Module 13: Soft Lithography

Lecture 18: Soft Lithography – 1
So far in this course we have discussed about various surface patterning techniques such as Photo Lithography and Nano Imprint Lithography. Now it is time for us to discuss the various “Soft Lithography” (SL) groups of methods. Soft Lithography essentially refers to a group of non-photolithographic strategies that primarily relies on self assembly and replica molding in soft material for nanofabrication. These methods convenient, effective, and low-cost as compared to optical lithography based techniques and can be implemented without major facilities and infrastructure, often in an undergraduate level laboratory. In fact, research in the field of patterning received a significant boost when the SL group of techniques was discovered around mid 90’S. We will, in course of the discussion in this chapter, notice that in addition to the inherent simplicity of the methods, there are certain unique capabilities that most of the methods offer, which cannot be achieved by any other patterning technique. It might be noted that SL is an area in which still active research is going on and a variety of methods are still being developed: while some of them are genuinely novel, others are essentially extensions of the existing techniques. Thus it is not unlikely that a reader glancing through the latest literature might come across names of new techniques. However, there are few major well established SL techniques, which we will discuss in the next two chapters. They include: 1) Replica molding (REM); 2) Microcontact printing (μCP); 3) Micromolding in capillaries (MIMIC); 4) solvent-assisted micromolding (SAMIM); 5) Capillary Force Lithography (CFL); and 6) Microtransfer molding (μTM). As already pointed out during the introduction of NIL, an elastomeric stamp with patterned relief structures on its surface is used for patterning. In fact, the first technique, Replica Molding (REM) is the method by which the elastomeric stamp is first fabricated. That way, we will soon realize that most of the SL techniques are largely dependent on REM for their successful implementation. The second method, Microcontact Printing (μCP) is also unique as it is the only method by which chemically patterned surfaces (surfaces with ordered domains of different wettability) can be created. Similarly, Microtransfer molding (μTM) is unique in the sense that it is the only SL method that allows the fabrication of 3-D structures.
18.1 Replica Molding (REM)

Replica Molding (REM) is one of the earliest Soft Lithography method developed by Whiteside’s group in mid 90’s and is extensively used to fabricate stamps necessary in other Soft Lithography techniques. Simply put, Replica molding is an easy and generic method for replicating or duplicating the information present on an original master pattern, fabricated by any other high end lithographic technique such as photolithography, micromachining, e-beam or FIB writing etc. or can even be a commercially available grating, hologram or a transmission electron microscope grid, on a cross linkable elastomer! The process is schematically shown in figure 18.1. In this method, the polymer to be molded (precursor, in liquid form) is first poured over the original master containing the relief pattern in a liquid form (frame B, figure 18.1). In majority of the cases, Sylgard 184, a two part PDMS based commercial thermo curable elastomer composition (Dow Corning, USA) is used as the pre-polymer. Specific care is taken to ensure that there is no bubble during pouring of the pre-polymer solution, as it is a high viscosity liquid. Upon pouring, the liquid polymer completely covers the master, either due to spreading or by spin coating. The pre-polymer faithfully replicates the contours of the original stamp.
Subsequently, the pre-polymer solution is transformed into a solid elastomer by thermal annealing, where the polymer cross links (frame C, figure 18.1). Once the cross linking is complete, the flexible solid polymer is simply peeled from the original master, as shown in frame D of figure 18.1. To achieve easy detachment during the peeling process, the master is generally silanized by exposing it either to silane vapor or by immersing it in a silane solution. The low surface energy silane coating ensures that the molded structures are not damaged during peeling, due to attachment of the polymer with the master during cross linking. Master silanization is not only important to prevent any distortion to the final molded structures but also ensures reusability of the original master, which is a key requirement for cost effective rapid prototyping. The quality of the molded patterns in REM, particularly the edge fidelity of the replicated patterns is influenced strongly by the van der Waals interactions and wetting property of the master material by the liquid pre-polymer. In this regard, viscosity of the pre-polymer solution is important, as it significantly affects the time required for mold filling. Under appropriate conditions, patterns with sub 50 nm lateral resolution are routinely fabricated by REM.

However, the use of a soft elastomer (Sylgard 184) has some associated problems, which needs to be highlighted: 1) Crosslinked PDMS undergoes about 1% shrinkage during curing, which can lead to dimensional distortion. Secondly, crosslinked Sylgard readily swells when in contact with several non polar organic solvents such as toluene and hexane. Thirdly, the elasticity and thermal expansion of crosslinked PDMS make it difficult to achieve high accuracy in patterning across a large area and may limit the utility of soft lithography in multilayer fabrication. Finally, the softness of an elastomer limits the aspect ratio of features that can be created. In case the aspect ratio (h/l) of the patterns is too high or too low, the elastomeric character of cross linked PDMS may cause the neighboring microstructures to get attached with each other and result in distortion in the final patterns. Frame F of figure 18.1 shows the likely deformations: pairing for very high and sagging in very low aspect ratio patterns, respectively.
Though extremely simple to execute, REM is an important and useful SL technique. Apart from fabrication of masters for other soft lithography techniques, REM is widely used for high throughput bulk production of various commercial items like optical storage discs (CD, DVD, Blue-Ray Disc etc.), Holograms, gratings, MEMS devices and micro tools etc. Further, REM can itself be implemented against a flexible stamp or a mold, examples of which include molding materials like polyurathine (PU) using a flexible PDMS stamp. The use of a flexible stamp allows an in plain compression of the patterns during molding. This can be used as an innovative approach to generate features with lateral dimension smaller than that of the master. The reduction in the lateral dimension achieved this way can often be as significant as ~ 30 – 40%. This approach, which is based on a combination of mechanical compression, bending and stretching during the molding process in presence of a flexible master makes it possible to fabricate topographically complex structures from simple planner stamps like a grating.

**Figure 18.2: Schematic of Micro Contact Printing (µCp)**

18.2 Micro Contact Printing (µCp)

Micro Contact Printing (µCp) is the only SL method which is capable of generating chemical patterns on a surface and is thus, is clearly distinct from all other SL techniques, all of which are result in the creation of structures with topographic patterns. Micro-contact printing (µCp) utilizes the essential physics of silanization in conjugation with the basic concepts of micro molding to generate ordered regions of different wettability. In silanization, the surface active
silane molecules self assemble on a substrate, forming a self assembled monolayer (SAM). The presence of a ligand (Y(CH2)nX), which is reactive toward the surface ensures the attachment of the silane molecules to the substrate. The binding of the SAM molecules to the surface is determined by the group Y. On the other hand, the surface properties of a SAM coated surface depends on the nature of the head group X. Some surfaces like gold or silver show excellent binding ability towards the silane molecules such as alkanethiolates. Alkylsiloxane molecules on hydroxyl-terminated surfaces such as Si/SiO\textsubscript{2}, Al/Al\textsubscript{2}O\textsubscript{3}, glass etc. also exhibit good attachment properties.

The basic mechanism of the process of \(\mu\text{Cp}\) is shown in figure 18.2. In the simplest configuration, a patterned cross linked PDMS stamp made by REM is first inked by immersing in a dilute silane solution (Kumar et al. 1993). The stamp in this case is not used for embossing but is used as a carrier to transfer the dissolved surface active molecules from the solution to the substrate to be chemically patterned. During inking, the entire stamp gets covered with the silane molecules (frame B, figure 18.2). The inking step can also be performed by vapor phase deposition of the silane molecules on the stamp, by keeping the stamp above a beaker containing the silane solution. Some times application of heat to the silane solution further facilitates the vapor phase deposition of the silane molecules on the stamp. The inked stamp is subsequently placed in conformal contact on the substrate to be patterned (Frame D, figure 18.2). It can be clearly seen from the figure that only the top of the stamp stripes come in conformal contact with the substrate and consequently the silane molecules stationed over these areas come in direct contact with the substrate. In contrast, the silane molecules over other areas on the stamp (valleys) do not come in contact with the substrate and therefore areas of the substrate below the stamp valleys remain devoid of any silane molecules. Thus, the silane molecules transfer from the stamp to the substrate only at the locations where the two are in direct contact, resulting in alternating SAM covered zones. The periodic variation in the number density of the attached silane molecules to the surface results in ordered wettability domains, or chemical patterns.
Under ideal transfer conditions, the width of each SAM covered zone should match the line width of the stamp protrusions. The success of μCp, particularly the dimension control and sharpness of the features depends on the rapid reaction and attachment of the surface active molecules to the substrate. The autophobicity of the resulting SAM layer is also important as it prevents the spreading of the silane molecules on the substrate, preventing lateral distortion and overlapping of the individual chemical patches. The intrinsic viscosity of the ink solution is also important, as a low solution viscosity leads to flooding of the ink on the surface. On the other hand, a very high viscosity hinders the transfer of the molecules from the stamp to the substrate within a finite contact time. Solvent evaporation rate is also a key parameter, as a very rapidly evaporating solvent would make the ink too dry even before evaporation and hinder the transfer of the molecules. In contrast, a very slow evaporating solvent may result in smearing of the patterns and possible joining of the near by structures. The typical contact time varies depending on the nature of the substrate. For example, it is ~10 – 20 seconds when a gold coated surface is imprinted with alkanethiol. In addition to the surface active molecules, μCp can also be utilized for making patterns with colloidal particles. The wide popularity of μCp is attributed to simplicity and inherently parallel nature of the process itself, where patterns can be created over large areas (~ cm²) in a single imprinting step.

18.3 Micro Molding in Capillaries (MIMIC)

Micromolding in capillaries (MIMIC) relies on capillarity driven flow of a polymer solution through a confined micro channel, and can be used to fabricate complex topographic microstructures on both planar and curved surfaces. The technique relies on the well known physics of capillary filling, where the flow of a fluid is triggered is engendered due to an imbalance in surface energy in the direction of the flow. The rate of capillary filling is given by:

\[
\frac{dz}{dt} = \frac{R \gamma \cos \theta}{4 \eta z} = \frac{R(\gamma_L - \gamma_{SL})}{4 \eta z}
\]  

(18.1)
where \( z \) is the length traveled by the liquid, \( R \) is the capillary radius, \( \gamma \) is the surface and interfacial tensions, depending on the subscript (SL: solid – liquid interfacial tension; S: Solid surface tension; L: Liquid surface tension) and \( \eta \) is the kinematic viscosity of the liquid.

![Figure 18.3: Schematic of the method of Micro Molding in Capillaries (MIMIC)](image)

For implementing MIMIC, a cross linked PDMS mold (fabricated by REM) is first placed in conformal contact with the substrate (frame A, figure 18.3). The relief structure on the mold forms a network of empty confined capillary channels on a bare substrate. It is important to note that unlike NIL, no initial film is coated in MIMIC. Subsequently, a liquid pre-polymer is dispensed at the open end of the channel network. In the simplest form, the pre-polymer can be a solution of a homopolymer in a solvent. However, it can be a liquid monomer or even a colloidal sol. Due to the preferred wettability of the stamp surface, the liquid spontaneously fills up the channels by capillary action, with a progressively advancing meniscus. The air initially present in the channels generally escapes through the permeable PDMS stamp, without obstructing the capillary flow. Once the capillary filling is complete, the pre-polymer is solidified by allowing the solvent to evaporate or by cross linking. Subsequently, the PDMS stamp is peeled off to reveal the desired pattern (frame D, figure 18.3). It is possible to achieve high fidelity patterns by MIMC, particularly if a low viscosity pre-polymer is used along with a highly wettable stamp.
higher viscosity pre–polymer is generally avoided as it takes longer time for mold filling, which is evident from equation (18.1). MIMIC as a technique was initially designed and developed for liquid pre-polymers that did not contain any solvent. This ensured very low shrinkage of the polymer during solidification (< 5%) and therefore, the final patterns dimensions replicated that on the original stamp perfectly. Subsequently MIMIC has been extended for systems containing solvents, which has allowed the method to be extended for patterning various classes of materials beyond simple homopolymers, some examples of which include ceramics precursors and sol–gel solutions, structural and functional polymers, colloids, biological macromolecules etc. In case a dilute polymer solution is used, there is significant shrinkage of the replicated structures during solvent evaporation, which might lead to distortion of the patterns. A major concern about the choice of the solvent is that it should not swell the cross linked PDMS stamp, which is a major problem with several common non polar solvents such as toluene and cyclohexane. The use of solvent containing precursor system has been particularly useful in fabricating ordered structures with colloids, which are otherwise impossible to create by any other patterning. Various functional micro electronic devices such as ferroelectric capacitors, Schottky diodes, field effect transistors (FET) and silicon metal oxide semiconductor FETs (MOSFETs) have been fabricated by MIMIC.

In spite of its simplicity and advantages, MIMIC has several major limitations. Firstly, it requires an interconnected network of capillaries and therefore cannot be used for fabricating isolated structures. Secondly, the rate of capillary filling progressively reduces with distance and therefore achieving patterns spanning over large areas becomes difficult by MIMIC. Further, the filling rate drops with reduced capillary dimension and therefore replicating very small features takes extremely long time. Finally, when a dilute polymer solution is used, there might be significant shrinkage in the patterns during the stage of solvent evaporation. However, the method has several advantages and unique properties, which has already been highlighted in the text. One key unique feature of this method is the ability to pattern colloids. Additionally,
patterns formed by MIMIC has also be used as resists in selective chemical etching of metals such as Au, Ag, and Cr, which acts as a new route for generating chrome masks necessary in photolithography.

Reference: