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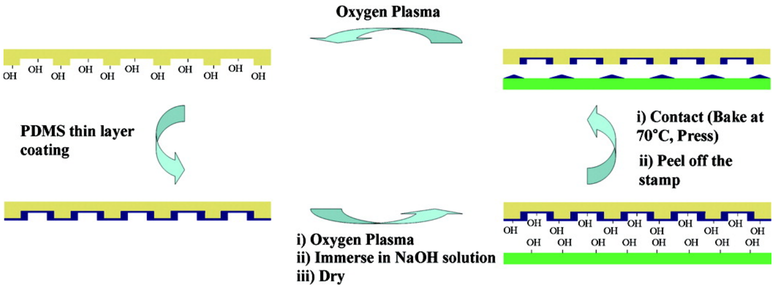

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Advancing Decal-Transfer Lithography with a Reusable PDMS-Coated Nanoscale Stamp

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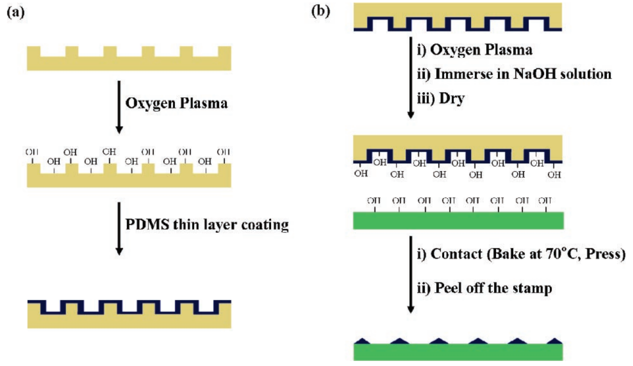
Many techniques, such as soft lithography,[1−3] are available for the fabrication of micropatterned surfaces in thin film form, their development sparked by the vast potential of applying such materials in modern science and technology. Soft lithography has particularly become a major means in the emerging technologies of biopatterning,[3] microfluidics,[4] organic circuits,[5] and nonplanar patterning,[6] owing to its use in patterning a wide variety of materials.

A series of recent reports has described decal-transfer lithography (DTL; decal transfer-microlithography (DTM)),[7−9] one of several forms of soft lithography. DTL, based on the adhesive transfer of a patterned poly(dimethylsiloxane) (PDMS) film from an elastomeric stamp to a substrate, offers useful new capabilities for the design and fabrication of advanced planar 3D microfluidic assemblies and microreactors.[7] Previous researches[7−11] have focused on several applications of DTL as an important type of patterning for thin film materials.

It must be noted, however, that DTL has some limitations that obstruct its applicability. First, as with other soft lithographic techniques, DTL is limited by the material properties of the elastomeric stamp used for patterning.[1] The most widely used elastomeric stamp for soft lithography, Sylgard 184 (Dow Corning), consists of a silicone "T-resin" cross-linked with a mixture of vinyl-terminated PDMS and trimethylsiloxy terminated poly(methylhydrosiloxane) polymers. The resulting material, Sylgard 184-PDMS, has a highly cross-linked three-dimensional structure that offers a high elongation level but a relatively low modulus that can lead to structural problems in the pattern transfer elements.[12] This is especially true with nanometer features, which can collapse or stick together or otherwise change shape. Second, in DTL, the features of a patterned PDMS decal stamp are physically torn away from it via a cohesive mechanical failure (CMF). Consequently, reuse of the stamp is intrinsically impossible.

In the present study, we were able to promote the capability of conventional DTL. First, we succeeded in progressing toward a DTL process that extends to the nanometer scale. Second, we were able to empower the DTL stamp to be used several times. On the first point, many researchers have recently focused on materials that can extend applicability to the nanoscale, as advanced techniques for nanofabrication are now essential for progress in many areas of science and technology. Several groups have attempted to avoid the elastomer problem by using stamps made from stiffer materials[12,13] or by employing composite stamps.[14] These endeavors have made it possible to pattern features at a submicrometer scale but have not completely eliminated the design limitations that can result from the elastomeric properties.[15] Recently, our group developed an antiadhesion release layer coating method[16] that can be applied to overcome the elastomeric stamp's limitations. The procedure used in this study was inspired by traditional DTL techniques, but a conventional PDMS stamp was alternated with a nanometer scale stamp covered with a thin film of PDMS.

Scheme 1. Schematic Illustration of Nanometer Scale DTL Patterning[a]



[a] Images show (a) PDMS thin-layer coating on the nanometer-sized mold and (b) a schematic illustration of PDMS transfer procedure, CMF decal method.

Scheme 1a shows the schematic illustration of a PDMS thin layer coating on a mold[16] used as nanoscale DTL. This mold was prepared using UV-curable polymer from a PDMS thin-layer coated nanotemplate.[17] In this study, we used pentaerythritol propoxylater triacrylate (PPT) as a UV-curable polymer. PPT (M_n = 530) precursor solution was prepared by mixing PPT and photoinitiator, 2-hydroxy-2-methylpropiophenone, in the ratio of 95:5 (v/v). Owing to the use of PPT, a strongly adherent coating material on an inorganic or organic substrate, we were able to replicate the nanoscale pattern on PPT on a PET film using a nanoscale master coated with a thin layer of PDMS as the antiadhesion release layer.[16] After curing with a ~365 nm, 135 mW/cm^2 UV light source for 30 min, the PPT mold was peeled off. The strategy of a PDMS thin layer coating onto the PPT mold was as follows. Aminosilane grafting on the surface of the PPT mold was attained by treating the surface of the mold with O_2 plasma (25 W, 20 s) and then immersing it in a 0.5 wt % aqueous solution of 3-(aminopropyl triethoxysilane) (APTES) for 10 min. After washing the unreacted APTES with distilled water, monoglycidyl ether-terminated PDMS (M_n = 5000) was dropped and heated at 80 °C for 4 h. Upon heating, the mold was immersed in 2-propanol and sonicated for 1 min to remove the unreacted PDMS. Scheme 1b shows the schematic for recently developed decal-transfer printing techniques[18] based on a silicate-forming reaction between NaOH and the surface SiO_x layer. A nanoscale stamp covered with a thin film of PDMS was oxidized in oxygen plasma (25 W, 30 s) to render the surface hydrophilic. Then the hydrophilic stamp was immersed in 100 mM NaOH for 1 h and brought into contact with an oxidized Si wafer (50 W, 10 min) after being dried under N_2. This assembly was

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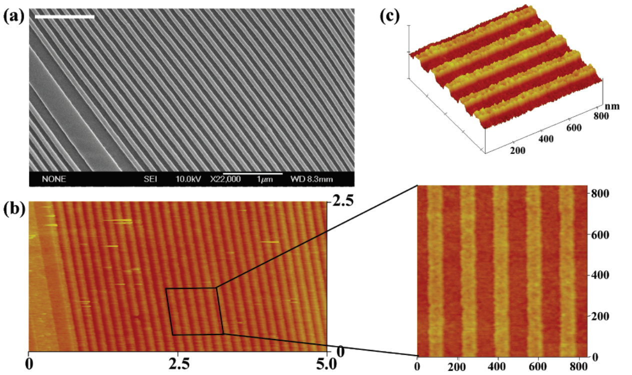

Figure 1. Nanometer scale patterning of PDMS thin layer via the CMF decal mechanism: (a) SEM image of the line patterns on PPT mold prior to DTL, scale bar = 1 μm; (b) AFM image of the transferred PDMS patterns via the CMF over 5.0 × 2.5 μm; (c) a higher magnified image of image b (the scan size was 840 × 840 nm).

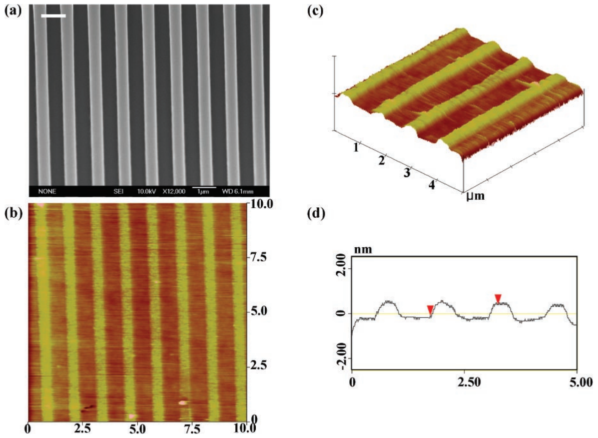

Figure 2. (a) SEM image of the line patterns on PPT mold prior to DTL, scale bar = 1 μm; (b) AFM image of the transferred PDMS patterns from recycled mold subsequent to DTL; (c) AFM image of the magnification of panel b; (d) cross section analysis of image c.

placed under a hot press (0.05 MPa) at 70 °C for 1 h and then the stamp was peeled off.

Figure 1 represents the results of using the nanoscale DTL technique. Figure 1a shows the SEM image of ~70 nm line patterns onto the PPT mold. Figure 1b shows the AFM image of the transferred PDMS patterns deposited by CMF with DTL technique over 5.0 × 2.5 μm. Figure 1c shows the highly magnified 2D, 3D images of Figure 1b. The width of the transferred PDMS pattern was ~70 nm, indicating that the PDMS patterns almost retained the dimensions of the master without there occurring any noticeable line spreading. The height of the PDMS pattern was about 1~2 nm, comparable to that of a densely packed tetradecylsiloxane monolayer (~2 nm).

In this PDMS thin layer coating, the covalent bonding formed by the epoxy-amine chemistry between monoglycidyl ether-terminated PDMS and an aminosilane-treated surface made it possible to establish a strong and highly stable coating without roughening the surface. The thickness of the PDMS thin layer was measured by means of an ellipsometer to be ≤10 nm.[16] Thus, owing to the PDMS thin-layer coating strategy, we were able to expand upon a traditional DTL. First we were able to extend the DTL to the nanoscale and second increase the number of times the stamp could be used.

Figure 2 represents the results of repeatedly using the DTL technique with the same stamp. A conventional PDMS stamp, which is torn away via DTL, was alternated with a nanoscale stamp covered with a thin film of PDMS. This allowed us to alleviate the inherent limitations of a conventional DTL in which the stamp is lost after only one use. In our strategy, by contrast, the mold was not affected by the multiple DTL, with merely the covered PDMS layer being torn. Figure 2a shows the SEM image of the PDMS thin-layer coated line patterns onto the PPT mold prior to DTL. Figure 2b shows the AFM image of the transferred PDMS patterns from Figure 2a subsequent to five rounds of DTL. Undeterred by five applications of DTL with the same mold, the results indicate that DTL reuse of the mold is attainable. The lines of the transferred PDMS pattern were ~500 nm, effectively corresponding to the PPT mold. Figure 2c shows the magnified 3D AFM image of Figure 2b, and Figure 2d shows a cross-sectional analysis of Figure 2c. It is reasonable to observe that the PDMS patterns almost retained the dimensions of the mold without any noticeable line spreading, despite the use of consecutive decal methods. An advantage in applying the PDMS thin-layer coating strategy is its efficiency in repeating the DTL method with the same stamp, in contrast to the methods used in previous DTL research.

In conclusion, we present nanoscale DTL in which the conventional PDMS stamp is alternated with a reusable PDMS-coated nanoscale stamp. Using the different types of PDMS, our strategy is expected to control the thickness of the transferred PDMS layer. This potentially considerable extension of traditional DTL supplies a unique predictive power over these patterning techniques.

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Supporting Information Available: Surface coverage and resist capabilities of the printed PDMS layers. This material is available free of charge via the Internet at http://pubs.acs.org.

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