from research. Of primary interest in this regard are issues related to manufacturing, registration, and restrictions inherent in the design rules supported by specific patterning methods.[64] Recent work in this field addresses itself to developing strategies that lift some of the limitations encountered with three prototypical soft-lithographic techniques: these are micromolding in capillaries (MIMIC); microcontact printing (μCP); and elastomeric membrane patterning (EMP). MIMIC[23] is a versatile technique that uses a molded PDMS stamp to form capillaries when it is placed in contact with a smooth substrate. Although still in contact, the channel system created in this way is filled with a liquid prepolymer or other material precursor via various driven filling methods, such as vacuum MIMIC[65] and the Channel Outgas Technique (COT).[66] Once cured, the PDMS mold can be peeled away to reveal patterns formed in a variety of materials, notable examples of which include: ceramics,[23] metals,[20,30] and polymers.[46,51] Major requirements exist for patterning via MIMIC. These include the following: the use of a precursor in the liquid state; a precursor with viscosity appropriate for filling a mold with a given design rule; and a continuous pattern to allow the filling of the mold in its simplest form based on a 2-D channel system. An array of discrete patterns (i.e., ones not part of a simple channel design) requires the use of a 3-D channel system to fill the mold, something which is impractical for smaller, high-feature-density patterns. The printing-based method, μCP, on the other hand suffers from no such design limitations.[20,21,40,41,67] A patterned stamp coated with a material to be patterned (the ink) is simply placed in contact with the substrate. Because the pattern transfer relies only on a controlled contact mechanism, μCP easily creates both continuous and discrete patterns. As another significant point

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of attraction, very small features can be created by μCP (features as small as 30 nm have been reported). Patterning by μCP does have associated with it a number of challenges as yet to be resolved by research. For example, many of the molecular inks used in μCP are prone to reactive spreading,[42,68] a feature which can impact the fidelity of the pattern transfer. This technique has been most successfully developed for the additive patterning of SAMs, but these materials themselves, although useful, can only serve in as yet limited capacities as resists.[42,44,69] As with any contact lithography method, registration also remains a significant challenge for μCP-based patterning. A final related technique, EMP, uses a thin PDMS membrane stencil-mask as a layer to mediate both additive and subtractive processing.[27,70,71] The ability to use these inert membranes in lift-off patterning and as etch resists derives from the reversible seal that forms spontaneously between the thin, patterned PDMS stencil and a smooth substrate. As with MIMIC, this technique also requires that the polymer membrane be continuous, and therefore, the material must be etched or added in a complementary form that is discontinuous. Most difficult though is the transfer and manipulation of the thin-film membranes which are inherently mechanically unstable (they are typically on the order of a few microns thick themselves).

A series of recent reports have described variations of soft-lithographic patterning that all depend in one form or another on the use of engineered adhesion as an integral part of the fabrication process. Rogers and co-workers have described a very powerful method for patterning metal thin-films called Nanoscale Transfer Printing (NTP).[72,73] This method uses a metal coated patterned PDMS stamp to transfer a metal film in what might be described as an almost inverse model of lift-off lithography. The substrate to which this metal decal is transferred is specially treated with an adhesion layer (a reactive mercaptosilane coupling agent for the case of Au thin film patterns) to promote the adhesive bonding of the metal and thus enhance the fidelity of the pattern transfer.

Another novel adhesion promoted patterning method has been described by Whitesides and co-workers. Their method, Micromembrane Sandwiching (μMS), is an attractive fabrication strategy for constructing complex 3D microfluidic architectures in PDMS. A central hallmark of this method is the use of an oxidative plasma processing step to promote the interlayer bonding of molded PDMS membranes, either in slab or membrane form, to develop the interconnected levels of a 3D architecture. This work highlights a leading example of the far more general potential that exists for 3D patterning building on sequential levels of polymer casting, molding, embossing, and stencil membrane bonding. As powerfully illustrated in the work of Whitesides,[74,75] Beebe,[76] and Hosokawa,[77] among others, such bonded architectures appear to hold important capabilities for patterning biological materials and lend themselves very naturally to the construction of three-dimensional microfluidic devices.

The present report describes a patterning method that bears some resemblance to aspects of these latter seminal contributions. We describe, specifically, a method for sealing PDMS irreversibly to a variety of solid substrate materials, including silicon, glass, quartz, PDMS, and silicon thermal oxide substrates. A UV/Ozone (UVO) pretreatment of the PDMS, the predominant elastomer used in soft-lithography, allows it to be irreversibly bound to these materials under mild conditions. This bonding is sufficiently strong as to allow the direct transfer of the features of a patterned PDMS stamp, a decal pattern transfer, to a substrate material. This method provides a way to pattern PDMS features, ones capable of serving as resist levels for fabrication or the structural components in microfluidic devices, using a chemically engineered and mechanically stable support layer to enable and mediate its manipulation, alignment, and subsequent deposition. In the first embodiment of this decal pattern transfer process, the features of a patterned PDMS decal stamp are physically torn from it via a cohesive mechanical failure (CMF patterning). The release properties of the decal also can be modified easily by rational molecular design. This selective pattern release (SPaR) is a novel complement to other soft-lithographic patterning techniques, one that is capable of patterning submicron features in both open and closed forms, over a very large range of design sizes and pitches, as well as three-dimensional integrated structures of continuous or discontinuous design. In particular, we demonstrate the utility of this methodology for forming PDMS resists, microfluidic channel systems, and membrane reactors with design rules not previously possible via soft-lithography.

Experimental Section

Materials Used. Poly(dimethylsiloxane) (PDMS) (Dow Corning Slygard 184), ⟨100⟩ boron doped silicon wafers (Silicon Sense, Inc.), quartz slides (Chem Glass, Inc.), glass slides (Gold Seal), (Tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (“No Stick”, Gelest), fluorescein (Aldrich), rhodamine B (Fisher), sulfuric acid (Fisher), hydrochloric acid (12.1N) (Fisher), hydrogen peroxide (30%, Fisher), 2(or 4)-[10-(dimethylamino)-3-oxo-3H-benzo[*c*]xanthene-7-yl]-benzenedicarboxylic acid, (SNARF, Molecular Probes), chloroplatinic acid hexahydrate (Strem), 1 M tetrabutylammonium flouride (TBAF) in THF (Aldrich), buffered hydrofluoric acid (6:1, NH_4F/HF) (Ashland Chemical) and common solvents were obtained from commercial sources. Silicon oxides were grown on silicon wafers under an ambient atmosphere by heating them to 800 °C for several hours to give an ∼2500 Å thick oxide layer. A home-built apparatus employing a low-pressure mercury lamp (BHK), (173 μW/cm^2) was used as UV source for the UVO treatments. Masters were produced using photolithography to pattern photoresist (AZ 5214, Clariant or SU-8 5, MicroChem) as described previously[78] using 5080 dpi transparencies as an exposure mask. All masters were cleaned with UVO and treated with “No Stick” (as a mold-release agent) in a closed container at around 5 mTorr for 2 h. Solvents used in processing these samples were of analytical grade or higher and used without purification.

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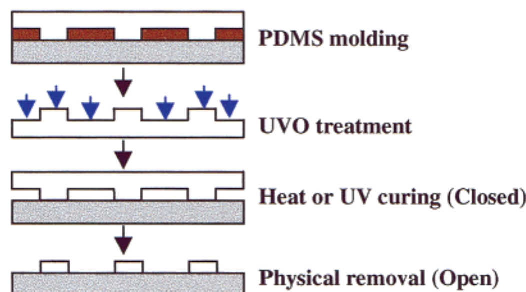

Figure 1. Schematic depiction of the steps involved in the use of CMF as a means to fabricate open form PDMS patterns.

General Analytical Methods. Optical micrographs were recorded using an Olympus BH-2 optical microscope with Panasonic GP−KR222 digital color camera. Electron micrographs were recorded using either a Zeiss DSM 960 or Hitachi S-4700 scanning electron microscope (SEM). For the SEM studies, 6 nm of a palladium/gold alloy was sputtered onto the samples prior to examination to facilitate the imaging. Fluorescence images were recorded using an Olympus Provis AX70 optical microscope with a dichroic mirror assembly (Olympus UM-WIB). This setup uses a 100 W Hg arc lamp to send excitation through a band-pass filter (470−505 nm) to excite a sample. The emission from the sample then passes through a high-band-pass filter (> 515 nm) for capture by an Asashi Pentax K1000 35 mm camera using Kodak Color Watch film. All of the images shown are unprocessed. Surface feature heights were determined by surface profilometry (Sloan Dektak^3 ST).

Sample Preparation and Adhesive Treatment. PDMS molds and stencils were prepared by mixing the commercially available oligomer and initiator in a 10:1 ratio as recommended by Dow Corning with the modification of reducing the pressure (∼50 Torr) in a vacuum oven (National Appliance Union) at room temperature for several minutes to remove entrained gas bubbles. The prepolymer was cast upon the master as illustrated schematically in Figure 1 and, after waiting 10 min for the solution to level, cured in an oven at 70 °C for 2 h. The newly patterned PDMS elastomer was then extracted from the master, washed with ethanol, and dried under a stream of high purity nitrogen. Substrates, which for these studies include silicon, quartz, glass slides, and PDMS, required specific methods of preparation. Silicon, thermally grown oxides, and quartz were rinsed with hexanes and ethanol, dried with nitrogen, and exposed to UVO for 15 min prior to use. Glass slides were cleaned in a piranha solution (3:1 H_2SO_4: hydrogen peroxide 30%) for 5 min, rinsed thoroughly with DI water, and dried under a stream of nitrogen. Caution! This solution is extremely corrosive and reactive with organic materials. PDMS, when used as a substrate, was prepared by exposing the surface to UVO for 20 min and then waiting for 5 to 10 min before rinsing the surface with ethanol, and drying with nitrogen. Finally, the PDMS elastomer's molded surface was modified by exposing it to UVO for 150 s, while holding it at a distance of 1 mm from the mercury bulb. The modified surface was then brought immediately into contact with the precleaned substrate. While maintaining contact, the sample was heated in an oven at 70 °C for a minimum of 20 min. The interfacial bond strength gradually increases and ultimately becomes irreversible over this time. The exposure distance, duration, and "aging" between exposure and substrate contact were all found to be significant experimental variables in the UVO bonding process. Samples exposed for 4 min or more, exposed farther than ∼2 mm from the source, or "aged" in the atmosphere for more than a minute after the UVO exposure did not demonstrate a reliable/reproducible irreversible adhesion to any of the substrates of interest. We also note that for the case of sealing PDMS to PDMS, it is essential to maintain a compliant contact on the more heavily oxidized substrate piece. In addition, heating for 40 min at 135 °C is recommended.

Cohesive Mechanical Failure Patterning (CMF). This patterning procedure follows simply from the bonding steps described above. After inducing adhesion between the molded PDMS elastomer and the silicon substrate, the elastomer patterns were transferred by using tweezers to grip one of the stamp's corners and physically peeling off the bulk pad as illustrated schematically in Figure 1. This procedure works best for patterns with small feature sizes and/or lesser extents of PDMS/substrate contact area (see below). For pattern forms with high symmetry content, we generally found that the best fidelity in the pattern transfer is obtained by peeling the stamp along a direction that minimizes the critical stress. Explicit examples are described below.

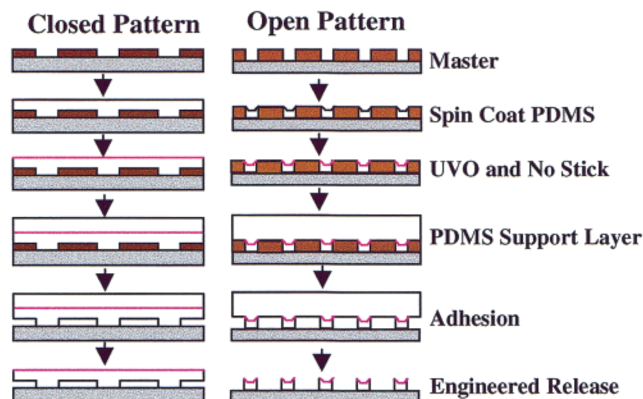

Figure 2. Schematic depiction of the steps involved in the use of SPaR to fabricate PDMS thin-film patterns exhibiting either closed- or open-pattern architectures.

Selective Pattern Release (SPaR). The second method of pattern transfer involves the creation of a well-defined layer of PDMS which is bound to a support layer that has specifically engineered release properties. The two patterning options generally accessible for this method, ones we term open and closed, are shown schematically in Figure 2. The procedure used in each case is identical except for the limits adopted in the first step, the spin-casting of the prepolymer onto the master. The height of the features on the master used must be known beforehand (a variety of feature heights can be easily rendered using photolithographic mastering techniques) and a PDMS spin-coating procedure used that adopts this dimension in one of two ways. If the PDMS prepolymer is cast below the feature height of the master, an open pattern will result; if the prepolymer is cast above the height of the master, then a closed (i.e., PDMS membrane sealed) pattern will result. After spin-casting, both types of decals are cured at 70 °C for 30 min. This PDMS thin-film is then modified for selective release by exposing the film, while still on the master (as seen in Figure 2) to UVO for 3 min, holding it only a few millimeters (1−2 mm) from the source. Immediately after the UVO exposure, the membrane-coated master was then closed in a dry atmosphere container with an open vial of (Tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (No Stick) at room temperature for 20 min. The "No Stick" treated PDMS thin-film/master was then covered with an additional, thicker level of the PDMS prepolymer, which was then cured in place at 70 °C for 2 h. The composite replica was extracted from the master using a scalpel to cut around the pattern's edge. The master was reusable for further patterning. Adhesion of the engineered stamp onto a substrate was then induced by exposing the patterned thin-film surface to UVO for 150 s, and placing the stamp in contact with the substrate, and curing at 70 °C for 20 min. In the last step, the supporting PDMS layer was easily removed using tweezers to uncover the SPaR decal.

XPS Studies of UVO Exposed PDMS. Four silicon wafers were coated with a thick PDMS prepolymer by spin-casting; these films were subsequently cured in an oven at 70 °C for 12 h. Three films were exposed to variations of the UVO treatment. The first surface was exposed for 150 s a distance of 1 mm, the second for 20 min at 1 mm, and the third for 150 s at 6 cm. A control received no UVO exposure. Immediately after their exposure, the samples were analyzed using a Kratos Axis Ultra XPS instrument using a Mg Kα source operating at

225 W and a pass energy of either 160 or 40 eV. A roughly 200 μm^2 analysis area was selected and a charge neutralizer used.

Integrated Microfluidic Devices. A decal comprising closed patterns with interconnected features yields a system of channels upon deposition of the PDMS thin-film onto a smooth substrate via SPaR. Prior to carrying out this transfer step, a metal leather-punch was used to create a hole through both the supporting layer and patterned thin-film so as to intercept a single (pre-designed) capillary that was remote from, but connected to, the entire pattern. In this way, the SPaR patterned thin-film creates a system of microfluidic channels with a single point of access for the addition of fluids (e.g., via COT).[66] Additional levels can be added to the microfluidic system by replicating these steps and transferring the decal to the top of a previously deposited decal. The thicknesses of the elastomers covering any SPaR channel system were found to be easily designed to range from essentially bulk dimensions (mm) to as little at 1 μm without tearing. The registration of the layers was followed using an optical microscope and errors corrected prior to the last heat treatment that effects the bonding of the decal to the substrate. This latter observation clearly establishes that the adhesion developed by the UVO bonding mechanism is sufficiently compliant as to allow correction of alignment errors.

Amorphous Silicon Planar Pixel Array. Low-temperature reactive magnetron sputtering (RMS) was used to deposit amorphous silicon films on glass slide substrates. These films were deposited using 1.5 mTorr of Ar as a sputtering gas. Surface profilometry was used to identify process conditions that yielded a film thickness of ~4000 Å. Using the procedure described above, CFM was used to deposit a thin PDMS resist on the amorphous silicon thin-film. The substrate was then processed by Reactive Ion Etching (RIE) using sulfur hexafluoride in a parallel plate plasma chamber (Plasmatherm 790 series). A detailed description of this RIE processing will be reported in a furture publication. Remnants of the PDMS resist were then removed by submerging the substrate for 30 s in 1 M TBAF in THF.

Patterned Metal Thin Films via Lift-Off Lithography. Using SPaR as described above, an open form PDMS pattern with discrete openings was deposited on a silicon substrate. This membrane-coated substrate was placed in a sputter deposition chamber (EMI Tech K575) and a 60% Palladium/40% Gold source sputtered to a 40 nm coverage. The membrane was then dissolved by sonicating (Cole-Parmer 8852) in 1 M TBAF in THF for 10 min. The patterned silicon wafer was washed with hexane, ethanol, and deionized water, and then dried under a stream of nitrogen prior to imaging.

Electroless Metal Deposition Using a Membrane Microfluidic Reactor. A closed form system of PDMS channels was deposited onto a quartz slide using SPaR. The decal used was designed so as to generate channels sealed by a 24 μm thick PDMS membrane. The channels used in this demonstration were ~13 × 75 μm in cross section (height to width). Following the procedure described above, a metal leather-punch was used to create a hole through both the supporting layer and the patterned thin-film so as to intercept a single capillary that was remote to the interconnected features of the pattern. A solution of chloroplatinic acid hexahydrate (157 mg, 0.303 mmol) in ethanol (0.5 mL) and deionized water (0.5 mL) was used to fill the channel system via COT.[66] A small thick pad of cured PDMS was used to seal the filling reserviour of the membrane-covered microfluidic system, and the system then placed under a passive hydrogen atmosphere at room temperature for 5 h. This exposure led to the formation of metal deposits on the quartz slide forming the bottom of the channel system. An inverted microscope (Zeiss Axiovert 100) with video camera (Sony) was used to image the platinum film from the quartz side of the slide.

Microfluidic Membrane Sensor. A system of PDMS channels was deposited onto a quartz slide via SPaR. The decal was designed so as to seal this channel system with a 27-μm thick PDMS membrane. The channels were then filled by COT using 0.25 mL of a 0.5 M solution of 2(or 4)-[10-(dimethylamino)-3-oxo-3H-benzo[*c*]xanthene- 7-yl]-benzenedicarboxylic acid (SNARF) diluted with 0.75 mL of pH 8.9 (Tris-HCl) buffer. After filling, the liquid reservoir was sealed using a PDMS slab. The quartz mounted membrane microfluidic reactor system was placed over the lens of an inverted fluorescent microscope (Leica TCS SP2) for imaging and analysis. Excitation was provided by a 514 nm argon laser through a 458/514 nm filter with a prism and three PMTs were set up to simultaneously monitor emission at 545−465, 580−600, and 620−640 nm. An open vial containing ~2 milliliters of concentrated HCl was placed two centimeters from the PDMS membrane system. Both the acid vial and membrane system were enclosed in an ambient atmosphere chamber and images recorded every 6.45 s.

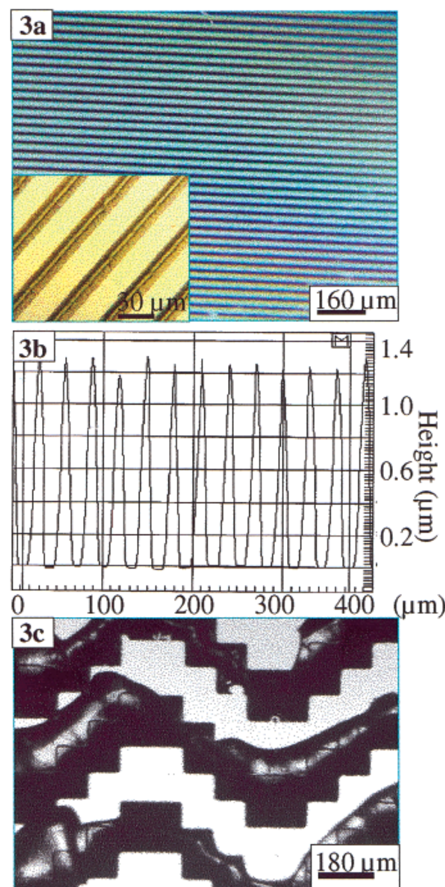

Figure 3. Use of CMF to deposit line structures with different design rules: (a) a straight pattern with small feature widths; (b) regular film thickness of the features in (a) as indicated by surface profilometry; and (c) a similar PDMS coverage with wider features that resulted in a loss of fidelity in the pattern transfer, a complex locus of cohesive failure, and irregular film distortions.

Results

The bonding of PDMS to a variety of smooth substrate surfaces that results from the UVO treatment described in this report provides a novel method for achieving pattern transfer. In the studies carried out here, we have identified two methodologies based on an adherent transfer mechanism that appear to work well as a form of decal lithography. In one, a patterned PDMS stamp is exposed to UVO and brought immediately into contact with and bonded to a smooth substrate surface. Once bonded to a surface in this way, peeling the stamp off the surface results in a cohesive failure within the PDMS itself. The locus of this failure is such that it directly transfers the stamp's surface features to the substrate as depicted schematically in Figure 1. Figure 3 shows two examples of

PDMS patterns with very different feature sizes and design rules that were created in this way. The pattern shown in Figure 3a was made by transferring PDMS lines to a planar silicon substrate. The origin of this pattern was a master of coplanar lines that are 15 μm wide with a depth of 1.5 μm and a separation of 20 μm. The image shown here reveals the cohesive failure caused by peeling the stamp off in a direction parallel to the direction of the lines, one leading to a failure in the stamp near the regions where the surface features join the bulk of the PDMS stamp. This catastrophic failure of the polymeric material leads to a necking which distorts the shape of the original rectilinear contours of the stamp's structures. Figure 3a demonstrates that the pattern transfer achievable with this design rule is quite good, in fact, remarkably so. There are few gross defects, and the pattern produced is both uniform and reproducible. It is particularly notable in the profilometry data shown in Figure 3b that the deposited lines share a uniformity of feature heights and spacing. Maintaining pattern fidelity with larger feature sizes proved problematic, however. This is well-illustrated by the specific example shown in Figure 3c. Although this larger line-width pattern has the same amount of PDMS surface coverage as the previous example, it required a much greater force to peel the pad from the substrate. The "yield strength," we have found, tends to follow both the PDMS contact area and feature sizes in a direct way, one that limits CMF patterning to feature sizes that are generally below 100 μm (see below). For the specific case shown here, the locus of cohesive failure was irregular, often extending away from the plane where the features join the stamp and into the bulk of the pad. Figure 3c displays a design based on contoured 180 μm lines with 180 μm line-widths, a depth of 8.6 μm, and a pitch of one. Although this pattern is faithfully reproduced at the adherent stamp surface/substrate interface (the pad here was peeled off in a direction perpendicular to the lines), undesirable overhanging protuberances were also formed. This latter problem was a general complication seen for patterns with component feature-sizes over 100 μm.

The CMF method excels at the transfer of PDMS patterns with small feature sizes over very large areas. An interesting aspect of this method is that it can do so in a manner that both allows registration (because the stamp is transparent and the bonding is activated, contact alignments can be checked with a microscope and corrected if in error) and enables micron scale patterning over large areas. We have found, though, that the locus of the cohesive failure of the stamp progressively approaches the surface features as their sizes approach the 1 micron level. Decal transfers in the (10−100 nm) thickness range were easily reached for a 1.0 μm design rule, based on a master with a 1 μm feature height as a specific example. The removal of the pad for these small features sizes also required less force. Several examples of small feature patterning by the CMF variant are shown in Figure 4. The first example, a set of lines 1 μm wide with a pitch of one, is shown in Figure 4a. The second representative pattern, a 2.5 × 2.5 cm pattern derived from a master composed of a square array of holes 2 μm in diameter, 1.5 μm deep, with a 2.7 μm center to center separation, is shown in Figure 4b,c. The view shown in Figure 4c is the widest field of view that we can photograph and still resolve individual pixels. The point to note here is that very few defects are seen in the entire 6.25 cm^2 area of the pattern.

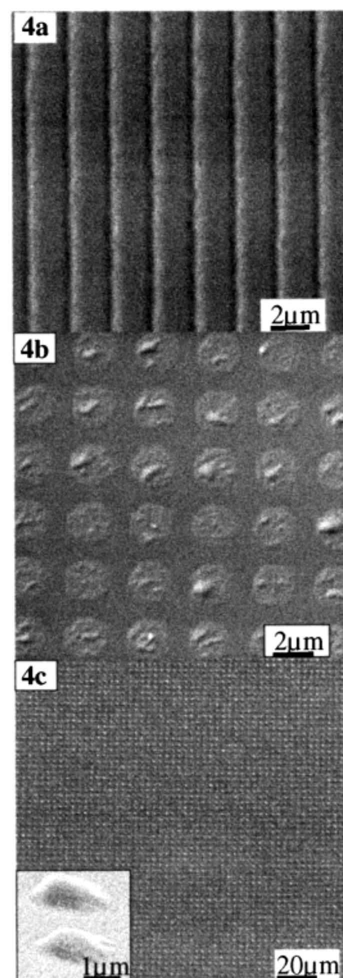

Figure 4. Micron scale, large area patterning of PDMS via the CFM mechanism: (a) a set of continuous 1 μm lines with a pitch of one; (b) discrete circles with a 2 μm diameter; and (c) segment of a nearly defect free 2.5 × 2.5 cm^2 pattern array (inset shows a representative pair of PDMS "droplets").

These data clearly show that, even at this early stage of development, DTM can produce PDMS structures with micron scale feature sizes over very wide substrate areas with few gross defects via the CMF variant. Our studies suggest that submicron design rules should be easily accommodated. One does note, though, that the structural character of the PDMS structures transferred in this instance (as regards their thickness) are somewhat complex. The 1 micron lines shown in Figure 4a illustrate that the transfer in this case yields patterns with a well-defined height profile; the line heights are well centered at the submicron level across the array. The 2 μm circular pixels, however, show a more complex PDMS coverage pattern throughout the pixel, but one that never showed a thinning of the polymer below a 5−10 nm thickness. As we show below, these latter structures still serve very effectively as resists for Si processing by both wet etching and RIE methods.

The mechanical and design-rule sensitivities noted above led us to develop a second methodology, selective pattern release (SPaR), to extend the design rules of DTM and lift the constraints imposed by the sometimes complex loci of mechanical failure seen in CMF. We used the procedure depicted in Figure 2, to accomplish this goal. The modified interface, incorporated between the surface features to be patterned and

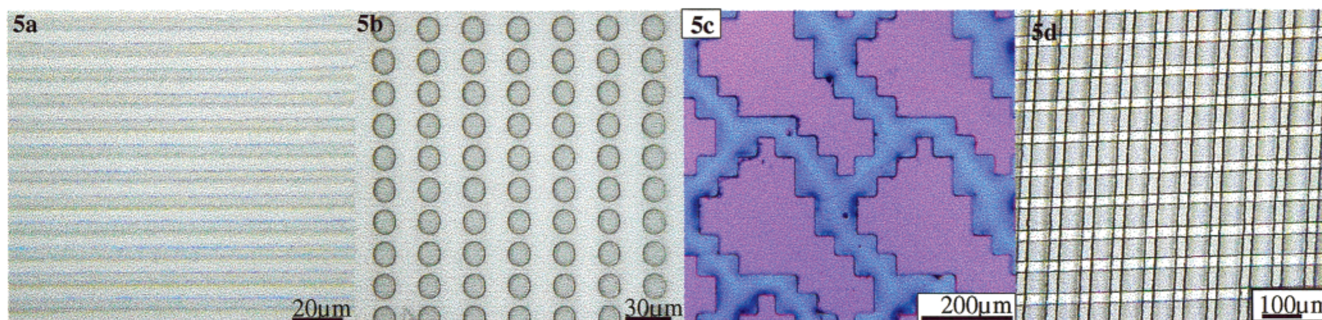

Figure 5. Micrographs of representative continuous, open patterns of PDMS deposited via SPaR. The examples show the following: (a) lines 5 μm in width, 600 nm high, and a pitch of 1 supported on silicon; (b) a stencil mask in a 2.8 μm thick PDMS sheet featuring holes 10 μm in diameter in a rectangular array supported on silicon; (c) complex topology in high aspect ratios lines that are 8 μm thick supported on a thermally grown silicon oxide; and (d) lines 70 μm thick with a separation of 20 μm deposited on and perpendicular to an identical set of PDMS lines supported on silicon.

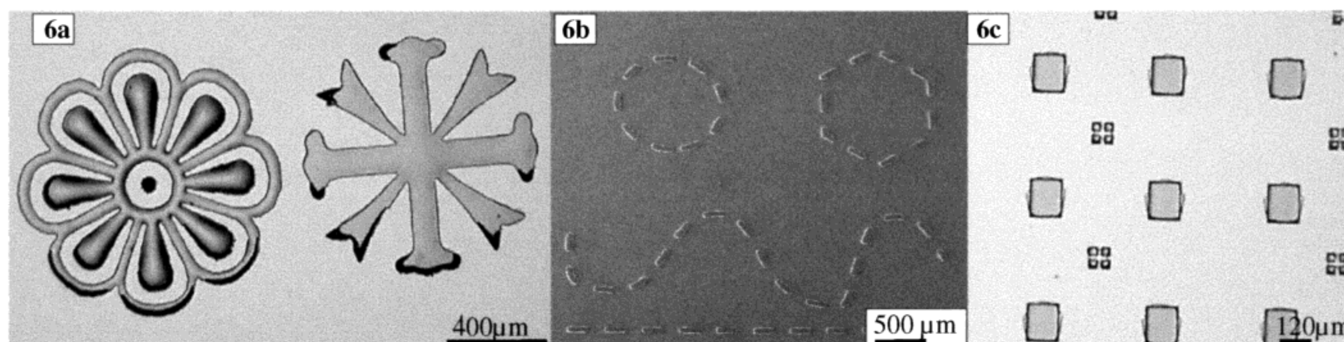

Figure 6. Large area deposition of discrete, open form PDMS thin-films with a defined thickness (8 μm): (a) complex pattern shapes and closures; (b) large area patterning that embeds significant variations in interfeature spacing; and (c) significant pitch and size variations shown by 30 μm^2 squares arrayed in 70 μm^2 clusters of patterns that embed a significant variation in the feature spacing.

the bulk PDMS pad that serves as their support, provides a designed control mechanism for the decal transfer. This interface allows the deposition of precisely designed polymer thin-films encompassing a broad range of design rules, integration properties, and feature sizes. The examples shown in Figure 5 demonstrates the ability of SPaR to produce a variety of continuous, open-form PDMS patterns. Such designs are trivially obtained by spin-casting the first application of the PDMS prepolymer below the height of the features on the master (right panel, Figure 2). The silicon-supported structures shown in

Figure 5a, a continuous open-form pattern of 5 μm lines with a pitch of one, were deposited by diluting the PDMS prepolymer 4:1 with toluene for the first application and spin-casting it to a thickness of 600 nm on a master with 5 μm high features. The structures shown in Figure 5, parts b and c, were similarly fabricated. The structure shown in Figure 5b was produced by spin-casting the PDMS prepolymer to a thickness of 2.8 μm on a master formed by circular posts that were 5 μm tall and 10 μm wide. The thermal oxide-supported example that is shown in Figure 5c used a prepolymer cast to a thickness of 8 μm on a master bearing features 13 μm tall. Finally, the composite set of PDMS lines shown in Figure 5d illustrates a set of continuous, open-form 70 μm wide lines separated by 20 μm which were deposited perpendicularly upon an identical set of lines previously deposited on silicon. Each level used PDMS lines that were 8 μm thick.

In many regards, the structures shown in Figure 5 extend pattern types that can also be fabricated by techniques such as MIMIC or EMP. The notable advance embodied in DTM, however, stems from the fact that it utilizes a bulk PDMS pad to support the decal during the pattern transfer. This enables the methodology to microfabricate structures not previously accessible, namely, discrete open-form patterns, and does so in a way that is in principle consistent with precision transference and manipulation for registration. It also allows film-thickness control over a very wide range and, as far as we have been able to determine, has no upper critical design rule limitations in either pattern array sizes or line-widths. An illustrative set of examples of this design flexibility is presented in Figure 6. Each of the noncontinuous patterns shown were cast to around 8 μm on masters with feature heights averaging 13 μm. Figure 6a is an example of computer symbols printed at a font size of 8, which makes the area of each thin-film character about 1 mm^2. This example shows that decals can still be released easily, even when they incorporate very large areas of physical contact. The structures shown in Figure 6b were generated from a pattern derived from a common component, rectangles that are 210 μm long and 50 μm wide. The range of the spacings shown here is a significant point of note. The example shown in Figure 6c provides a demonstration of patterning that entangles a range of features sizes and pitches in a complex array. In the micrograph, one clearly sees the successful release of the square arrays of four 30 μm^2 squares on 40 μm centers, which in turn interpenetrates a larger square array of 120 $\times$ 140 μm rectangles spaced by 420 μm centers. Again, the significant features sizes and pitches demonstrated here is a point of considerable interest.

DTMs ability to define and release patterned PDMS thin-films through the SPaR methodology suggests other possibilities for microfabrication. This latter method, as schematically depicted in Figure 2, simply involves casting the prepolymer solution to a thickness greater than the master's feature height. The pattern shown in Figure 7a, for example, was derived from

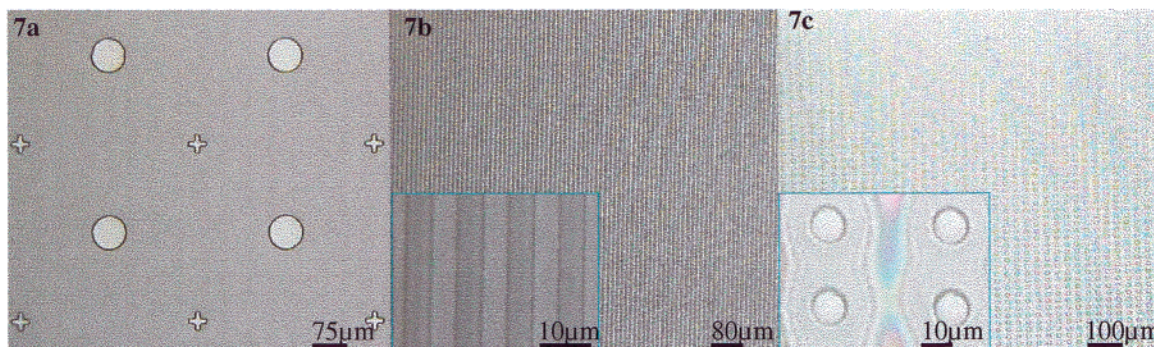

Figure 7. Using SPaR to pattern PDMS over large areas in closed-form patterns of cavities sealed by membranes of known thickness: (a) 25 μm thick membrane enclosing large area 75 μm diameter cylinders and smaller crosses; (b) 5 μm wide, 5 μm tall channels with a pitch of one and sealed with an ultrathin 2 μm thick membrane; and (c) 5μm diameter cylinders, 5 μm tall, and sealed with a 2 μm thick membrane.

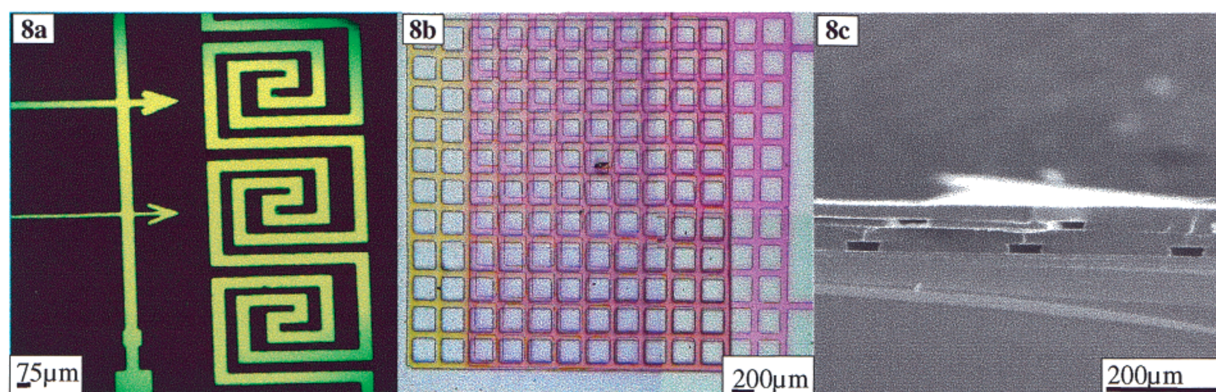

Figure 8. Micrographs of PDMS membrane microcapillary channels. Representative fluorescein-filled microfluidic channels: (a) a complex interconnected array of 20−75 μm wide channels, 12 μm high and covered a 10 μm thick membrane; (b) a composite image showing two sets of microfluidic channels, 75 μm wide, 13 μm high and covered by a 10 μm thick membrane. The separate microfluidic systems are filled with solutions containing fluorescein (bottom, yellow) and rhodamine B (top, purple); and (c) a SEM cross-section of stacked PDMS microcapillaries.

a PDMS prepolymer that we spin-cast upon a master to give a film thickness of 37 μm. Because the master's features were only 12 μm tall, the pattern produced consists of an interpenetrating square array on 400 μm centers of 75 μm diameter cylindrical and 40 × 10 μm cross-shaped cavities, all of which are sealed under a 25 μm thick PDMS membrane. The examples shown in Figure 7b,c were made from the same masters used to produce the patterns shown in Figure 5a,b, except that the film was cast this time to a thickness of 7 μm to cover the 5 μm features of the master. These masters give 5 μm channels with a pitch of 1 and a rectangular array of 10 μm holes with centers separated by 20 μm vertically and 30 μm horizontally, each respectively covered by 2 μm thick membrane. Taken together with the insets shown in Figure 7b,c, the SPaR method clearly demonstrates remarkable design tolerances and impressive capabilities for wide area patterning. The essentially defect-free structures shown in Figure 7b,c appear to hold particular promise for sensor applications based on microfluidic devices. We now turn to consider this prospect in more detail.

The ability to form PDMS reactors and channel systems sealed with a precisely defined ultrathin membrane suggests that DTM could make a major contribution to the microfabrication of three-dimensional microfluidic devices[28,48,74−76,79,80] and microreactors.[81,82] As noted above, soft lithography has been receiving considerable attention in research focused on the microfabrication of microfluidics for on-chip technologies. The examples presented in Figure 8 suggest the possibilities that DTM offers in this area of interest. These examples were chosen to highlight issues related to the design rules that can be accommodated in the fabrication of membrane microreactors of advanced design. Figure 8a shows a portion of a large PDMS channel system; to collect the fluorescence image the device was filled with fluorescein using the COT method.[66] This pattern's feature sizes vary widely; from 20 μm wide channels to 600 μm^2 square sections. The decal used to construct this channel system had a height of only 22 μm. Because the master's features were 12 μm high, this complex channel system is sealed by a membrane that is only 10 μm thick. Figure 8b features an example of two identical microfluidic systems stacked one on top of the other, and each filled with different solutions. Both levels were cast to a thickness of 23 μm over a 13 μm height profile master; a permeable membrane with a thickness of only 10 μm separates the fluids in the two levels of this microfluidic system. Because of the device's large size, the image shown is a composite of several micrographs that have been stitched together to image the channels; the bottom capillary was filled with fluorescein and the top filled with rhodamine B. The grid's channels are 75 μm wide with intersections spaced on 240 μm centers. An SEM micrograph of a similar stacked channel system is shown in Figure 8c; the structure shown here has 75 μm wide channels that are 12 μm

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high and covered with a 20 μm thick membrane. The feature sizes and membrane dimensions shown in Figures 7 and 8 compare quite well with the most sophisticated PDMS-based structures reported in the literature.[74,76] DTM thus provides a very convenient and design-tolerant route to fabricating devices of this sort.

XPS was used to study the effects of UVO exposure on PDMS samples. The data proved rather unremarkable when considered in the context of the data currently available in the literature.[83−85] We generally found that PDMS samples are oxidized in this ambient. Samples held 1 mm from the light source are more heavily oxidized than those held for similar length of time at a distance of 6 cm. The extent of oxidation, as deduced from the observed C1s:Si2p ratio, is progressive in time. The sample surfaces became extensively degraded after a 20 min exposure, for example (a 50% reduction in the C1s: Si2p ratio was noted). Perhaps most interesting, the sample surfaces treated by UVO under the conditions that lead to strong adherent bonding showed only modest signs of oxidation of the PDMS near surface regions (as indicated by a reduction of only 8% in the C1s or Si2p line-shapes). The data thus suggest that the UVO treatment minimally oxidatively degrades the PDMS surface. The molecular characteristics of the surface it renders remain unclear. We note, however, that physical properties such as wetting clearly suggest the polar character of the PDMS surface phase created by the UVO treatment; these surface are in fact somewhat hydrophilic and only slowly reconstruct to give the hydrophobic properties expected for PDMS. In total, the results are qualitatively similar to those reported by earlier studies of UVO and plasma surface modifications of PDMS.[86,87]

We carried out several experiments to demonstrate the potential of DTM as a means of constructing resist levels for applications in microfabrication processes. Representative examples are illustrated in the micrographs shown in Figures 9 and 10, which profile the fabrication of amorphous silicon (α-Si) pixel arrays supported on a glass substrate and Au/Pd thin-films microstructures supported on a Si(100) test wafer, respectively.

Figure 9a shows a high magnification micrograph of one PDMS structure deposited by the CMF method that served as the resist level for the fabrication of the α-Si pixel array. The low mass coverage and irregular shape of the resist is evident in this micrograph. Perhaps the most stringent test of their effectiveness as a resist is their performance when subjected to a RIE process environment (wet etching or lift-off patterning being less demanding chemical environments for an organic thin film resist). The sequence and outcome of this RIE processing is illustrated in the images shown in Figure 9b−c. After etching in a sulfur hexafluoride plasma the Si pixels and a residue of the PDMS resist are clearly seen (Figure 9b). A brief immersion in TBAF in THF strips the resist residue leaving behind the isolated α-Si pixel array (Figure 9c and d). The structural quality

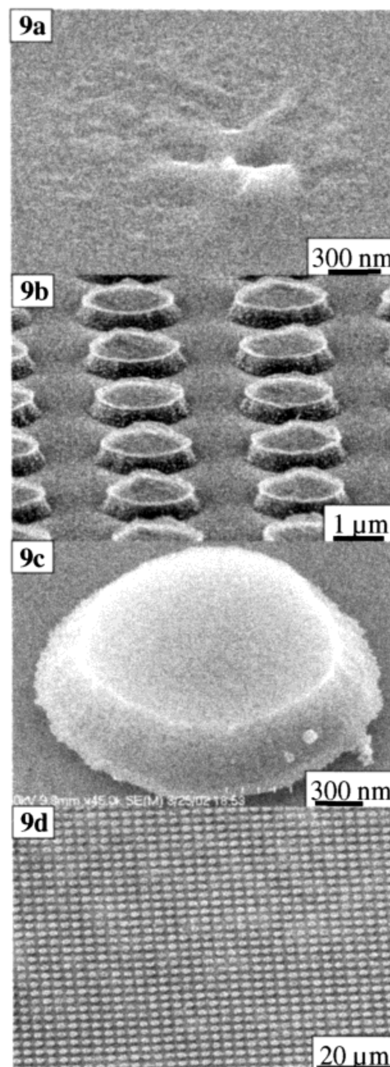

Figure 9. An example showing the use of DTM as a RIE patterning method. A thin CMF deposited PDMS resist was used to pattern an amorphous Si pixel array on a glass substrate via the following process: (a) 2 μm diameter, thin PDMS circles were deposited by CMF onto a ~4000 Å thick amorphous silicon film; (b) the PDMS-resist covered silicon pixels supported by the underlying silicon oxide substrate after plasma dry etching with SF_6; (c) the silicon pixels after dissolving the PDMS resist using 1M TBAF in THF; and (d) a lower magnification image of the pixel array.

of the silicon pixels obtained are less than ideal (side wall undercutting being noted) and the RIE processing remains far from optimized. All the same, the fact remains that etching selectivities in excess of 10^3 to 10^4 appear to be possible using this system and improvements appear likely with further process development.

Figure 10 shows Au/Pd thin film structures patterned on Si-(100) using a lift-off patterning method. The 5 μm thick PDMS resist level in this case was deposited by SPaR. The resist itself is shown in Figure 10a, a micrograph that fully reveals the challenging feature pitch associated with this test structure. The Au/Pd sputter-deposited structures, after the resist stripping, are shown in Figure 10, parts b and c. Several subtle points of interest are brought out in this example. The resist level shown here could be deposited by other soft-lithographic methods, in particular MIMIC and EMP, and as such these methods deserve comparative evaluations. The resists from MIMIC tend to be much thicker than is true in the case for this demonstration (and

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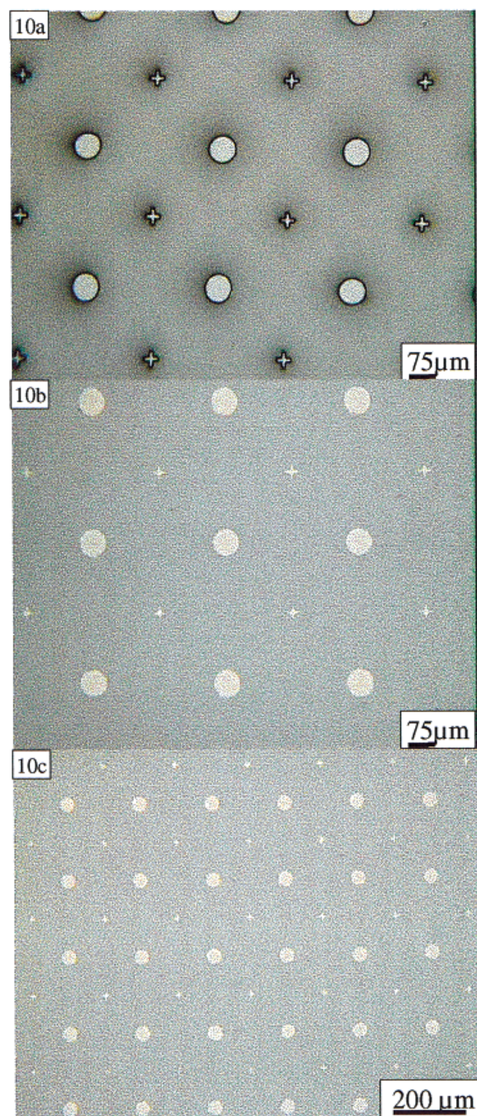

Figure 10. Example showing the use of DTM in the lift-off patterning of metal thin films. A SPaR deposited pattern was used as a stencil mask as illustrated in the optical microscopy images: (a) a 5 μm thick PDMS stencil mask with a square array on 400 μm centers of 75 μm diameter circular openings and 40 × 10 μm cross shaped cavities supported on a planar silicon substrate; and (b) the same substrate after depositing 40 nm thick films of 60% palladium/ 40% gold via sputtering. The PDMS stencil was removed using TBAF; (c) a larger view of the metal thin-film pattern. The area patterned in this way was 1 × 1 cm.

as a result tend to lead to shadowing effects in the deposited features),[46] and would have great difficulty accommodating the pitch of this layout (due to the large distances the elastomeric mold would have to span). Residues from the molding also tend to complicate the adhesion of deposited films and thus requires careful cleaning steps to avoid this problem. EMP resists would perform better, but are mechanically very difficult to manipulate at the scale of this demonstration. The PDMS resist levels from SPaR compare very well in this regard as they perform well as lift-off resists for metal patterning and are extremely easy to process.

SPaR's ability to pattern useful membrane-sealed microfluidic reactor systems is illustrated by the example shown in Figure 11. The pattern of 75 μm wide and 17 μm high channels separated by 200 μm spaces was open only to a large liquid reservoir which was subsequently sealed by a bulk PDMS slab several millimeters thick. The channel system itself was filled with a solution of chloroplatinic acid dissolved in an ethanol−water mixture. When exposed to a hydrogen atmosphere, a reaction ensues that leads to the deposition of a Pt thin film. This reaction is very selective in that the metal is formed (as best we can tell) only on the bottom of the channel system's capillaries. Most notably, the deposition proceeds only in the membrane sealed portions of the pattern (it did not extend back into the reservoir itself). A control not exposed to hydrogen was stable, showing no signs of metal deposition after many hours.

The example above suggest applications lying outside the interests of microfabrication. Specifically, we examined a model system to illustrate SPaR's utility as a means for fabricating membrane sensors. To do so, we patterned a PDMS thin-film on a quartz slide to create a similar microfluidic system with channels 75 μm wide, 21 μm tall, and separated by 200 μm into an interconnected grid pattern, here covered by a 27 μm thick membrane. These channels were filled with a pH ∼8.9 solution of the acid sensing fluorophore SNARF, whose emission shifts from 640 nm at pH 9.0 to about 580 nm at pH 6.0[88] and ceases to fluoresce appreciably at lower pH values. For this experiment, the excitation was set at 514 nm (argon ion laser) and an image collected every 6.45 s. The images shown in Figure 12 correspond to ones collected using a PMT data channel set to image a wavelength (620−640 nm) that optimized the weighted fluorescent response of the basic form of the SNARF dye used. The sequence of these images (Figure 10a−c) were extracted from the series of acquisitions made over a period of 90 s. Upon exposure to a diffuse source of HCl (a point source of concentrated HCl was placed in the sample box at a distance of 2 cm), the sample is rapidly acidified by molecules diffusing through the thin PDMS membrane. The data shown here demonstrate clearly that this transport rate is fast, a property that is a reflection of both the permeability of the PDMS to HCl vapor as well as the short diffusion path length of the membrane used to seal the channel system. As expected, a control sample that was scanned in this manner for an hour in the absence of an HCl vapor source showed no change in the measured fluorescence intensity.

Discussion

Decal Transfer Microlithography is a unique patterning technique that exploits a rich interplay of several main processing steps. Each contributes in some fashion to the design rules (demonstrably broad ones even at this early stage of development) that it supports. These include the casting, mold wetting, adhesion, and the cohesion steps used to form and transfer a decal pattern. DTM, like other soft lithographic techniques, uses PDMS as the material of choice to develop the microstructures of its decals. As we show in the representative examples provided in this report, the PDMS patterns are able to serve as resists or templates suitable for patterning a wide variety of materials and provides a natural complement to other soft lithographic techniques. Because PDMS is optically transparent above 230 nm,[76] it also serves as an ideal material for applications requiring photochemical activation, multilevel alignment, or spectroscopic investigation. Although not directly

(88) Catalog from Micro Probes.

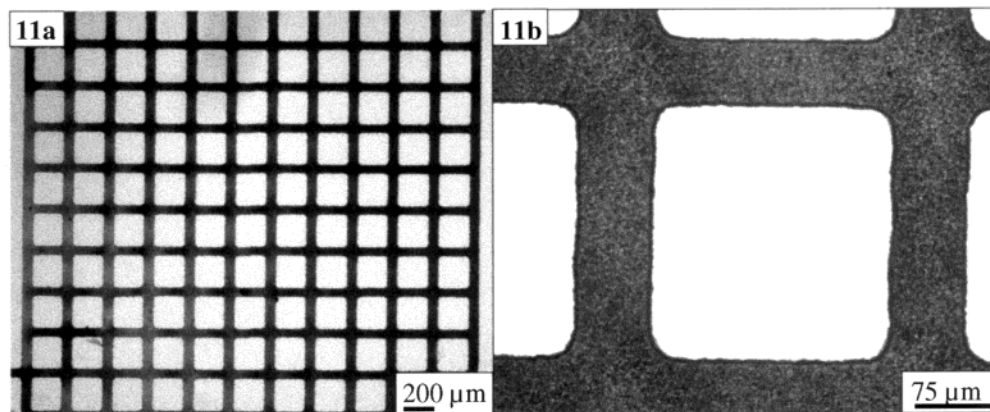

Figure 11. Use of SPaR to pattern PDMS membrane-covered microfluidic reactors. The micrographs show: (a) a low magnification image of a Pt thin film selectively deposited at the bottom of a glass supported PDMS channel system after filling it with a solution of H_2PtCl_6 and exposing it to a H_2 atmosphere; and (b) a higher magnification of a capillary intersection evenly coated by Pt.

examined in this work, the compliant nature of the PDMS stamp suggests that DTM should similarly inherit the ability demonstrated in other soft lithographic methods (e.g., MIMIC and μCP) to pattern PDMS in decal form upon nonplanar or 3-D substrates.[41,46] Potential disadvantages of PDMS as the material used for DTM patterning are also suggested by past research on soft lithography. Given that PDMS shrinks by ~1% upon curing, has an experimentally significant coefficient of thermal expansion, and that the elastomer is easily swelled by solvents, achieving multilevel registration for submicron design rules remains a significant challenge and stands as an area of need for progress in research.[19] We consider each of these issues in some detail in the discussions that follow.

The starting point for the DTM method is the replication of a pattern embedded in a master, a feature shared with other methods of soft-lithographic patterning. In this work, we typically used templates based on patterned photoresist to generate our decal constructs. The choice of photoresist is not a completely innocent one in our experience. Most of the patterns shown here were derived from replicas formed by casting against patterns fabricated in an SU8 photoresist. This material is well-suited for forming features sizes down to the micron scale with a wide range of heights and aspect ratios.[89]

For example, feature heights ranging from 200 to 5 μm are easily obtained using this resist, dimensions well-suited to the limiting ranges appropriate for constructing resists at the one end and microfluidic devices at the other.[89] This material is also amenable to the rapid prototyping method used to generate many of our masks.[78] We note that the most important sensitivity we have observed related to the choice of the photoresist was actually seen later in the processing. Notably, the use of the SU8 resist always yielded replicas that bonded well to substrates after the UVO treatment; an alternative resist, AZ 5214, was found to give replicas that on occasion could not be made to bond (and thus transfer a decal imprint) to a substrate. We were not able to determine the cause of the failures, but believe low molecular weight components were transferred from the resist that modified the adhesion properties of the PDMS in some way.

The most important point to note is that the DTM method appears to combine many of the best features of two prototypical soft-lithography patterning methods, namely MIMIC and μCP. It does so, however, in ways that lift many of the constraints that limit these methods, whereas at the same time engendering new capabilities for patterning. The most obvious point of note here is that DTM, whether via the CMF or SPaR variants, transfers a polymeric film with mass coverages that can span (in a designed fashion) from tens of nanometers to microns to essentially millimeters or beyond. In some senses, the method appears to follow closely the design rules enabled by MIMIC. Both can be used to form polymeric structures and resists. MIMIC, while having an advantage in that many possibilities exist for the types of polymers that can be molded, requires that the mold for a pattern formed be filled by a fluid. This leads to very direct limitations in the feature types and designs that can be easily accommodated, and the level of the defect densities that can be reached.[23] In most of our applications of MIMIC in electronics microfabrication, for example, the resist structures used were generally constrained to patterns that describe a continuous form and had no limiting feature sizes below ~20 μm or above ~200 μm.[46,51] The latter constraints derive from the difficulties encountered in filling small channel features with a viscous prepolymer and the sensitivity of the elastomeric molds to sagging and other gross mechanical deformations. The mass transfer of these polymer constructs/resists via DTM has some advantages as regards these latter constraints and is further benefited by the very real improvements it affords in limiting the surface contamination that typically attends the molding of liquid prepolymers.

The alternative soft-lithographic method, μCP, is a very powerful technique and has been used to generate high-quality feature sizes that are well below the micron level; these latter dimensions are ones that generally speaking are not accessible to MIMIC. The structures made by μCP can also be rendered in both continuous and discrete form (the latent image's mass transfer being sensitive only to the need of effecting a point of contact between the substrate and features present on the stamp). The method requires a suitable chemistry for the ink, and for this reason the most extensive use and most developed applications of μCP have involved the patterning of self-assembled monolayers (SAMs).[21] These structures, although of considerable interest and utility, have limitations regarding their applications in microfabrication. First, SAMs have only limited utility as resists; the best applications involve the patterning of

(89) Zhang, J.; Tan, K. L.; Hong, G. D.; Yang, L. J.; Gong, H. Q. *J. Micromech. Microeng.* **2001**, *11*, 20.

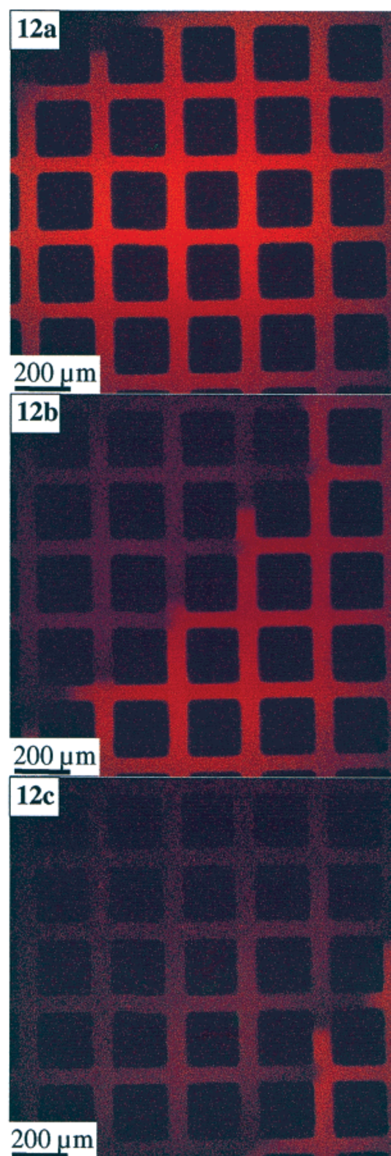

Figure 12. Use of SPaR to pattern a model PDMS membrane-covered sensor. The images are constructed from CCD intensity scans of the emission of SNARF, a pH sensitive fluorophore, between 620 and 640 nm. The system was excited at 514 nm using an Ar ion laser. The images document the loss of the emission of the basic form of the dye as the media is acidified as a result of the facile diffusion of HCl gas from a fixed effusive source through a 27 μm thick PDMS membrane: (a) intensity loss monitored in the upper left corner array (that closest to the source) at 52 s; (b) the progression of the intensity loss monitored at 90 s; and (c) the intensity monitored at 122 s.

metals such as Au, Ag, and Pd via wet etching, metals for which inks forming high quality SAMs are available (these metals, in turn, can be used as secondary resists to pattern a material such as silicon). Reactive spreading of the adsorbed ink, though, is a concern noted in the literature regarding the use of SAMs as templates for microfabrication.[42,68] Perhaps most important are the difficulties associated with achieving registration in multiple printing levels. Because the mass transfer of the ink in μCP occurs promptly at the time and point of contact, the alignments cannot be inspected easily and errors corrected.

DTM appears to have a number of unique characteristics when viewed in the context of the points outlined above. The most notable of these is the fact that the design rules embraced by the method are very broad. We have demonstrated high quality, large area, micron scale patterning via CMF; the PDMS structures transferred here easily span thicknesses in the range of 10 to 80 000 nm. There seems to be considerable promise for engineering research to further develop and improve the performance of this method as a general technique of submicron patterning. The decal pattern transfers demonstrated by the SPaR variant complement these metrics well. We note successful examples of large area patterning that reached limiting design rules with features sizes as small as 5 μm, and feature heights ranging upward from 0.6 μM (the thinnest resist examined here). The edge definition of the SPaR demonstrations reported here are ones that simply follow from the quality of the master (except in one important regard, see below). The lack of mechanical deformation that attends the use of a release layer (ones clearly seen for CMF) is a significant advantage of the SPaR version of DTM. We note, though, that further improvements are required to extend the scope of SPaR in a general way beyond the 5 μm limit demonstrated here. The issue of concern is one related to the different release properties needed for the engineered interface in the composite stamp on one hand and the master on the other. Clearly, a submicron capable SPaR method would hold enormous advantages over CMF-based decal transfers. The problem we have encountered in doing this is that the composite stamps are very hard to release from the molds without inducing mechanical failures when the feature sizes are very small. Currently, the duration of the master/thin-film exposure to the UVO treatment is used to control the extent of the surface oxidation and thus the ultimate amount of the mold release agent that can be adsorbed.[90] We have optimized this parameter in a qualitative way at this point and it is likely that some further improvements are possible. We note that the absorbance of this release agent by a PDMS surface exposed to UVO has been examined by Genzer and co-workers, and they estimate that this treatment yields a surface coverage of about 1.5×10^{14} molecules/cm^2 after an hour of UVO exposure (as compared to the $\sim 5 \times 10^{14}$ molecules/cm^2 limiting coverage reached on silicon/silicon oxide). This suggests that considerable room for improving the adhesion and release properties still exists. As it is now, however, the range of the differential adhesion strengths afforded by the use of a common silane release agent on both the mold and release interfaces (and for some cases, the mechanical and tensile properties of the PDMS) are simply not adequate to support a general submicron patterning method based on SPaR. We are currently developing a release mechanism that can be activated photochemically as one means of addressing this problem and will describe these efforts in a future publication.

Another interesting point of comparison for SPaR is provided by the EMP soft lithography technique. This comparison is most relevant to the open-form structures shown in Figure 5. Both EMP and SPaR use a common spin-casting procedure to form a PDMS thin-film stencil. The use of a backing layer to support the fragile stencil is unique to SPaR. This enables not only a more practical approach to microfabrication, but also allows the transfer of discrete polymer patterns as well (i.e., the inverse image of an EMP stencil). We should note that one important topographical aspect that is common to both methods is the presence of a shape meniscus around the features of the PDMS

(90) Genzer, J.; Efimenko, K. *Science* **2000**, *290*, 2130.

stencil. This structural feature is illustrated schematically in the right panel of Figure 2. The wetting properties of the prepolymer and master's surface give rise to this phenomenon. It is clearly a property that future research might seek to eliminate as a nonplanar topography could frustrate the development of complex, multilevel designs based on multiple membrane stacking. We believe that this might be done by using recently developed "constrained" molding steps,[76,79] but only if the desired thickness of the film matches the feature height of the master. This latter constraint is not relevant, however, to the fabrication of the closed-form structures that can also be obtained via SPaR. We should note that, although most of the spin-casting work used undiluted prepolymer (appropriate for forming films between 100 μm and 1.7 μm), we have also cast some submicron films by diluting the PDMS prepolymer solutions with toluene. This dilution also effects the meniscus seen, as does the side-wall aspect pitch (and possibly aspect ratios as well). We have not examined any of these sensitivities systematically, but simply note their possible relevance.

The membrane microfluidic systems obtained by the SPaR patterning method bear some resemblances to the metrology of the structures yielded by another soft-lithographic patterning method, micromembrane sandwiching (μMS).[74,75] This latter method has been extensively developed by Whitesides et al. as a general fabrication strategy for 3D microfluidic systems. The latter method uses a plasma-based protocol to effect the bonding of multiple PDMS levels, one that appears to complement well the UVO protocol reported here. The μMS method offers one capability that we have not explored in the development of the SPaR patterning method, namely the simultaneous development of molded forms on both sides of a PDMS membrane structure. This appears to be a useful direction to pursue in future research. We simply note here that, as currently developed, the two methods appear to complement each other very well and have interesting contrasts as to their abilities to form very thin membrane sealed microfluidic systems.

As noted earlier, the surface treatment of the PDMS by UVO prior to its contact with the substrate is the most critical step underlying the performance of both DTM methodologies. CMF and SPaR both require the formation of a strong adhesive bond between the surface features of the patterning tool and the surface of the substrate in order to transfer a decal. Treating the substrate and the PDMS stamp's surface with UVO immediately prior to contact, followed by heating modestly, proved to be a very successful method for doing this. A clean substrate is absolutely necessary, as is the proximity of the samples to the UV source during the exposure. It is most striking that the adhesion is lost when the samples are held farther than $\sim$2 mm from the UV source bulb. We have also found that contact between the substrate and the stamp must be made promptly as the modifications induced by the UVO treatment are unstable, and their decay serves to limit the adhesive bond strength. The bonding is not immediate, however, and thus alignment errors can be corrected rather easily. We have also found that the heat treatment needed to develop the bonding can be eliminated by modifying the procedure in one of two ways, but only so long as the contacts are made promptly as described above. In the first case, if the surfaces were left in contact at ambient temperature for 16 h, then a strong bond was generally obtained. We also found that the contacting assembly could also be irradiated through the PDMS from the backside with 365 nm light, and this too promoted the strong bonding of the assembly. This latter method was not fully developed, however, and a more careful examination will be required to establish whether the bonding results from heating or a separate photochemical pathway.

This brings us to a consideration of the mechanisms that might underlie the adhesion of a treated PDMS surface to the substrates used here. Unfortunately, this aspect of the patterning method is not entirely understood, but interesting insights may be gleaned both from our studies and recent literature. Perhaps the most striking observation that we have made is that the UVO-based method of adhesion is only successful when the low-pressure mercury lamp is held from the samples at a distance of $\sim$1 mm. Neither UV irradiation from the same source at a distance or exposure to ozone alone have been able to produce strong bonding. The XPS studies that we and others[85] have conducted reveal that the PDMS is in fact oxidized by the UVO treatment at essentially any distance from the source. The bonding then embeds some sensitivity other than this qualitative aspect, one clearly related to the molecular details of the species present in the near surface region of the decal. The UVO treatment is known to generate atomic oxygen (a very potent species for effecting the surface oxidation of polymers)[91] by converting oxygen to ozone at 185 nm and then converting that ozone (in part) to atomic oxygen via a subsequent irradiation at 254 nm. This method of modifying PDMS has been described in detail in studies by Koberstein and co-workers.[83−85] Their conclusions indicate the treatment of PDMS with UVO leads to the oxidative removal of surface organic groups with the concurrent formation of Si−O bonds resulting in surface properties approaching that of silicon oxide over time. This could explain the formation of the silanol groups that would be necessary to support a proposed adhesion mechanism based on a condensation reaction of these moieties with oxide bearing surfaces. It is less clear whether it can explain the lack of adhesion observed when the stamp's surface was exposed to UV at somewhat greater distances from the source (the earlier study used a sample to source distance of 5 mm and did not examine the adhesion properties that resulted). The source of this latter mechanistic sensitivity is unlikely to be related to the sensitivity of the reaction to the ozone concentration because independent control experiments show that the latter by itself does not promote the formation of strong adhesive bonds. It seems likely that the flux of atomic oxygen to the sample, on the other hand, would vary quite sensitively in a spatially dependent way. This species is very reactive and would be rapidly depleted by gas-phase reactions. The moieties created by this species, then, might play an important role in the bonding ultimately developed. It is necessary to point out here that the shortest wavelengths given off by the source are strongly attenuated in air. A sample placed in close proximity would receive a greater exposure to them as a result, and as such pathways that result from photochemical activation of the PDMS might also be of importance.[87] Further work will be needed to clarify this point. The results of the UVO treatment all the same closely follow those seen in the use of oxygen and other plasmas, procedures that have been used extensively to modify

(91) Phely-Bobin, T. S.; Muisener, R. J.; Koberstein, J. T.; Papadimitrakopoulos, F. *Adv. Mater.* **2000**, *12*, 1257.

the surface and adhesion properties of PDMS.[11,64,76] Whatever the chemistry underlying this adhesion process, it will be useful to examine whether the duration or distance requirements of the UVO treatments might be mitigated in DTM by using an enriched oxygen feed, an enriched ozone feed, or a UV lamp which emits radiation more efficiently at 185 and 254 nm.

The pattern of fractures seen in CMF are most intriguing. Clearly, the film patterns obtained in this way are constrained by the cohesive/mechanical properties of bulk PDMS: an isotropic, amorphous material with a tensile strength of 6.20 MPa and a tear strength of 2.6 kN/m at room temperature.[92] The mechanical forces needed to promote a useful failure mode were least problematic for small decal feature sizes. The locus of the failure induced in this pattern transfer is clearly a parameter that responds very sensitively to the design rules adopted in the patterning. In all of the cases we have examined, the pattern transfer always occurs due to a cohesive failure of the PDMS. The point of interest, though, is to note the regions where these failures occur. Large features generate yield behaviors that tear deeply into the pad region of the stamp. Smaller feature sizes yield failures that move progressively toward the surface of the decal stamp's patterns. This scaling with feature size is presumably due to an aspect of the complex fracture mechanics elicited by the peeling step. Although the pattern fidelity can be impressive in CMF, better control of the mechanics will clearly be needed to foster its further development.

What then are the future prospects for this patterning method? In our view, decal transfer microlithography is likely to make its strongest contributions to patterning in applications where it complements photolithography. Because we can pattern PDMS as a resist with a wide range of thicknesses, and then subsequently remove it after additive or subtractive lithography, the utility of DTM for use in lift-off patterning naturally suggests itself. The examples shown in Figure 10 clearly support and bear these expectations out. The more striking observation, however, is provided by the results of the RIE studies carried out using a very thin CMF resist. That these thin decals could serve to pattern silicon thin films in this way is quite promising and speaks powerfully to the potential utility of PDMS (in conjunction with an appropriate stripping agent) to serve as an RIE resist.

Our past experience with soft lithography also suggests that DTM should excel in cases where a need exists to pattern very high aspect ratio or three-dimensional polymer structures (e.g., MEMS and photonics), for patterning materials on nonplanar substrate surfaces (e.g., sensors and optics), and the growing number of cases where the patterning of micron scale or larger features inexpensively on large format substrates is required (e.g., displays, bioMEMS, microvias, etc.). Again, the specific examples shown in Figures 9−12 speak to these points of interest. Details of the processing methods used to fabricate these demonstration structures and extensions to nonplanar patterning will be discussed in detail in future publications. We simply note from these illustrations that DTM may prove invaluable for serving and extending areas traditionally reserved for screen printing due to its superior feature resolution over this method and the large area patterning capabilities it seems to enable.

Finally, we note that DTM is somewhat unique in its ability to form complex channel systems that are sealed by ultrathin membranes. The representative demonstrations performed in this work suggest that these latter structures may have significant impacts that extend beyond a traditional electronics-centered interest in microfabrication. Of primary interest in this regard is the design of sensors, bioanalytical systems, and bioMEMS devices where gas and analyte permeation are required, especially those where performance can be benefited when these processes are separated from fluid mass transfer (research along these lines is currently underway in our laboratory). Thus, the greatest potential for DTM may lie in its significant capabilities as a means for fabricating closed-form microstructures in PDMS. Indeed, the model examples described here demonstrate a significant competency of DTM as a means for forming microfluidic systems that match and in some ways possibly exceed the current state of the art and thus should have broad impacts on the design and fabrication of microfluidic systems and membrane microreactors.

With this in mind, our future work will focus on developing these applications and expanding the range of materials and substrates that can be patterned using a decal-based protocol. The development of DTM as a method for effecting the large-area nonplanar patterning of semiconductors and metals and the construction of analytical devices based on microfluidic membrane architectures is well advanced and will be reported on shortly in subsequent papers.

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(92) Dow Corning Tech Sheet.