Abstract

Microfabrication is essential in the field of science and technology. The development and innovations in this field are already prominent in the society through microelectronics and optoelectronics. The lithography or transfer of pattern to the substrate/surface of a layer is an important process step in microfabrication and is usually carried out with photolithography. Though photolithography is a well-established technique, it suffers from drawbacks such as limited feature size due to optical diffraction, requirement of high-energy radiation for small features, and high-cost involvement for sophisticated instruments. Also, it cannot be applied to nonplanar surfaces. Soft lithography is complement to photolithography which overcomes the above-mentioned drawbacks. Soft lithography is a simple and inexpensive method, and also, it suits to wide range of materials and very large surface areas. High-quality micropatterns or nanopatterns can be made using a patterned elastomeric stamp. This article briefly describes the various soft lithography techniques to obtain high-resolution structures for nanofabrication.

Keywords: soft lithography, polydimethylsiloxane, SU8, UV lithography, photoresist

1. Introduction

Microfabrication is essential in the field of science and technology. The development and innovations in this field are already prominent in the society through microelectronics and optoelectronics. The lithography or transfer of pattern to the substrate/surface of a layer required in microfabrication is usually carried out with photolithography. Photolithography is the basic technology used for making all microelectronic systems. Photolithography is limited to materials for various layers or substrates due to the etching chemistry. Also, photolithography is limited to geometries it can produce. At the same time, photolithography technique is expensive and can only pattern a small area at any given time. Also, the feature
size of the pattern is limited by diffraction of light. As photolithography is confined to extremely flat silicon substrates, one cannot fabricate electronic circuits on a plastic sheet or curved surface. Soft lithography is an alternate technology which provides a good control over an infinite range of structures and chemistries. The dimension can be defined from nanoscale to mesoscale, and it finds applications in developing devices in different fields from consumer product to life sciences and industrial processes.

Conventional photolithography has its own disadvantages such as the following:

i. The feature size is limited by optical diffraction

ii. Complex facilities and technologies for high-energy radiation needed for small feature sizes (EUV, E-beam, or X-ray lithography techniques)

iii. The system is very expensive

iv. Not suitable for nonplanar surfaces

v. No control over the chemistry of patterned surfaces

Due to the above difficulties in photolithography, nonphotolithography technique called soft lithography came into picture, which overcomes the above problems. It does not have the diffraction limits and provides access to three-dimensional structures, chemically inert, inexpensive, and simple processes suitable for molecular scientists. A high quality of patterns with lateral dimensions of about 30 nm–500 μm can be obtained using this technique. Soft lithography is a complement to conventional lithography system and has numerous advantages such as possibility to pattern UV sensitive materials without degrading the performance, to pattern nonplanar surfaces, to pattern large surfaces, to control the chemistry during patterning, ideally does not have any diffraction limits, short time between idea and prototype, clean room free operation, etc.

This chapter explores the fabrication of micromolds with polydimethylsiloxane (PDMS). PDMS is a Si-based organic polymer that has found wide applications in MEMS for soft lithography. PDMS has several desirable properties, which are:

i. Visco-elasticity: PDMS is flexible

ii. Biocompatibility

iii. High chemical inertness

iv. Optical transparency

v. Adhesion to metals: Applications as inert substrate material

Initially, the fabrication of polymer molds has been investigated to explore the nonconventional lithography technology called “soft lithography.” As this technique requires the cycle time of less than 24 hours from design to implementation, many researchers are using this technique for rapid prototype development. The use of polymers for microfluidics is the major research area in the field of Medical Diagonostics and Tissue Engineering. Soft lithography using PDMS molds had been first developed by Whitesides in 1998 at Harvard University [1, 2].
The disadvantages of conventional optical lithography and the advantages of soft lithography had been well demonstrated by his team. He also established the various soft lithography techniques to get the feature size in the range of 30 nm to 500 μm. Many researchers reported on the various techniques of soft lithography in detail [3–8]. Research has been carried out to develop various microdevices using this technique in the field of optics and biosensors. Huang et al. reported about the replication of polymeric microring optical resonators with soft lithography and found an excellent agreement in the optical properties between molded replicated devices and master devices [9]. Chang-Yen reported on PDMS waveguide system using soft lithography [10]. The attenuation and temporal stability were excellent at low cost, low toxicity, and biocompatibility with yield of 96%. Golden et al. reported on array biosensor with PDMS mold which can be used for the simultaneous detection of multiple targets in multiple samples within 15–30 minutes [11]. Liu et al. have reported the fabrication of microchannels, in which with the aid of Si-reinforced PDMS molds, Au dots and wires have been successfully generated on the sidewalls and bottom surfaces of microchannels through hot-embossing processes [12]. Tarbague et al. discussed about the development of new PDMS microfluidic chip molding for Long Wave Biosensor to realize a detection cell of bio-organisms in liquid media [13].

2. Various methods of soft lithography

There are various methods of soft lithography to get precise micropatterns or nanopatterns on the planar or nonplanar surfaces. The following soft lithography process methods have been well established for various commercial devices: (i) replica mold (REM) technique (ii) Microcontact printing (μCP) technique (iii) Micromolding in capillaries (MIMIC) (iv) Solvent-assisted micromolding (SAMIM) (v) Microtransfer molding (μTM) and (vi) Hot embossing technique.

2.1. Replica mold (REM) technique

Replica molding is a very old, simple, and reliable method, in which the micro- or nanopatterns on the surface of the prime (master) mold is duplicated on the polymer material [14]. The minimum feature size of less than 100 nm can be accurately replicated using this technique. It has been successfully used for mass production of devices such as compact disks (CDs) [15, 16], diffraction gratings [17], holograms [18], and microtools [19]. The prime or master mold is generally fabricated on a rigid material (silicon, nickel, glass, or SU8 photore sist) using a standard photolithography and micromachining techniques. The elastomeric stamp or replica mold is fabricated by cast-molding technique. A prepolymer of the elastomer is poured over the master, cured, and then peeled off. Poly(dimethylsiloxane) (PDMS) is a widely used elastomer all over the globe compared to other elastomers such as polyurethanes, polyimides, and Novolac resins. PDMS is a unique combination of an inorganic siloxane and organic methyl groups. Since the glass transition temperature of PDMS is very low, it is available in the form of fluid at room temperature. This can be readily converted into solid elastomers by cross-linking. Nowadays, PDMS is readily available in the market as a two-part material containing prepolymer and curing agent.
Figure 1 shows the process flow for the fabrication of master mold. The master is made up of SU8–2075 negative photoresist (Microchem, USA), which helps us to get high-aspect ratio structures precisely. SU8–2075 is spin coated on flat silicon substrate for the required thickness. For example, to get the photoresist thickness of 100 $\mu$m, spinning was carried out with the spin speed of 2230 rpm for spin time of 30 sec with an acceleration of 500 rpm for 5 sec. The sample was soft baked for 5 minutes at 65°C then for 12 minutes at 95°C. Now, the mask plate (written by laser writing on Chrome coated glass plate) was kept above the sample, and UV light (365 nm wavelength) was exposed for 15 seconds using Karl Suss Mask Aligner. Then, the sample was post baked for 5 minutes at 65°C then for 10 minutes at 95°C. Then, it was developed for 7 minutes using SU8 developer solution. Finally, the sample was hard baked for 1 hour at 95°C, and the patterns on SU8 photoresist were observed under the microscope. The master made on SU8 can be used repeatedly for more than 50 times to make polymer replicas.

Figure 2 shows the process flow for the fabrication of PDMS stamps using the master. The elastomeric stamp or mold is prepared by cast molding. PDMS elastomer Sylgard 184 was...
obtained from Dow Corning. It comes as a two-part material containing the silicone base and a curing agent. The base and the curing agent were taken in the ratio of 10:1, and vigorous agitation by manual stirring is required for mixing. During this process, air bubbles may form in this mixture. To remove the air bubbles, the mixture was kept in vacuum desiccators for 1 hour. Then, it was poured on the SU8 master mold structure and cured at 70°C for 3 hours. After cooling down to room temperature, the PDMS layer was peeled off from SU8 pattern. The resulting PDMS micromold pattern is a reverse pattern of SU8 structure. Figure 3 shows the SEM images of three different master molds made up of SU8–2075, and Figure 4 shows their corresponding PDMS replica patterns.

Replica molding is extensively used to fabricate microfluidic devices as a rapid prototype [20–25]. The microchannels are formed on the PDMS mold with SU8 as prime mold. Then, this PDMS structure is placed on a glass cover plate and bonded together by oxygen plasma treatment of both surfaces. The PDMS is punched to form inlet and outlet ports, and tygon tubes with luer connectors are inserted on the ports. The photograph of the microfluidic device fabricated using the above method is shown in Figure 5.

Replica molding technique has been adapted for the fabrication of topologically complex, optically functional surfaces that would be difficult to fabricate with other techniques. Experimenting with various feature size of photo lithography and test the replica molding for its best replication is also necessary. PDMS shrinks by approximately 1% upon curing. Also,

Figure 3. SEM images of three different SU8 master mold patterns (i), (ii), and (iii).

Figure 4. SEM images of three different PDMS mold patterns: (i)–(iii) corresponding to SU8 master mold patterns shown in Figure 3 (i)–(iii).
the cured PDMS gets swelled while treating with organic solvents such as toluene and hexane. Due to low Young’s Modulus and thermal expansion of PDMS, there are variations in the dimensions especially while working with multilayered structures. Also, while fabricating PDMS with microstructures, if the aspect ratio \( h/l \) is too high or too low, the elastomeric character of PDMS will cause the defects in the microstructures as shown in Figure 6. During fabrication, stress is induced on PDMS due to gravity, adhesion, or capillary forces and generates defects in the pattern that is formed. Main technical problems are given below [1]:

i. If the aspect ratio is too large, the PDMS microstructures fall under their own weight as shown in Figure 6. Figure 6 A(i) shows the expected structure, and A(ii) shows the resultant structure due to high aspect ratio. Aspect ratios between 0.2 and 2 are the best to get defect-free stamps.

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Figure 5. Photograph of the spiral microfluidic device fabricated using replica molding on PDMS.

Figure 6. Defects in patterns due to high or low aspect ratio structures: A(i) expected structure with high aspect ratio (ii) resultant collapsed structure; B(i) expected low aspect ratio structure with (ii) resultant sagged structure.
ii. If the aspect ratio is too small, the relief structures are not able to withstand the compress forces and adhesion between the stamp and the substrate. This will lead to sagging as shown in Figure 6 B(i) and (ii). Nonfunctional posts or rigid supports have to be included in the design to avoid sagging.

2.2. Microcontact print (μCP) technique

Microcontact printing (μCP) is a simple and efficient method for precise microscale pattern transfer for biotechnology applications. This technique enables tailoring the properties of surface at molecular level using self-assembled monolayers (SAMs). SAMs can be easily formed by immersion of the stamp in the solution containing a ligand \(Y(CH_2)_nX\) reactive toward the surface or by exposure of the stamp to the vapor of a reactive species [2]. The thickness of a SAM can be controlled by change in the number \(n\) of methylene groups in the alkyl chain. Changing the head group \(X\) can modify the surface of the monolayer. The binding of the anchoring group \(Y\) is selective to substrate material. Well-established methods of SAMs of alkanethiolates on Au and Ag and alkylsiloxanes on hydroxyl-terminated surfaces such as Si/SiO\(_2\), Al/Al\(_2\)O\(_3\), glass, mica, and plasma-treated polymers are reported.

Figure 7 shows the process steps for microcontact printing. A thin metal film such as gold (Au), silver (Ag), copper (Cu), palladium (Pd), or platinum (Pt) is deposited on the substrate by physical vapor deposition (thermal evaporation or e-beam evaporation). PDMS stamp (as shown in Figure 7(a)) is wetted with a hexadecanethiol in ethanol (as shown in Figure 7(b)) and is brought into contact with the surface of Au for 10:20 seconds. The hexadecanethiol transfers from the stamp to the gold upon contact resulting in a hexadecanethiolate and generates patterns of SAMs on the surface of gold as shown in Figure 7(c).

![Figure 7](image-url)

**Figure 7.** Process steps for microcontact printing (a) PDMS stamp (b) PDMS stamp immersed in hexadecanethiol solution and (c) SAM pattern transferred to the substrate with gold coating by bringing the stamp in contact upon the substrate.
2.3. Micromolding in capillaries (MIMIC)

Micromolding in capillaries (MIMIC) is another technique of generating microstructures using PDMS stamps. In this method, top portion of microchannel structures is made on the PDMS stamp. Then, this stamp is placed on a substrate with the channel structure facing down on the substrate. This forms capillaries on the substrate. When a polymer material such as polyurethane or epoxy is placed at one end of the channel, it started flowing into the channels due to capillary action. After some time, the capillaries are filled by the above material. Finally, this polymer material is cured by UV or heat or using a curing agent. Once the polymer is cured, the PDMS stamp can be removed. The fill rate of the polymer inside the capillary depends on viscosity of the fluid, radius of the channel, pressure difference at the ends of the capillaries, surface tension, contact angle, and the length of the capillary. Figure 8 shows the process flow for micromolding in capillaries (MIMIC).

2.4. Solvent-assisted micromolding (SAMIM)

In solvent-assisted micromolding (SAMIM) technique, a PDMS mold with microchannels is placed on a substrate. As PDMS is hydrophobic in nature, it is treated with oxygen plasma to improve its wettability. A good solvent that can dissolve a polymeric material without affecting PDMS mold is allowed to fill the microchannels. The solvent gets evaporated and the resulting fluid or gel which solidifies and made available in the molded structures defined by the PDMS mold. The solvents such as methanol, ethanol, Iso-propane alcohol, toluene, and acetone having high surface tension are generally being used. The problem with SAMIM is the formation of a very thin film at the bottom of the structure. This film has to be removed by RIE or by a suitable etchant before use for the preferred application. Figure 9 shows the step-by-step process flow for the SAMIM technique of patterning.

Figure 8. Process flow for micromolding in capillaries (a) PDMS mold with microchannels on silicon substrate (b) Polyurethane or epoxy in the form of fluid at the end of the microchannels (c) fluid flows inside the microchannels by capillary force and (d) cured epoxy and removal of the PDMS mold.
2.5. Microtransfer molding (μTM)

Microtransfer molding (μTM) is a simple soft lithography technique to form patterned microstructures of polymers such as organic polymers or polyurethane on a large area. The polymer may also be doped with fluorescent material like rhodamine. In this method, the patterned surface of a PDMS mold is filled with a prepolymer of required polymer material as shown in Figure 10(a). The excess fluid is removed by another flat PDMS block to get a flat surface as shown in Figure 10(b). This combined block is turned upside down and placed on a substrate as shown in Figure 10(c). Now, the prepolymer is cured by UV light or by heating. Once the prepolymer is solidified, the PDMS mold is peeled out leaving the patterned polymer structure on the surface of the substrate as shown in Figure 10(d). In this method, a very thin layer (100 nm) of polymer is formed in-between the raised structure. This can be etched by reactive ion etching (RIE). This method is established for the fabrication of optical waveguides, couplers, and interferometers.

2.6. Hot embossing

Hot embossing also referred as soft embossing denotes stamping of micropatterns onto a polymer softened by raising the temperature just above its glass transition temperature. The stamp used to define the pattern may be made up of a hard material such as Silicon or metal.
using any of the micromachining technique like bulk silicon etching or LIGA. The preferred polymer materials suitable for making the replicas using this technique may be polystyrene (PS) or poly methyl methacrylate (PMMA) or polycarbonate (PC). In this method, dimensions of micropatterns less than 1 μm are highly possible.

The process involves three steps namely heating, embossing, and demolding as shown in Figure 11. During the first step of heating, the metal or silicon mold and the polymer substrate are aligned and placed in between two stainless steel supporting plates. This setup is brought into a heating chamber, and the sample is kept at the specified embossing temperature for a soaking time of 30 minutes. During the second step of embossing, the load is applied gradually by a pneumatic (servomotor controlled) press and hold at a specific load for few minutes. This is followed by gradual unloading. The third step is demolding, in which the temperature is gradually reduced. After it is cooled down, the mold and the polymer replica are taken out of

**Figure 11.** Process flow of hot embossing technique: (a) Step 1: prepare the metal mold and keep over the required polymer sheet; (b) Step 2: apply pressure and heat for hot embossing; (c) Step 3: cool and detach the polymer replica.
the chamber and separated out. For better precision, a vacuum chamber is preferred which maintains the temperature and helps for perfect embossing of microstructures.

3. Challenges

Though soft lithography seems to be simple and promising low-cost technique to achieve nanostructures, there are many challenges in bringing this technique to market. The major problem is the distortion of elastomeric materials, which limits high-resolution registration in soft lithography. This problem can be reduced by using thick samples and rigid supporting structures. The micropatterns or nanopatterns in the stamp or mold may distort due to pairing, sagging, swelling, and shrinking of elastomer. The process may also introduce defects due to dust particles, poor adhesion to substrate, or poor release from the stamp and bubbles in the prepolymer. The presence of thin film of polymer in soft lithography is generally removed by reactive ion etching. But, this may damage small features. Soft lithography is still in its early stage of development, and researchers and manufacturers of microdevices are working in establishing this technology toward reliability, reproducibility, and stability of the micro/nanostructures.

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