

Decal Transfer Lithography

William R. Childs

Final Seminar

July 15, 2004

The advancement of microelectronics over the past three decades has relied upon a microfabrication technique known as photolithography.¹ The semiconductor industry uses photolithography to produce computer processors by simultaneously constructing millions of transistors on a single silicon wafer. This means that microchips, no matter how elaborate, are produced in bulk at relatively low cost. Photolithography accomplishes this task by allowing for these transistors to be produced in parallel, rather than serially, which is the same advance a printing press confers over writing by hand. Photolithography is nearly perfect for the manufacture of microelectronics, since it was developed for the patterning of flat objects with metals, ceramics, and polymers.

But even photolithography has limitations. As resolution is increased in an effort to enforce Moore's law, the depth of field for photolithography decreases, so that non-planar surfaces cannot be patterned without major changes to existing protocols.^{2,3} Photolithography also requires the use of harsh chemicals and expensive equipment. None of this is a problem for the semiconductor industry, since they process only metals, semi-conductors and ceramics on planar surfaces. However, research in integrated optics and lab-on-a-chip applications seek to process materials other than electrons, and require a patterning technique compatible with curved substrates⁴ and biological materials.⁵

My research concerns the invention and development of a type of soft lithography called Decal Transfer Lithography (DTL), which represents a possible solution to these limitations. Soft Lithography is a non-photolithographic patterning technology based on molding which is capable of transferring patterns to an object using a flexible elastomeric stamp made out of a clear silicone rubber known as poly(dimethylsiloxane) (PDMS).⁶ PDMS may be poured onto an object in liquid form, and then heated to capture the object's shape as the liquid becomes a solid rubber. The clear rubber stamp is brought into contact with a surface such that the raised parts make contact, but the relief pattern does not. Soft lithography complements photolithography by providing a parallel patterning scheme with high resolution, while possessing the versatility to pattern a variety of materials into devices, and the capability of patterning non-planar surfaces.

DTL is a new soft lithographic patterning technique that is based on the transfer of elastomeric decal patterns via the engineered adhesion and release properties of a compliant PDMS stamp.⁷ When a PDMS stamp is exposed to UV/Ozone (UVO), a chemical change occurs on the surface of the stamp that allows for adhesion to a glass or silicon substrate upon heating. The bond formed in this manner exceeds the cohesive strength of the stamp itself, such that physical removal of the stamp causes the mechanical failure of the material composing the stamp. This results in the deposition of the stamp's material in areas of contact, so that an exact PDMS copy of the stamp's pattern is transferred onto the silicon surface. The PDMS pattern controls the deposition and removal of materials in a fashion similar to the photoresists used in photolithography. This DTL patterning mode is called Cohesive Mechanical Failure (CMF) molding, and

has been used to pattern both a semiconductor material, amorphous silicon, and a conductor, gold, onto the convex surfaces of a spherically curved lens.⁸

A second mode of DTL patterning was designed to augment the design rule limitations of CMF. Here a thin layer of PDMS pre-elastomer is cast on the surface of a mold and cured. This thin film of PDMS is then irradiated by UVO and treated with a fluorinated silane prior to the addition of a thicker layer of PDMS. The result is a PDMS stamp engineered with two functional parts for a Selective Pattern Release (SPaR), a thin patterned decal weakly adheres to a thick PDMS support layer [Figure 1]. Exposing the

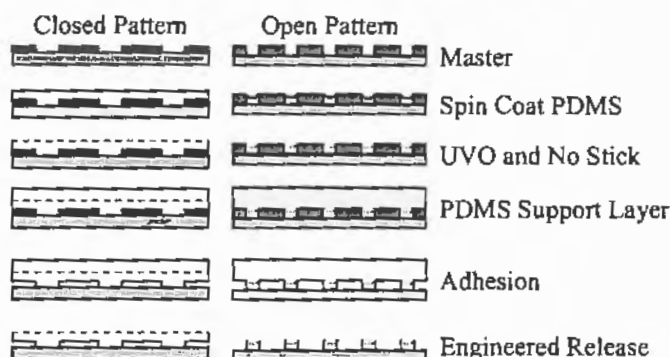


Figure 1 A schematic depiction of the Selective Pattern Release (SPaR) protocol for patterning open and closed PDMS structures.

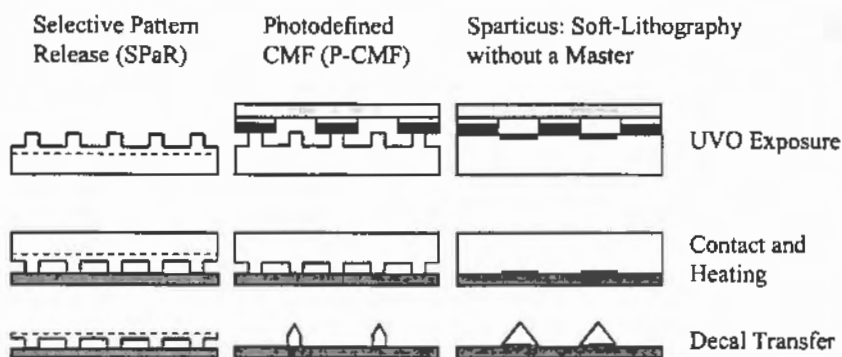
face of the PDMS decal to UVO allows the PDMS decal to be adhesively transferred onto silicon dioxide surfaces in open or closed form over large areas. This technique is ideal for patterning ultra thin PDMS microfluidic networks covered by a thin PDMS membrane.

The greatest limitations of the DTL technique is the reliance of the technique on adhesion for decal transfers. For sufficient adhesion to take place, surfaces must be compatible with silane bonding (i.e. oxides). Two general methods for modifying the surfaces of noble metals to promote the adhesive transfer of PDMS thin-film structures are presented. The first method involves the functionalization of a surface, here those of gold and silver films with a thiol terminated silane coupling agent, (mercaptopropyl) trimethoxysilane (MPTMS). This SAM, when hydrolyzed to its silanol form, provides a robust adhesion-promoting layer suitable for use in DTL patterning. The second method employs the deposition of a silicon oxide capping layer onto a surface, here for the case of copper films, using e-beam evaporation. Both surface modification strategies enable PDMS decal transfers suitable for large area micron-sized patterning of gold, silver, and copper thin films via wet-etching and lift-off procedures.

One of the great limitation of soft lithography is imposed by the mechanical properties of the PDMS stamps used.⁹ When the distance between features is too large, the stamps sag and pattern fidelity is lost.¹⁰ DTL need not suffer this limitation, since UVO exposure and contact are the means of pattern transfer. Two new surface patterning techniques are presented; photo-defined-cohesive-mechanical-failure (P-CMF) and

Masterless Soft-Lithography (Spartacus) [Figure 2]. Both significantly extend the design rules of DTL. A novel UVO mask is developed, which allows the photopatterning of UVO modifications of polymer surfaces. In a second explicit innovation, the photooxidative modifications were carried out using a D₂ discharge lamp as an excitation

Figure 2



source. These modifications in turn enable the direct photoinitiated patterning of resist patterns transferred by P-CMF, which fuses the design rules of the contact based adhesive transfer of PDMS in DTL with those of photolithography. The second, so-called Spartacus method, transfers the design rules of photolithography directly onto PDMS surfaces, enabling a photodefined adhesive transfer of PDMS films onto silicon dioxide surfaces. Both methods have been used to pattern complex, large area PDMS patterns with design rules difficult to achieve by microcontact printing, in this case 2 μm lines with an overlay of pitches ranging from 1 to 20 μm . The chemistry of the UVO modification of the PDMS surfaces, which enables the PDMS to adhere to these various surfaces, was investigated using ToF-SIMS. These investigations confirmed that wavelengths below 230 nm were required to effect a UVO modification that produces strong adhesion, and that the functional groups responsible may be a carbonyl moiety (rather than silanols).

References

1. Leuschner, R.; Pawlowski, G. "Photolithography,," *Mater. Sci. Technol.* **1996**, *16*, 173-249.
2. Madou, M. *Fundamentals of Microfabrication*; CRC Press: Boca Raton, Florida, **1997**.
3. Xia, Y.; Whitesides, G. M. "Soft Lithography," *Ann. Rev. Mater. Sci.* **1998**, *28*, 153-184.
4. Rogers, J. A. "Techniques and applications for non-planar lithography,," *Mater. Res. Soc. Symp. Proc.* **2003**, *739*, 31-38.

5. Whitesides, G. M.; Ostuni, E.; Takayama, S.; Jiang, X.; Ingber, D. E. "Soft Lithography in Biology and Biochemistry," *Annu. Rev. Biomed. Eng.* **2001**, *3*, 335-373.
6. Xia, Y.; Whitesides, G. M. "Soft Lithography," *Angew. Chem., Int. Ed.* **1998**, *37*, 550-575.
7. Childs, W. R.; Nuzzo, R. G. "Decal Transfer Microlithography: A New Soft-Lithographic Patterning Method.," *J. Am. Chem. Soc.* **2002**, *124*, 13583-13596.
8. Childs, W. R.; Nuzzo, R. G. "Patterning of Thin-Film Microstructures on Non-Planar Substrate Surfaces Using Decal Transfer Lithography.," *Adv. Mater.* **2004**, In Press.
9. Delamarche, E.; Schmid, H.; Michel, B.; Biebuyck, H. A. "Stability of molded polydimethylsiloxane microstructures.," *Adv. Mater.* **1997**, *9*, 741-746.
10. Bietsch, A.; Michel, B. "Conformal contact and pattern stability of stamps used for soft lithography.," *J. Appl. Phys.* **2000**, *88*, 4310-4318.