

Nanofabrication with molds & stamps

by Byron D. Gates

A number of methods can be used to fabricate patterns with features having dimensions < 100 nm. These techniques, however, can require specialized equipment and are often restricted to a cleanroom environment. Nanofabrication can be made accessible to multiple users by using elastomeric molds or stamps to transfer high-resolution patterns into other materials. These techniques are inexpensive and can transfer patterns into functional materials and onto a number of surfaces. This review describes recent advances in fabricating nanostructures using these techniques.

Fabricating functional structures in a variety of materials with arbitrary patterns is central to the development of many technologies. An example is the development of microelectronic devices and data storage technologies. Advances in these technologies often depend on continual improvements to specialized techniques – primarily photolithography and electron-beam lithography – to fabricate increasingly complex patterns with minimum dimensions ≤ 100 nm. These specialized techniques are, however, restricted primarily to patterning planar semiconductor substrates. Alternative techniques are essential for transferring patterns into organic substrates other than photoresist, and into other functional (and often fragile) materials.

This review focuses on new approaches to nanofabrication using topographically patterned elastomers, including molding, embossing, printing, and edge lithography. A number of polymers can be used to transfer the patterns. One of the most successful materials for pattern transfer is poly(dimethylsiloxane) or PDMS¹⁻³. This elastomer is durable, chemically resistant, and deforms reversibly without permanent deformation of the surface topography. PDMS also has a low surface free energy⁴ (21.6 dynes/cm²), and reversibly conforms to different surfaces – even nonplanar structures – over areas > 1 cm². Precursors to this material are commercially available and inexpensive^{5,6}. PDMS can, therefore, sometimes be used as a disposable component of pattern transfer. A common formulation of PDMS from Dow Corning (Sylgard 184) has a tensile modulus of 1.8 MPa⁷.

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Formulations of PDMS with higher tensile moduli include a ultraviolet (UV)-cured PDMS (hv-PDMS)⁷ and a thermally cured PDMS (h-PDMS)⁸⁻¹¹, which have moduli of 3.4 MPa and 8.2 MPa, respectively. Further silicone elastomers for nanofabrication include block copolymer thermoplastics^{12,13} and fluorocarbon-modified siloxanes¹⁴. Highly fluorinated elastomers easily release from molds and resist swelling upon exposure to organic solvents and monomers¹⁵. These materials have a surface free energy similar to poly(tetrafluoroethylene) (PTFE) and other types of Teflon®¹⁵.

Molding

Molding is the transfer of a topographic pattern from one material to another by curing or solidifying a liquid precursor against the original patterned substrate. This fabrication method can replicate a three-dimensional structure into a range of materials (Fig. 1a)^{3,16}. The replication steps include: (i) fabricating the desired topographic patterned master; (ii) transferring this pattern to PDMS by curing a PDMS prepolymer in contact with the master and releasing the PDMS from the master; and (iii) solidifying a liquid precursor against the PDMS mold and releasing the solidified structure to isolate a replica of the master. Examples of these solidified structures include polymers, gels, precursors to ceramics and carbons, luminescent phosphors, salts, and colloids^{1,3}. The PDMS mold releases easily from both the original master and the replica without damage to either surface. Repeating the replication procedure can pattern numerous molds from each master and multiple replicas from each mold. The process replicates structures with high fidelity and accuracy down to length scales similar to the size of large molecules. For example, replica molding with PDMS can transfer a pattern of periodic features with vertical deflections <2 nm into a UV-cured polyurethane (Fig. 1b-d)^{11,17,18}. The ultimate resolution of replication with a PDMS transfer element is currently unknown and may be limited by capillary and van der Waals interactions. Another useful property of this elastomer for nanofabrication is size reduction by mechanical or thermal deformation of the PDMS mold^{19,20}.

Another approach to molding is necessary to fabricate isolated features from a topographically patterned master. One method is microtransfer molding (μ TM) – replication of the recesses of a topographically patterned mold and transfer of these features to another substrate (Fig. 2a)²¹. The first step of this molding process is to fill the recesses of the mold

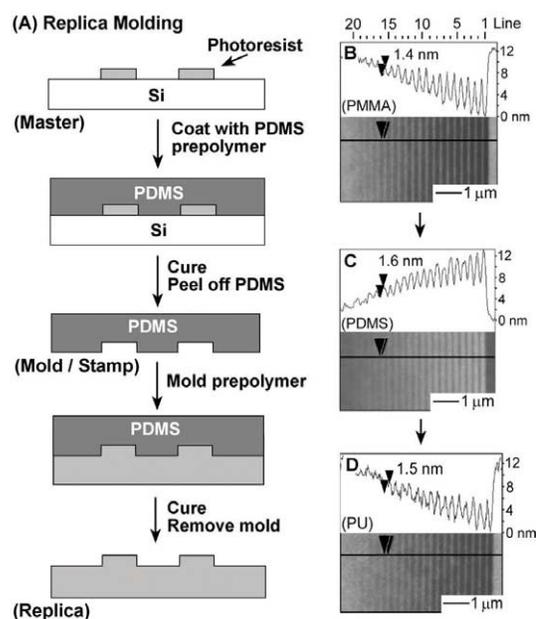


Fig. 1 Replica molding. (a) Schematic illustration of the procedure to form elastomeric molds from topographically patterned masters, and molding of this elastomer with another prepolymer to fabricate a replica of the original master. (b-d) The smallest structures replicated using PDMS are ~ 1.5 nm vertical deflections¹¹. Atomic force microscopy (AFM) images show: (b) a poly(methyl methacrylate) or PMMA master with periodic lines patterned by direct writing with a focused electron beam; (c) a complementary h-PDMS mold; and (d) a polyurethane (PU) replica. (Reprinted with permission from¹¹. © 2003 American Chemical Society.)

with a polymer precursor and remove the excess material. In the second step, the prepolymer is cured after placing the mold onto another substrate (e.g. semiconductor, oxide, or polymer). The PDMS mold is optically transparent down to wavelengths ~ 280 nm and it is, therefore, possible to mold UV-curable prepolymers while in contact with nontransparent substrates (e.g. Si wafers). After curing the prepolymer, the last step is to remove the mold. This step leaves the replicated structure on the new substrate. It is possible to fabricate complex three-dimensional structures by repeating this process in a layer-by-layer fashion^{21,22}. μ TM can also transfer patterns onto curved or other nonplanar surfaces. A limitation of this technique is that a thin residue of polymer can connect the isolated features (Fig. 2a). This residue is removed using reactive ion etching. It may be possible to prevent the formation of this residue by fabricating a mold with an appropriate surface chemistry (e.g. fluorinated silanes) to dewet the prepolymer from the raised regions of the PDMS mold.

An alternative approach to molding isolated features is micromolding in capillaries (MIMIC). This molding technique fills a series of channels with a low-viscosity liquid that either

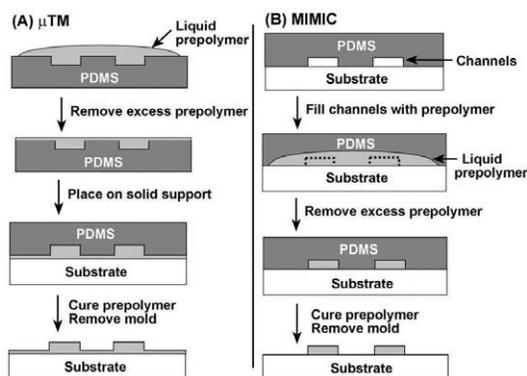


Fig. 2 Extensions of replica molding. Schematic diagrams illustrate (a) μ TM²¹ and (b) MIMIC²³. In μ TM, the liquid precursor coats the recessed regions of the mold prior to placing the mold on a solid substrate, and in MIMIC the liquid precursor fills the recessed regions by capillarity after placing the mold onto the substrate.

deposits material or chemically modifies a substrate (Fig. 2b)²³. A network of connected channels is formed by placing a topographically patterned PDMS mold onto a solid substrate. Placing a liquid at one end of the channels, the liquid fills the series of channels by capillarity. This liquid either deposits or removes material in the exposed regions of the underlying substrate. Deposited materials include polymers, prepolymers, sol-gel precursors, proteins, and colloids^{1,23}. The solution filling the channels can also etch the substrate or modify the surface chemistry in a pattern defined by the network of channels. This patterning technique is simple and can pattern continuous structures with isolated features. A microfluidic system can assist with filling the channels. This system directs the delivery of liquids from reservoirs to the channels by changes in external pressure (e.g. applying a vacuum or high pressures to pump the liquid)²⁴. A network of multiple reservoirs and channels can pattern different materials in parallel. It is, however, still a challenge to fill <100 nm wide channels with the desired solutions. The resistance to liquid flow through the channels increases with decreasing size of the channel. It may be slow to fill the channel with the liquid, but applying a vacuum to the channel or heating the liquid can assist the filling process.

Embossing

Another form of nanofabrication is solvent-based embossing. Solvent-assisted micromolding (SAMIM) uses a solvent to restructure a polymer film by swelling or dissolving the polymer²⁵. This room-temperature processing avoids thermal cycling of the substrate^{26,27}, which can be time intensive and lead to oxidation of the substrates. Instead of heat, an

organic solvent softens the polymer film. After coating the surface of a PDMS mold or polymer film with the solvent, the mold is brought into contact with the polymer film. The softened polymer film adapts to the topography of the PDMS mold (Fig. 3a). The PDMS is gas permeable, which prevents trapping of gas pockets at the mold-polymer interface. The solvent also passes through the PDMS mold and evaporates. During solvent evaporation, the restructured polymer film hardens with a topographic pattern complementary to that of the PDMS mold. The mild processing conditions of SAMIM are conducive to patterning fragile optical components, such as organic light-emitting diodes (OLEDs) and organic-based distributed feedback lasers²⁸.

SAMIM can pattern nanoscale structures^{9,25}. For example, SAMIM can pattern linewidths of at least 60 nm, such as the lines in the Novolac-based photoresist in Fig. 3b²⁵. Pattern transfer into polymers depends on finding an appropriate solvent to soften the polymer and also to evaporate by transport through the PDMS in a reasonable period of time. This evaporation process is a limiting factor in the throughput of SAMIM. Understanding the interaction of the solvent with the PDMS is also important for controlling the swelling and distortion of the PDMS upon uptake of the solvent. A recent study has increased our understanding of compatibility, swelling, and retention of solvents within a PDMS mold²⁹.

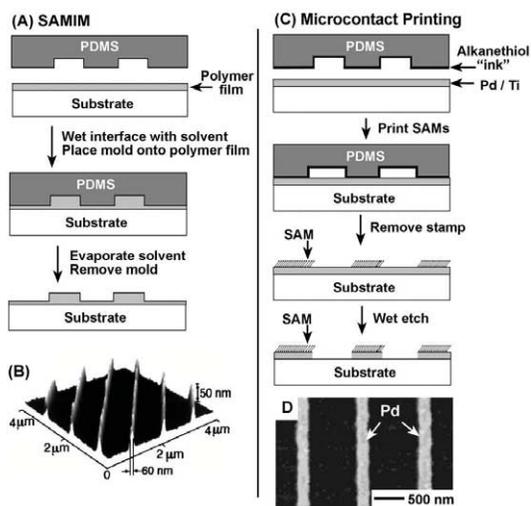


Fig. 3 Embossing and printing. (a) Schematic illustration of SAMIM. This embossing technique can pattern linewidths of at least 60 nm, as shown in the AFM image in (b) of a patterned Novolac photoresist²⁵. (Reproduced in part with permission from²⁵. © 1997 Wiley-VCH Verlag GmbH.) (c) Schematic illustration of μ CP. An application of this technique is to pattern SAMs on noble metals as etch resists. For example, the scanning electron microscopy (SEM) image in (d) shows ~150 nm wide lines of Pd patterned by μ CP with eicosanethiol, which protects these regions of the metal during a solvent-based etch³³. (Reproduced in part with permission from³³. © 2003 American Chemical Society.)

Printing

Printing using a topographically patterned stamp is a straightforward method of projecting a pattern onto a surface. Microcontact printing (μ CP) transfers an 'ink' onto a surface in a pattern defined by the raised regions of a stamp (Fig. 3c)³⁰. This is a simple method for fabricating structures in an additive process. An elastomeric stamp coated with the ink is brought into conformal contact with the surface of interest. The ink transfers from the stamp to this surface by a process of chemisorption or physisorption. Releasing the PDMS stamp from the surface reveals the printed pattern of ink. The first application of this technique³⁰ was to pattern alkanethiols on Au. Upon contact with the Au film, the thiol group binds to the Au surface and van der Waals interactions between the alkane chains direct these molecules to form dense, ordered monolayers (i.e. self-assembled monolayers or SAMs)^{3,31}. This printing technique can also transfer silane- and phosphonic-terminated alkane chains to oxidized surfaces³, and can pattern planar and nonplanar surfaces³² over areas >50 cm². Transferring the pattern of printed molecules onto the substrate is straightforward. These printed patterns of SAMs can protect the substrate during a subsequent solvent-based etch (Fig. 3d). Structures patterned by this technique include electrodes^{33,34} and components for display devices³⁵. The recessed features of an elastomeric stamp can, however, deform on the nanoscale and distort the printed structure. To minimize this deformation and exploit the beneficial properties of PDMS, a base layer of h-PDMS is backed with a softer PDMS layer (e.g. Sylgard 184 from Dow Corning) to form a composite stamp that retains the structure of nanoscale topographic patterns⁸. This modification to the stamp and improvements in the etch resistance of the SAMs improve the edge roughness of patterned structures to <100 nm^{36,37}.

Nanoscale fabrication by printing extends beyond transferring molecules to a surface. Elastomeric stamps can also print colloids^{38,39}, dendrimers⁴⁰, organic reactants⁴¹, and proteins⁴². An elastomeric stamp can also serve as a 'handle' for manipulating and transferring continuous or discontinuous structures onto different surfaces. An example of this approach to fabrication is decal transfer printing – the placement and transfer of membranes and isolated features of PDMS using a PDMS 'handle' to assist in the transfer process⁴³. Minimum features patterned by this technique are, however, currently on the micron scale. A similar technique

transfers thin, solid films from a PDMS stamp to other surfaces. Nanotransfer printing (nTP) avoids the need to expose a substrate to harsh solvents (e.g. acids and bases) (Fig. 4a)⁴⁴. This patterning process includes the following steps: (i) coating the stamp with a thin film (e.g. 20 nm thick Au); (ii) bringing the stamp into contact with a surface to be patterned; and (iii) releasing the thin film as a continuous structure or as isolated features by removal of the stamp. The thin film transfers to the printed surface by covalent binding to reactive SAMs (e.g. alkanedithiols)⁴⁵, cold welding between two metal layers⁴⁶, or condensation between silanol or titanol groups⁴⁷. nTP simplifies nanofabrication by eliminating the need for developers and etchants during pattern transfer, and can transfer complex patterns in a single step (Fig. 4b). A layer-by-layer process can pattern three-dimensional structures⁴⁶. Structures fabricated by nTP include organic thin film transistors⁴⁸, capacitors⁴⁷, and electrostatic lenses⁴⁴. The transfer of patterned metal films to a fragile surface avoids exposing the sample to the high temperatures common in conventional metal deposition techniques. The 'soft contact' of nTP is a nondestructive method for establishing electrical connections to fragile surfaces and structures.

Reversible soft contact is also possible if an adhesion layer is deposited between the metal film and the PDMS stamp. Electrical microcontact printing (e- μ CP) is a technique for

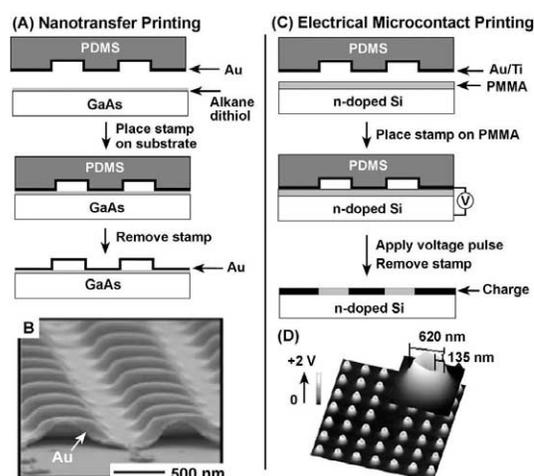


Fig. 4 Extensions of μ CP. (a) Schematic illustration of nanotransfer printing (nTP). This printing method can pattern complex topographies, such as the hollow structures shown in the SEM cross-section image (b) of a 20 nm thick Au film transferred onto a GaAs substrate functionalized with 1,8-octanedithiol⁴⁵. (Reproduced in part with permission from⁴⁵. © 2004 Wiley-VCH Verlag GmbH.) (c) Schematic illustration of e- μ CP. KFM measurements indicate changes to the surface potential of an electrode as shown by the image in (d) of a thin film of PMMA after patterning by e- μ CP⁴⁹. (Reproduced in part with permission from⁴⁹. © 2001 American Association for the Advancement of Science.)

transferring a pattern to thin films of electrets – materials that accept and maintain an electrostatic potential – using this flexible electrode (Fig. 4c)⁴⁹. The PDMS-based electrode is brought into contact with the electret (e.g. a thin film of poly(methyl methacrylate) or PMMA) supported on a conductive or semiconductive substrate, such as an *n*-doped Si wafer. A short voltage pulse (10–30 V for ~10 s; ~10 mA/cm²) applied between the metal layer on the stamp and the substrate coated with the dielectric film can change the electrostatic potential of the electret in contact with the flexible electrode. Kelvin probe force microscopy (KFM) can measure the changes in electrostatic potential across the surface of the electret (Fig. 4d). Not only can this technique pattern electrostatic charge over areas >1 cm² with ~100 nm resolution, but it is also a convenient method to print patterns with high feature densities for data storage (>5 Gbits/cm² in <20 s)⁴⁹. These patterned substrates can also attract nanoparticles, such as carbon and iron oxide, to the regions of trapped charge^{49,50}. Removable soft contact electrodes may find a number of other applications in printing charge, preparing substrates for xerography, and probing the electronic properties of nanostructures.

Edge lithography

Edge lithography is another simple form of nanofabrication. An example is phase-shifting edge lithography using an elastomeric stamp for pattern transfer⁵¹. The vertical edges of a topographic pattern within a PDMS stamp can induce a phase shift in incident UV light to pattern photoresists with nanoscale features (Fig. 5a). In contrast to phase-shift photolithography using a rigid mask⁵², a PDMS phase-shift mask is inexpensive to fabricate and conforms to the photoresist surface. The transparent PDMS stamp, placed in contact with the thin film of photoresist, induces abrupt changes in the phase of incident, collimated light. Constructive and destructive interference results at the vertical edges of the stamp. Fig. 5a shows the light intensity from destructive interference of collimated light. These interference patterns can be predicted^{53,54}. The interference forms light or dark regions of light that overexpose or underexpose a positive photoresist to pattern trenches or ridges, respectively (Fig. 5b). These nanoscale features can direct the assembly of nanoparticles⁵⁵ or the crystallization of inorganic salts¹⁰. The patterned photoresist can also mask the underlying substrate during pattern transfer by thin film

deposition or reactive ion etching. This process can fabricate free-standing, single-crystalline nanostructures of Si⁵⁶ and frequency-selective optical filters⁵⁷.

Edge lithography is also the transfer of structures that are thin in the vertical direction – such as a thin film – to structures that are thin in the lateral direction^{58–62}. This reorientation of thin films is a convenient method for fabricating nanostructures. Depositing a thin film onto the topographic pattern of a polymeric mold and taking its cross section can form patterned arrays of nanoscale edges (Fig. 5c)⁶¹. The first step of this process is to cast and cure an epoxy prepolymer against a PDMS mold. After releasing the epoxy mold from the PDMS, the surface of the epoxy is selectively coated with a thin film (e.g. Au). A brief exposure to oxidizing plasma removes organic residue from the surfaces of this substrate prior to encapsulating the entire substrate with the epoxy prepolymer. A clean surface is important to prevent (or at least minimize) delamination between the epoxy and the deposited thin film while taking a cross section of the encapsulated structure using a microtome. Cooling the sample to -120°C during sectioning

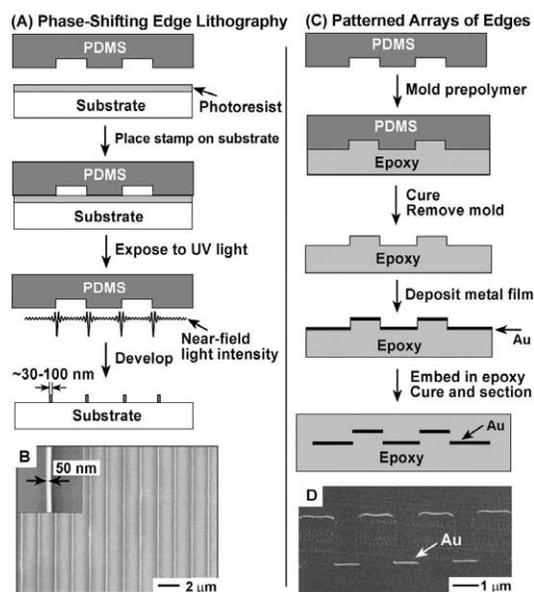


Fig. 5 Edge lithography. (a) Schematic illustration of phase-shifting edge lithography using a PDMS stamp in contact with a photoresist. The schematic also illustrates the modulation of the light intensity at the interface between the PDMS stamp and the photoresist (i.e. the near-field region). This technique can pattern narrow linewidths as shown in the SEM image in (b) of 50 nm wide lines of positive-tone photoresist supported on Si⁹. (Reproduced in part with permission from⁹. © 2002 American Chemical Society.) (c) Schematic illustration of the fabrication of patterned arrays of conductive edges embedded in epoxy. The SEM image in (d) shows 50 nm wide Au edges exposed by sectioning the encapsulated structure with the glass knife of a microtome⁶¹. (Reproduced in part with permission from⁶¹. © 2004 American Chemical Society.)

minimizes the surface roughness (~10 nm). The cross section exposes the deposited thin film as a patterned array of edges with nanoscale lateral dimensions (Fig. 5d). It is a simple process to fabricate structures with different compositions, dimensions, and structures. These exposed edges can be conductive or magnetic. Applications of these structures include insulated nanoscale electrodes⁶¹ and directing the assembly of nanoparticles⁶³.

Conclusions

Advanced lithography tools can fabricate complex patterns of nanoscale features covering large areas of a semiconductor substrate. New tools are, however, necessary for fabricating nanostructures in fragile substrates, such as functional

organic materials. Simple, inexpensive, and versatile methods for patterning nanostructures include molding, embossing, printing, and edge lithography using an elastomeric mold or stamp. These techniques can make multiple copies of arbitrary patterns with high throughput and fidelity of pattern transfer. These tools have also made nanofabrication accessible in multiple research environments. The development of these methods will continue to lead to advances in both fundamental and applied science in many fields of study, such as materials science, chemistry, physics, and biology.

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