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UNCONVENTIONAL NANOFABRICATION

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edge lithography

■ **Abstract** Nanostructures are fabricated using either conventional or unconventional tools—that is, by techniques that are highly developed and widely used or by techniques that are relatively new and still being developed. This chapter reviews techniques of unconventional nanofabrication, and focuses on experimentally simple and inexpensive approaches to pattern features with dimensions <100 nm. The techniques discussed include soft lithography, scanning probe lithography, and edge lithography. The chapter includes recent advances in fabricating nanostructures using each set of techniques, together with demonstrated advantages, limitations, and applications for each.

INTRODUCTION

Nanofabrication is an extension of microfabrication, and central to the evolution of electronics and information technologies to ever-smaller structures. The process of making functional devices with well-defined structures—fabrication—includes patterning, interfacing with other components (e.g., wiring, optical alignment, and making other connections that require registration), and packaging. Patterning has, in the past, been accomplished almost entirely by photolithography. This review focuses on unconventional techniques for patterning materials to make functional nanostructures.

A number of techniques can pattern nanostructures. We describe these techniques as either conventional or unconventional. Conventional techniques—projection lithography and scanning beam (or maskless) lithography—are highly developed and widely used for fabricating microelectronic circuits. The most common type of projection lithography is photolithography. Diffraction of the light used to expose a photoactivated film of resist limits the dimensions of the features produced by photolithography. The use of short wavelengths (down to 157 nm), reduction optics between the mask and substrate, phase shifting corrections to intensity, and immersion optics have permitted a reduction in features size to

less than 50 nm (1). Extending these processes to wavelengths below 157 nm (deep UV and soft X-ray wavelengths) brings increasing technical difficulty, particularly in developing new optical elements (2–8).

Scanning beam lithographic techniques, such as electron beam and focused ion beam lithography, offer alternative approaches to patterning small features. These serial techniques are, however, slower than the parallel approach of projection lithography. A pattern is carved out line-by-line by scanning a high-energy (> 10 kV) beam of electrons or ions over a resist material (chemically, this process typically depolymerizes, polymerizes, or ablates the film of resist). The resolution of electron beam lithography is limited by high-energy secondary electrons and by scattering of electrons from the primary beam within the resist and from the substrate. Increased accelerating voltages (> 50 kV) produce fewer secondary electrons in the resist, but edge roughness limits the reproducible patterning of resists to features > 10 nm in the smallest dimension (9). A focused ion beam (FIB) can deposit or remove material with resolution down to ~ 5 nm (10).

Each of these conventional fabrication tools, except for soft X-ray lithography, is commercially available (albeit expensive). These techniques are highly developed and optimized for semiconductor fabrication. The cost of purchasing, installing, and maintaining the tools they require limits their application in areas other than microelectronics. These tools are also often incompatible with nonstandard problems in fabrication (for example, patterning nonplanar surfaces, or reactive organic polymers). Access to fabrication facilities may also be restricted when using “dirty” materials—for example, organic compounds that are not photoresists. In fact, it is difficult or impractical to pattern many organics and biological samples using photolithography. Slow turnaround for sample processing using commercial and shared user facilities has also inhibited exploration of these techniques outside of microelectronics and related areas, and has stimulated efforts to develop alternative tools for nanofabrication.

A number of unconventional methods developed for nanofabrication enable new types of fabrication and circumvent limitations—both technical and financial—of conventional methods. Usually these techniques are not directly competitive with the conventional processes; in fact, conventional approaches are often used in fabrication when, in fact, nonconventional techniques would be better suited for the particular task.

This review focuses primarily on advances in three areas: soft lithography (11–13), scanning probe lithography (SPL) (14–17), and edge lithography (18). These approaches can fabricate nanostructures with a range of topographies in a range of materials.

Soft lithography is a suite of techniques that uses organic (that is, soft) materials to enable replication and pattern transfer on multiple length scales (from nanometers to centimeters). We use the term soft to refer to the stamp and/or to the substrate when they are composed of soft matter (e.g., polymers or self-assembled monolayers). The pattern transfer consists of three steps: (a) fabricating a topographically patterned master, (b) molding this master to generate a patterned stamp, and

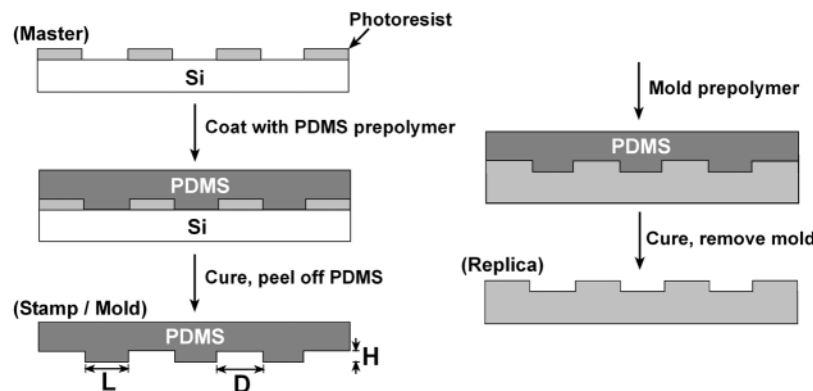


Figure 1 Schematic illustration of the fabrication of the topographically patterned elastomeric pattern-transfer agent (a mold or stamp depending on the application of soft lithography) by casting and curing an elastomer against a patterned relief structure, usually in photoresist (a master). A replica of the master is generated by molding against the patterned elastomer. PDMS is poly(dimethylsiloxane).

(c) generating a replica of the original template in a functional material or a 1:1 projection of the pattern on a surface by applying the stamp (Figure 1). Fabrication of the master usually employs conventional tools. Soft lithographic techniques can, however, produce numerous molds and replicas from the same master and thus provide nanofabrication capabilities not commonly available in academic research laboratories.

The area of soft lithography includes a wide variety of procedures. This review organizes soft lithography into three categories—replica molding, embossing, and microcontact printing—to clarify the differences among them. Replica molding is any process that transfers topographical features from a rigid or elastomeric mold into another material by solidifying a liquid in contact with the original pattern (19). Molding techniques include microtransfer molding (μ TM) (20), micromolding in capillaries (MIMIC) (21), and step-and-flash lithography (22). Embossing is the process of imprinting a pattern into an initially flat substrate by pressing a mold into the surface; this term includes techniques such as nanoimprinting (using either rigid or soft mold) (23) and solvent-assisted micromolding (SAMIM) (24). These methods thermally imprint a polymer film with a rigid mold or use solvent assistance to imprint a polymer film with a soft polymeric mold. The term nanoimprint is sometimes used in the microelectronics community (25–28); for economy in nomenclature, we include nanoimprint lithography as a soft technique. Microcontact printing (μ CP) is the transfer of a pattern from a stamp as defined by the regions of the stamp in contact with a surface (29). Historically, the term referred to patterning molecules that are covalently attached to the surface. Decal transfer, or transfer of the patterned topography of an elastomeric stamp (30),

and nanotransfer printing (release of a conformal surface coating from the stamp) (31–33) are two recent extensions of this technique.

Scanning probe lithography is a second major class of techniques of unconventional nanofabrication—localized modification of a surface by oxidation or by material transfer using a sharp probe in contact with the surface (14, 15, 17). SPL is primarily serial; recent advances, however, have enabled a multiprobe, or more parallel, application of this technology (34–36).

Edge lithography is the third major class of techniques. We define edge lithography as either pattern transfer directed by the edge of a feature or the process of transforming an edge of one feature into a feature with smaller dimensions (18, 37).

This review includes only unconventional nanofabrication techniques capable of making features with the smallest dimensions < 100 nm in at least one (lateral or vertical) direction. The techniques covered are largely top-down approaches, as opposed to bottom-up approaches that assemble atoms or molecules into nanostructures. (Other chapters of this volume review bottom-up strategies.) In this context, we review techniques capable of nanofabrication, or patterning of nanoscale features, by design. We focus on techniques that require a low capital expenditure (12, 38–43), are easy to learn, and experimentally straightforward to apply.

FABRICATION OF MASTERS

The primary use of soft lithographic pattern transfer is replication. A brief overview of the procedures used to obtain a master (or mastering) is, however, important in understanding the capabilities and current limitations of pattern generation. Numerous procedures can generate masters (12, 13). Conventional methods commonly employed include photolithography, electron beam lithography, and FIB lithography. These techniques create arrays of lines without difficulty. Alternative, or nonstandard, procedures for fabricating masters can occasionally offer simple routes to specialized patterns. A few commercially available substrates—for example, diffraction gratings and other diffractive optical structures—can sometimes be used as masters (44). Crystalline substrates, such as silicon (100) wafers, can be etched anisotropically to generate well-defined, narrow patterns (44–46). Thin films deposited by a number of techniques can also be patterned by selectively etching exposed regions of the film, while masking with a photoresist or with a self-assembled monolayer (SAM) of organic molecules (46–50). These patterned substrates can be used as masks for further pattern transfer into an underlying substrate (46, 49, 50) or for selective dewetting of prepolymer solutions to create relief structures (44).

A number of techniques can also generate soft masters. Polymer films can be patterned by holography and replicated by electroplating; this technique has been highly developed for holograms on credit cards (51, 52). Electric field-induced formation of structure in a polymer bilayer has patterned polymer films with dimensions < 100 nm (53). Crystalline lattices of polymer beads can also be assembled over large areas ($> \text{cm}^2$) (54–60). These crystalline arrays can be molded,

incorporated into a mold (44, 61), or used directly as a pattern transfer mask (62, 63).

Masters can also be formed by self-assembly; an example is the formation of a polymer mask from a block copolymer film (64). Biologically inspired materials with nanoscale dimensions also self-assemble: examples include two-dimensional lattices of DNA (65), and two-dimensional crystalline lattices of proteins (66–68).

SOFT LITHOGRAPHY

Soft lithographic techniques are especially useful for inexpensive prototyping of a test pattern. They also allow <100 nm patterning of curved surfaces and of large areas. They do not provide the lateral fidelity and stability of the pattern that one can achieve using, for example, high-resolution photolithography. A mold is prepared by casting a liquid polymer precursor against a suitable master. A number of polymers (e.g., polyurethanes, epoxides, and polyimides) are readily available for molding and provide a range of possible materials and properties of the final mold. We commonly use poly(dimethylsiloxane) (PDMS) elastomer (or silicone rubber) for the mold because it has a number of useful properties: PDMS (*a*) is inert to many chemicals and unreactive toward most materials being patterned or molded; (*b*) has a low surface free energy ($\gamma = 21.6 \text{ dyn/cm}^2$) (69) that facilitates release from templates and printed structures; (*c*) is optically transparent down to ~ 300 nm and thermally stable (below $\sim 150^\circ\text{C}$)—a feature that permits UV or thermally induced cross-linking of materials being molded; (*d*) is physically tough (tensile modulus of 4.77 MPa); and (*e*) is flexible (elastic modulus of 1.8 MPa and elongation up to $\sim 160\%$) (70).

Polymers have a number of properties that make them attractive for molding and replication of topographically patterned templates. Distortion of nanoscale features, however, limits the number of materials that can be used in nanofabrication. One cause for distortion of replicated features is a difference in thermal expansion between the master and replica. A second factor that influences the fidelity of replication is polymer shrinkage during curing of a prepolymer through solvent evaporation and/or cross-linking of the polymer. A third type of distortion of the molded material can result from adhesive forces during separation of the master and stamp. A fourth distortion is collapse of the features owing to mechanical instability of a polymer (e.g., flexibility and polymer chain mobility).

PDMS has a number of properties that prevent or minimize these distortions. In curing PDMS, there is no solvent evaporation, and low-temperature curing (room temperature to 60°C) minimizes thermal expansion (71). PDMS has a low surface free energy, and a solvent can be used to reduce further the strength of interaction between the master and stamp or the mold and replica (72, 73).

The low elastic modulus for Sylgard 184 PDMS (1.8 MPa) (70) make it difficult to replicate nanoscale features with high-aspect ratios using soft lithography. A number of alternative PDMS formulations address this problem. For example, the elastic modulus of a thermally cured so-called hard PDMS (h-PDMS) (74) and

UV-cured PDMS ($h\nu$ -PDMS) (70) are 8.2 and 3.4 MPa, respectively. Composite stamps comprising a thin layer ($\sim 40\text{ }\mu\text{m}$) of h -PDMS supported by a thick layer ($\sim 1\text{ mm}$) of Sylgard 184 replicate lateral features below 100 nm with aspect ratios $>4:1$ without collapsing (74, 75).

Replica Molding

REPLICA MOLDING USING A RIGID MOLD Replica molding fabricates objects with a specific topography by solidifying a liquid polymer precursor against a topographically patterned mold. There are numerous approaches to replica molding using both rigid and soft topographic molds. Willson and colleagues have developed one approach—step-and-flash lithography—that uses a rigid, transparent (usually quartz) master (76). The process proceeds by placing this rigid mold in contact with a low-viscosity, photocurable polymer (Figure 2*a*). A fluorosilane [e.g., $\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{SiCl}_3$] is typically covalently linked to the surface of the mold to lower its surface free energy and to make it easier to separate the mold and the photocured polymer. The liquid prepolymer conforms to the rigid mold and requires only slight pressure (50 mbar–1 bar) be applied to the mold to minimize the thickness of the residual film between isolated features. Exposing the prepolymer to UV light through the transparent mold initiates photoinduced cross-linking. Little mechanical stress is imposed on the system during molding—mostly from a decreasing volume of the polymer during cross-linking. This technique also is “self-cleaning” because particulate matter on the surface of the rigid mold is captured mechanically in the cross-linked polymer replica and thus removed from the mold.

Step-and-flash lithography avoids thermal- and pressure-induced deformations of nanostructures and can replicate features with lateral dimensions as small as 30 nm (Figure 3) (22); this dimension will certainly decrease with development. High-aspect ratio (up to 8:1) lines can also be patterned by step-and-flash lithography. The polymer replica can serve as an etch resist to transfer the pattern into a second material by reactive ion etching (RIE). This technique has been applied to pattern a polymer gate for a functional metal oxide semiconductor field-effect transistor (MOSFET) (77) and to fabricate arrays of micropolarizers using the polymer as a mask for wet etching of a metal film (78). Two advantages of step-and-flash molding for fabricating nanostructures are the rapid cycle time ($<5\text{ min/replication cycle}$) and the ability to align the mold optically with features on the underlying substrate (76, 79). Limitations of this replica molding technique include the difficulty of patterning nanostructures on nonplanar surfaces and that of replicating isolated features in the mold due to air trapped at the mold-polymer interface. For multilayer structures, the dimensional fidelity and stability of the replicated pattern and the ability to carry out registration remain unresolved issues.

REPLICA MOLDING USING A SOFT MOLD We have also demonstrated replica molding with deformable templates, using elastomeric molds of PDMS (11, 80, 81). Figure 2*b* outlines the general procedure for replica molding using a PDMS

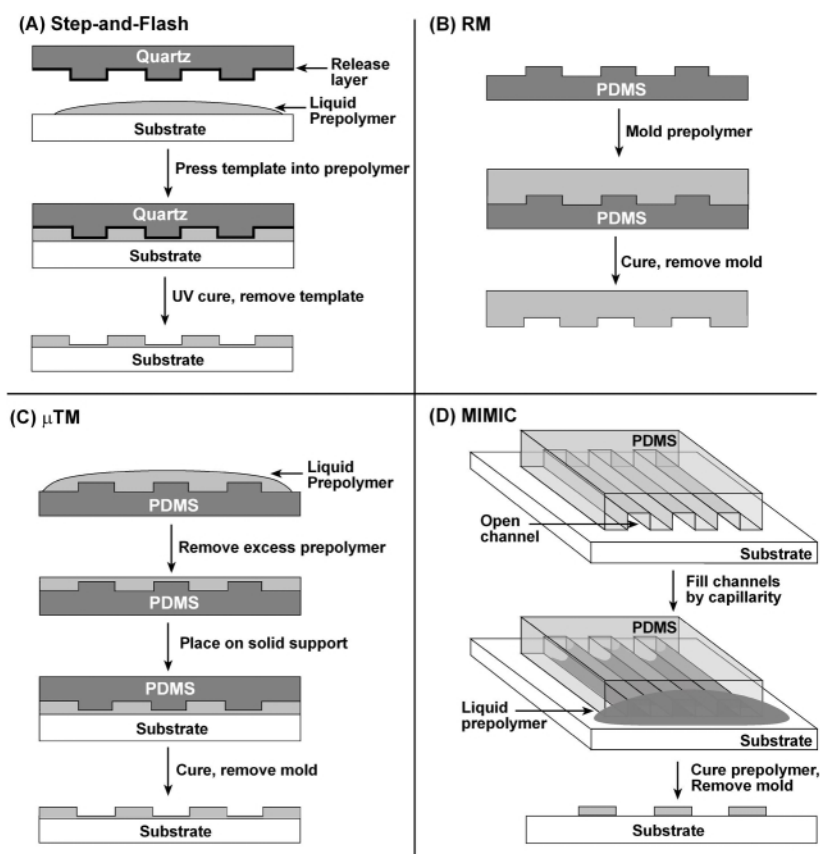


Figure 2 Schematic diagrams of four approaches to replica molding: (a) step-and-flash lithography, (b) replica molding (RM), (c) microtransfer molding (μ TM), and (d) micromolding in capillaries (MIMIC).

mold, and photo- or thermally curable prepolymers. Low-molecular-weight monomers (e.g., styrene) often dissolve in PDMS (82). Prepolymers, however, typically do not penetrate into PDMS. Each PDMS mold can be used for multiple replications (>20 times from the same stamp). A benefit of replica molding with PDMS is the ability to mold against nonplanar, rigid, and soft topographic surfaces (unlike step-and-flash techniques, which require a planar, rigid mold). The ability to mold a range of materials and topographies, the potential for large area molding, and the ability to generate multiple PDMS molds inexpensively from a single master, make this technique potentially useful for applications where low costs are required.

PDMS can be used to replicate nanostructures having dimensions <100 nm. A diffraction grating with ~ 10 -nm vertical features and a template with ~ 30 -nm lateral features—created by compressing a PDMS stamp with 50-nm features—were

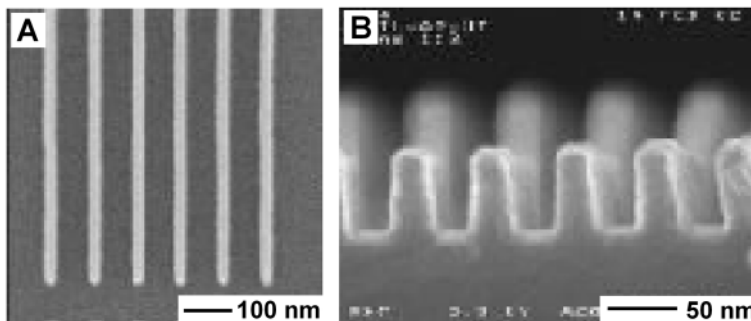


Figure 3 (a) Scanning electron microscopy (SEM) image of 30-nm wide lines molded into UV-cured 1,3-bis(methacryloxypropyl)tetramethyldisiloxane as patterned by step-and-flash lithography (22) (reprinted with permission, © SPIE 2002). The image in (b) shows a cross-section of these lines.

both replicated into polyurethane (PU) (81, 83). The replication of an array of trapped air bubbles with nanoscale features was also shown using a polystyrene template with 20-nm wide and 27-nm deep holes created from a block copolymer film (Figure 4a–c) (84).

The smallest features replicated using PDMS are periodic vertical patterns with peak-to-trough dimensions of ~ 1.5 nm (85). Figure 4d shows a tapping mode AFM image of a test structure in PMMA with ~ 0.5 to ~ 5 -nm deep lines spaced by 250 nm; this structure was fabricated by direct writing with a focused electron beam. We used this structure as a master, and fabricated a PDMS mold from it by replica molding (Figure 4e) and rereplicated the features from PDMS into PU (Figure 4f). The ability of soft-lithographic molding to replicate features below 1 nm is an unresolved issue because the surface roughness of the PDMS and PU are of this magnitude. Replication of nanoscale features with molecular precursors of polymers is, in principle, limited by the size of these molecules and by the atomic-scale separation of the master and mold. We estimate a lower limit of 0.1 to 0.2 nm from van der Waals contacts (86), but this limit remains to be verified experimentally.

A variant of replica molding is microtransfer molding (20). In this technique, liquid prepolymer fills the recessed regions of the mold, and excess prepolymer is removed from the top surface using a flat edge (a so-called doctor blade). After placing the mold in contact with a rigid substrate, the prepolymer is cured by appropriate means (Figure 2c). The permeability of the PDMS mold to gas prevents trapping of air at the interface and allows replication of noncontinuous features. Microtransfer molding has been used to pattern planar or curved surfaces. The patterned features are cured while in contact with a surface, and the elastomeric mold peeled away (20). Repeating this process multiple times on a single surface can build multilayer structures. Sub-micrometer wide pyramids with tips having a radius of curvature < 100 nm across have been fabricated using anisotropically etched Si (100) substrates as the master (80). The disadvantage of

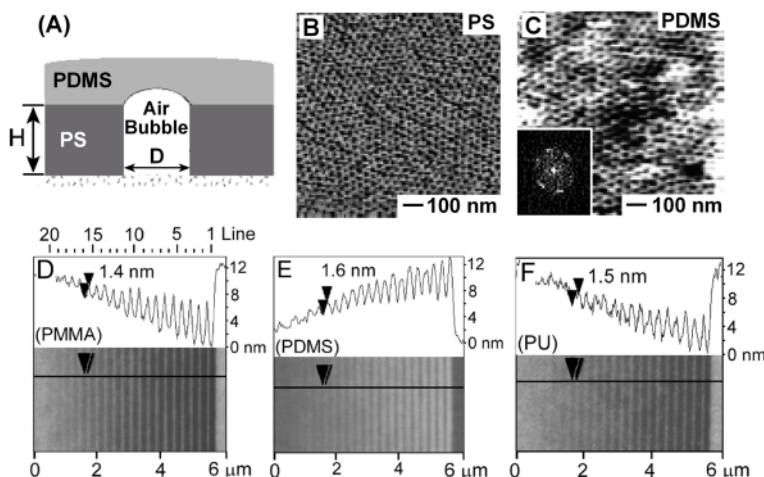


Figure 4 Replica molding of nanoscale polymer templates. (a) Schematic illustration of the replication of air bubbles trapped within a polystyrene (PS) master during molding. Atomic force microscopy (AFM) images of (b) blockcopolymer template (PS-*b*-PMMA) after selective removal of the poly(methyl methacrylate) (PMMA) to expose ~ 20 -nm wide holes, and (c) a PDMS replica of air bubbles trapped in this master with an inset showing a two-dimensional Fourier transform of the same area (84) (reprinted with permission, © WILEY-VCH 2003). Topographic AFM images with cross-sections of (d) a PMMA film with parallel trenches spaced by 250 nm with vertical displacements varying from ~ 0.5 to 5 nm, (e) a h-PDMS mold of this master formed by spin-casting and curing the prepolymer, and (f) a polyurethane (PU) replica (85) (reprinted with permission, © ACS 2003).

μTM is that a thin film of cured polymer precursor (sometimes called scum) often connects topographic features. This film can be removed by RIE to create free-standing or isolated structures (20), but this removal requires an additional step of processing.

Another variant on molding is micromolding in capillaries (21, 87–89). This technique uses capillarity to fill a series of channels in a topographically patterned PDMS stamp with a fluid, low-viscosity polymer or ceramic precursor; because the PDMS stamp is in contact with the substrate before the polymer is introduced, this method does not leave residue between the patterned features (Figure 2d) (21). A patterned elastomeric stamp placed in contact with a flat surface forms a network of open micro (or nano) channels. A low-viscosity precursor placed at one end of the channels fills them by capillarity. Precursor material is cured within the channels, and the mold is peeled away to reveal a positive reproduction of the open network. The speed of filling is determined by the combined influence of precursor viscosity, channel radius, interfacial free energy of the surfaces, and distance the precursor has traveled along the channel (21). A vacuum is sometimes applied to one end of the capillaries to assist the capillary flow (90).

It is not clear what role—if any—nanosized channels will play in nanofabrication, because filling nanosized capillaries is slow. Channels with <100 -nm diameters have been filled by capillarity over short distances (91, 92). Micrometer and submicrometer channels are, however, efficient templates for directing the self-assembly of smaller, nanosized components. MIMIC has been used to pattern block copolymers (93), mesostructured silicates (94), colloidal particles (94), and bacterial S-layer proteins (95).

Embossing and Nanoimprinting

Embossing a flat thermoplastic against a rigid mold is a common patterning technique used in mass production (19, 96, 97). These methods have been used to manufacture compact discs, digital versatile discs (DVD), holograms, diffraction gratings, microtools, and plastic parts (11). Embossing techniques have been extended to nanofabrication with resolution well below 50 nm (23).

EMBOSSING USING A RIGID MOLD Nanoimprint lithography is the term coined for a procedure that transfers a pattern from a rigid mold into a deformable material coated on a rigid surface. The material, typically a polymer, is heated above its glass-transition temperature (e.g., 90 – 200°C), while pressure is applied to the rigid mold (e.g., 50 – 130 bar) (26, 27, 98). The mold is removed after cooling the substrate to below this glass-transition temperature (T_g) (Figure 5*a*). Imprinting can replicate structures with aspect ratios up to 10:1 and as small as 10 nm (Figure 6*a*) (98). Nanoimprint has been used to pattern Fresnel lenses (Figure 6*b*) (99), MOSFETs (100), and electrical contacts for nanowire FETs (101). Pattern transfer takes about 5 to 10 min (and sometimes longer) depending on the efficiency of heat transfer within the system. A room-temperature approach to embossing polymer films was introduced by applying high pressures ($\sim 10^7$ bar) to a rigid mold for ~ 20 s to pattern features down to 80 nm (102).

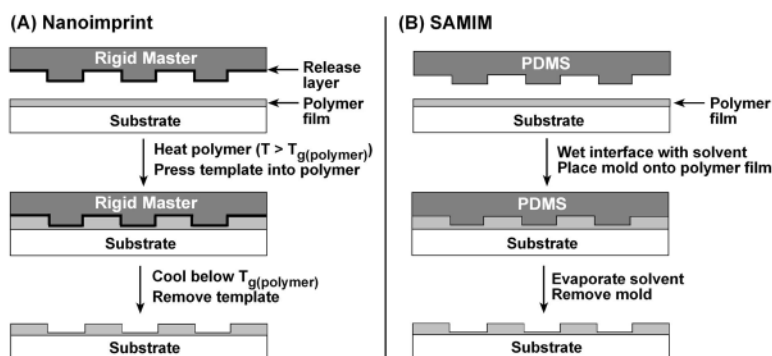


Figure 5 Schematic illustration of embossing procedures for (a) nanoimprint lithography and (b) SAMIM.

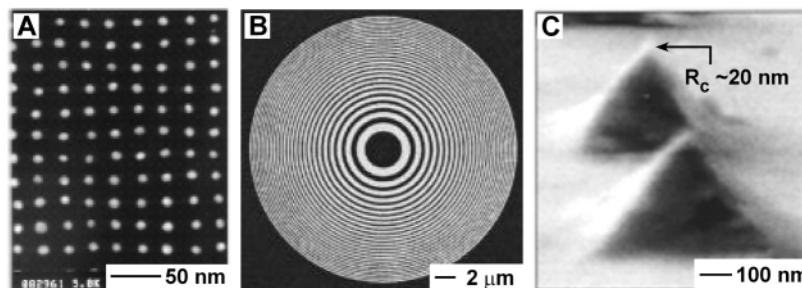


Figure 6 (a,b) SEM images of structures patterned by nanoimprint: (a) 10-nm diameter metal dots with a periodicity of 40 nm (98) (reprinted with permission, © AIP 1997), and (b) Fresnel zone plates with a 125-nm minimum line width (99) (reprinted with permission, © AIP 2000). (c) SEM image of features patterned by SAMIM (75) (reprinted with permission, © ACS 2002).

Nanoimprint lithography, as with step-and-flash lithography, can be carried out in a step-and-repeat fashion similar to those currently applied in commercial processes of manufacturing. There are challenges, however, that must be overcome to transfer patterns uniformly over large areas: for example, the rigid mold and the spin-cast polymer film must be parallel, and the pressure applied across the mold must be uniform (27, 28). Embossing a polymer film can also trap air pockets within the recessed regions of the rigid mold, and high pressures can be required to fill these features (103). Thermal cycling can oxidize some substrates and can extend the processing time to allow for a complete heating and cooling cycle. It also makes the dimensional fidelity and stability of the pattern transfer problematic. Nanoimprint seems—at this relatively early stage of development—to be substantially more complicated and difficult than step-and-flash lithography.

EMBOSSING USING A SOFT MOLD Solvent-assisted micromolding uses an elastomeric PDMS mold in combination with an appropriate solvent—instead of a rigid mold and high temperatures and pressures—to emboss the polymer film. The solvent, rather than temperature, softens the polymer (Figure 5b). Solvent is either briefly applied to the PDMS mold (24) or retained in the polymer film (104) before placing the two surfaces in contact. Polymer is drawn into the crevices of the mold as solvent is removed from the mold-polymer interface by transport and evaporation through the mold. The permeable mold prevents trapping of air pockets and nonuniform solvent evaporation. The mold is removed (after evaporation of the solvent) to reveal a relief structure complementary to the topography of the mold. Line widths down to $\sim 60 \text{ nm}$ and aspect ratios of at least 1:1 have been patterned in a Novalac photoresist and poly(vinyl pyridine) by SAMIM (24, 104). A composite elastomeric mold with a h-PDMS surface has embossed features with critical dimensions down to $\sim 20 \text{ nm}$ (Figure 6c) (75). The application of SAMIM to smaller features has been limited primarily by the

lack of appropriate masters rather than by the fundamental characteristics of this process.

One advantage of molding using an elastomeric rather than a rigid mold is that it can conform to nonplanarity in surface topography over large areas ($> \text{cm}^2$); a second advantage of the elastomeric mold is that release layers are often unnecessary to prevent material transfer while embossing. Swelling of the elastomer, however, can cause distortion of the topographic features. Understanding the ability of solvents to swell PDMS (82) will improve the capabilities of this technique.

It is difficult to use embossing to pattern features that are not connected to one another because a thin layer of polymer is left between the features. The thickness of this thin film depends, inter alia, on the volume of polymer that can be displaced, the rate of removal of solvent, and the ability of the polymer to dewet from the underlying substrate. Typically a $> 10\text{-nm}$ thick layer of polymer is left between patterned features; this layer can usually be removed by RIE.

Microcontact Printing

Microcontact printing is one of the most useful techniques for generating patterns of functional organic surfaces over large areas ($> \text{cm}^2$) (11–13, 80, 105–111). The general procedure brings a topographically patterned PDMS stamp, wetted with a solution of an alkanethiol or other molecules (phosphonic acids, alkylsiloxanes, isocyanides) that can form SAMs, into contact with the surface of a metal, metal oxide, or semiconductor for a few seconds; an ordered monolayer forms rapidly at the points of contact (Figure 7). This procedure works best with alkanethiols and derivatives on gold, silver, palladium, and platinum; other types of microcontact printings give lower-resolution features. This methodology can tailor properties (wettability, biocompatibility, reactivity) of the surface, by transferring organic films that are only 1 to $\sim 2\text{ nm}$ thick (112, 113).

Applications of patterned SAMs on surfaces include resists for selective wet etching (29, 49), templates for promoting or resisting adhesion of polymers, biomolecules, and whole cells (114–119), and patterns for additional functionalization of the surface (120). The advantages of microcontact printing for fabricating small structures are (a) the physical dimensions of the stamp (not optical diffraction) define the minimum feature sizes of the pattern; (b) the *flexibility* of the stamp allows conformal (i.e., molecular level) contact between the stamp and the substrate for a range of topologies, including planar and curved substrates; and (c) a large variety of types of molecules can act as “inks” on a number of different materials. Some of the disadvantages are the blurring of the pattern by lateral diffusion of the ink, the deformation in the pattern that reflect deformations in the stamp, and the substantial number of defects in the film (121–124).

Selective wet etching of regions on metallic thin films patterned with SAMs can yield pinhole defects and rough edges in the final structures (47, 121, 125–127). The addition of an organic amphiphile, such as octanol, to an etchant solution

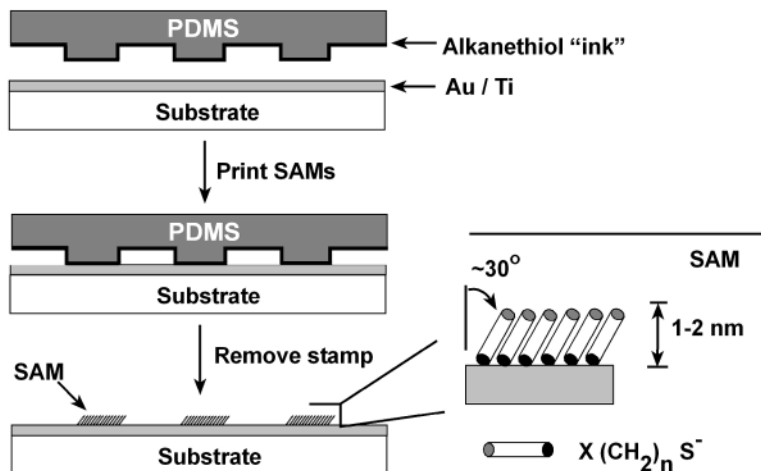


Figure 7 Schematic illustration of a procedure used to pattern SAMs on the gold surface by μ CP.

decreases the number of pinhole defects formed (Figure 8a) (128). Thin films of palladium offer a good alternative substrate for patterning nanostructures by microcontact printing because the film consists of smaller grains (~ 10 – 15 nm diameter) than gold or silver. SAMs formed from alkanethiolates on palladium also provide better etch resistance, and thus fewer defects, than those on gold or silver substrates because a thin (10 Å) layer of palladium sulfide forms between the bulk palladium and the SAMs (Figure 8b) (47, 121, 122, 125, 128). Linear nanostructures have been etched into palladium with lateral dimensions of ~ 50 nm (D. Wolfe, unpublished results).

Microcontact printing has produced features with critical dimensions smaller than 50 nm on metal surfaces (128, 129). Composite stamps comprising a thin layer (~ 40 μ m) of h-PDMS supported by a thick layer (~ 1 mm) of Sylgard 184 replicate lateral features on masters below 50 nm without collapsing (74, 75, 129). Although the lateral dimensions of the PDMS stamp, in principle, should determine the minimum resolution of the pattern transferred to the surface, lateral diffusion of the thiols contributes to (and may dominate) the formation of broadened features. Low concentrations (< 1 mM) of eicosanethiol have yielded patterns of SAMs of alkanethiolates on metallic surfaces with the highest fidelity (128). Macromolecules with high-molecular weights (> 5 kD), such as dendrimers and proteins, exhibit limited lateral diffusion and can generate linear features with widths of ~ 50 nm (Figure 8c) (129). Surfaces patterned by μ CP have been used as etch resists (29, 49) and as templates to direct the deposition of ~ 50 -nm diameter particles in ordered two-dimensional arrays (130, 131).

The key idea in microcontact printing is the transfer of the organic molecules to the surface of the substrate at the regions of contact. Three examples that extend

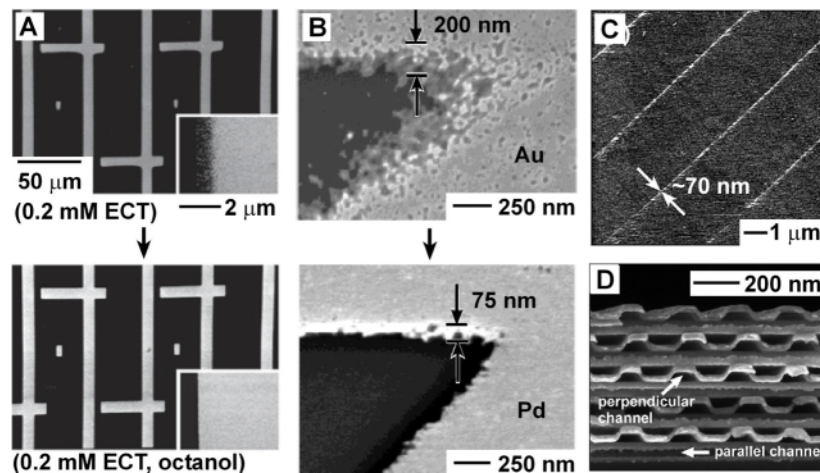


Figure 8 Patterns formed by microcontact printing. (a) SEM images of 15-nm thick Au patterned with eicosanethiol (ECT) at 0.2 mM (*bright regions*) show improved etch resistance and edge clarity with the incorporation of octanol in the gold etch bath (128) (reprinted with permission, © ACS 2002). (b) SEM images of the corner of a diamond pattern on Au and Pd printed with hexadecanethiol (47) (reprinted with permission, © ACS 2002). (c) AFM images of ~70-nm wide lines of titin multimer protein on silicon printed from a composite PDMS stamp (129) (reprinted with permission, © ACS 2003). (d) SEM image of a cross-section from a sample of 10 consecutively printed layers of 100-nm thick gold that were cold welded together with alternating layers rotated by 90° (132) (reprinted with permission, © ACS 2003).

this concept to include other types of materials and multiple layers of material are decal-transfer printing (30), nanotransfer printing (31–33, 132), and electrical microcontact printing (133). Discrete PDMS structures could be transferred onto a range of substrates from a PDMS stamp coated with an organic material (e.g., a perfluorinated alkylsiloxane) that facilitates release (30). A thin film of gold or other metal evaporated onto a PDMS stamp will transfer to another substrate when no adhesion layer (e.g., Ti or Cr) is used to bind the gold film to the stamp (31–33, 132). Repeating this procedure can produce three-dimensional nanostructures consisting of layers of topographically patterned metallic films (Figure 8d). Charge can be patterned in electrets (electrets are materials that can store charge) by electrical microcontact printing (133). In this technique, a gold-coated stamp is brought into conformal contact with a thin electret (e.g., PMMA) supported on a silicon wafer, and a voltage pulse is applied between the stamp and the supporting silicon wafer for ~20 s. A pattern of charge remains in the electret upon removal of the stamp. This technique can pattern regions of charge with lateral dimensions down to at least 100 nm.

SCANNING PROBE LITHOGRAPHY

Proximal probe techniques—scanning tunneling microscopy (STM) and AFM—are also potential new tools for nanofabrication (14–16, 134). One of the most striking examples of nanoscale fabrication by SPL has been the precise positioning of atoms with an STM tip (Figure 9*a,b*) (134, 135). These structures are interesting scientifically, but not yet demonstrations of a practical technology.

Serial Patterning of Surfaces

The deposition of individual atoms or clusters of atoms by SPL is a powerful method to pattern a surface (136–138). Dip-pen nanolithography (DPN) is one approach to fabricating nanoscale structures by the selective deposition of nanoparticles, SAMs, or other molecules onto a surface (17, 139–143). AFM tips are “inked” with a solution of the material to be transferred. The material adsorbed on the tip transfers to the substrate when scanning the probe across surface (Figure 9*c*). Patterns made by DPN can be as small as 15 nm (Figure 9*d*). The mechanism of this process is not yet clear. One possibility is that a water layer between the tip and surface mediates material transfer. Another is that transfer involves solid-solid interactions. Spreading of the ink is dependent on humidity, chemical interaction

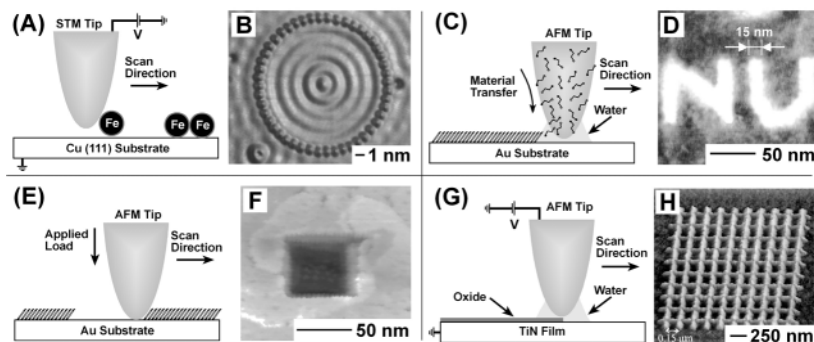


Figure 9 Schematic representations of four approaches to SPL and patterns produced using them: (a) A scanning tunneling microscopy (STM) can position atoms to pattern structures with high precision, such as (b) a quantum corral of a 48-atom Fe ring formed on Cu enclosing a defect-free region (135) (reprinted with permission, © AAAS 1993); (c) Dip-pen nanolithography can direct the deposition of SAMs (e.g., 16-mercaptohexadecanoic acid) on a Au surface to pattern (d) features down to ~15-nm (142) (reprinted with permission, © AAAS 1999); (e) Nanoshaving can remove regions of SAMs to pattern features, such as (f) a square hole within octadecane thiolate SAMs on Au (150) (reprinted with permission, © ACS 2000); and (g) Scanning electrochemical oxidation can selectively oxidize a surface to pattern (h) ~50-nm wide lines of oxide written on TiN (160) (reprinted with permission, © AIP 1999).

with the substrate, radius of curvature of the probe, and linear velocity of the probe. Defects within these patterns have not been characterized, nor is it clear what sizes of features can be made routinely. Although 10-nm-scale features have been shown, most seem to be closer to 50 nm.

A second, complementary, approach to patterning surfaces with a SPL is the selective removal of material from a surface. Polymers, liquid crystals, bilayers, and other types of resists have been patterned by mechanical abrasion using a scanned AFM probe (144–146). The scanned probe displaces a thin film when the contact load between the tip and substrate is higher than the displacement threshold of the surface layer. This process, referred to as nanoshaving, is typically applied to the patterned removal of SAMs (Figure 9*e,f*) (147–149). For reasons that are not entirely clear, this patterning of SAMs is typically carried out while immersing the surface in a good solvent in which the molecules can be removed (150). Alternatively, material abrasion can occur after multiple scans when the contact load of an AFM tip is below the displacement threshold of the material (151–153). Irregularities in the pattern can result from nonuniformities in the topography, such as step-edges in the underlying substrate.

A third, distinct area of SPL is the localized chemical modification of a surface, such as the electrochemical anodization of a metal or semiconductor using a conductive AFM or STM tip (154–161). Figure 9*g,h* show a TiN substrate patterned by localized electric-field induced oxidation using a conducting AFM probe (160). This pattern is composed of crossed lines, with each set of parallel lines having a 150-nm periodicity. The final topographic features have a height of ~ 4 nm (the oxide occupies more volume than the original TiN film). Lateral resolution of this proximal probe patterning method has so far been limited to ~ 50 nm. Chemical modifications of a surface may have applications in high-resolution customization for mask fabrication or for mask and device repair.

The commercial availability of AFM and STM instrumentation and probes makes SPL a convenient approach for nanoscale patterning. The inherent serial nature of SPL using a *single* tip, however, results in undesirably slow writing.

Parallel Patterning of Surfaces

Serial patterning of surfaces by scanning probe lithographic techniques can show excellent registration between features and can, in principle, fabricate single devices. A more parallel approach is necessary, however, for high-throughput application of this technology. A practical parallel technology may emerge by writing using multiple, independently controlled probes (35, 36, 143, 162–164). Arrays of cantilevers allow lithographic applications and improved sample throughput (higher density of features/time) (34, 162). The concept of the “Millipede” was developed as a two-dimensional array of independently addressed AFM probes for high-density data storage (Figure 10) (35, 162). Each probe can be mechanically deflected in the vertical direction and resistively heated. A layer of 50-nm thick PMMA has been patterned with ~ 40 -nm wide holes by heating the polymer to T_g

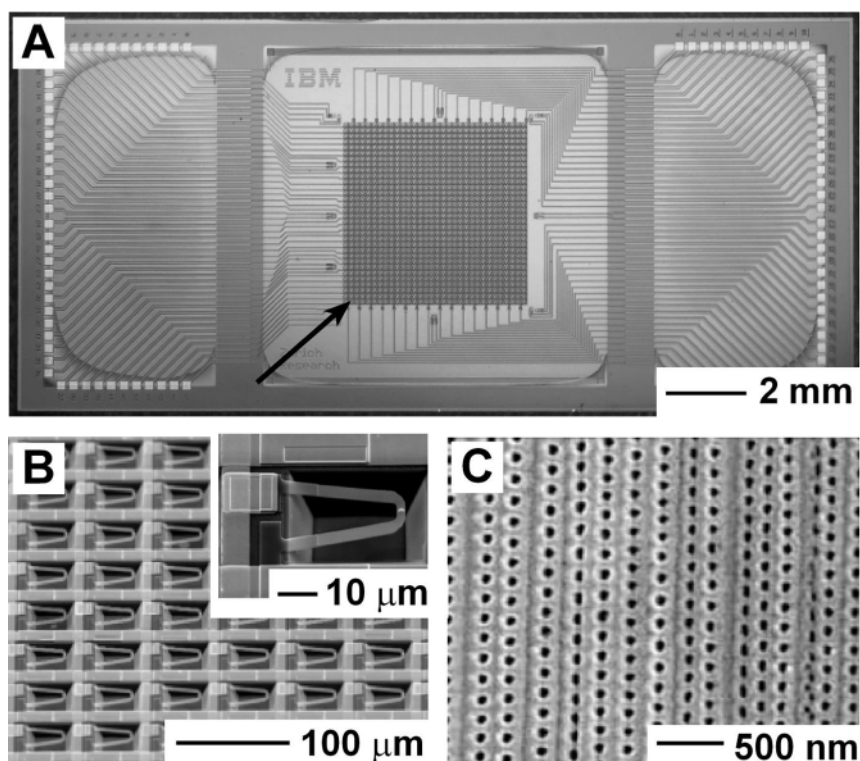


Figure 10 The Millipede: an approach to parallel SPL microscopy (35, 162–164). (a) Optical and (b) SEM images of a 32×32 array of cantilevers (163) (reprinted with permission, © IEEE 1999). The arrow in (a) denotes the position of the array. (c) AFM image from a portion of a pattern of holes spaced by ~ 70 nm created by thermal imprinting with the array of probes (35) (reprinted with permission, © IBM J. Res. Develop. 2000).

with the AFM probe (35). Densities > 200 Gb/in² have been realized using a 32×32 array of cantilevers. Recently, a linear array of eight tips was used to create eight copies of a pattern by DPN (36, 143).

EDGE LITHOGRAPHY

Edge lithography is the collective name for a class of techniques that use topographic edges in the fabrication of nanoscale features (18, 37, 165–169). These methods pattern arrays of < 100 nm structures in parallel in a range of materials. Edge lithographic techniques can be classified as either those using topography-directed pattern transfer or those obtained by cutting or cleaving a substrate to expose an edge with nanoscale features.

Pattern Transfer Directed by Topography

DECORATION OF STEP-EDGES The selective deposition of metal and other materials at the step-edges of single-crystalline surfaces has been pursued previously (170–175). This “decoration” of step-edges can generate continuous nanowires. For example, oxides (e.g., MoO_x , MnO_2 , Cu_2O , and Fe_2O_3) and metals (e.g., Ag, Pd, Cu, and Au) have been electrodeposited with lateral dimensions down to ~ 15 nm at the step-edges of highly oriented pyrolytic graphite (HOPG) (176–179).

ELECTRODEPOSITION OR ETCHING AT EDGE-DEFINED DEFECTS IN SAMs Nanostructures can also be patterned by selective removal or deposition of material at the edges of lithographically defined topographic features (18, 166, 180–184). For example, sharp metal corners within a topographically patterned metal substrate prevent the formation of well-ordered SAMs and expose the underlying metal at these edges (18, 183). Selectively etching the exposed metal transfers the outline of the patterned metallic topography into the underlying film with line widths down to ~ 50 nm. An extension of this technique included a titanium layer (typically 5-nm thick) between a patterned silver film and a planar silver substrate (Figure 11*a*) (184). Self-assembled monolayers form on the silver, but not on titanium, when immersing this patterned substrate in a solution of alkanethiols. The exposed Ti/ TiO_2 layer forms a ~ 5 -nm wide gap in the SAMs and serves as a nanoelectrode upon which metal can be electrochemically deposited (Figure 11*b*). An adhesive, such as Scotch tape, can remove these structures and transfer them onto a curved and flat substrate. Arrays of parallel copper lines supported on an adhesive can polarize incident light (Figure 11*c*).

CONTROLLED UNDERCUTTING AT EDGES A different approach to the use of topographic edges for the fabrication of nanostructures is the controlled undercutting of topographic features by isotropic wet etching, followed by deposition of a thin film (Figure 11*d*) (166). A thin metal film on a silicon or CaF_2 substrate covered with a patterned photoresist was isotropically wet etched with controlled undercutting of the photoresist and coated with a second metal film. Lift-off of the photoresist revealed well-defined trenches at the edges of the pattern of photoresist (Figure 11*e,f*) and has been used to pattern frequency-selective surfaces (Figure 11*f*).

PHASE-SHIFTING PHOTOLITHOGRAPHY The vertical edges of a transparent, topographically patterned substrate can induce abrupt changes in the phase of incident, collimated light to create narrow regions of constructive and destructive interference. Phase-shifting photolithography uses this phenomenon to project dark or bright spots of incident light onto the surface of a photoresist (Figure 12*a*) (169, 185–188). Optimally, the light should have a phase-shift of π at the photoresist-mask interface. Phase-shifting edge lithography using an elastomeric phase mask is a simple approach to pattern features down to ~ 30 nm (Figure 12*b*) (169, 186). Similar patterns of photoresist served as etch masks to pattern nanoscale rings in

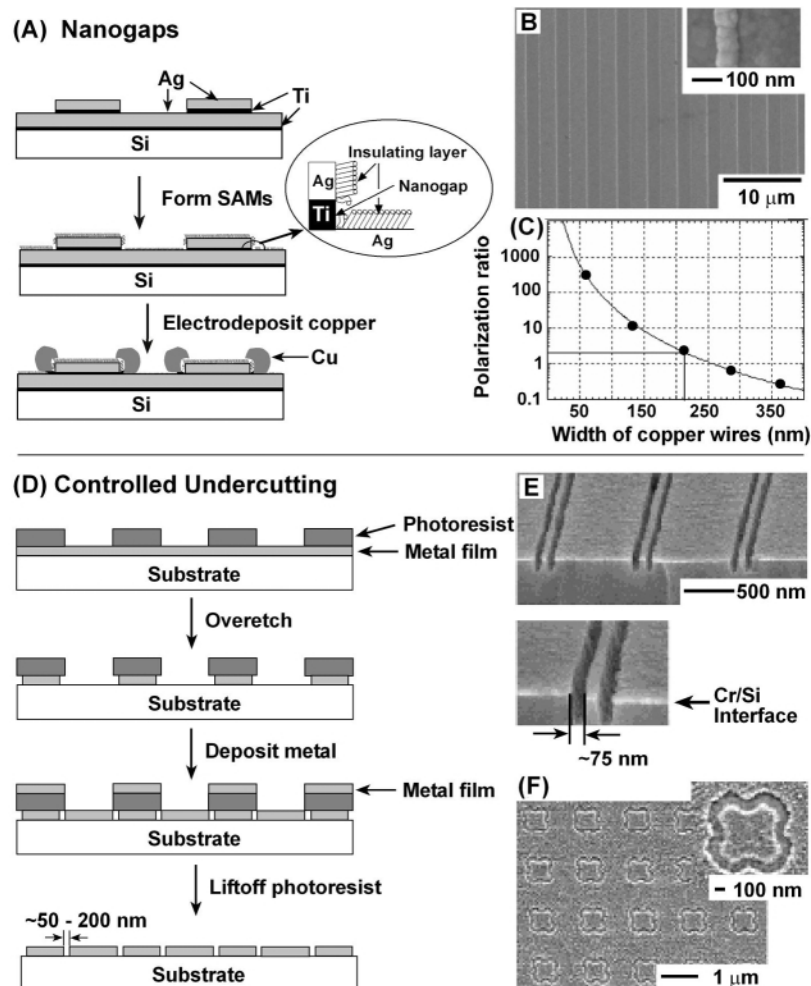


Figure 11 (a) Schematic illustration of one approach to making nanogaps by engineering defects in SAMs on Ag. The SEM image in (b) shows 70-nm wide lines of copper selectively electrodeposited on these nanogaps (184) (reprinted with permission, © ACS 2002). These nanowires can serve as optical polarizers as accurately predicted in a theoretical plot (c) of polarization ratio (parallel versus perpendicular polarization) of the electric component of light as a function of line width (184) (reprinted with permission, © ACS 2002). (d) Schematic illustration of the use of controlled undercutting to pattern trenches with lateral dimensions down to ~50 nm. SEM images are shown for (e) a cross-section of ~75-nm wide trenches in silicon and (f) a frequency-selective surface of 100-nm wide trenches in Al (166) (reprinted with permission, © WILEY-VCH 2001).

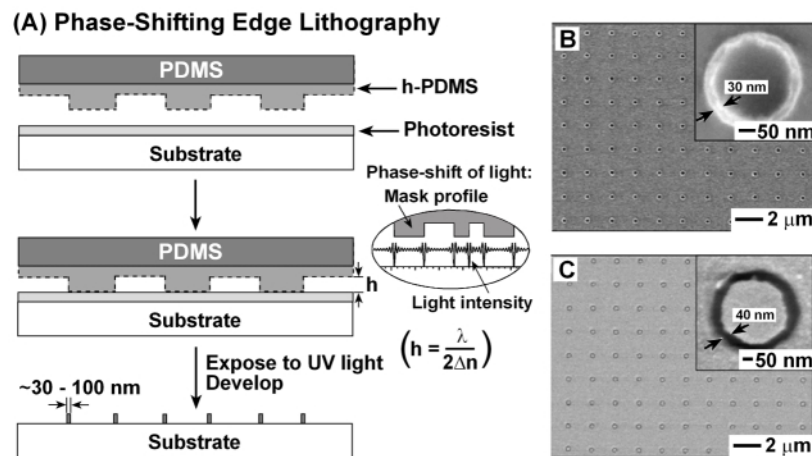


Figure 12 (a) Schematic illustration of phase-shifting edge lithography using a topographically patterned composite PDMS stamp in contact with a photoresist. The phase-shift is optimal when the thickness of the air-gap (h) is equivalent to the ratio of the wavelength (λ) of light to twice the change in refractive index (Δn) between PDMS and air. Patterns with narrow line widths can be fabricated using this technique, as shown in SEM images of (b) 30-nm wide rings in a positive-tone photoresist and (c) 40-nm wide rings transferred into a Pd film supported on silicon (169) (reprinted with permission, © ACS 2002).

a Pd film on a silicon substrate (Figure 12c) (169) or Al on CaF_2 (as a frequency-selective surface) (189). Photoresist patterns were also used as etch masks for producing uniform, single-crystalline silicon nanostructures of a variety of shapes (e.g., wires and loops) with well-defined widths down to 40 nm, and lengths > 1 cm (190).

Cleaved or Cut Edge Nanostructures

There are many ways to grow thin films with well-controlled thickness between 1 and 50 nm over large areas of surface. One can take advantage of this capability to fabricate nanostructures by converting these structures—which are thin along the z -axis—into structures that are thin along the x -axis (37, 167, 168, 191).

EDGES PRODUCED BY FRACTURE The cross-sections of multilayer films prepared using molecular beam epitaxy (MBE) have been exploited as templates to pattern simple quantum structures (37, 192–194). For example, MBE-grown substrates consisting of alternating layers of AlGaAs and GaAs have been used to fabricate FETs with a 20-nm gate length (37). Selectively etched, multilayered MBE-grown GaAs/AlGaAs substrates have also been used as physical templates with narrowly spaced grooves for patterning parallel arrays of nanowires by physical vapor

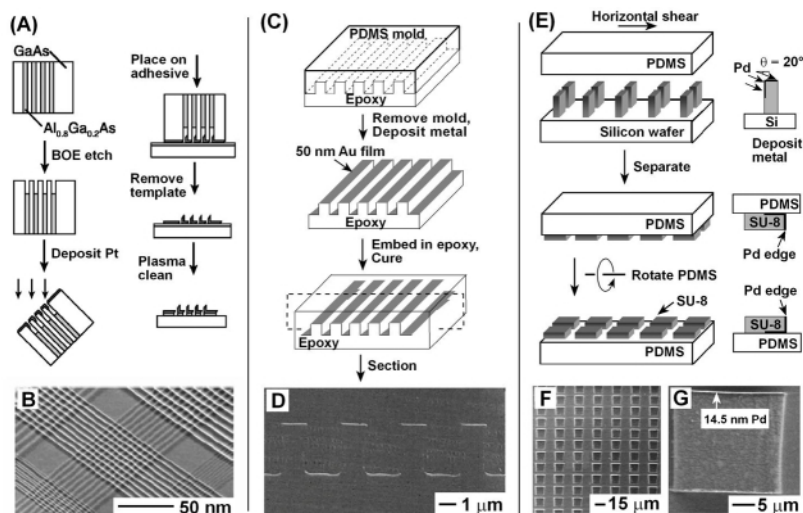


Figure 13 (a) Schematic illustration and (b) SEM images of 8-nm diameter Pt nanowire arrays patterned by physical vapor deposition on a template fabricated by MBE and etching in buffered oxide etch (BOE) (167) (reprinted with permission, © AAAS 2003). (c) Schematic diagram showing the fabrication of a patterned array of epoxy-embedded conducting metal edges. (d) SEM image of such metal edges (50-nm thick Au lines) exposed by sectioning with the glass knife of a microtome (198) (reprinted with permission, © ACS 2004). (e) Schematic illustration of an array of microdominos (posts of SU-8 photoresist) uniformly collapsed by applying a horizontal shear using a slab of PDMS. Selectively depositing a Pd film to coat the top and part of one side of each post prior to collapse can generate an array of Pd edges. (f) SEM images of the array of collapsed microdominos adhered to the PDMS slab, and (g) a ~15-nm wide edge of Pd on a collapsed post (199).

deposition (Figure 13a) (167). The thickness of the GaAs layers determines the width of the wires, and the AlGaAs layers determine the spacing between the wires. Platinum nanowires were fabricated with diameters down to 8 nm and center-to-center distances of ~16 nm. The authors fabricated a cross-bar array (Figure 13b) by overlapping two sets of parallel platinum nanowires and removed each set of nanowires from the template with an adhesive.

EDGES PRODUCED BY SECTIONING WITH A MICROTOME Embedding a thin film in a matrix and taking its cross-section also exposes a nanostructured edge. One approach to exposing the edge of an embedded film is to remove the matrix material by repeated sliding against a rough surface (i.e., sand-coated paper) (195, 196). We extended this technique using a microtome to section a polymer-encapsulated metal film, which had been patterned by soft lithography (Figure 13c) (197, 198). Sectioning at temperatures below -120°C significantly minimized the delamination

between the epoxy and metal film. The exposed edges of an encapsulated, 50-nm thick, patterned gold film (Figure 13*d*) can be electrically addressed from the opposite edge of the encapsulating matrix (198). The roughness of the microtomed surface was ~ 10 nm. Because soft lithography can generate complex three-dimensional structures, and stacking multiple layers is straightforward, it should be possible to generate substantially more complex features than those shown in Figure 13*d*.

EDGES POSITIONED BY REORIENTATION Ordered array of nanoscale edges over large areas ($> \text{cm}^2$) have been patterned using a method to tip a periodic array of posts—each capped with a metal film—onto one side (Figure 13*e*) (199). Arrays of epoxy pillars (or microdominos) patterned by conventional photolithography were fractured from the supporting substrate under a horizontally applied shear force. When shearing Pd-capped microdominos, this process generated regular arrays of features with nanometer-scale lateral dimensions in-plane (Figure 13*f,g*). Transferring these microdominos onto a film of conductive polymer establishes an electrical connection to each of the arrayed edges. This array of narrow electrodes could be used to print, in parallel, multiple regions of charge in a film of PMMA (199).

CURRENT DIRECTIONS IN UNCONVENTIONAL NANOFABRICATION

Conventional nanofabrication will continue to dominate nanoelectronics. There is little motivation for large companies to adopt new, unproven technologies unless the risk is low and the potential advantage large. Nanostructures fabricated in silicon and other semiconductors will, probably, continue to be patterned by photolithography, although the nature of the optical systems will require new materials and light sources and extensive use of front-surface optics. Electron beam and X-ray methods will also continue to develop. Where then do unconventional nanofabrication techniques fit into this world of ever-shrinking components? To answer this question, we must consider where nanofabrication brings new functions or improved economics.

One area where nanotechnology is beginning to have an impact is new materials. Nanoscale structures have a number of important properties—superparamagnetism (200) and quantum-confinement effects on electronic structure and optical properties (201–203)—that differ from microscale structures. An increasing number of methods have evolved to form nanostructures by chemical growth (201–204) and by deposition on physical templates (91, 205, 206). It is difficult, however, to organize these nanostructures into well-defined patterns for integrated, functional devices. Fusing top-down and bottom-up approaches may provide a means to control the placement of these materials. Examples include the alignment of nanowires within microfluidic channels (207, 208), assembly of nanoparticles within templates (57), and growth of aligned carbon nanotubes on patterned arrays of catalyst (209).

A significant advantage of techniques for unconventional nanofabrication is the ability to prototype new structures rapidly, often using ordinary laboratory facilities, without specialized equipment. Soft lithography provides an inexpensive method to reproduce patterns created by other lithographic means and can generate numerous molds and replicas from the same master. This process can replicate and pattern nanoscale features over large areas ($>\text{cm}^2$). Soft lithography can also pattern materials other than photoresist and nonplanar surfaces.

Soft lithography is well suited for fabricating microscale (~ 10 to $100\ \mu\text{m}$) structures, but extension of these techniques to generate nanostructures is not straightforward. On a larger scale, flexible displays can be fabricated by patterning multiple layers of organic semiconductor using soft lithography (210). The fabrication of complex functional nanostructures using soft lithography techniques will, however, require a further understanding and control of several issues. These issues include (a) distortion or deformation of polymer nanostructures, (b) optimization of conditions for pattern transfer and replication of nanoscale features, and (c) registration of nanoscale features in soft materials for patterning multilayered structures.

SPL currently lacks the ability to pattern a high density of features over large areas, but this technique may be a complementary tool to other nanofabrication techniques. SPL has the ability to pattern individual features and may find applications in mask design or repair. This technique is limited to a small set of materials (e.g., thin films of semiconductors or polymers, and some organic molecules). A parallel approach to SPL promises increased throughput of patterning. Technical challenges may limit the widespread application of this technique. For example, it is difficult to fabricate an array of functioning probes with high yields and to pattern complex designs by simultaneously addressing each probe.

Edge lithography is a simple approach to size reduction, but these techniques are still in the developmental stages. Structures fabricated by edge lithography are typically linear patterns that cover relatively small areas ($<\text{mm}^2$). The parallel nature of simultaneously patterning an array of structured edges over $\sim 1\ \text{cm}^2$ (e.g., shearing of microdominos) is a step in the right direction. Further work is necessary to increase the density of the patterned features over large areas, and to establish electrical connections with individual features.

Unconventional techniques will continue to complement conventional methods in the nanofabrication of structures for academic research. Electronics is an obvious area for application of these tools, but other areas may be just as important. Nanostructures are the right size for tools to probe biological systems (e.g., cells are microscale objects). The applications—single-cell bioanalytical systems (211), ultradense gene chips (212), and nanofluidics for biophysics (213)—are only just being explored.

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