Masterless Soft Lithography: Patterning UV/Ozone–Induced Adhesion on Poly(dimethylsiloxane) Surfaces†

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A novel microreactor-based photomask capable of effecting high resolution, large area patterning of UV/ozone (UVO) treatments of poly(dimethylsiloxane) (PDMS) surfaces is described. This tool forms the basis of two new soft lithographic patterning techniques that significantly extend the design rules of decal transfer lithography (DTL). The first technique, photodefined cohesive mechanical failure, fuses the design rules of photolithography with the contact-based adhesive transfer of PDMS in DTL. In a second powerful variation, the UVO masks described in this work enable a masterless soft lithographic patterning process. This latter method, UVO-patterned adhesive transfer, allows the direct transfer of PDMS-based polymer microstructures from a slab of polymer to silicon and other material surfaces. Both methods exploit the improved process qualities that result from the use of a deuterium discharge lamp to affect the UVO treatment to pattern complex, large area PDMS patterns with limiting feature sizes extending well below 1 μm (≥0.3 μm). The use of these structures as resists is demonstrated for the patterning of metal thin films. A time-of-flight secondary ion mass spectroscopy study of the process provides new insights into the mechanisms that contribute to the chemistry responsible for the interfacial adhesion of DTL transfers.

Introduction

Lithography is a general term that has come to denote a broad range of processes that can be used to pattern materials, ones essential to the technologies of modern life.1 Photolithography is the most important of these methods, and central to the advancement of microelectronics2 and information technologies.3 It is, for example, the central technique used to fabricate the transistors (and other components) of advanced integrated circuits and memory storage devices. The drive toward more complex integrated device technologies has placed exceptional demands on the great, but not unlimited,4,5 capabilities of photolithography. It remains of limited utility for applications lying outside the typical foci of the microelectronics industry. For example, new and complementary patterning techniques are needed to realize the potential of lab-on-chip devices for proteomics6,7 and integrated optical systems supported on nonplanar surfaces.8,9

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Soft lithography provides an increasingly important set of means to meet these needs. Soft lithography comprises a class of patterning techniques that is based on forms of mass transfer that occur during the physical contact of molded polymer stamps (usually poly(dimethylsiloxane), PDMS) with substrates.10 The power of soft lithography resides not only in its capacity for effecting submicrometer feature resolution11 but also in its versatile scope of patterning. Soft lithography has been used to pattern a wide variety of materials including cells,12 proteins,12 organic polymers,13 ceramics,14 and metals.15 As such, it has become a major player in the developing technologies of bio-patterning,16 microfluidics,17 organic circuits,14 and nonplanar patterning.17

The present report is concerned with decal transfer lithography (DTL),16 one of several forms of soft lithography that transfers a pattern from a PDMS stamp onto a surface using adhesion.18–21 In particular, DTL uses an
adhesive bond created between a molded PDMS stamp treated with UV/ozone (UVO) and (most typically) an oxide-bearing surface (e.g., a native silicon oxide layer on silicon) to transfer PDMS thin-film materials in a patterned form from the stamp to the substrate surface. The transfer of material from a PDMS stamp takes place only in areas of contact and may transfer a PDMS pattern in two ways: cohesive mechanical failure (CMF) using a standard PDMS stamp that, when removed by peeling, fails cohesively (and so transferring features) or a selective pattern release that uses engineered stamps to release PDMS films of controlled thickness and design.18

DTL, like all forms of soft lithography, is limited by the materials properties of the stamps used for patterning.10 For PDMS stamps made from Sylgard 184, it has been shown that the raised features of a stamp may be separated by a distance no greater than approximately five times the height of those features.21 The implications of this constraint for DTL and other soft lithographic patterning techniques using Sylgard 184 stamps is that the interference spacings are intrinsically limited by the elastic deformation of the PDMS.22,23 Several groups have attempted to circumvent this problem by using stamps made from stiffer materials24,25 or by employing composite stamps.21,26 These protocols have made it possible to pattern features with submicrometer resolution but have not completely eliminated the design limitations that can result from the elastomeric properties of the patterning tool.

The present work describes the fabrication and use of novel UVO masks—ones based on a microreactor design (Figure 1)—that allow the high spatial resolution patterning of a UVO treatment on a PDMS surface. This in turn provides a means for extending the design rules of DTL in ways that circumvent some of the aforementioned limitations, namely, by allowing the transfer of material from only proscribed regions of a PDMS stamp.19 As shown schematically in Figure 2, the photodefined cohesive mechanical failure (P-CMF) technique exploits both conformal contact and a patterned UVO treatment to seal the molded features of a stamp to an oxide-bearing (or otherwise suitably modified) substrate surface. The UVO mask in this case allows the transfer of design elements embedded in the original pattern of the PDMS stamp but according to an overlay of domains defined by the UVO mask. As we will show, this approach enables the untreated features of a stamp to function as supports that alleviate sagging and pattern deformation while preventing those same unmodified features from being transferred during the patterning step.

Materials Used. PDMS (Dow Corning Sylgard 184), (100) boron-doped silicon wafers (Silicon Sense, Inc.), quartz slides (Chem Glass Inc.), polystyrene Petri dishes (WVR), glass slides (Gold Seal), (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (TFOTS, Gelest), sulfuric acid (Fisher), hydrochloric acid (12.1 N; Fisher), hydrogen peroxide (30%, Fisher), 1 M tetrabutylammonium fluoride (TBAF, Gold Seal), (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (Aldrich), 3-(mercaptopropyl)trimethoxysilane (Aldrich), 2,2,2-trifluoroethanol (Aldrich), buffered hydrofluoric acid (6:1, NH₄F/HF; Ashland Chemical), hydrofluoric acid (49%, Fisher), TFA Gold Etch (Transcene), 3-mercaptopropanoltrimethoxysilane (Aldrich), 2,2,2-trifluoroethanol (Aldrich), and common solvents were obtained from commercial sources. Masters were produced using photolithography to pattern photoresist (AZ 5214, Shipley; 1805, Shipley, or SU-8 5, MicroChem) as described previously27 using 5080 dpi transparencies as exposure masks or chrome on quartz patterns purchased commercially. All photoresist masters used as molds were cleaned using a UVO treatment and treated with TFOTS (as a mold release agent) in a closed container at around ~150 mTorr for 2 h. Solvents used in processing these samples were of analytical grade or higher and used without purification unless noted otherwise. A home-built apparatus employing either an ozone active low-pressure mercury lamp (BH2) or a deuterium lamp (Hamamatsu D101BS) was used as a UV source for UV treatments. The intensities for each bulb, measured from 230 to 250 nm using a Mimil model 100 optical powermeter were determined to be 100 μW/cm² at 3 cm distance from the mercury bulb and 530 μW/cm² at 1 cm from the deuterium source. A DREC 03V5-5 ozone generator was used as an UV independent source of ozone.

Analytical Methods. Film thickness measurements were made by surface profilometry (Sloan Dektak6 ST). Atomic force microscopy (AFM; Digital Instruments Dimension 3100) images were processed using V5.12 software (Digital Instruments). Area scans were recorded with unmodified silicon tips in tapping mode with a tip velocity of 2 Hz or less. Optical micrographs...
were recorded using an Olympus BH-2 optical microscope interfaced with a Panasonic GP-KR222 digital color camera. 

**Fabrication of UVO Microreactor Exposure Masks.** Quartz slides were cleaned in a piranha solution for 10 min, washed with deionized water, and dried under flowing nitrogen. A 30-Å titanium layer and a 1000-Å-thick gold film were evaporated (Temescal FC-1800 electron beam evaporator) onto the surface of quartz slides as shown schematically in Figure 1 and patterned using one of the photoresists mentioned above (the choice of resist determines the aspect ratios of the features on the exposure mask, see below). This patterned quartz slide was descummed in an oxygen plasma for 15 s, the exposed gold areas were etched in a dilute (4:1) solution of TFA Gold Etch, and the exposed titanium layer was etched by a 1% HF solution. Care was taken to retain the unstriped layer of the photoresist as part of the final product.

**P-CMF Pattern Transfer.** The patterned face of a molded PDMS stamp was optically aligned and manually placed into contact with the patterned side of a UVO exposure mask as schematically illustrated on the left side of Figure 2. When the pattern on the surface of the photomask was dense enough to prevent the reversible seal that PDMS forms on contact with smooth surfaces, the photomasks were held in contact by placing weights (four ~6-g steel weights) around the plate edges to prevent accidental shifts in the photomasks during UV exposure. The PDMS stamp was irradiated through the UVO photomask for 6 min at a distance of ~3 cm from the mercury bulb or ~1 cm from the deuterium source. After the exposure, the PDMS stamp was peeled away from the UVO photomask, and the patterned face of the stamp was optically aligned by hand and placed promptly into contact with an appropriate substrate (in less than 1 min). While maintaining contact, the stamp and substrate were placed in an oven at 70 °C for 20 min. Tweezers were used to peel the stamp away (starting typically from a corner) to reveal a patterned film based on overlapping areas of irradiation and contact. The procedure used for preparing gold surfaces for decal adhesion has been described elsewhere.28

**UVO-Patterned Adhesive Transfer.** The flat unpatterned face of a PDMS slab was placed into contact with the patterned side of a UVO exposure mask as schematically depicted on the right side of Figure 2. Slabs of Sylgard 184 were cured for a minimum of 24 h at 70 °C to minimize irregularities within the PDMS elastomer. The rest of the procedure followed was identical to that described above for P-CMF, except that, in this case, the features deposited correspond solely to the pattern of irradiation used.

**Multilayer UVO-Patterned Adhesive Transfer.** Two layers of PDMS were transferred one on top of the other through two separate transfer steps. A set of parallel lines was transferred onto a glass slide using the protocol described above with a 30-min exposure time. The first set of lines was exposed to UVO for 20 min by the mercury discharge lamp as described previously for sealing PDMS to PDMS.18 Then the same UVO photomask was brought into contact with an unused PDMS slab and irradiated for 15 min by the mercury discharge lamp. Keeping the orientation of the UVO-induced pattern in mind, this second stamp was aligned optically so that the lines would be transferred perpendicular to and on top of the first set of lines. This assembly was heated at 140 °C for 40 min as required for forming PDMS–PDMS bonds using DTL.18

**Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS).** Spectra were obtained using a Phi Technics III ToF SIMS with a 15 keV Ga+ LMIG source. The ion beam was maintained at either 660 pA or 1 nA and rastered over an area of 800 × 800 μm². The dose for negative ion data acquisition was maintained at ~10¹² ion/cm² to produce stable surface analytical conditions. The mass resolution (m/Δm) was 5000–6000. Charge compensation was employed, and peaks corresponding to O or H ions were filtered out prior to data acquisition. Mass calibrations were made using the spectra of polymer standards. The ToF-SIMS Sample Preparation. PDMS samples were spin-cast at 1000 rpm for 30 s onto a clean silicon wafer (~2 × 2 cm²) and cured at 70 °C for at least 16 h. These samples were exposed to UVO under the conditions indicated in the results section. For vapor-modified samples, PDMS films were exposed to a mercury source through a UVO photomask for 6 min, and placed in a closed container with an open vial of TFOTS or 2,2,2-trifluoroethanol at room temperature under ambient pressure. All samples were inserted into a vacuum for ToF-SIMS analysis within 20 min of their exposure.

**Results**

In previous work, we established that treating PDMS, in particular Sylgard 184, surfaces with UV radiation in air was sufficient to promote strong adhesive bonding of PDMS to glass and other substrate surfaces.18 This adhesion provides the basis of a soft lithography patterning technique we refer to as DTL.18 The DTL method uses this UVO-induced adhesion as a vehicle for transferring PDMS patterns onto substrates for subsequent lithographic processing. Our original work flood exposed the surface of PDMS stamps, and as a result, all of the features of a stamp were modified by UVO and, on the basis of the patterns of conformal contact, subsequently transferred to a second substrate. The present work shows that it is possible to pattern the UVO modification of surfaces using a conformal photomask that creates a microreactor chamber in which reagent gases can be activated by short wavelength excitation. The PDMS stamps modified in this way adhesively transfer pattern features only in those areas where both contact and irradiation coincide. Most interestingly, this pattern transfer is effected irrespective of whether the treated PDMS sample is a patterned stamp, which leads to the embedding of a secondary design in the photoactivated pattern transfer, or a flat slab, which transfers PDMS only in the image of primary irradiation. The microenviron and short path lengths created by the composite mask are essential to the success of this process. These sensitivities, and the mechanisms of materials modification they support, are described in the sections that follow.

**Development of a Contact UVO Microreactor Photomask.** We designed an easily fabricated UVO photomask that provides the atmospheric reactants necessary for carrying out a patterned UVO modification of a polymer surface. The design rules of the device are critical to its success; short path lengths are used that provide sufficient oxygen to modify the PDMS surface while still limiting multiple reflections of light and the diffusion of reactive species outside of the exposed pattern boundaries. The general design of this mask is shown in Figure 1. In a prototypical design, a quartz lens coated with a 1000-Å-thick gold film was patterned into a square planar array of rectangular 45 × 55 μm² cavities with identical separations using SU8-5. Typically this photoresist would be removed after the gold and titanium layers were etched away. In this case, however, the resist was retained so as to provide a shim material of uniform thickness (17 μm) while the gold served as an optical stop for UV irradiation. As noted above, the SU8 shims define a local microreactor volume element, the gas content of which is then activated by UV light.

**P-CMF Pattern Transfer.** In a prototypical procedure, a PDMS stamp with a square array of posts, whose dimensions measured 2 μm in diameter and 0.5 μm in height with a center-to-center separation of 2.7 μm, was placed into contact with the patterned side of the UVO photomask and irradiated using the deuterium discharge lamp for 8 min. The UVO photomask was removed, the treated PDMS surface placed into contact with a glass substrate, and the assembly heated to 70 °C for 20 min. The resulting pattern transfer obtained after peeling the stamp away is shown in Figure 3. The decal in this case

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consists of PDMS microstructures that extend across the entire 1 cm × 1 cm area of contact (Figure 3a). The size and spacing of the PDMS domains transferred matched the 45 × 55 μm² cavities in the photomask (Figure 3b, inset at identical magnification) with an edge resolution exceeding that of the 2.0-μm pixel size of the PDMS posts. Not only did the spacing and diameter of the posts inside each domain match the pattern of the original master, but AFM scans indicated that essentially all of the PDMS posts transferred measured ~800 ± 51 nm in peak height. This is illustrated by the AFM area and line scan of a representative section shown in Figure 3c,d. These decal feature heights exceed the heights of the PDMS posts on the original stamp. The additional PDMS material, some 250-nm thick, is removed from the bulk polymer via a very high fidelity pattern of cohesive failure. Further comment on this point is deferred until later in the paper.

**UVO-Patterned Adhesive Transfer: A Masterless Soft Lithography.** The data presented below illustrate two model demonstrations of the UVO-patterned adhesive transfer method. In each, flat slabs of PDMS were used to transfer PDMS patterns corresponding to the fully irradiated areas of a flat stamp. Figure 4 shows representative examples of PDMS decals transferred onto a glass substrate in this way. For the first demonstration, flat stamps 3-mm thick were cast and cured against the glass substrate in this way. For the first demonstration, the surface of a PDMS slab was placed into contact with a UVO photomask, one patterned with a set of parallel transmissive lines 3.0-μm wide with 3.0-μm separations, and exposed to UV irradiation from a deuterium arc lamp for 30 min. The treated surface of the PDMS slab was then placed into contact with a clean glass substrate, heated at 70 °C for 20 min, and the PDMS slab was peeled away to deposit a set of parallel PDMS lines on the glass surface. Another PDMS slab was exposed through the same UVO photomask using a deuterium source for 15 min, while the first glass supported set of PDMS lines was flood exposed to UVO (here using a mercury source). The treated PDMS slab was aligned in contact with a clean glass slide and heated to 70 °C for 20 min, and the stamp was peeled away from the surface to transfer the PDMS decal pattern. In this instance, AFM images revealed a remarkable high resolution transfer of tapered PDMS lines: ones 4 μm wide, ~890 ± 40 nm tall, and separated by 4 μm, as illustrated by the representative AFM scans shown in Figure 4a,b. A second PDMS pattern was used to demonstrate the ability of this technique to pattern discrete micrometer-scale features over large areas. A UVO mask patterned with a rectangular array of cylindrical cavities 10 μm in diameter and 3 μm deep with a center-to-center separation of 20 × 30 μm was placed into contact with a flat slab of PDMS and treated using the same conditions described above. When the PDMS stamp was peeled away from the glass surface, a rectangular array of PDMS microfeatures was deposited across a 1 × 2 cm² area as shown in Figure 4c. AFM scans of a representative area indicated that the PDMS features were conical in shape with a 10-μm base diameter and a highly uniform peak height of ~1.26 ± 0.06 μm as shown in Figure 4d.

**Multilevel UVO-Patterned Adhesive Transfer.** We found that the conformal nature of contacts made to PDMS slabs allows the UVO-patterned adhesive transfer method to be applied in a hierarchical form. In one representative illustration, PDMS lines were patterned onto the surface of a glass substrate (as described above) and the UVO-patterned adhesive transfer protocol was then used to superimpose a second set of PDMS lines perpendicular to and on top of the first set. For this demonstration, the surface of a PDMS slab was placed into contact with a UVO photomask, one patterned with a set of parallel transmissive lines 3.0-μm wide with 3.0-μm separations, and exposed to UV irradiation from a deuterium arc lamp for 30 min. The treated surface of the PDMS slab was then placed into contact with a clean glass substrate, heated at 70 °C for 20 min, and the PDMS slab was peeled away to deposit a set of parallel PDMS lines on the glass surface. Another PDMS slab was exposed through the same UVO photomask using a deuterium source for 15 min, while the first glass supported set of PDMS lines was flood exposed to UVO (here using a mercury source). The treated PDMS slab was aligned in contact with the patterned glass surface, heated at 140 °C for 40 min (following the PDMS-on-PDMS sealing protocol as described previously), and finally removed to deposit a second set of PDMS lines on the glass substrate perpendicular to the first as illustrated by the AFM scan shown in Figure 5a. This AFM scan of the PDMS lines confirmed that the second set of lines transfers as a continuous pattern over the top of the first pattern with no observed discontinuities. Line scans measured parallel
Adhesive Transfer. Interactions or the covalent bonds formed by the reactions of oxide-bearing substrates. By this line of reasoning, polar interactions produce modifications of the PDMS that are effective in transferring the PDMS pattern dimensions into the underlying gold surfaces in patterns of PDMS lines with a base width of 4.1 µm and peak height of ~700 nm and cones with a 10 µm base diameter and a peak height of 1.1 µm. The gold films were patterned by their respective resists into parallel lines 4-µm wide (c) and a rectangular array of gold circles 10 µm in diameter (d).

To each set of lines indicated that the base width and height of the lines were consistent with PDMS lines transferred previously using the UVO-patterned adhesive transfer protocol (data given as Supporting Information): a base width of 3.0 µm and peak height of 400 nm, but with a peak height at each intersection that doubled in size to ~730 nm (Figure 5b). This modulated pattern of feature heights is found throughout the large area decal transfer. It is interesting to note that a UVO-patterned adhesive transfer decal similar to that shown in Figure 5a can also be transferred in a single transfer using the same mask. In this case, two sequential exposures were carried out first and the pattern subsequently transferred in a single step (data given as Supporting Information).

We were able to transfer submicrometer decal features using the UVO-patterned adhesive transfer method. These results warrant further consideration as they highlight mechanistic issues of the photooxidation processes involved. The point of particular interest here is that the oxygen content of the subnanoliter reactor created by the contact masks needed to create these features is exceptionally small. The pattern shown in Figure 5c,d was created using a UVO mask based on a 300-nm design rule. The shim height used (based on a Shipley 1805 resist) was 300 nm, which limits the total number of moles of oxygen available as a reactant across the entire sample to be of the order of 1 \times 10^{-12} mol. Even so, this quantity is sufficient to mediate the chemistries needed to effect a decal pattern transfer. As shown in Figure 5c, a line pattern is transferred, albeit one of a more uneven quality than was obtained for the other, larger design rule examples (as illustrated by the line scan of Figure 5d). We defer comment on this latter result and its implications until later in the manuscript. We simply note that, absent of oxygen, UV exposures at these wavelengths cannot produce modifications of the PDMS that are effective in promoting strong adhesion of the sample to other (typically oxide-bearing) substrates. By this line of reasoning, polar interactions or the covalent bonds formed by the reactions of polar functionality are implicated as being important.

**Etch Resists from P-CMF and UVO-Patterned Adhesive Transfer.** To demonstrate the potential utility of these PDMS features, we conducted model experiments that used them as resists. In one, a PDMS stamp with an unbroken pattern of lines (2-µm wide and separated by 2 µm) was irradiated through a UVO photomask by a deuterium discharge source for 10 min. The mask was patterned with a square array of 45 × 55 µm² transparent areas and a spacing layer 17-µm thick. This PDMS stamp was placed into contact with a gold surface functionalized using 3-(mercaptopropyl) trimethoxysilane and heated to 70 °C for 20 min. A P-CMF pattern of 2-µm-wide lines in domains of 45 × 55 µm² (Figure 6a) was obtained when the stamp was peeled away. As a control, we found that no pattern transfer is effected without the silane coupling agent. The lines of the PDMS resist pattern were then transferred to the underlying gold film by wet etching the gold and titanium layers and then stripping the PDMS resist. The resulting hierarchical pattern of gold lines produced, following the contours of the UV exposure, is shown in Figure 6b.

In a similar demonstration, a flat PDMS stamp was irradiated through a UVO photomask using the deuterium discharge source (a mask patterned with a series of 4-µm-wide lines with 10-µm separations) to effect PDMS transfer using the UVO-patterned adhesive transfer technique. The mask set for this demonstration used a 450-nm-thick Shipley 1805 level as a spacer in conjunction with an exposure time of 6 min. The stamp was then placed into contact with a silanized gold surface of a 100-nm-thick gold thin film supported on a glass substrate. After heating to 70 °C for 20 min, the PDMS slab was peeled away to reveal a high quality resist decal (not shown). The PDMS lines transferred were determined by AFM to be 4-µm wide with a peak height of 698 nm (data not shown). These lines served as an exceptionally effective etch resist for the removal of both the gold film and titanium adhesion layers as shown by the data presented in Figure 6c. In a second demonstration, a similar procedure was used to deposit a rectangular array of PDMS resist cones with 10-µm base diameters and center-to-center separations of 20 × 30 µm. The total area of the pattern transferred in this case was 1 × 2 cm². The underlying 100-nm gold film was wet etched, and the PDMS resist was stripped.
away using a solution of 1 M TBAF in THF to produce the resulting rectangular array of gold circles with 10-μm diameters shown in Figure 6d.

UV Exposure Dependencies. The decal pattern transfer processes described above differ in a marked way from the earlier work reported by us. The DTL process exploits the strong adhesive bonding generated by a near surface photooxidation process to effect the pattern transfer. The UVO oxidation described in these reports and others \(^{(29,30)}\) is generally believed to result in the formation of silanol groups, which in turn form the covalent bonds that mediate the strong interfacial bonding seen on certain oxide-bearing substrate surfaces. In point of fact, however, the irreversible bonding of PDMS to a surface in this way is extremely sensitive to the experimental conditions used in the oxidation step.\(^{(29,30)}\) In the present work, we found an experimental modification that leads to substantial improvements in the results obtained from UVO processing steps, namely, the substitution of the conventional unfiltered Hg discharge lamp by a higher intensity deuterium discharge source. The section below illustrates the profound sensitivity of the UVO processing of PDMS to this substitution for both P-CMF and UVO-patterned adhesive transfer (and DTL more generally).

Figure 7 shows two P-CMF patterns that are similar in design to the example shown in Figure 3. A similar UVO mask was used in each case with the exception that either a Hg (Figure 7a,b) or a D₂ (Figure 7c,d) discharge source was used. These two lamps differ most markedly in the radiant power they deliver. The Hg source emits discrete, intense peaks at the wavelengths necessary for UVO (185 and 254 nm; BHK no. 412). The emission profile of the D₂ source is more continuous, and far more intense, at wavelengths below 200 nm. As these data implicitly establish, the decal pattern transfer is strongly dependent on these differences. One notes in Figure 7a,b that the pixel transfer effected by the Hg source is irregular; the feature heights are quite tall at the domain edges (≈1 μm) but fall markedly to a few tens of nanometers near the center. Uniform, high aspect ratio pixel transfers are seen throughout the domains for the patterns deposited using the D₂ source (Figure 7c,d). Slight excitation sensitivities, albeit of a somewhat more complex nature, are seen in the UVO-patterned adhesive transfer variant of DTL as well.

To develop an understanding of the factors contributing to these differences, we carried out an AFM study to characterize the surface of PDMS slabs treated with each source. These data, shown in Figure 8, strongly support the conclusion that the D₂ source leads to a much more marked modification, and likely cross-linking, of the irradiated near surface regions of the PDMS. In these experiments, identical flat PDMS films were exposed to radiation from the two sources using a UVO photomask, one patterned with a rectangular array of 10 μm diameter holes with a 20 × 30 μm spacing and a shim thickness of 2.0 μm. Tapping mode AFM images showed that, after an exposure time of 4 min, the deuterium source produced marked circular depressions from 3 to 5 nm deep in the PDMS in an overlay correlated with the mask design rules (data not shown). The depth of these depressions increased with more extended exposure times, and by 20 min reached to a depth of ≈34 nm as illustrated by the data shown in Figure 8a,b. PDMS films illuminated by a mercury source were less markedly impacted even after 20 min of exposure. The AFM data (Figure 8c,d) indicate that the depressions obtained are less sharp, with trenches 16-nm deep running along directions aligned parallel to the closest areas of exposure. These data clearly showed that substantial, source-dependent kinetic effects are evidenced in the UVO process. The nature of these dependencies, and the modifications they produce, are described in the Supporting Information.

ToF-SIMS Surface Characterization of Modified and Unmodified PDMS. To develop a mechanistic understanding of the oxidative chemistries that mediate pattern transfer, we examined SIMS spectra from a PDMS surface modified with a standard UVO adhesion protocol and compared these results to ones obtained from a control. Samples from a single batch of PDMS were cast by spinning onto silicon wafers and cured at 70 °C for 16 h. A quartz slide was placed over the PDMS film with a 40-μm spacer prior to irradiation by either the deuterium or the mercury source as described in the experimental section.

Negative ToF-SIMS spectra were recorded for each sample (and a control) using identical acquisition times and conditions. At low resolution, the spectra plotted over a range of 30–100 m/z (available in the Supporting Information) exhibited few apparent differences. At higher resolution, though, marked differences are seen in the ToF-SIMS data. The spectra presented in Figure 9


PDMS and a polar surface, always produced a modification of the surface conditions that lead to strong adhesive bonds between the materials. The UVO modifications, when carried out under the appropriate conditions, led to distinct differences noted in these data. For example, the intensity of the UVO-induced fragment in this region appearing at 59.00 amu (SiOMe) was observed for a peak at 45.00 amu, which corresponds to a COOH group for PDMS surfaces that were unmodified or modified by either irradiation from a mercury or a deuterium source. Interestingly, the intensity of the COOH peak at 45.00 amu increased significantly after the UVO treatment. These intensity changes were quite marked over a period of several minutes for samples left standing in air and still progressed measurably for samples stored in the vacuum environment of the spectrometer for a period of several hours.

**Chemical Reactivity of UVO-Modified PDMS.** To gain some understanding of the chemical reactivity of UVO-modified surfaces, several additional SIMS studies were carried out. In one of these, a PDMS-coated wafer was exposed to UVO for 3 min and placed in a closed container with an open vial of TFOTS for 20 min along with another PDMS-coated control wafer. These data (not shown) reveal significant uptake of the silane reagent by the UVO-modified sample relative to the control, a pattern of reactivity expected for a polar surface presenting either oxides or silanol groups.

In a second experiment, two PDMS-coated wafers were exposed to UV through a UVO mask patterned with a square array of 100 × 100 μm² transparent cavities using a 17-μm resist spacer. The mask was removed, and one sample was placed into a closed container with an open vial of TFOTS for 20 min while the other was exposed to a vapor of 2,2,2-trifluoroethanol for 20 min. The surfaces were characterized byToF-SIMS with image maps created using either the (F⁻) peak at m/e = 19.00 amu or the (COOH) peak at m/e = 45.00 amu. In Figure 10a, one sees that the fluorine intensity due to the TFOTS correlates strongly with areas of exposure. Interestingly, the intensity of the UVO-induced m/e = 45.00 peak (COOH) is retained after the TFOTS exposure (Figure 10b). Image maps from the surface of the UVO and 2,2,2-trifluoroethanol-treated surface also indicated a selective albeit lesser uptake of a fluorine containing species in the exposed areas (Figure 10c); the latter reaction, though, eliminates essentially all measurable contributions from the COOH peak (Figure 10d). Finally we note that, in both cases, maps made of the SiOH (m/e = 49.98 amu) peak were completely uniform (data not shown). These results reveal that the UVO chemistry may effect a specific functional group transformation, one that correlates with a capacity for promoting strong adhesion and is susceptible to specific types of chemical reactions.

**Discussion**

There has been considerable progress made in recent years in developing new forms of soft lithography that are based on processes for printing solid inks. DTL is an exemplary process in this class. To print a polymeric decal, DTL uses a UVO treatment to modify the surface of a PDMS stamp. This treatment provides capacities for strong adhesive bonding using a chemistry that has been exploited for the purpose of transferring PDMS microstructures from a stamp to a substrate. Like most forms of soft lithography, DTL generates patterns based on the

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forms of conformal contact induced between a substrate surface and the raised contours of a molded stamp. As such, the design rules for DTL, as for all forms of soft lithography, are limited in some manner by the mechanical properties of the materials used to make the stamps (in general practice almost exclusively Sylgard 184).\textsuperscript{18} Printing methods using stamps fabricated from this elastomer are typically limited by the form factors that PDMS can sustain. Schmid and co-workers\textsuperscript{24} have shown, for example, that the features present on a stamp may not be farther apart than \( \sim \) five times the height of those features or a loss in the fidelity/resolution of the pattern transferred will occur. Several groups of researchers have engineered stamps using materials with a higher Young’s modulus (\( >3\text{ MPa} \))\textsuperscript{24} or stamps with firm back planes\textsuperscript{21,26} to extend the reachable design rules of soft lithographic patterning techniques, especially microcontact printing.

The current work demonstrates that DTL need not be restricted by these same constraints, because the transfer of PDMS decals requires both contact and specific, activated reactions enabled by the UVO oxidation process, a procedure that the current work demonstrates can be directly patterned in both large areas and high fidelity with submicrometer feature size resolution. In previous publications,\textsuperscript{18} DTL procedures were described that used the UVO process to modify the entire molded surface of a stamp; as a result, all areas of the treated decal that were brought into contact with the polar substrate were subsequently transferred. These PDMS decals serve as useful resists, and several methods have been reported that use them to pattern a variety of thin-film materials.\textsuperscript{28} In this study, we describe several innovative procedures that can be used to pattern the UVO treatment itself and thereby extend the scope of the patterning that can be supported by DTL.

The modification and patterning of polymer surfaces (including PDMS) by UVO has been the subject of earlier investigations that generally employed a simple shadow mask during the irradiation step.\textsuperscript{32} This technique, while similar in concept to the subject of this report, has two drawbacks. First, it requires a self-supporting stencil mask (e.g., a wire grid).\textsuperscript{33} Second, it is a low-resolution patterning method and, as described in the literature, provides no generally useful capacities for fabricating polymer resists for thin film patterning processes.\textsuperscript{32}

The qualities of such patterning can be improved substantially, however, using a UVO mask based on an optical quartz flat that embeds its own photochemical microreactor. As shown in the present work, the short path lengths of the UVO mask and the chemistry of PDMS together provide remarkable new capacities for patterning thin-film resists—ones that seem all the more intriguing given the design rules and process modifications they support.

**Significance of Oxygen Availability.** The volume element defined by the shim structure is a critical design rule for the process and directly restricts the feature resolution it can sustain. For ease of fabrication, we employed a photoresist material, SU8 or Shipley 1805 most typically, to construct this part of the mask. The use of a photoresist as a spacer material provides three advantages. First, the spacer is directly integrated with the process used to pattern the gold film used as an optical stop and provides for an intrinsic alignment between the transparent openings and the polymer microreactor cavities. Second, the polymer resist effectively constrains photogenerated reactive species from reaching other areas of the sample. Third, the photoresist spacer allows for the construction of precise air gaps in the UVO mask, a parameter critical to the resolution and utility of the PDMS resist patterns obtained. The SU-8 series of photoresists proved to be quite durable in our hands, and patterned layers with thicknesses ranging from 1 \( \mu \text{m} \) to as much as 200 \( \mu \text{m} \) are easily fabricated using rapid prototyping methods.\textsuperscript{34} From a practical standpoint, UV exposure times of 6 min were sufficient to ensure irreversible adhesion for shim thicknesses of 3 \( \mu \text{m} \) or more. Thinner shims (100–300 nm) required 30 min of continuous irradiation to generate complete pattern transfer. Both protocols proved sufficient to generate high quality, large area pattern transfers of PDMS by both the P-CMP and UVO-patterned adhesive transfer methods with limiting feature sizes lying near and significantly below 1 \( \mu \text{m} \).

The critical role of oxygen in this process has been established by detailed studies—ones summarized here and reported more fully in the Supporting Information section. First, we found that UV treatments of the PDMS carried out with either UV source in an inert atmosphere did not provide modifications of the material that supported the formation of strong adhesive bonds. Second, UVO treatments carried out in air but under conditions in which light at wavelengths below 220 nm was filtered out also failed to induce modifications that lead to strong adhesive bonding. Perhaps most interesting, this filtered source was found to be highly effective at promoting adhesion when the processing was carried out in an ambient enriched in ozone. In this latter case, the data obtained from ToF-SIMS and other surface characterization methods (data given in the Supporting Information) could not be differentiated from that obtained from samples treated in oxygen using an unfiltered UV source.

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Ozone by itself (i.e., absent UV irradiation), however, was completely ineffective in eliciting a strong adhesive bond to PDMS.

**Source-Dependent Cross-Linking.** These observations implicitly establish the nature of the critical species involved in the UVO process and fully rationalize the most significant general technical advance brought forward in this research. It follows that the chemistries that lead to strong adhesive bonding are efficiently elicited on the PDMS surface by the photodecomposition products of ozone—species that notably include both atomic and singlet oxygen.35,36 The key advances in this work—the short path length UVO microreactor mask and the use of a deuterium discharge source—both support this latter inference. For example, the cross-linking process is most efficient when the concentration of ozone is high. The generation of ozone from oxygen requires excitation at wavelengths below 244 nm, the range where the D₂ source has a higher fluency than the conventional Hg-discharge source. More importantly, though, the data clearly show that the ozone must be photoactivated and that the products so formed must be generated in close proximity to the PDMS surface (less than 1 mm in air at 1 atm).37 The latter observations again support the critical intermediacy of short-lived reactive species in the reactors that lead to the formation of strong adhesive bonds.

As noted above, the PDMS pattern transfers of the P-CMF and UVO-patterned adhesive transfer methods involve contributions of both chemically activated-adhesive bonding and cohesive material-failure processes. In this sense, then, they both share similar mechanistic underpinnings. Several trends evidenced in the data warrant special comment here. First, it is especially notable that the introduction of the deuterium discharge lamp has completely changed the pattern qualities of the PDMS resists transferred by the CMF variant of DTL. As noted in an earlier report, PDMS structures transferred by CMF, when bonded using a mercury discharge lamp as the UV source, tended to be quite thin for stamps bearing features in the micrometer and submicrometer size range (representative examples are presented in the Supporting Information).28 The cohesive failure in this case generally tends to remove a lesser portion of the features present on the stamp rather than its full aspect ratio. The photoactivated chemistries supported by the deuterium discharge source, while similar in qualitative terms (it induces strong interfacial adhesion), leads to very different quantitative metrics in the CMF-pattern transfer. The PDMS structures in this case tend to be much thicker. This in turn provides a capacity for transferring PDMS resist structures with thicknesses approaching 1 μm or more.

The latter values are all in a range that reflects an ~10-fold increase in the effective throwing power of CMF-based decal transfer. This result is best understood, we believe, as being reflective of a higher degree of cross-linking34 that results from the use of the deuterium source. This higher modulus material, then, serves as the template for mechanics that ultimately pull a significant quantity of lower modulus (unmodified) PDMS from the more distant bulk. The data presented in this report, especially that provided in Figure 8, strongly supports the centrality of photooxidation processes that leads to a significant degree of cross-linking in the PDMS. Such cross-linking has been noted and characterized in considerable detail by others.58 Most striking here, though, is that this cross-linking induced by the modified procedures leads to a substantial and far reaching change in the modification of the mechanical properties of the PDMS—affecting the transfer of material residing within micrometers of the surface. We see little that might preclude the use of this method as a general tool for large-area micrometer scale patterning as illustrated by the representative examples shown in Figure 3.

**Insights into the Adhesion Mechanism.** Many aspects of the photomeditated bonding process remain poorly understood even though there is an abundance of research concerning the oxidative changes brought about by corona discharge,39 oxygen plasma,40–43 and UVO treatments42,44,45 of PDMS surfaces in the literature. Most of these efforts center around attempts to change the wetting properties of PDMS or modify the surface for grafting procedures. Surface studies concerning the UVO modification of PDMS generally agree on the following points: UVO modification requires the photolytic production of atomic oxygen from ozone;46 UVO effects are limited to the first several micrometers of PDMS material by the absorbance of UV by bulk PDMS and the limited diffusion of reactant species;32,45,46 UVO treatments eventually oxidize methyl and silicon hydride groups to silanols that undergo subsequent condensation;44,45,47,48 and this increase in cross-linking leads to a reduction of volume, a higher modulus, and with longer exposures, cracks in the PDMS surface.45,46

Our interests in this report extend to UVO modifications of PDMS surfaces that support material transfers through adhesion. The ToF-SIMS and AFM data, when taken together with the documented impacts of UVO treatments on the polymer’s modulus, suggest that reactions occurring within the first few nanometers of the PDMS surface as well as modifications occurring more deeply in the bulk are both critical to the adhesion and pattern transfer characteristics seen. The critical intermediates appear to be produced relatively early during the oxidation process, as extensive oxidation has been noted to preclude adhesion by ourselves and others.49 It is notable, in this regard, that the intensity of the UV sources used in this work are two to three orders of magnitude less intense than those employed in earlier published works.32,45,44,50,51 In addition, the modification protocols presented here and in previous publications50,52 limit either the exposure time or the

amount of oxygen available as a reactant. As one figure of merit, the exposure conditions used here to induce adhesion do not produce marked changes in the wettability of the PDMS by water, a result strongly correlated with the negligible differences seen between treated samples and controls in high resolution XPS data.

With these observations in mind, we close with a consideration of the UVO-induced adhesion mechanisms that mediate the DTL processes described in this study. The idea that reactive carbon-centered species are formed on PDMS surfaces during a UVO (or other) oxidation as an intermediate is not a novel one. Indeed, attenuated total reflection Fourier transform infrared experiments performed on UVO modified PDMS films by Wirth and co-workers and Nuyken et al. have presented evidence for the formation of carboxylic acid or aldehyde groups, respectively. Our data support the formation of such a species generally but also serve to advance a theory that reactive carbon-centered intermediates must also directly participate in the formation of the covalent bonds that mediate the interfacial adhesion that we observe under our exposure conditions (i.e., that the chemistry of the adhesion process involves more than the condensation reactions of silanol groups, a model proposed by others for closely related non-UVO processes). This insight is derived largely from the ToF-SIMS data. The present data clearly correlate strong adhesion with the presence of a negative ion fragment yield at 45.00 amu in the treated samples. The high mass resolution of the current data clearly establishes that this correlated fragment is, in fact, one derived from a carbon-centered species. These data also show that the presence of silanols does not provide, in and of itself, a similar correlation. The identity of the functional group that gives rise to this fragment is, therefore, of some interest but unfortunately remains incompletely understood. One possibility is that this fragment might arise from a silyl-ester moiety created by a reaction of the PDMS with an activated oxygen species. The apparent reactivity of this inferred intermediate with 2,2,2-trifluoroethanol, a very weak protic nucleophile, is consistent with the expected properties of such a species. It remains an interesting and unresolved question, however, one that further studies will be needed to answer.

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Supporting Information Available: Details of the UVO spacing effects for photomask design, UVO irradiation time dependence of P-CMF, surface topography of stamps used for DTL patterning, one-step multiple exposure UVO-induced adhesive transfer, ToF-SIMS surface characterization of modified and unmodified PDMS, ToF-SIMS characterization of the UVO oxidative adhesion mechanism, optical micographs, AFM scans, and ToF-SIMS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.