# New Approaches to Nanofabrication: Molding, Printing, and Other Techniques

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## 1. Introduction

"Nanofabrication" is the process of making functional structures with arbitrary patterns having minimum dimensions currently defined (more-or-less arbitrarily) to be ≤100 nm. Microelectronic devices and information technologies have improved and will continue to improve as a result of large-scale, commercial implementation of nanofabrication. The motivation for these improvements is to increase the density of components, lower their cost, and increase their performance per device and per integrated circuit.

The smallest physical gate length of a microprocessor currently in production is 37 nm,[1] and current half-pitch, or periodicity, of manufactured dynamic random-access memory (DRAM) is 90 nm. The International Technology Roadmap for Semiconductors (ITRS), published by the Semiconductor Industry Association (SIA), projects reaching the 45-nm node in 2010 (corresponding to transistor gate lengths down to 18 nm and DRAM spacing of 45 nm).[1] It is likely that a number of new technologies will evolve with further developments in nanofabrication.

Many materials with minimum dimensions on the nanoscale have properties different than those observed for the bulk material. For example, quantum

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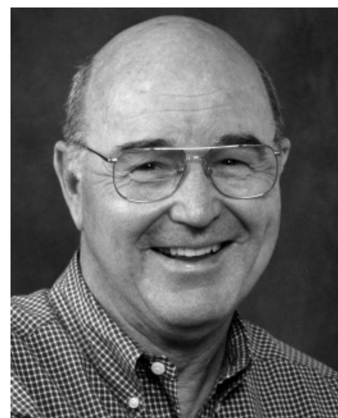

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dots can exhibit single-electron tunneling,[2-5] carbon nanotubes can have high electrical conductivity and mechanical strength,[6-12] and thin polymer films can have glass-transition temperatures higher or lower than thick films.[13-16] There is an expectation that

new technologies will emerge from the fabrication of nanostructures and nanostructured materials and also that nanofabrication will have new applications beyond information processing and storage in areas such as optics, biomedicine, and materials science.[17−19]

Methods used to generate nanoscale structures and nanostructured materials are commonly characterized as "top-down" and "bottom-up". The top-down approach uses various methods of lithography to pattern nanoscale structures. This approach includes serial and parallel techniques for patterning features—typically in two-dimensions (2D)—over length scales approximately 4 orders of magnitude larger (in linear dimension) than an individual structure. The bottom-up approach uses interactions between molecules or colloidal particles to assemble discrete nanoscale structures in two and three dimensions.

This manuscript first briefly reviews "conventional" techniques for nanofabrication; this review serves as background for discussions of "unconventional" techniques. These top-down techniques include photolithography and scanning beam (or maskless) lithography (e.g., electron beam and focused ion beam lithography). The limitations of these conventional approaches—such as their high capital and operating costs, the difficulty in accessing the facilities necessary to use them, and their restricted applicability to many important classes of problems—motivate the exploration and development of new, or "unconventional", nanofabrication techniques. These unconventional approaches, of course, have limitations of their own.

Unconventional nanofabrication—the focus of the review—includes both top-down and bottom-up approaches. We discuss advances in unconventional nanofabrication within the areas of molding,[20,21] embossing,[22,23] printing,[24−27] scanning probe lithography (SPL),[28−34] edge lithography,[35−43] and self-assembly.[44−47] The first three techniques are primarily top-down approaches to nanofabrication. Scanning probe lithography and self-assembly, however, bridge top-down and bottom-up strategies for nanofabrication; these two techniques often use templates fabricated by top-down methods to direct the bottom-up assembly of components.[48−50]

"Conventional" and "unconventional" techniques are at different stages of development. Conventional techniques for nanofabrication are commercially available and widely implemented in manufacturing. Conventional techniques have relatively high cost and low throughput; they are also largely restricted to planar fabrication in semiconductor materials and are incompatible with many problems in nonstandard fabrication (e.g., fabrication on nonplanar substrates, large area and low-cost fabrication, and three-dimensional fabrication). Conventional fabrication techniques also expose substrates to corrosive etchants, high-energy radiation, and relatively high temperatures. Alternative techniques are necessary when patterning relatively fragile materials, such as organic materials (especially biological materials) other than photoresist.

Unconventional routes to nanofabrication are often followed in research; they may also offer alternatives to photolithography in manufacturing. Tools for molding on the nanometer scale are just entering commercial production. These techniques create opportunities for fabrication on nonplanar surfaces (particularly smooth, curved surfaces) and over large areas and may offer competition in nanofabrication where cost and materials make photolithography difficult. They are probably the only techniques that are applicable to biological materials and to sensitive organic and organometallic materials. The ability of any technique—conventional or unconventional—to prototype nanoscale structures rapidly and inexpensively will be a factor that influences the acceptance of that technique. Unconventional techniques have the potential to be the ultimate, low-cost method for nanomanufacturing; approaches based on reel-to-reel processing are particularly important for low-cost processes. Unconventional approaches are also operationally much simpler to use than are conventional techniques and thus help to open nanoscience and nanotechnology to exploration by a wide range of disciplines, especially those historically weakly connected to electrical engineering and applied physics.

We focus this review on research published in nanofabrication during the interval from 1999 to mid-2004 and to specific techniques demonstrated to be capable of patterning a substrate with features $\leq 100$ nm in both lateral and vertical dimensions. In general, this definition excludes techniques with control over nanoscale features in only one direction, such as the deposition of thin films. Inorganic thin films, self-assembled monolayers (SAMs),[51] or Langmuir–Blodgett (LB) films offer precise control over a structure only in the vertical direction. These materials can, however, sometimes be used to fabricate two-dimensional structures with nanoscale lateral dimensions.

The first area of unconventional nanofabrication that we review is a set of techniques that uses organic materials to replicate nanoscale patterns or masters. These patterns are transferred into the materials by molding, embossing, or printing. The second area of unconventional nanofabrication that we review (albeit in less detail) is scanning probe lithography (SPL). Techniques based on SPL are serial but can pattern features on a surface with atomic resolution.[28,52] We also sketch advances in the development of a parallel approach to SPL. Our review of SPL is brief as this technique has been reviewed elsewhere.[32,34,53,54] The last two areas that we review—edge lithography and self-assembly—are more limited than conventional lithography in generating arbitrary patterns but are promising approaches to low-cost, regular arrays of nanostructures. We believe that these approaches will be useful in research laboratories wishing to explore ideas in nanoscience. There are many forms of edge lithography; generally, they are techniques in which the *edges* of one pattern become the *features* of a second pattern. One approach to edge lithography converts films that are thin in the vertical direction into structures that are thin in the lateral direction. A second approach to edge lithography transfers the edges of a patterned thin film into another material. Self-assembly (both templated and untemplated) offers a final set of new

**Table 1. Capabilities of Conventional and Unconventional Nanofabrication Techniques**

| technique | current capabilities (2004) | | |
|---|---|---|---|
| | minimum feature[a] | resolution | pattern |
| photolithography[1,b] | 37 nm | 90 nm | parallel generation of arbitrary patterns |
| scanning beam lithography[88,c] | 5 nm | 20 nm | serial writing of arbitrary patterns |
| molding, embossing, and printing[116,123,168,d] | ~5 nm | 30 nm | parallel formation of arbitrary patterns |
| scanning probe lithography[28,52] | <1 nm | 1 nm | serial positioning of atoms in arbitrary patterns |
| edge lithography[39,e] | 8 nm | 16 nm | parallel generation of noncrossing features |
| self-assembly[353–357,f] | >1 nm | >1 nm | parallel assembly of regular, repeating structures |

[a] Refers to the minimum demonstrated lateral dimension. [b] A resolution (pitch) of 45 nm is projected for 2010 using 157-nm light, soft X-rays, or optical "tricks" (e.g., immersion optics). [c] Obtained with a focused ion beam. Limited by photoresist sensitivity and beam intensity. [d] Limited by available masters and, ultimately, van der Waals interactions. [e] Potentially smaller sizes could be obtained using atomic layer deposition. [f] Self-assembly produces structures with critical feature sizes from 1 to 100 nm or larger.

approaches to nanofabrication. We believe that templated self-assembly will be very important in nanoscience but is early in its development.

Table 1 compares the current capabilities of conventional and unconventional methods for patterning nanostructures. This table summarizes the current minimum feature size (minimum lateral dimension), the highest resolution (pitch), and the types of patterns that can be generated reproducibly by each technique. The sections of the review that follow also discuss the current applications and limitations of these techniques as well as areas that may lead to further advances in nanofabrication.

## 2. Conventional Techniques for Nanofabrication

### 2.1. Overview

The microelectronics industry has developed a sophisticated infrastructure for patterning nanoscale features by conventional lithography. There are two dominant methods for conventional lithography: photolithography and particle beam lithography. Photolithography is the method of choice for manufacturing in the microelectronics industry. The most advanced photolithographic systems project collimated light through a quartz plate that supports a patterned chromium coating. The chromium mask has openings with linear dimensions approximately four times larger than the final image projected onto a photoresist located at the focal plane. This projection lithography can expose an ~8 cm$^2$ area of photoresist coated on a planar substrate—typically a semiconductor wafer—in a few seconds. A photoresist is an organic material that cross-links and becomes insoluble or that changes chemically and becomes more soluble in a basic solution upon exposure to high-energy short-wavelength light (e.g., UV light).[55–57]

The exposed photoresist is immersed in solvents that dissolve the exposed (positive photoresist) or unexposed (negative photoresist) regions and provide patterned access to the surface of the substrate. The patterned photoresist masks the substrate during a subsequent step that chemically modifies the exposed regions of the substrate (Figure 1). A modern "step-and-scan" photolithography system can pattern over one hundred 300-mm diameter wafers per hour with 65-nm resolution; it can also cost tens of millions of dollars.[58]

Scanning beam lithography is a serial process most often used to produce photomasks for projection lithography rather than for actual device fabrication. Writing time for scanning beam lithography depends on pattern density and feature size. Patterning dense arrays of sub-20-nm features over an area of ~1 cm$^2$ requires ~24 h; this rate of patterning restricts scanning beam lithography techniques to small areas or low densities of features.

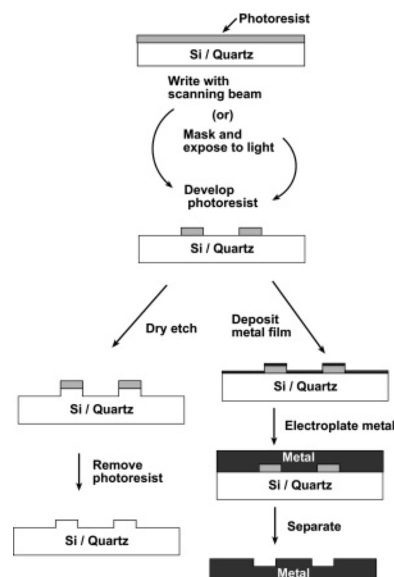


**Figure 1.** Schematic illustration of the fabrication of topographically patterned surfaces in hard materials by conventional photolithography and electroplating.

### 2.2. Photolithography

In current semiconductor nanofabrication photolithography can pattern 37-nm wide features with 193-nm wavelength light. The microelectronics industry plans to pattern minimum features below 37 nm using photolithography.[1] Continuing this trend with 193-nm light will require optical proximity correction (OPC) or phase-shifting mask technology, which significantly increases the cost of photomasks.

Another potential route to features with sub-50-nm resolution using 193-nm light is "immersion lithography".[59–64] Immersion lithography is analogous to the better known concept of immersion microscopy often used with biological specimens.[65] Imaging resolution for immersion microscopy is improved by increasing the refractive index of the medium between the imaging lens and the imaging

plane.[65] Increasing the index of the fluid between the final lens element and the imaging plane improves depth of focus while also allowing lenses with larger capture angles (numerical aperture) to be used in the imaging system. Switching the immersion fluid from air ($n = 1$) to water ($n = 1.47$ at 193 nm) allows the lens systems to be designed with numerical apertures approaching 1.3, thus significantly improving ultimate achievable imaging resolution.[66] The technical challenges of contacting the photoresist-coated substrate and mask with water (or another solvent) and fabricating complex, aspheric, catadioptric (both reflective and refractive) lenses must be solved before immersion lithography can be implemented, but this technology offers a potential route to high-volume production of devices with sub-50-nm resolution.

To pattern still smaller features, photolithography will require further advances, such as decreasing the imaging wavelength to 157 nm[67,68] or to soft X-rays (~13.5 nm)—known in the microelectronics industry as extreme ultraviolet (EUV) light.[69,70] The shift to shorter wavelengths of light requires new photoresists to alter the wavelength sensitivity and resolution of the resist[70-73] as well as new light sources and, especially, new types of optics based on reflection rather than transmission to focus the light.[74-77]

Photolithography has a number of advantages over scanning beam lithography in nanofabrication, but the time and cost required to fabricate the photomask—typically patterned by scanning beam lithography—can be a significant drawback. There is, however, one photolithographic method that can produce simple patterns (e.g., diffraction gratings) without using a photomask. This process is interferometric lithography,[78,79] which involves the constructive and destructive interference of multiple laser beams at the surface of a photoresist. This method does not require a photomask or most of the expensive projection optics, but the projected patterns are restricted to regularly spaced arrays of lines or dots. Some of the smallest features—patterns of 40-nm wide parallel lines separated by 57 nm—produced by photolithography have, however, been generated using interferometric lithography.[80]

## 2.3. Scanning Beam Lithography

Scanning beam lithography is a slow process relative to photolithography. This serial technique can, however, generate high-resolution features with arbitrary patterns. There are three main classes of scanning beam lithography: (i) scanned laser beams with ~250-nm resolution are the least expensive; (ii) focused electron beams with sub-50-nm resolution (depending on tool settings and the choice of photoresist) are expensive to purchase and maintain; and (iii) focused ion beam (FIB) systems with sub-50-nm resolution are primarily (and extensively) used in research. Typically, high-resolution photomasks are patterned using laser writers and electron-beam tools.

There are tradeoffs for high-resolution patterning with an electron or ion beam. Increasing the resolution requires decreasing the diameter of the particle beam, which decreases the beam current (charge—charge repulsion makes small, high-current beams unstable). These changes increase the time necessary to achieve the same imaging dose. Some improvements can be realized by using very sensitive resists. Resists that require a lower dose of electrons or ions, however, usually have lower resolution than photoresists that require a higher dose. A chemically amplified photoresist requires a low dose of electrons (~10 $\mu$C/cm$^2$ for an accelerating potential of 100 kV) to pattern features with a resolution >50 nm.[81] A photoresist requiring a higher dose of electrons, such as poly(methyl methacrylate) (PMMA), however, can have resolution below 20 nm but requires a dose of ~400 $\mu$C/cm$^2$ (at 50 kV).[82] A cold developer (<10 °C) may improve the resolution and clarity of features in both types of resists.[83]

A focused ion beam can write patterns into a photoresist or directly onto the substrate.[84] This technique can "mill" substrates by selectively removing material through ion bombardment or create patterns in an additive process by ion deposition or a localized chemical vapor deposition.[85-87] This lithography technique can pattern features in a semiconductor with resolution down to ~20 nm and with the smallest lateral dimensions down to ~5 nm.[88] Common sources of contamination in FIB lithography are from implanted ions or material displaced from the substrate after milling. Implantation of ions can, however, be useful for transistor fabrication and repair, and the ability to write with different ions is potentially useful in tuning the properties of electronic nanostructures.

## 3. Nanofabrication by Molding and Embossing

A number of different procedures—molding, embossing, and printing—have been developed for patterning nanoscale structures. We divide molding and embossing techniques into two categories: (i) molding and embossing of nanostructures with a hard mold and (ii) molding and embossing of nanostructures with a soft (elastomeric) mold. Molding involves curing a precursor (usually a monomer or a prepolymer) against a topographically patterned substrate. This method of pattern transfer is used by techniques such as step-and-flash imprint lithography (SFIL),[20] replica molding (RM) with a soft mask,[21,89] microtransfer molding ($\mu$TM),[90] and micromolding in capillaries (MIMIC).[91] Embossing (or imprinting) techniques transfer a mold with a structured topography into an initially flat polymer film. These techniques include nanoimprint lithography (NIL)[92] and solvent-assisted micromolding (SAMIM).[93]

## 3.1. Hard Pattern Transfer Elements

Techniques such as relief printing and injection molding use hard molds or stamps to transfer a patterned topography into a monomer, prepolymer, or polymer substrate. Commercialized processes that use hard molds include patterning of compact discs (CDs), digital versatile discs (DVDs), diffraction gratings, holographic gratings (e.g., for identification markings on credit cards and currencies), and plastic parts.[94-101] Hard molds can also transfer nanoscale

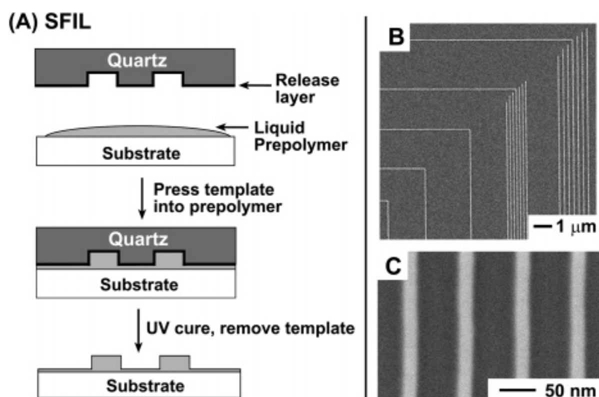


**Figure 2.** (A) Schematic illustration of the procedure for step-and-flash imprint lithography (SFIL).[20] Scanning electron microscopy (SEM) images of (B) 40-nm wide lines and (C) 20-nm wide lines patterned by step-and-flash lithography. The mold for the pattern in B was used for more than 1500 previous imprints. (Reprinted with permission from ref 20. Copyright 1999 SPIE.)

features into polymer films for nanofabrication. Nanostructured hard molds are prepared by transferring a structure patterned in photoresist into a hard substrate using reactive ion etching (RIE), wet chemical etching, or electroplating (Figure 1). Hard molds have been fabricated out of quartz, silicon, and metals.[20,92,102−106] The most commonly used hard materials have been quartz and silicon. The smallest features transferred into a silicon mold are ~10-nm wide lines written using electron-beam lithography.[107] The smallest features produced in a quartz mold are 20 nm.[108−110]

A hard mold offers a number of advantages for nanofabrication. The rigid mold of silicon or quartz retains nanoscale features with minimal local deformation (the pressures required for embossing can cause long-range distortions in the substrate). A hard mold is thermally stable at temperatures used to cross-link most polymer precursors. Silicon and quartz molds are chemically inert to precursors used to mold polymers. Surface fouling of the pattern transfer element is, however, dependent on the surface free energies of the mold and the polymer, and a fluorosilane [e.g., $CF_3(CF_2)_6(CH_2)_2SiCl_3$] is usually covalently linked to the surface of a hard mold to facilitate the release of the mold from the polymer and reduce surface fouling. One of the main differences between silicon and quartz substrates is that quartz is transparent to ultraviolet and visible wavelengths of light and silicon is not. It is, therefore, possible to align the quartz mold optically to features on the underlying substrate and initiate photoinduced cross-linking of a molded prepolymer by exposure to UV light through the pattern transfer element. Step-and-flash imprint lithography exploits these properties of a quartz mold for nanofabrication.[20]

### *3.1.1. Step-and-Flash Imprint Lithography (SFIL)*

Step-and-flash imprint lithography is a technique that replicates the topography of a rigid mold using a photocurable prepolymer solution as the molded material.[20,104,105,111−113] In SFIL (Figure 2A) a low-viscosity, photocurable liquid or solution fills the void spaces of the quartz mold. The solution consists of a low-molecular-weight monomer and a photoinitiator. Exposing this solution to UV light polymerizes and hardens the precursor while in contact with the mold. Removing the mold leaves a topographically patterned (inverse) replica on the substrate.

Step-and-flash techniques avoid incomplete mold filling—a problem for embossing polymers with a rigid mold—by using a monomeric fluid with a low viscosity ($<$5 cPs). This lithographic technique is also insensitive to the effects of pattern density reported for NIL.[114,115] Hydrodynamic forces, however, prevent complete displacement of the fluid by the mold, even for low-viscosity precursors. The incomplete displacement of fluid leaves a residual layer of cured material between patterned features. The substrate and mold must be parallel and both must be rigorously flat to ensure that the residual layer is uniform in thickness over the entire imprinted area. This residual layer can be removed by etching (e.g., RIE).

An important consideration in all nanomolding techniques is the lifetime of the mold. A release layer reduces the surface free energy of the mold and minimizes adhesion of cross-linked polymer to the mold. If the release layer fails, the cured polymer can adhere to the mold and foul its surface or break its features. The first reported release layer was a fluorinated silane[20] with a lifetime of less than 100 patterned substrates. New surface treatments have been developed (but not described in detail) for patterning that claim to provide more than 1500 consecutive substrates.[116]

Figure 2B,C shows topographic patterns generated using the SFIL technique. The SFIL process patterns features down to at least 20 nm across a field size of 6.25 $cm^2$ per molding step.[116] This process can pattern dielectric gates for the fabrication of a metal oxide semiconductor field-effect transistor (MOSFET)[104] and is compatible with semiconductor device manufacturing. Step-and-flash imprint lithography is also being developed to pattern curved surfaces and topographies with multiple depths in a single step.[117,118]

Step-and-flash imprint lithography uses a rigid, transparent mold to print features at a constant temperature (~22 °C) with low applied pressures ($<$1 lb/in.$^2$). This combination of factors gives SFIL an inherent advantage in its potential for fine layer-to-layer alignment, which is necessary for multilayer device fabrication. Distortions caused by differential thermal expansion are not an issue since the mold and substrate are not heated. The low printing pressure allows imprinting on brittle substrates and reduces distortion caused by flexing of the mold or substrate. The alignment accuracy in SFIL has been reported as high as $\pm$10 nm ($3\sigma$).[119]

The development of SFIL techniques has focused primarily on semiconductor nanofabrication. The successful implementation of SFIL to other applications will require the development of new photocurable monomers and appropriate economics for the application. The precursors currently available for molding do not include the functional materials

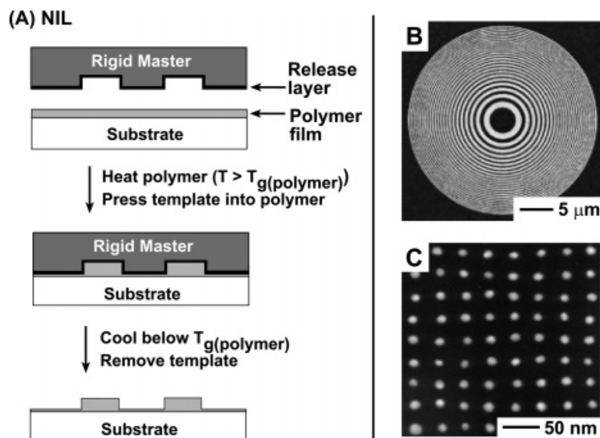


**Figure 3.** (A) Schematic illustration of nanoimprint lithography (NIL).[22,131] The SEM images (B,C) show typical NIL experimental results. (B) Fresnel zone plates with a 125-nm minimum line width. (Reprinted with permission from ref 131. Copyright 2000 American Institute of Physics.) (C) Metal dots with a 10-nm diameter and a periodicity of 40 nm. (Reprinted with permission from ref 22. Copyright 1997 American Institute of Physics.)

required for optoelectronics and ferromagnetic coatings.

#### 3.1.2. Nanoimprint Lithography (NIL)

Nanoimprint lithography[23,103] refers to the pressure-induced transfer of a topographic pattern from a rigid mold (typically silicon) into a thermoplastic polymer film heated above its glass-transition temperature (Figure 3A). Another term for this method is "hot embossing" since the process involves heating the molded polymer above its glass-transition temperature. For example, to transfer the pattern from a mold into a thin polymer film of PMMA by NIL requires heating the polymer film above ~110 °C.

Nanoimprint lithography is a parallel plate printing process. Entire 100-mm wafers have been patterned in a single imprinting step.[102,120] A second version of NIL uses "rolling molds" to emboss sheets with a repeating pattern.[121] A third approach uses a modified commercial flip-chip bonder to imprint several fields across a substrate.[122]

Nanoimprint lithography can mold a variety of polymeric materials (Figure 3B,C) and pattern features as small as ~5 nm[22,123] and aspect ratios up to ~20 (height-to-width).[124] Materials that have been patterned successfully include biomolecules,[125] block copolymers,[126] conducting polymers,[127,128] and fluorescently labeled polymers.[129] This process has been used to pattern components for a range of microelectronic, optical, and optoelectronic devices.[130,131] For example, gate lengths in a MOSFET have been defined by NIL with a minimum feature size as small as 60 nm.[102]

Nanoimprint lithography has made great progress in a relatively short period of time. One of the important issues still to be resolved is the useful lifetime of the mold. Presently, nanoimprint molds require replacement after ~50 consecutive imprints.[130] Heating and cooling cycles and high pressures (50−130 bar), applied during embossing, produce stress and wear on nanoimprint molds. This stress also presents a challenge for alignment during multilayer fabrication. Thermal cycling of the substrate also limits throughput to one imprint per 10 min. A laser-induced flash heating process may, however, reduce thermal cycling times.[132,133] To prevent temperature cycling of the substrate, materials such as poly(dimethylglutarimide)[134] are imprinted at room temperature at an unstated pressure and polystyrene (PS) printed with pressures above ~300 atm.[135] Chou et al. imprinted patterns at room temperature using a transparent mold and UV-initiated cross-linking of the molded polymer.[136] The difference between UV-based NIL and SFIL is not distinct.

The high viscosity of the polymer films presents another challenge for nanofabrication using NIL. There appears to be an optimal pattern size and feature density for NIL.[137] Embossing micrometer-scale features can be more challenging than nanoscale features: filling large recesses within the mold requires more lateral displacement of the polymer than smaller recesses and thus increased process times (or higher temperatures and pressures). A mold containing a range of feature sizes may introduce distortions within the embossed film because of uneven displacement of the polymer and trapping of air bubbles. The thickness of the residual layer can also vary across the imprinted region depending on the pattern density or layout of the pattern. Nonuniformities in the residual layer present a challenge for transferring the pattern uniformly into the underlying substrate by RIE.

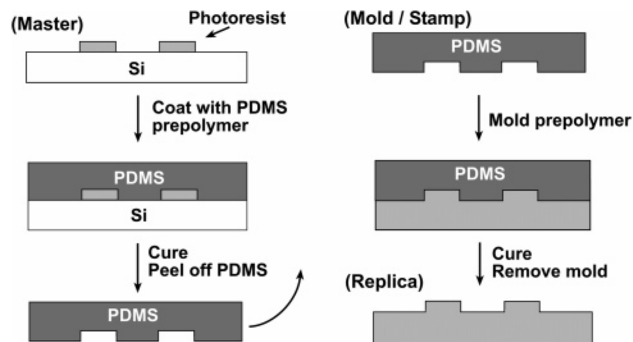


**Figure 4.** Schematic illustration of the formation of topographically patterned molds (or stamps, depending on the application) and replication of the master into a third functional material.

### 3.2. Soft Pattern Transfer Elements

Techniques that prepare a soft mold or stamp by casting a liquid polymer precursor against a topographically patterned master are commonly referred to as soft lithography (Figure 4).[24,27] A number of polymers could be used for molding. Elastomers are a versatile class of polymers for replication of a topographic master. The most widely implemented and successful elastomer for nanofabrication is poly(dimethylsiloxane) (PDMS).[24,27,54] Other elastomers tested as pattern transfer elements include polyurethane (PU), polyimide, and cross-linked Novolac resins (a phenol formaldehyde polymer).[138] Other siloxane elastomers are being developed for soft lithography, such as block copolymer thermoplas-

tics[139,140] and fluorocarbon-modified siloxanes.[141] A particularly interesting new class of polymers is highly fluorinated elastomers,[142,143] which show excellent release properties and resistance to swelling by organic solvents and monomers. Molds from other polymers are also finding applications in nanofabrication, including polyolefins,[144] acrylate-based UV-curable polymers,[145] and an amorphous fluoropolymer.[146]

Poly(dimethylsiloxane) has a number of useful properties for nanofabrication. This material is durable, unreactive toward most materials being patterned or molded, chemically resistant to many solvents,[147] and transparent above a wavelength of ~280 nm. Commercially available kits or precursors for this polymer can be obtained inexpensively.[148,149] One of the major advantages of PDMS is that fabrication of molds or stamps (by replica molding) is so inexpensive that a large number of uses may not be necessary. In fact, sometimes the mold or stamp becomes a disposable reagent.[150,151] This material can be deformed reversibly and repeatedly without permanent distortion or relaxation of the surface topography.[21] The cured elastomer has a low surface free energy (21.6 dynes/cm$^2$);[152] this low surface free energy allows PDMS to be easily released after molding. Fluorosilane chemistry can be used to decrease the surface free energy to ~12 dynes/cm$^2$—a value similar to poly(tetrafluoroethylene) or Teflon.[142,153] Another method to reduce the noncovalent interactions of the mold−substrate interface during release is immersion in a solvent (e.g., methanol or hexane) or exposure to an organic vapor.[154,155] Poly(dimethylsiloxane) is chemically inert, an advantage for patterning many different types of materials. These materials include polymers, precursors to carbons and ceramics, sol−gel materials, organic and inorganic salts, colloids, biological macromolecules, thiols, phosphonic acids, and silanes.[24,27] An important limitation of PDMS is that it absorbs many nonpolar, low-molecular-weight organic compounds.[147] The swelling of the PDMS both compromises dimensional stability and leads to unwanted adhesion after polymerization of monomers. Other materials may circumvent this limitation.[142]

The tensile modulus of 184-PDMS (Dow Corning) is relatively low (1.8 MPa) and limits the replication of nanoscale features.[156−160] High-resolution masters are reproduced accurately in composite stamps of hard PDMS (h-PDMS)[159,161−163] or UV-curable PDMS ($h\nu$-PDMS)[164] with tensile moduli of 8.2 and 3.4 MPa, respectively.

### 3.2.1. Replica Molding (RM)

Replica molding consists of three steps (Figure 4): (i) creating a topographically patterned master (usually by conventional techniques; see, for example, Figure 1); (ii) transferring the pattern of this master into PDMS by replica molding; and (iii) fabricating a replica of the original master by solidifying a liquid precursor against the PDMS mold.[27,89,165] The replica can be cast from a photo- or thermally curable prepolymer. Nonpolar monomers and other low-molecular-weight molecules often dissolve in PDMS.[147] Oligomers and prepolymers (and polar or highly fluorinated monomers), however, typically do not penetrate into PDMS. This low solubility extends the usefulness of each PDMS mold beyond 20 replications; ultimate limits to the number of cycles over which a mold can be used are not established. A benefit of molding with PDMS is the ability to mold against nonplanar, rigid, and soft topographic surfaces (unlike a hard mold, which requires a planar, rigid surface).

Replica molding can produce numerous molds, replicas, and patterned surfaces from each master and provide capabilities for nanofabrication not commonly available in an academic setting. Replication of the high-cost, high-resolution masters reduces the financial burden of patterning nanostructures and conveniently extends nanofabrication to a range of materials.

Replica molding has transferred ~30-nm lateral features from a diffraction grating, a compressed PDMS stamp,[21,89] and a nanoscale crystal into PU.[166] Air bubbles with sizes as small as ~20 nm were also replicated into PDMS.[167] A phase-separated block-copolymer film—with one component removed—trapped air bubbles in a regular array during molding with PDMS (Figure 5A−C). Features down to at least 1.5 nm were also replicated into PDMS from a regular pattern of vertical deflections.[163] Periodic patterns of rings (Figure 5D) or lines (Figure 5G) written into a PMMA film using an electron beam were molded into h-PDMS (Figure 5E,H) and replicated into PU (Figure 5F,I). Surface roughness of the PMMA, PDMS, and PU are each ~0.5 nm over an area of at least 1 $\mu$m$^2$. The smallest features replicated using PDMS are ~3-nm wide structures[168] and ~0.5-nm vertical deflections.[169] In the later experiment the surface roughness is ~0.2 nm for each substrate over an area of 1 $\mu$m$^2$. It is still not clear what the ultimate limit to replication using PDMS (or other materials) is, but the limit, based on the physics of van der Waals interactions, should be less than 0.5 nm.

Two techniques related to RM are micromolding in capillaries (MIMIC) and microtransfer molding ($\mu$TM). Micromolding in capillaries can fabricate isolated structures by using capillarity to fill channels in a PDMS mold with low-viscosity liquid solutions, such as a photo- or thermally curable prepolymer.[91] Nanosized channels can be filled with liquids.[170,171] These nanochannels are, however, slow (or impossible) to fill completely since resistance to flow in pressure-driven flow increases rapidly as the size of the channel decreases. The capillary flow can be assisted by applying a vacuum to one end of the capillaries, heating the liquid, or applying an electric field.[172,173] Microtransfer molding also fabricates isolated structures but has been limited to a minimum feature size >100 nm.[90,174−176]

### 3.2.2. Solvent-Assisted Micromolding (SAMIM)

Solvent-assisted micromolding uses an elastomeric mold and an appropriate solvent to emboss polymer

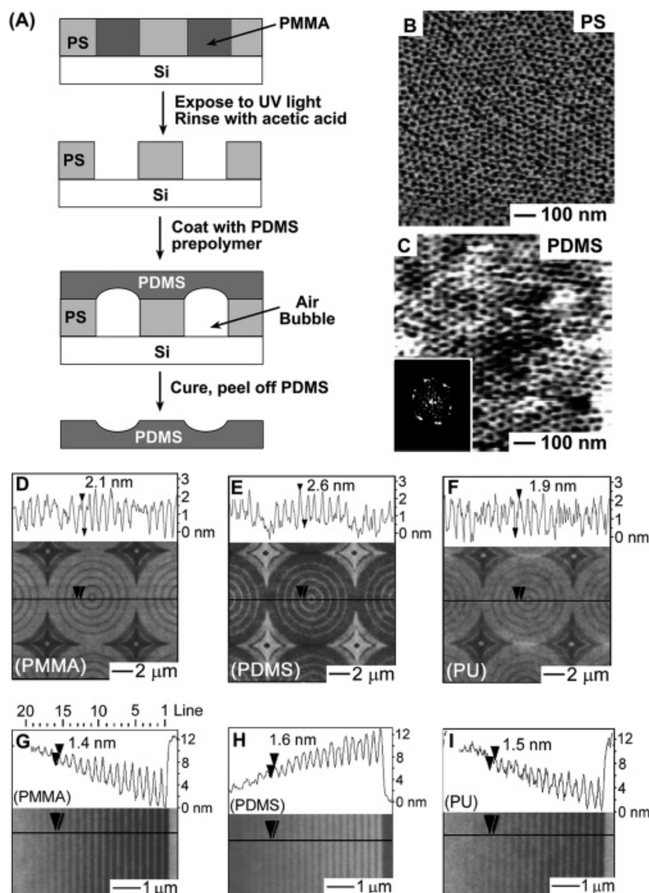


**Figure 5.** (A−C) Replica molding of air bubbles trapped within a porous polystyrene (PS) surface.[167] (Reprinted with permission from ref 167. Copyright 2003 Wiley-VCH Verlag GmbH.) (A) Schematic depiction of this replication. (B) Atomic force microscopy (AFM) image of the PS-*b*-PMMA copolymer master after selective removal of the poly(methyl methacrylate) (PMMA), and (C) a PDMS replica of air bubbles trapped within this master of ∼20-nm wide holes. The inset shows a two-dimensional Fourier transform of the PDMS replica. (D−I) Replica molding of nanoscale vertical deflections (∼1−5 nm) patterned in PMMA by direct writing with a focused electron beam.[163] The series of AFM images include the (D,G) PMMA master, (E,H) h-PDMS mold, and (F,I) polyurethane (PU) replica.

films (Figure 6A).[93] This technique processes the polymer at ambient conditions with soft molds rather than at elevated temperatures with rigid molds. For SAMIM, a solvent swells or dissolves the polymer; swelling of the elastomeric mold is crucial to the process but limited by the amount of solvent contained in the polymer being molded and by the solubility and mobility (usually by diffusion) of the solvent in the PDMS. During solvent evaporation the softened polymer conforms to the surface of the PDMS mold. The gas and solvent permeability of the mold prevents nonuniform solvent evaporation and trapping of air bubbles at the interface. The precipitated polymer film retains an imprint of the surface topography from the mold.

Solvent-assisted micromolding has two characteristics useful in nanofabrication. It avoids cycling of the temperature of the sample and thus limits thermal oxidation or degradation of other system components. Elastomeric molds are also especially useful in embossing because the mold conforms to the polymer substrate—even when it is not planar—over areas >1 cm$^2$ and allows uniform pattern transfer over that area. This process has been demonstrated for a number of polymers including Novolac photoresists, PS, PMMA, cellulose acetate, poly(vinyl chloride) (PVC), and the precursors to conjugated organic polymers.[27,93,177−179] The mild processing conditions of SAMIM are compatible with patterning polymer-based distributed feedback lasers[178] and organic light-emitting diodes (OLEDs).[177]

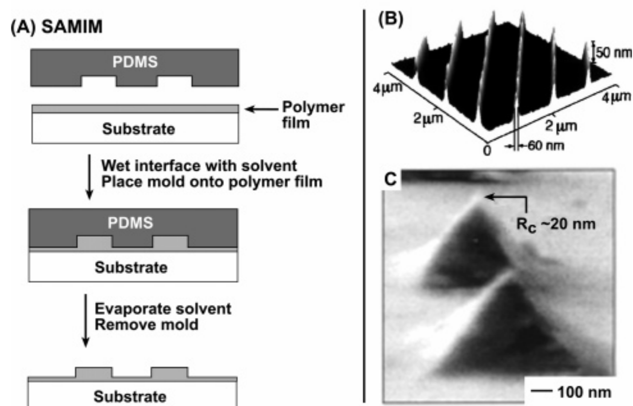


**Figure 6.** (A) Schematic illustration of solvent-assisted micromolding (SAMIM). (B) AFM image of 60-nm wide lines in a Novolac photoresist supported on a silicon substrate patterned using SAMIM.[93] Ethanol coated on the PDMS mold softened the photoresist. (Reprinted with permission from ref 93. Copyright 1997 Wiley-VCH Verlag GmbH.) (C) SEM image of square pyramidal structures showing a well-defined apex with an ∼20-nm radius of curvature ($R_c$) molded with a composite PDMS mold using SAMIM.[159]

Although SAMIM makes it possible to mold polymers that are difficult to manipulate by SFIL and NIL, the in-plane dimensional stability of soft masks is believed (or simply *assumed*) to be lower than for hard masks. Whether this belief is justified by practice remains to be established. The application of SAMIM to patterning nanoscale features has been limited primarily by the lack of appropriate masters rather than by the fundamental characteristics of this process. Line widths as small as ∼60 nm and aspect ratios of at least 1:1 have been patterned in a Novolac photoresist (Figure 6B) and poly(vinyl pyridine) by SAMIM.[93] A composite elastomeric mold with a h-PDMS surface has embossed features with minimum dimensions as small as ∼20 nm (Figure 6C).[159]

As with other embossing techniques, SAMIM using PDMS leaves a residue between isolated features (molding using fluorinated elastomers—with their lower interfacial free energies—may obviate this problem[142]). The processing time for SAMIM depends on solvent transport through the PDMS. Swelling of the PDMS by the solvent can cause distortion of the topographic features. Understanding the interactions of solvents with PDMS, such as compatibility and swelling of the elastomer, will improve the capabilities of this technique.[147,180]

### 3.3. Fundamental Limits of Molding and Embossing

The *resolution* of nanofabrication by molding and embossing is primarily limited by five factors: (i) the practicality of fabricating masters with small features; (ii) the ability of a material to mold, with high fidelity, the features of the master; (iii) the distortion of features in the transferred pattern; (iv) the swelling of the master by the monomers used or the solvent used to dissolve polymers; and (v) the ability of the molded material to fill the mold completely, the tendency of the system to trap bubbles of gas, the kinetics of filling of the mold, the thickness of the residue or "scum" layer (if any) between isolated features, and related issues concerning the mold, substrate, and polymer as a system. The *practicality* of nanofabrication by molding and embossing is limited by release of the mold from the polymer, cycle time, mold maintenance, and registration (or exact alignment) of features on the mold with structures on a substrate.

Advances in the capabilities of conventional lithographic tools will continue to decrease the smallest lateral dimensions in the masters. For example, direct-write electron-beam lithography can pattern a minimum feature size down to 5 nm.[82] The ability to arrange and assemble small molecules or particles could also present a new strategy for fabricating masters with nanoscale features (further details are provided in section 7). The minimum feature size replicated by molding and embossing has, so far, decreased steadily with improvements in fabricating masters.

A number of factors limit the fidelity of replicating nanostructures by molding and embossing. The fidelity is, in principle, limited by the size of the molecular precursors of the polymer and the separation between the mold and master. A minimum separation of $\sim$0.1 nm is predicted by van der Waals contacts, and $<$0.5 nm is suggested by current experimental data.[163,169,181] There is, thus, no fundamental physics-based limitation to molding in the nanometer range, although the actual limit to replica molding remains to be determined experimentally. The size and shape of the molded species—that is, molecules making up the material used in the polymer—and the polymer (and filler) making up the mold also limits the fidelity of pattern transfer. The granularity of matter at the atomic and molecular scale (0.1−1 nm) thus provides a chemical limit to resolution. As a consequence, small molecules such as monomers and prepolymers and amorphous materials such as silica gels may give better resolution for molding than higher molecular weight precursors (i.e., polymers).

The distortion of nanoscale features in the master, the mold, or the replica product limits the number of materials that can be used in molding and embossing for nanofabrication. One cause for distortion of replicated features is a difference in thermal expansion between the materials used to fabricate the master, mold, and replica. A second cause for distortion, which influences the fidelity of replication, is polymer shrinkage upon curing a precursor to a polymer due to solvent evaporation and/or cross-linking during polymerization. A third cause for distortion is collapse or deformation of the molded features (or features on the mold) due to mechanical instability of the polymer (e.g., flexibility and polymer chain mobility): capillary and van der Waals interactions can be very important at small scales. A fourth cause for distortion is the forces required to overcome adhesion between the master and mold.[182] One approach to reducing the adhesion between a polymer mold and a silicon or quartz master is to reduce the surface free energy of the master by modifying its surface with a fluorosilane. A second approach is to carry out the separation between mold and molded material in the presence of a vapor or liquid with very low viscosity, such as methanol.[154,155] Further work is necessary to develop surface release layers for high-resolution masters.

Elastomeric molds are susceptible to distortion because of their low elastic modulus and high thermal expansion coefficient. Hard molds can also experience distortion even with relatively minor pressure differentials.[115,183] The alignment of patterns with nanoscale precision is challenging for two reasons: (i) distortion of the mold and (ii) the low contrast in refractive index between the master (e.g., PDMS or quartz) and polymer precursor. These limitations often restrict molding and embossing techniques to fabricating structures with one or at most two layers. Quartz molds have been aligned with an accuracy as small as $\pm$10 nm (3$\sigma$);[119] similar values will ultimately be achievable with other hard (and perhaps soft) molds.

### 3.4. Summary

Molding and embossing are the most widely pursued and successful techniques for unconventional nanofabrication. There are a number of molding and embossing techniques that can pattern, in parallel, nanometer-scale features over large areas (i.e., entire silicon wafers). These techniques have been used to pattern functional structures for inorganic- and organic-based microelectronics and optics.[25,104,184] The formation of these structures requires a high-resolution master, typically generated by conventional nanofabrication techniques. These masters can, however, be inexpensively replicated by molding or embossing. The replication process can be repeated a number of times for a range of organic materials. The number of replications is limited by surface fouling, which is related to interfacial free energies. Another limitation is the variation in thickness of the residual layer (the so-called "scum layer") between nanoscale features. It is challenging to transfer the pattern uniformly into an underlying substrate by RIE because of this variation in thickness. The number of replicas, surface area of each replica, and range of materials that can be patterned by molding and embossing have steadily increased, while the resolution and minimum feature size have steadily decreased.

# 4. Nanofabrication by Printing

## 4.1. Introduction

Transferring a material onto a substrate by printing from a topographically patterned stamp is also useful in nanofabrication. A process known as microcontact printing (μCP) transfers molecules from a patterned PDMS stamp to a substrate by the formation of covalent bonds.[138,185−191] In this process a solution of molecules (e.g., 5 mM alkanethiol in ethanol) is inked onto the surface of the PDMS, and this stamp is brought into contact with an appropriate substrate (e.g., a thin gold, silver, or palladium film). The molecules are transferred in a pattern defined by the topography of the stamp (i.e., the regions of atomic-level contact between the stamp and substrate) with a minimum feature size as small as ~30 nm.[138,192−196] The flexibility of the PDMS stamp and the ability to achieve conformal, atomic-level contact between the stamp and the substrate are both advantageous for printing over large areas (>50 $cm^2$)[197,198] and on curved surfaces.[199−201] This patterning technique has been developed primarily for PDMS stamps, although recent demonstrations have explored surface modifications of these stamps and other soft materials.[202−205] Further details concerning μCP of SAMs on metal films are covered in another article of this issue.[51]

## 4.2. Extensions of Microcontact Printing

Microcontact printing has patterned a number of materials other than self-assembled monolayers (SAMs), such as biomolecules,[206−213] colloidal particles,[202,214−217] and polymers.[218−220] In this section we focus on more recent extensions of μCP for patterning nanostructures. These extensions include patterning of surfaces by electrical contact (electrical μCP, or e-μCP)[221] and release of material coatings from a patterned stamp (nanotransfer printing, or nTP).[222] Both techniques use a PDMS stamp or a PDMS substrate to achieve compliant, conformal contact and uniform pattern transfer.

### 4.2.1. Electrical μCP (e-μCP)

Electrical microcontact printing uses a flexible electrode to pattern a thin film of a material that is an electret (i.e., that accepts and maintains an electrostatic potential), probably by injecting and trapping charges.[26,221,223,224] The electrode was a PDMS stamp coated with ~5 nm of chromium (adhesion layer) and ~80 nm of gold (electrode material) (Figure 7A). This flexible electrode was brought into contact with a thin dielectric film (the electret, a material such as PMMA) supported on a second electrode (typically n-doped ⟨100⟩ silicon). Electrical microcontact printing uses the flexibility of the PDMS stamp to allow conformal contact between the top, patterned electrode and the dielectric film. A voltage pulse (10−30 V) was applied between the two electrodes for ~10 s with current densities of ~10 mA/$cm^2$. Charge remained in the electret where the flexible electrode contacted the dielectric film. After

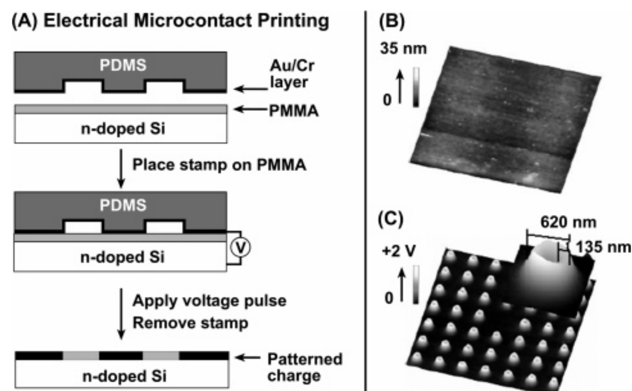


**Figure 7.** (A) Schematic illustration depicting the procedure for electrical microcontact printing (e-μCP). Kelvin probe force microscopy (KFM) measurements of a thin film of PMMA after patterning charge by e-μCP show (B) no change in the surface topography and (C) a surface potential with positive features for a test pattern of 620-nm diameter rings.[221] The full-width half-maximum (fwhm) is ~135 nm for the positive ring of charge in the plot of surface potential. (Reprinted with permission from ref 221. Copyright 2001 American Association for the Advancement of Science.)

removing this electrode the changes in surface potential across the thin dielectric were measured by Kelvin probe force microscopy (KFM).[225] Figure 7B and C shows the measured topography and corresponding surface potential, respectively, for an 80-nm thick PMMA surface patterned using a current density of 20 mA/$cm^2$ (+18 V).[221]

A number of methods exist for charging electrets, such as corona discharge and tribocharging.[226−228] Typically, these methods pattern charge in electrets with micrometer-scale lateral resolution. Scanning probe techniques can pattern charge in electrets over multiple length scales and have demonstrated feature densities of 7 Gbits/$cm^2$ for 120-nm wide features at a resolution of 100 nm.[229−231] The writing speed is, however, slow: a pattern covering ~1 $cm^2$ requires ~24 h to write. Alternatively, e-μCP can pattern charge over areas >1 $cm^2$ in less than 20 s with a resolution of ~100 nm.[221] The minimum feature size, the maximum area that can be patterned in one impression, and the maximum charge density that can be patterned by e-μCP remains to be established. The stability of the patterned charge (for periods greater than months) is unexpectedly high.[221]

The patterned, flexible electrode used in e-μCP is reusable and serves as a tool for fundamental studies of thin film electrets with high lateral resolution. Recent studies have explored the application of e-μCP in high-density data storage (>5 Gbits/$cm^2$)[221] and electrostatic printing of particles, such as graphitized carbon, carbon toner, and iron oxide.[221,224,232,233] Similar procedures can pattern thin-film waveguides in <90 s over large areas (>1 $cm^2$) by changing the local index of refraction of a doped polymer.[223]

Current limitations of e-μCP include buckling of the PDMS stamp after metal deposition from thermal expansion and contraction of the surface.[221] Depositing metal onto small features or cooling the PDMS prevents buckling.[223] Other studies have explored alternative designs for the electrodes using a pat-

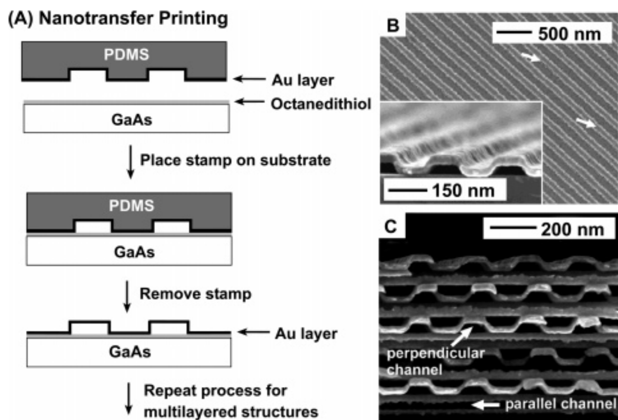


**Figure 8.** (A) Schematic illustration of one approach to nanotransfer printing (nTP)—transferring thin films from a topographically patterned PDMS stamp by forming bonds between the thin film and the surface chemistry of another substrate. SEM images of (B) a 20-nm gold layer transferred onto a GaAs substrate functionalized with 1,8-octanedithiol and (C) a multilayered stack of 20-nm thick layers of gold containing parallel grooves with each layer oriented perpendicular to the one below.[236] After printing the initial gold layer each subsequent layer is transferred by cold welding.

terned array of nanometer-scale, in-plane edges (further details are provided in section 6.2).[41]

#### 4.2.2. Nanotransfer Printing (nTP)

The process of transferring a thin, solid film from a stamp with nanoscale-patterned features to a substrate is referred to as nanotransfer printing.[39,222,234−242] The stamp can be either a soft or a hard material, such as PDMS or silicon. Figure 8A illustrates a typical procedure for this contact printing technique using a PDMS stamp. The stamp was coated with a continuous layer of gold (~20-nm thick) without an adhesion layer between the gold and the PDMS. This stamp was brought into contact with a substrate coated with a dithiol (e.g., 1,8-octanedithiol).[222,237] The dithiol formed a SAM on the substrate (GaAs in this case) and the exposed thiol group covalently bound to the gold layer in the regions of contact. Removing the elastomeric stamp from the substrate left the gold layer bound to the SAM and the underlying substrate (Figure 8B). Alternatively, cold welding[243,244] between two metal surfaces could also transfer the structured metal film. Three-dimensional structures can be fabricated by repeating this procedure (Figure 8C).[236] Another method of releasing the structured film relies on condensation reactions between surface-bound silanols (Si−OH) and/or titanols (Ti−OH).[222,234] Techniques relying on noncovalent interactions between the metal film and the substrate have also been explored, although the minimum dimensions of transferred features are currently >100 nm.[239,245]

A number of methods can pattern nanoscale metallic structures such as narrow, periodic lines. Conventional methods include lift-off, wet chemical etching, RIE, and shadow evaporation. These patterning techniques require exposure to high temperatures, basic or acidic solutions, and/or organic solvents. Nanotransfer printing avoids harsh processing conditions and transfers nanostructures in one step.[222,235] Nanotransfer printing can pattern features with a lateral resolution of at least 70 nm and an edge roughness down to 10 nm.[222,246]

Nanotransfer printing is well suited for transferring electrodes to fragile surfaces. For example, this contact printing technique can pattern parallel lines and circular dots as electrical contacts on SAMs.[246] These discontinuous structures adhere to the substrate under Scotch tape adhesive tests.[235] The components of devices fabricated directly on plastic substrates include complementary inverter circuits, organic thin-film transistors,[235] capacitors,[234] and electrostatic lenses.[222] This patterning technique can also transfer arrays of sacrificial etch masks[236] and stable ferromagnetic stacks of cobalt.[237]

The morphology and continuity of the transferred metal structure is important for functional devices. Uniformity of the metal film is dependent on the wetting and grain size of the metal on the stamp. A thin adhesion layer (<2-nm thick) improves the uniformity of a gold layer on the PDMS stamp and in the transferred layer.[236,237,242] A metal film on an elastomeric stamp can crack from thermal expansion during metal deposition. These cracks can be prevented by rapid deposition of metal (rates ≥ 0.3 nm/s to minimize thermal stress on the PDMS) and by cooling the stamp.[223,237] The stress in the metal film from thermal expansion is also avoided by depositing the metal onto a stamp with a higher thermal conductivity than PDMS (e.g., silicon or gallium arsenide). The surface of these stamps must, however, be modified with a release layer. Mechanical stress during printing can also introduce cracks into the metal structure as indicated by the arrows in Figure 8B.[236] The consequences of mechanical deformations on nanofabrication using nTP remain to be established.

An alternative approach to printing structured materials is decal transfer printing.[150,151] This process transfers a structure (e.g., PDMS membrane or isolated PDMS features) from one planar surface to another. The PDMS decals can be made to adhere reversibly to the first substrate (i.e., a PDMS slab)[247,248] while forming covalent bonds with the second substrate. The PDMS slab serves as a handle for patterning continuous or discontinuous features that are otherwise difficult to manipulate. Decal transfer printing can transfer submicrometer features, but extending this technique to nanoscale features will require further investigation of the interfacial adhesion between the PDMS (or other) substrate and the decal.

### 4.3. Fundamental Limits of Printing

A number of factors determine the smallest features that can be printed by soft lithography. The fundamental limits to printing are determined by three main constraints: (i) minimum size of features in the stamp; (ii) lateral dimensions and resolution of the transferred material; and (iii) preferential adhesion of the printed material to the second surface.

The smallest feature in the stamp depends on the size of features within the master, the fidelity of the

molding process, and the ability of the mold to retain nanoscale features. Further details on these limitations are provided in section 3.3. Distortion of the stamp while in contact with the printed surface also limits the minimum size of the transferred feature. The elastic deformation of a PDMS stamp can collapse high-aspect ratio features.[156,158] A composite stamp of h-PDMS with a 184-PDMS backing can, however, retain nanoscale features without collapse.[159,161]

Resolution and lateral dimensions of nanoscale features transferred from these stamps depends, among other things, on the interaction of the "ink" with the printed surface. Lateral spreading of the pattern (either by transport across the surface or by transport through the vapor) can result from diffusion of molecular ink on the printed surface. For example, alkanethiols patterned on gold by $\mu$CP while immersing the substrate in water illustrates the effect of lateral surface diffusion of alkanethiol across gold on broadening of the printed pattern.[194] In this example the lateral dimensions of the exposed gold decreased from 500 to ~35 nm by a time-dependent surface-mediated diffusion as the stamp was left in contact with the substrate for longer intervals of time. Diffusion of the ink and blurring of the features can be minimized by using high-molecular-weight inks. Patterns of dendrimers printed by $\mu$CP can have lateral dimensions as small as ~40 nm.[220,249] The outline of the edge of features printed using $\mu$CP often follows the edges of grains in the metal film used as a substrate; grain size is, thus, also an important determinant of resolution.

The resolution and minimum feature size of thin films transferred by nTP also depends on the integrity of the transferred material. The wetting of the stamp by a metal determines the minimum thickness and lateral dimension of isolated features. The grain size of the metal determines the thickness required to produce a continuous film. For example, the minimum thickness of a continuous film of Pd (grain size of ~20 nm) is less than that required for Au (grain size of ~50 nm) when deposited by electron-beam evaporation onto titanium-coated silicon.[190] Cracks in the metal film can also form as a result of mechanical deformation during printing.[236] Other sources of defects in the printed pattern include disparities in the stamp or on the printed surface.

The preferential adhesion of the material to be printed onto a second surface is a third limiting factor in printing nanoscale features. The stamp can be coated with a release layer to assist the removal of this material (e.g., a metal film) from the stamp by decreasing the surface free energy of the stamp. This release layer can, however, also decrease the wetting of metal deposited onto the stamp.[237] The formation of covalent bonds between the transferred material (e.g., molecular ink or metal film) and the printed surface also improves release from the stamp.[222,234,236,237]

### 4.4. Summary

Printing materials onto a surface using a topographically patterned stamp changes the properties of the surface in well-defined, nanometer-scale regions. High-resolution printing normally requires a mechanically compliant stamp. The surface can be modified with covalently bound molecules (e.g., SAMs) or thin films (e.g., gold or silica). The printed material can have applications as etch resists, reversible or permanent electrical contacts, patterns for use in biotechnology, and bits of information in high-density data storage. Resolution is, however, limited by surface diffusion of printed molecules and distortion of the features within the stamp during printing. Different materials are being developed to improve the fidelity of pattern transfer from nanometer-scale features. These printing techniques are easily implemented and attractive because the stamps are generated inexpensively from readily available commercial precursors.

## *5. Scanning Probe Lithography (SPL) for Nanofabrication*

Scanning probe lithography provides a versatile set of tools for both manipulating and imaging the topography of a surface with atomic-scale resolution.[31−34] At present, these tools seem well suited for applications in research but will require substantial development before they can be used for patterning large areas in manufacturing. The most important SPL techniques include scanning tunneling microscopy (STM), atomic force microscopy (AFM), and near-field scanning optical microscopy (NSOM). A striking example of the potential of these techniques for nanoscale fabrication is the precise positioning of individual Fe atoms with an STM tip (Figure 9A,B).[28,52] This atomic-scale manipulation is interesting scientifically but is not yet a practical technology. Our review of the current capabilities of SPL for nanofabrication is brief as this topic is extensively reviewed elsewhere.[32,34,53]

### 5.1. Serial Patterning of Surfaces Using SPL

Scanning probe lithography is a versatile method for depositing clusters of atoms or molecules onto a surface in a well-defined pattern.[30] One approach to deposit nanoparticles or molecules selectively onto a surface is dip-pen nanolithography (DPN).[30,31,250−252] An AFM tip is "inked" with a solution of the material to be transferred to the surface. The material adsorbed onto the AFM tip transfers to the surface in an arbitrary pattern "written" with the scanning probe (Figure 9C). This technique can, with care, reproducibly pattern lateral features as small as 50 nm.[32] Molecules patterned by this technique include SAMs for binding oligonucelotides, proteins, and viruses.[253−256] Similar SAMs can also mask the substrate during wet etching to pattern nanostructures of metals such as Au, Pd, and Ag (Figure 9D).[257] This process can fabricate trenches with lateral dimensions from 12 to 100 nm.[258] The mechanism of material transfer by DPN is not yet clear. One possibility is that water between the tip and surface mediates the process;[259] another is the transfer of solid material as a result of tip−surface interactions. The spreading of the ink on the substrate depends

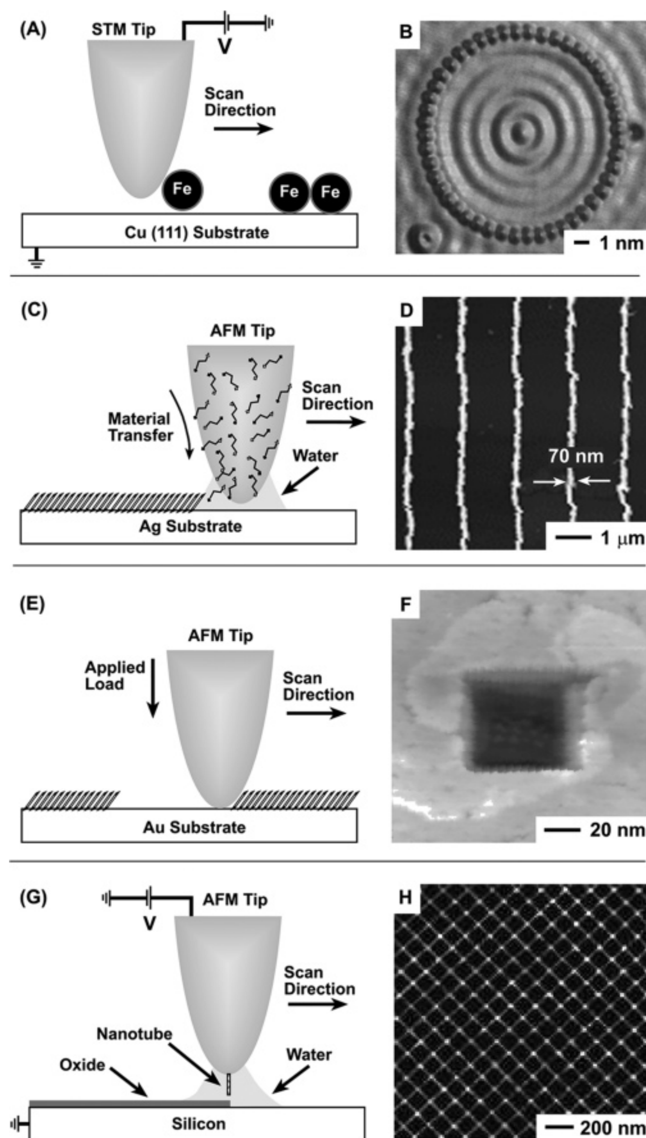


**Figure 9.** Schematic representations of four approaches to scanning probe lithography, and patterns produced using them: (A) Scanning tunneling microscopy (STM) can position atoms on a surface with high precision to generate patterns, such as (B) a quantum corral of a 48-atom Fe ring formed on Cu enclosing a defect-free region.[52] (Reprinted with permission from ref 52. Copyright 1993 American Association for the Advancement of Science.) (C) Dip-pen nanolithography can direct the deposition of SAMs (e.g., 16-mercaptohexadecanoic acid) on Ag as an etch resist to pattern (D) 70-nm wide features.[257] (E) Nanoshaving can remove regions of SAMs to pattern features such as (F) a square hole within octadecanethiolate SAMs on Au.[266] (G) Scanning electrochemical oxidation with a carbon nanotube-modified AFM tip can selectively oxidize a surface to pattern (H) 10-nm wide (2-nm tall) silicon oxide lines spaced by 100 nm.[278] (Reprinted with permission from ref 278. Copyright 1999 American Institute of Physics.)

on the humidity, the reactivity of the ink with the substrate, the radius of curvature of the probe, and the linear velocity of the probe.[259−264]

Another approach to nanofabrication by SPL is the selective removal of material from a surface by force-induced patterning.[265−267] An AFM tip in contact with the surface can displace SAMs in a process referred to as nanoshaving (Figure 9E).[266] This process removes SAMs from a surface in a well-defined pattern (Figure 9F). Irregularities in these patterns can result from variations in surface topography and, therefore, a nonuniform contact between the tip and substrate. A second material (e.g., SAMs or nanoparticles) can replace the removed film.[265,268] This substitution lithography is a convenient method for patterning multiple types of SAMs on a surface. Mechanical displacement of a thin polymer film with an AFM tip, or "nanoplowing",[269] can also generate nanoscale holes or trenches. These nanoscale pits are templates for the growth of nanowires[270] or the formation of nanosized electrical contacts with the supporting substrate.[271]

Scanning probe lithography is also used to modify a surface chemically.[272] One example is the localized oxidation of a surface (metal, semiconductor, or SAM) in a pattern scanned by a conductive AFM or STM tip (Figure 9G). [267,272−277] A local electric field between the conductive tip and the surface induces oxidation of the surface. Typically, this method can generate ~50-nm wide features. A carbon nanotube-modified AFM probe can, however, pattern ~10-nm wide lines of silicon oxide on a silicon hydride surface (Figure 9H).[278] A conductive AFM tip can also locally modify organosilane SAMs to direct the deposition of $Au_{55}$ nanoclusters.[279,280] Another SPL method for chemically modifying a surface is photochemical oxidation by NSOM.[281−283] For example, the photochemical oxidation of SAMs of mercaptoundecanoic acid (with 244-nm light), followed by selective wet chemical etching of the unmasked substrate, can pattern ~55-nm wide trenches in gold.[281]

The commercial availability of AFM, STM, and NSOM make these tools convenient for nanofabrication. These instruments are also capable of nanoscale registration. This approach to writing nanoscale patterns with a single tip is, however, fundamentally slow. The serial nature of SPL results in a low sample throughput. Single-probe methods are probably restricted to research applications and possibly to fabrication of customized patterns or mask repair.

## 5.2. Parallel Patterning of Surfaces Using SPL

A practical approach to SPL for large-volume, parallel production may emerge by simultaneously writing patterns with multiple probes.[53,250,251,284−288] An array of cantilevers scanned in parallel may allow higher sample throughput. The concept of the "Millipede" was developed as a 2D array of independently addressable AFM probes for high-density data storage.[53,284−286,289,290] Each probe in this array can be mechanically deflected in the vertical direction and resistively heated. These arrays of cantilevers can locally heat a thin polymer film to pattern ~40-nm wide holes with feature densities $>10^{11}$/in.$^2$.[284,285] A parallel approach to patterning surfaces by DPN is also being explored.[250,251,287,288] The current capabilities of parallel DPN include writing multiple copies of a pattern using a linear array of passive (i.e., nonactuated) probes or writing a series of different patterns (e.g., alkanethiols in the pattern of numerals 0−9) using thermally actuated probes.[287]

### 5.3. Summary

Scanning probe lithography can precisely position atoms on a surface and selectively deposit or remove regions of etch resist to pattern surfaces. These techniques may find applications in mask or device repair and information storage. Parallel approaches in SPL are being developed to overcome the serial limitations of standard SPL technologies. Surface diffusion of molecular inks and colloidal suspensions broadens the features patterned by SPL. It is also challenging to generate reproducible structures between scans because of variations in the surface topography of the substrate and differences in the shape of the tip (and variations in this shape with time and use).

## 6. Edge Lithography for Nanofabrication

We define edge lithography as either pattern transfer directed by the edge of a feature[36,42,291,292] or the process of transforming a feature that is thin in the vertical direction into a feature that is thin in the lateral direction.[37,39,40,293] General interest, as measured by volume of publications, in these two areas has increased markedly in the past few years.[35−43] These methods are, currently, limited in the types of patterns they can form but can be used to pattern arrays of $<$100-nm structures in parallel for a range of materials.

### 6.1. Pattern Generation Directed by Topography

In this section we discuss varieties of edge lithography that use the edge (e.g., the perimeter or the outline) of a topographic feature to generate nanoscale structures. We divide this area into four strategies for generating nanostructures: (i) depositing material at step edges of crystalline lattices;[43,294−297] (ii) adding or removing material at edge-defined defects in SAMs;[36] (iii) depositing or undercutting at lithographically defined step edges;[38,298] and (iv) patterning photoresists at regions defined by vertical edges in a soft stamp using phase-shifting photolithography.[42,292]

#### 6.1.1. Material Deposition at Step Edges of Crystalline Lattices

The exposed edges of steps within a crystalline lattice can have properties that are different from those of the bulk material. For example, gas-phase catalytic studies have shown that the exposed edges of the catalyst can promote a number of reactions and are often the sites of highest reactivity.[295,299−301] The step edges on single-crystalline surfaces can also direct the growth of metal nanostructures.[43,294,296,297,302−306] Particles of Cu, Co, and Ag have been deposited at the step edges of crystalline metallic substrates (e.g., Mo (110), Ag (111), and Cu (111)).[303−305,307] These metals are often deposited by physical vapor deposition.

Material deposition at atomic step edges has been extended to the growth of continuous nanowires by electrodeposition on highly oriented pyrolytic graphite (HOPG) (Figure 10A−C).[43,308] This approach can generate nanowires of metals (e.g., Ag, Pd, Cu, and Au), oxides (e.g., $MoO_x$ and $Cu_2O$), and semiconductors (e.g., $MoS_2$ and $Bi_2Te_3$).[43,308−313] These nanowires can have lateral dimensions down to ~15 nm[43] and can be used in the fabrication of gas sensors.[310,314] For example, palladium nanowires, transferred to a cyanoacrylate polymer film, can be used to detect the presence of hydrogen gas.[310,315,316] Nanowires grown by this method are, however, randomly positioned on the substrate in a pattern determined by the orientation and spacing of the step edges in the HOPG substrate. Their grain structures and edge roughness have not been characterized. The diameter of these nanowires can also vary across the substrate, and nanoparticles can nucleate on defects in the substrate.

#### 6.1.2. Patterning at Edge-Defined Defects in SAMs

Another strategy for patterning nanostructures by edge lithography is the selective deposition or removal of material in regions defined by defects at the edges of topographic features.[36,291,317,318] For example, SAMs form polycrystalline lattices on a planar metallic surface but remain disordered at the edges of this surface.[35,36] Sharp metal corners within a topographically patterned metal substrate prevent the formation of well-ordered SAMs and expose the underlying metal at these edges.[36,291,317] Selectively etching the exposed metal transfers the outline of the patterned metallic topography into the underlying film with line widths as small as ~50 nm.

A modification of this technique included a thin titanium layer (~5-nm thick) between a patterned silver film and a planar supporting layer of silver.[318] Immersing this patterned substrate in a solution of alkanethiols formed SAMs on the silver but not on the titanium. The exposed edge of titanium formed a gap (~5-nm wide) in the SAM-coated substrate. This edge served as a well-defined nanoelectrode for the electrodeposition of copper.[318] Electrodeposition on edges made by engineering defects in SAMs has generated nanowires with lateral dimensions as small as 70 nm.

These edge lithographic techniques generate nanostructures in a pattern defined by the outline of a topographic template. Photolithography can pattern regular arrays of topographic features, and electrodeposition on edges within this well-defined surface can generate aligned nanowires.[318] Removing an array of parallel nanowires with Scotch tape transfers these nanostructures to a transparent, flexible substrate and generates an efficient optical polarizer.[318] Nanowires supported on this adhesive substrate can also conform to a curved or flat substrate.

#### 6.1.3. Controlled Deposition and Undercutting at Lithographically Defined Step Edges

Thin-film deposition onto a topographic template and selective etching of the substrate can also generate nanoscale features. For example, shadow evaporation of metal onto the side walls of topographic features, followed by the selective etching of the substrate, generates narrow, vertical structures.[319] White et al. used this method to fabricate an array

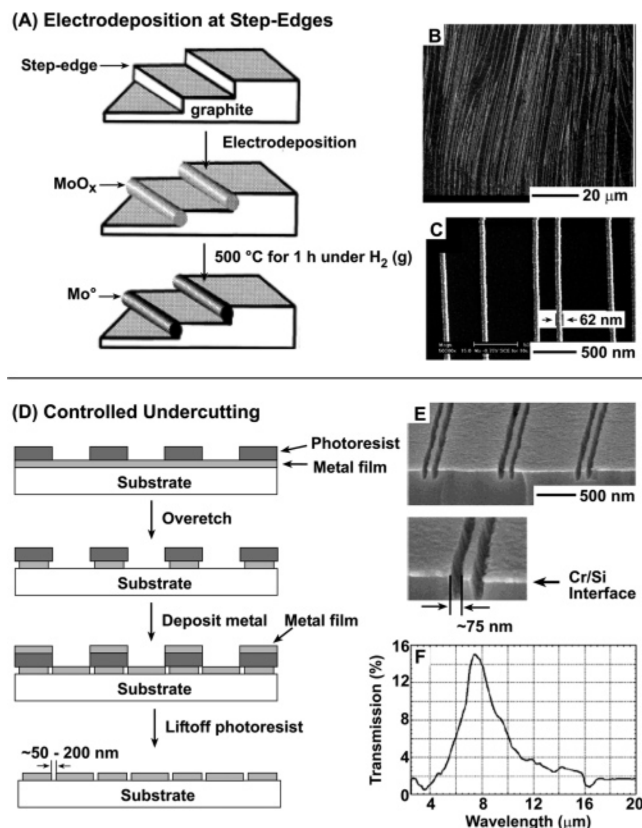


**Figure 10.** (A) Schematic illustration of the process used to generate nanowires at step edges of a graphite surface by electrodeposition of a material such as molybdenum oxide ($MoO_x$).[43] SEM images (B,C) show dense arrays of $MoO_x$ nanowires deposited from 1.0 mM $MoO_4^{2-}$. (Reprinted with permission from ref 43. Copyright 2000 American Association for the Advancement of Science.) (D) Schematic illustration of the use of controlled undercutting to pattern trenches with lateral dimensions as small as ~50 nm. (E) SEM images for a cross-section of ~75-nm wide trenches transferred into a silicon substrate through a patterned chrome mask. (F) An infrared transmission plot showing the frequency selectivity of 100-nm wide trenches in Al on a $CaF_2$ substrate, prepared by selective undercutting.[298] (Reprinted with permission from ref 298. Copyright 2001 Wiley-VCH Verlag GmbH.)

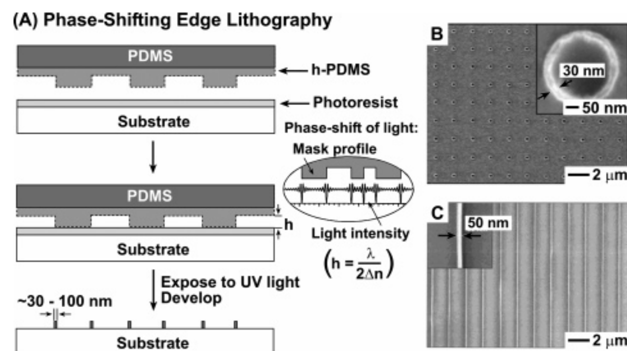


**Figure 11.** (A) Schematic illustration of phase-shifting edge lithography using a topographically patterned composite PDMS stamp—"hard" PDMS (h-PDMS)[161] with a soft PDMS backing[159]—in contact with a photoresist. The schematic depicts the intensity profile for a destructive modulation of the phase-shifted light—a constructive modulation is also possible (see text for further details). The phase shift is optimal when the thickness of the air gap (h) is equivalent to the ratio of the wavelength ($\lambda$) of light to twice the change in refractive index ($\Delta n$) between PDMS and air. The SEM images show (B) 30-nm wide rings[162] and (C) 50-nm wide lines[159] patterned in a positive-tone photoresist using phase-shifting edge lithography with a PDMS stamp and destructive modulation of the phase-shifted light.

of 30-nm wide lines of silica with heights of ~300 nm.[38] Depositing a low-temperature oxide uniformly over topographic features and etching the substrate by RIE can also pattern nanoscale features at the outline of each feature.[320] Somorjai et al. used this method to generate ~10-nm wide vertical structures.[321]

Patterned arrays of nanostructured trenches can be fabricated by the controlled undercutting of topographic features using isotropic wet etching, followed by deposition of a thin film (Figure 10D).[298] In this approach to nanofabrication the initial step was to pattern a photoresist supported on a metal-coated substrate (e.g., chromium on silicon). The exposed metal film was isotropically wet etched with controlled undercutting of the photoresist. Coating this substrate with a second metal film, followed by liftoff of the photoresist, produced nanostructured trenches at the edges of the photoresist (Figure 10E). This method has patterned well-defined trenches with lateral dimensions as small as ~50 nm.[298] Controlled undercutting of photoresist has also patterned ~50-nm wide islands of gold for growing ZnO nanowires.[322] The controlled undercutting of thin films is not limited to semiconductor substrates. For example, patterning an aluminum film supported on a calcium fluoride ($CaF_2$) substrate generated a frequency-selective surface (Figure 10F).[298]

Each of these techniques is limited in its ability to pattern arbitrary features by the features whose edges are being used and by the characteristics of light. Photolithography and electron-beam lithography can pattern regular arrays of topographic features, and nanoscale structures generated at the step edge of these features are regularly spaced. Patterning intersecting (crossing) lines of metal using these methods is, however, not straightforward.

### 6.1.4. Phase-Shifting Edge Lithography

Another approach to nanofabrication directed by the edges of a topographic feature is near-field phase-shifting photolithography (Figure 11A).[42,162,241,292,323−325] In this technique the vertical edges of a transparent, topographically patterned substrate induce abrupt changes in the phase of incident, collimated light over short distances (an edge in a conformal, transparent, PDMS stamp). This shift in phase of the incident light creates narrow regions of constructive and destructive interference. Phase-shifting photolithography uses this interference to project "dark" or "bright" regions of incident light onto the surface of a photoresist. The smallest lateral dimensions are produced when the light has a phase shift of $\pi$ radians at the photoresist−mask interface (Figure 11A).

Masks for phase-shifting edge lithography must be transparent and situated as close as possible to the films of photoresist. (Ideally the mask and photoresist should be in conformal contact.) These

requirements limit the choice of materials. A hard mask for phase-shifting edge lithography (e.g., quartz) is expensive to design and requires accurate control of the distance between the phase mask and the photoresist; accidental contact between the two easily damages or contaminates the mask. An elastomeric mask is much less expensive to fabricate and use. A PDMS mask spontaneously and nondestructively achieves conformal contact with the photoresist; conformal contact eliminates any gap between the mask and the resist and places the resist directly in the optical near-field of the mask. Phase-shifting edge lithography using an elastomeric phase mask has patterned features as small as ~30 nm (Figure 11B,C).[162,292,323,324,326,327] Soft masks for phase shifting can also conform reversibly to nonplanar surfaces.[162,292,323,328]

Near-field phase-shifting photolithography has been used to fabricate a number of simple patterns, such as rings and lines of photoresist (Figure 11B,C). These patterns can be transferred into a metal film by lift-off or selective wet etching.[162,292,323,327] The narrow photoresist features can also mask a substrate during RIE. This method produced uniform, single-crystalline silicon nanostructures with well-defined features as small as 40 nm and lengths >1 cm.[326] Components of devices fabricated by phase-shifting edge lithography include optical polarizers[329] and gates for organic transistors[327] having dimensions as small as ~100 nm. An array of patterned features in Al can generate a frequency-selective optical filter,[328] and nanostructured holes patterned in photoresist can direct the crystallization of various salts[162] or the deposition of nanoparticles.[330]

Phase-shifting lithography using a soft, conformal mask requires that the mask have vertical, straight sidewalls. Distortions in the mask broaden the features in the photoresist. A composite stamp (Figure 11A) of h-PDMS with a "soft" PDMS backing such as Sylgard 184 improves the fidelity of the sidewalls in comparison to a stamp of only Sylgard 184-based PDMS. These composite stamps can pattern ~30-nm features by phase-shifting edge lithography.[162]

## 6.2. Generating Nanostructures by Exposing the Edge of a Thin Film

A second type of edge lithography takes advantage of the numerous methods[331,332] that can grow thin films over large areas with a thickness between 1 and 50 nm. Converting these films—which are thin in the vertical direction—into structures that are thin in the lateral direction is an approach to fabricating nanostructures.[37,39,293,333,334] There are now three demonstrated approaches to exposing a nanostructured edge: (i) fracturing a thin film;[37] (ii) sectioning an encapsulated thin film;[40,335] and (iii) reorienting posts capped with a thin film.[41]

### 6.2.1. Edges by Fracturing Thin Films

Thin films deposited onto a crystalline semiconductor substrate, such as silicon, can be exposed as a uniform narrow edge by fracturing the substrate. Multilayered structures grown by molecular beam epitaxy (MBE) are the most common substrates for

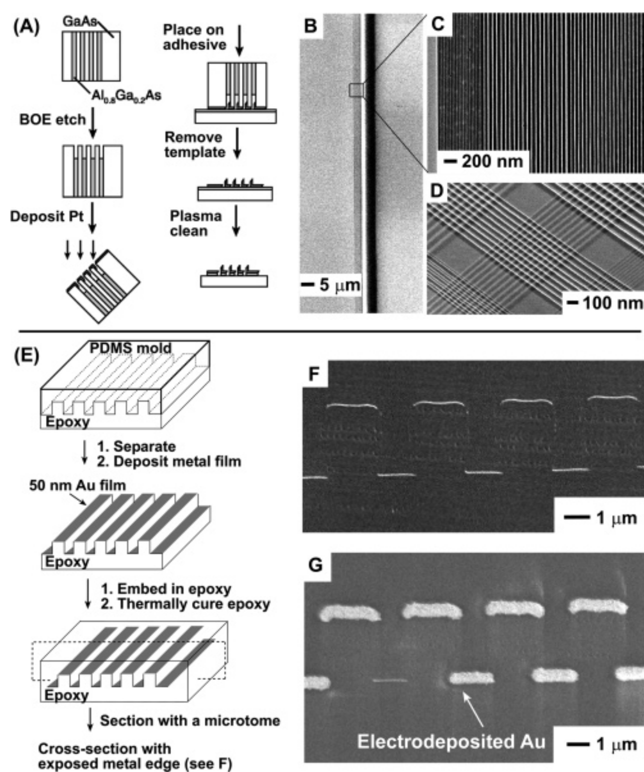


**Figure 12.** (A) Schematic illustration of a method to create nanowires by physical vapor deposition on a structured edge, which was fabricated by molecular beam epitaxy (MBE) and etching in buffered oxide etch (BOE).[39] (Reprinted with permission from ref 39. Copyright 2003 American Association for the Advancement of Science.) (B,C) SEM images showing the edge of the MBE-grown substrate with an array of deposited Pt nanowires. The higher resolution micrograph (C) shows 10-nm diameter Pt nanowires with a pitch of 60 and 30 nm. (D) SEM image of a cross-bar array of Pt nanowires fabricated from two sets of nanowires transferred to adhesive substrates. (E) Schematic diagram showing the fabrication of a patterned array of epoxy-embedded conducting metal edges.[40] (F) SEM image of 50-nm thick Au lines exposed by sectioning with the glass knife of a microtome. (G) Electrochemical deposition of a metal onto the exposed metal edge identified the conductive regions.

this approach to nanofabrication. For example, Pfieffer et al. fractured multilayered MBE-grown substrates to direct the growth of quantum wires and quantum dots.[37,336,337] An MBE-grown substrate consisting of alternating layers of AlGaAs and GaAs was also used to fabricate an array of field-effect transistors (FETs) with ~20-nm gate lengths.[336]

The edge of a multilayered substrate that has been fractured can also template the formation of parallel nanowires by physical vapor deposition (Figure 12A).[39] Selectively etching one of the components (e.g., AlGaAs in a buffered oxide etch) reveals an array of narrowly spaced grooves. These grooves are partially coated with a metal by selective angle deposition to generate parallel nanowires supported on the fractured edge (Figure 12B,C). The width of the groove, corresponding to the original thickness of the etched film, determines the spacing between the nanowires. Modifying the thickness of each layer of the substrate will change the spacing between the nanowires and the width of the nanowires.

An adhesive tape can remove the deposited lines of metal from the edge of the substrate. Free-standing Pt nanowires have been fabricated with diameters down to 8 nm at a pitch of ~16 nm.[39] Parallel nanowires supported on adhesive substrates can be overlapped perpendicular to each other to create a cross-bar array (Figure 12D). A narrow edge can also direct the assembly of nanorods.[338] For example, nanorods of cadmium selenide (7-nm diameter, 35-nm long) can align along an exposed edge of ZnS (5-nm wide) functionalized with SAMs of hexanedithiol.

### 6.2.2. Edges by Sectioning Encapsulated Thin Films

A nanostructured edge can also be fabricated by embedding a thin film in a soft matrix and cutting or sectioning the matrix to expose its cross-section.[40,335] An early approach to exposing the edge of an embedded thin film was to polish the substrate with an abrasive film (e.g., silica-coated paper).[335] In this approach a Pt film deposited on mica was encapsulated in an epoxy matrix. Sanding this soft matrix exposed the edge of the Pt. Another approach to expose the edge of the encapsulated film is to section a polymer-encased metal film with the glass knife of a microtome.[40] This approach to edge lithography can be combined with soft lithography to generate a patterned edge structure (Figure 12E). The surface roughness of the sectioned epoxy was ~10 nm. This smooth surface encapsulated arrays of isolated, narrow gold lines with line widths as small as 50 nm (Figure 12F).

Exposed edges can direct the deposition of material into a well-defined pattern. For example, these edges can be electrically addressed from the opposite side of the encapsulating matrix for the electrodeposition of metal (Figure 12G).[40] This backside electrical connectivity cannot be easily achieved for structures patterned by conventional techniques. We believe the combination of edge lithography with molding and embossing will be a useful method for generating substantially more complex features than those currently demonstrated.

A major challenge in fabricating encapsulated nanostructures by sectioning a soft matrix is minimizing delamination at the matrix−metal interface. Sectioning the matrix at temperatures below −120 °C significantly minimized the delamination between epoxy and an embedded metal film.[40] Exposing the surfaces to an oxygen plasma before embedding also improved adhesion between the interfaces.

### 6.2.3. Edges by Reorientation of Metal Capped Posts

Ordered arrays of nanoscale edges have been patterned by capping an array of posts with a thin film and tipping each post onto one side (Figure 13A).[41] Arrays of epoxy posts were patterned by photolithography on a silicon substrate. A thin metal film, deposited by selective angle deposition, coated the top and part of one side of each post. These structures (“microdominos”) fractured from the supporting substrate under a horizontally applied shear force. They collapsed in a uniform pattern determined by the direction of the applied shear (Figure 13B,C). These patterned, collapsed arrays can cover large

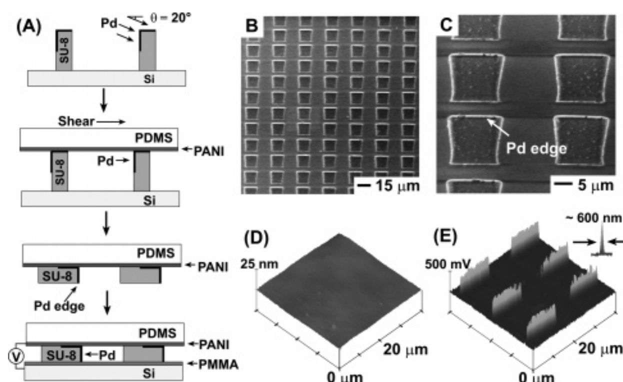


**Figure 13.** (A) Schematic illustration of an array of microdominos (posts of an epoxy-based photoresist) uniformly collapsed by applying a horizontal shear using a slab of PDMS. Selectively depositing a Pd film to coat the top and part of one side of each post prior to collapse generated an array of nanometer-scale Pd edges after collapse.[41] (B) SEM images of the array of collapsed microdominos adhering to the PDMS slab, and (C) a ~15-nm wide edge of Pd on a collapsed post. (D) Topography and (E) surface potential of a 100-nm thick PMMA surface after patterning regions of charge (~400 mV peak surface potential). The inset in E shows the side profile for one region of charge. (Reprinted with permission from ref 41. Copyright 2004 Wiley-VCH Verlag GmbH.)

areas (>1 cm$^2$). The reorientation of the microdominos also generates an array of metal features (edges) with nanometer dimensions in the plane of the array.

The collapsed microdominos adhere to the PDMS slab that is used to apply the shear force. If a conducting polymer [e.g., polyaniline (PANI)] had been grafted onto the surface of the PDMS before using it to shear the microdominos, this layer established an electrical connection to each of the arrayed edges.[41] This array of narrow electrodes supported on a conducting, elastomeric substrate can be used as a flexible electrical contact for printing charge into electrets (Figure 13D,E). Multiple regions of charge can be patterned in parallel by simultaneously addressing all of the nanoscale edges.

A nonuniformly applied shear force can result from uneven contact between the microdominos and the horizontally translated substrate. An elastomeric slab, such as PDMS, applies a shear force evenly across the substrate by conforming to asperities in the surface. A limitation of the current approach is the inability to address each nanoscale edge individually. Patterning the conductive substrate in contact with these edges may overcome this limitation.

## 6.3. Summary

Edge lithographic techniques are, currently, restricted to generating certain, limited types of line structures (e.g., noncrossing lines) in one step of fabrication. Crossed lines can sometimes be generated by stacking features.[39,40] These techniques are still being developed as tools for research. Recent developments include “wiring-up” nanostructures to external magnetic or electric fields[40,41] and directing the formation of parallel nanowires with applications in nanoelectronics[39] and tunable optical polarizers.[318] We believe the formation of more complex nanostruc-

tures will result from a combination of edge lithography with other—conventional and unconventional—nanofabrication techniques.

## 7. Self-Assembly for Nanofabrication

Self-assembly is defined as the spontaneous organization of two (or more) components into larger aggregates using covalent and/or noncovalent bonds.[339] We described a number of techniques for nanofabrication that use top-down approaches to patterning nanostructures. Self-assembly, a bottom-up approach to nanostructures or nanostructured materials, is a second strategy for nanofabrication. This approach relies on cooperative interactions of small components that assemble spontaneously in a predefined way to produce a larger structure in two or three dimensions.

We will focus on two types of self-assembly: (i) nontemplated self-assembly, where individual components interact to produce a larger structure *without* the assistance of external forces or spatial constraints, and (ii) templated self-assembly, where individual components interact with each other *and* an external force or spatial constraint. In this section we review recent advances in both nontemplated and templated self-assembly and evaluate the current status of self-assembly for nanofabrication. For other aspects of self-assembly we direct the interested reader to recent reviews.[46,340−344]

### 7.1. Nontemplated Self-Assembly

One of the most appealing aspects of self-assembly is the *spontaneous* assembly of components into a desired structure. The notion that a fabrication strategy requires only the mixing of components to achieve an ordered structure is appealing both for its simplicity and its potential efficiency. We refer to this type of self-assembly as "nontemplated self-assembly." Examples of materials fabricated using this approach include SAMs[51] and structures that self-assemble from block copolymers[345,346] and nanoparticles.[343,347] Recent advances in the fabrication of functional nanostructures using self-assembly include self-assembled arrays of magnetic nanoparticles that can be used as magnetic data storage devices[348] and self-assembled arrays of nanorods that display birefringence.[349]

Nontemplated self-assembly, while attractive for its minimalist use of materials and energy (in contrast to conventional lithography), is not widely used for nanofabrication. Examples where this approach is used for nanofabrication include patterning arrays of nanoelectrodes[350] and generating arrays of metal nanoparticles for sensing biomolecules.[351] Self-assembly is, however, prone to producing defects, and the perfect periodicity of self-assembled structures from nanoscale components is generally limited to micrometer-sized areas. The components also have a limited number of different ordered arrangements and generate a limited number of functional structures.

### 7.2. Templated Self-Assembly

By templating self-assembly it is possible to introduce an element of pattern into the self-assembled structure and sometimes increase the order of the self-assembled structure. Self-assembly can be directed using surface topography, electric and magnetic fields, or shear forces. Templated self-assembly[352] often uses top-down strategies to fabricate components that direct the bottom-up assembly of molecules, macromolecules, or colloidal particles. Templated self-assembly is an alternative to nontemplated self-assembly for the controlled fabrication of patterned structures with nanometer-scale local order and for the generation of micrometer-size, or larger, domains of defect-free patterns.

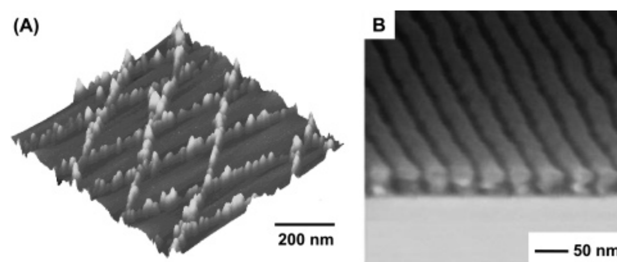


**Figure 14.** (A) AFM image of a 2D array of DNA strands that templates the electroless deposition of palladium nanowires.[364] (B) SEM image of poly(styrene-*block*-methyl methacrylate) self-assembled onto a photopatterned template of SAMs with a periodicity of 48 nm.[366] (Reprinted with permission from ref 366. Copyright 2003 Macmillan Magazines Ltd.)

#### 7.2.1. Templating from Molecules

Molecular and supramolecular chemistry[45,339,353,354] can produce structures that range in size from 1 to 100 nm and beyond.[46,174,353,355−359] Generation of these nanostructures has, largely, remained an academic exercise in design and synthesis because they are not functional—they are not, for example, electrical conductors, transistors, or motors. These organic nanostructures have, however, been used as templates to mask the deposition of metal[360] or guide the growth of metal nanoparticles[361−363] and nanowires (Figure 14A).[364] The inorganic nanoparticles or nanowires are often fabricated at electrodes and are electrically conductive.[365]

The combined use of a top-down approach, such as photolithography, and bottom-up self-assembly has been used to pattern block copolymers (Figure 14B).[366−369] Patterns of oxidized SAMs (or random copolymers)[370] on silica can be produced using extreme ultraviolet interferometric lithography that exhibit a periodicity on the order of the lamellar spacing of poly(styrene-*block*-methyl methacrylate) copolymer (that is, in this instance, ∼48 nm). When this block copolymer is allowed to self-assemble on the patterned SAM (or random copolymer), this pattern acts as a template that guides the phase separation of the polymer. Annealing a block copolymer film confined by physical boundaries can also direct the assembly of the copolymer into a regular structure.[371,372] These methods illustrate the use of templating to overcome the major disadvantages of nontemplated phase separation as a method of generating regular structures: that is, the high level of defects, the inability to control or pattern the phase-

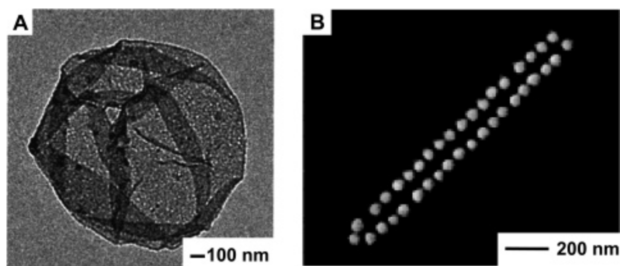


**Figure 15.** (A) Transmission electron microscopy (TEM) image of a polymer shell fabricated using layer-by-layer assembly of alternating layers of poly(styrenesulfonate) and poly(allylamine hydrochloride) assembled onto a spherical template.[380] In this example the template—a melamine–formaldehyde bead—has been selectively removed. (B) SEM image of 50-nm diameter gold nanoparticles assembled into wells defined by electron-beam lithography.[400] Capillary forces generated by an evaporating solvent directed the particles into these wells.

segregated regions, and the uncontrolled drift in the pattern over nonlocal dimensions.

#### *7.2.2. Templating from Particles*

Charged polymers, or polyelectrolytes, can be used to modify the surfaces of colloidal particles.[373−375] The electrostatic attraction between a charged surface and a charged macromolecule is sufficient for adsorption. Often the charged polymer has excess charge and reverses the charge on the surface.[376] This reversal of charge permits a second polymer, with charge opposite to the first, to assemble on the first layer of polymer. The layer-by-layer assembly[377,378] of polyelectrolytes can be repeated to produce robust multilayers of self-assembled polymers.

Layer-by-layer assembly has also been used to fabricate hollow colloidal particles (Figure 15A).[379−383] A multilayer polyelectrolyte shell around a colloidal particle is robust enough to survive the removal of the core, generally achieved by dissolving the core template in a solvent. The hollow and permeable shell that remains encapsulates an attoliter volume.[377,384] Colloidal particles have also been used to template the self-assembly of nanoparticles.[385−388] Typically, the diameter of these particles is larger than 100 nm, but the assembly of thin, metallic shells may be important for nanofabrication.

#### *7.2.3. Templating Using External Forces*

Nanospheres that are monodisperse in size and shape self-assemble to produce thin films of close-packed, ordered lattices. Electric[389] and magnetic fields[390] as well as shear forces[391] and spatial constraints[392,393] have been used to direct the assembly of nanoparticles and nanorods into different configurations. For example, template-assisted self-assembly[394] has been used to direct the assembly of spherical and tetrapod-shaped nanoparticles where the capillary force exerted by the edge of a drop of evaporating solvent confines particles against an edge,[395] in a narrow channel,[396−399] or in a well (Figure 15B).[400]

The assembly of nanowire arrays is more challenging than the assembly of nanoparticles and nanorods due to the anisotropic shape of the object.[401] Nanowire self-assembly results in partially ordered, small superlattices. This issue has been addressed by several new methods that direct the assembly of nanowires, including the use of microfluidic channels[402] and electric fields.[403] Another review in this issue contains a full account of methods available to assemble nanowires.[404]

### 7.3. Summary

Self-assembly—as a stand-alone method for nanofabrication—is presently unable to produce structures with precise spatial positioning and arbitrary shapes with a low concentration of defects and functionality that can be achieved using conventional nanofabrication. It is also unable to generate the range of patterns required for even simple electronic functionality. Nontemplated self-assembly may represent a useful method of generating materials for information technology. For example, crystalline arrays of magnetic nanocrystals can store large amounts of information.[348]

Neither nontemplated nor templated self-assembly strategies have yet demonstrated a route to the level of functionality necessary to contribute to microelectronics other than by generating materials or positioning objects with large (~100 $\mu$m) dimensions.[197,405−409] We are, however, optimistic that self-assembly will play a significant role in nanofabrication in the future, particularly when we consider the potential for fabrication in three dimensions, the opportunity for reversible[410] and reconfigurable self-assembly,[411] and the implication that self-assembled structures can undergo self-repair or self-replication.[412] The cell is the ultimate demonstration and inspiration for continuing work in nanometer-scale self-assembly, and it is much *more* sophisticated than current microelectronic systems. A demonstration of the principle for *very* complex and functional forms of self-assembly thus already exists.

## *8. Outlook and Conclusions*

The expectations surrounding nanotechnology and nanofabrication are high. Governments and companies around the world are spending billions of dollars on research related to nanotechnology. The U.S. government promoted an initiative announced in 2000 based on optimistic (probably *very* optimistic) predictions that it would eventually lead to "materials with ten times the strength of steel and only a fraction of the weight, the ability to shrink the information housed in the Library of Congress into a volume the size of a sugar cube and the ability to detect dangerous cancerous tumors when they are only a few cells in size".[17] This initiative predicts nanotechnology will add a trillion dollars to the gross national product and add 2 million new jobs to the U.S. economy by 2013. Whether nanotechnology will or will not have a revolutionary economic impact is not certain but also not highly relevant at this early, exploratory stage in its development. It is unquestionably fascinating science, and it will certainly lead to significant technologies.

Nanoscience and nanotechnology cover many different areas, but one key set of methods for both is

nanofabrication. The development of microelectronic circuits with <100-nm-scale features is proceeding rapidly by extensions of existing, conventional photolithographic techniques. Unconventional techniques and new materials will be required, if at all, for structures with dimensions below ~20 nm and to change the cost structure of this very capital-intensive industry. New products and technologies outside the field of microelectronics, but still requiring nanoscale fabrication, are being developed in widely different areas such as biology, materials science, and optics. Our intuition is that there will be many opportunities for the application of unconventional nanofabrication in these areas. Some possible areas of application include the following: (i) printed, low-cost organic microelectronics; (ii) subwavelength optics; (iii) tools for biology for investigating individual cells and cell−cell interactions; (iv) nanofluidics; (v) nanoelectrical mechanical systems (NEMS); and (vi) single-molecule studies.

The high capital and operating cost of conventional equipment for nanofabrication (photolithographic steppers and scanning beam tools) has given an opening for unconventional techniques in nanofabrication, initially in the areas of research and product development. Molding, embossing, and printing techniques have demonstrated usefulness, at least at the level of generating prototypes. A new generation of nanofabrication tools is emerging—mainly from small businesses located in the United States, Europe, and Asia—that enable various forms of stamping, molding, and embossing. These products vary in sophistication and capability. Most of the tools that are being sold are going to research laboratories or to fabrication facilities for products other than semiconductor-based devices. The nanofabrication equipment manufacturers are selling tools to companies that are reportedly developing a variety of single-layer products such as surface acoustic wave devices, photonic crystals, microfluidics, and biosensors. We expect that unconventional nanofabrication will play an important role in the commercialization of nanotechnology-based devices that require low-cost manufacturing of nanoscale structures over large areas, on nonplanar surfaces, and with new materials.

Historically, the motivation for developing unconventional nanofabrication techniques was to continue patterning semiconductor devices beyond the predicted resolution limit of photolithography—to forestall an end to "Moore's Law".[413] Photolithography continues to overcome obstacles to achieve new resolution requirements.[1] These improvements have not always been simple. This challenge is reflected in the increasing costs of conventional photolithography processes when shifting to shorter imaging wavelengths, improved imaging optics, phase-shifting masks, and optical proximity correction. Complex engineering challenges remain. It is, however, now clear that it is not feature sizes (or even registration) that is the limitation in microelectronic device performance. The major challenges are connections within or from the chip, power distribution, and heat dissipation. These areas may offer opportunities for unconventional nanofabrication.

The intrinsic limits of photolithography are inescapably related to the diffraction of light. The attraction of many unconventional nanofabrication techniques is that their intrinsic limitations are *not* set by optics and diffraction but by van der Waals interactions and the granularity of matter at the molecular or atomic scale. The resolution of molding methods in the laboratory is currently ~1 nm,[163,169] but extensive development will be required to achieve <10-nm feature sizes reliably in manufacturing. Unconventional nanofabrication methods may, however, offer higher resolution patterning at a lower cost than photolithography. Conventional scanning beam lithography also has high initial equipment costs. Scanning beam lithography is, however, required by many nanofabrication techniques to pattern the master or mask. The major advantage most unconventional methods have over conventional scanning beam techniques is the high throughput in replicating the original pattern.

Each technique for nanofabrication has certain characteristic advantages, and it is unlikely that a single technique will dominate all areas of application. For example, molding, embossing, or printing from a cylindrical drum[121,184] or by wave printing[414,415] or perhaps self-assembly have the potential to generate regular patterns over very large areas inexpensively. Photolithography will, however, probably remain the exclusive method for producing high-performance integrated circuits for years to come.

Regardless of their ultimate commercial applications, unconventional techniques for nanofabrication provide uncomplicated methods for the research communities in a broad range of disciplines to explore nanoscience and begin to develop nanotechnology. Their variety, low cost, operational simplicity, and broad collective applicability open the door to surveying and exploring many areas to which high-resolution photolithography and particle-beam writing simply are not applicable. Unconventional techniques for nanofabrication are being widely accepted and developed in this exploratory spirit and are thus a key part of the development of nanoscale research and development. From them may come unexpected inventions and technologies that will allow nanotechnology to live up to the optimistic expectations for its future.

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## 10. References


(1) Anon (http://public.itrs.net/Files/2003ITRS/Home2003.htm).
(2) Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403.
(3) Feldheim, D. L.; Keating, C. D. *Chem. Soc. Rev.* **1998**, *27*, 1.
(4) Kastner, M. A. *Phys. Today* **1993**, *46*, 24.
(5) Klein, D. L.; Roth, R.; Lim, A. K. L.; Alivisatos, A. P.; McEuen, P. L. *Nature* **1997**, *389*, 699.
(6) Venema, L. C.; Wildoer, J. W. G.; Janssen, J. W.; Tans, S. J.; Tuinstra, H. L. J. T.; Kouwenhoven, L. P.; Dekker, C. *Science* **1999**, *283*, 52.
(7) Avouris, P. *Acc. Chem. Res.* **2002**, *35*, 1026.
(8) Zhou, C.; Kong, J.; Yenilmez, E.; Dai, H. *Science* **2000**, *290*, 1552.
(9) Liang, W.; Bockrath, M.; Bozovic, D.; Hafner, J. H.; Tinkham, M.; Park, H. *Nature* **2001**, *411*, 665.
(10) Bockrath, M.; Liang, W.; Bozovic, D.; Hafner, J. H.; Lieber, C. M.; Tinkham, M.; Park, H. *Science* **2001**, *291*, 283.
(11) Bockrath, M.; Cobden, D. H.; McEuen, P. L.; Chopra, N. G.; Zettl, A.; Thess, A.; Smalley, R. E. *Science* **1997**, *275*, 1922.
(12) Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; De Rossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* **1999**, *284*, 1340.
(13) Torres, J. A.; Nealey, P. F.; de Pablo, J. J. *Phys. Rev. Lett.* **2000**, *85*, 3221.
(14) Tsui, O. K. C.; Zhang, H. F. *Macromolecules* **2001**, *34*, 9139.
(15) Fryer, D. S.; Peters, R. D.; Kim, E. J.; Tomaszewski, J. E.; de Pablo, J. J.; Nealey, P. F.; White, C. C.; Wu, W. L. *Macromolecules* **2001**, *34*, 5627.
(16) Singh, L.; Ludovice, P. J.; Henderson, C. L. *Thin Solid Films* **2004**, *449*, 231.
(17) US-NNI US National Nanotechnology Initiative (http://www.nano.gov/).
(18) Whitesides, G. M. *Nat. Biotech.* **2003**, *21*, 1161.
(19) Maier, S. A.; Brongersma, M. L.; Kik, P. G.; Meltzer, S.; Requicha, A. A. G.; Atwater, H. A. *Adv. Mater.* **2001**, *13*, 1501.
(20) Colburn, M.; Johnson, S.; Stewart, M.; Damle, S.; Bailey, T. C.; Choi, B.; Wedlake, M.; Michaelson, T.; Sreenivasan, S. V.; Ekerdt, J.; Willson, C. G. *Proc. SPIE-Int. Soc. Opt. Eng.* **1999**, *3676*, 379.
(21) Xia, Y.; Kim, E.; Zhao, X.-M.; Rogers, J. A.; Prentiss, M.; Whitesides, G. M. *Science* **1996**, *273*, 347.
(22) Chou, S. Y.; Krauss, P. R.; Zhang, W.; Guo, L.; Zhuang, L. *J. Vac. Sci. Technol. B* **1997**, *15*, 2897.
(23) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Science* **1996**, *272*, 85.
(24) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550.
(25) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823.
(26) Gates, B. D.; Xu, Q.; Love, J. C.; Wolfe, D. B.; Whitesides, G. M. *Annu. Rev. Mater. Res.* **2004**, *34*, 339.
(27) Xia, Y.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153.
(28) Eigler, D. M.; Schweizer, E. K. *Nature* **1990**, *344*, 524.
(29) Quate, C. F. *Surf. Sci.* **1997**, *386*, 259.
(30) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, *283*, 661.
(31) Ginger, D. S.; Zhang, H.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 30.
(32) Kraemer, S.; Fuierer, R. R.; Gorman, C. B. *Chem. Rev.* **2003**, *103*, 4367.
(33) Nyffenegger, R. M.; Penner, R. M. *Chem. Rev.* **1997**, *97*, 1195.
(34) Wouters, D.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2480.
(35) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *Nature* **1999**, *398*, 495.
(36) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *Nature* **1998**, *394*, 868.
(37) Pfeiffer, L.; West, K. W.; Stormer, H. L.; Eisenstein, J. P.; Baldwin, K. W.; Gershoni, D.; Spector, J. *Appl. Phys. Lett.* **1990**, *56*, 1697.
(38) Flanders, D. C.; White, A. E. *J. Vac. Sci. Technol.* **1981**, *19*, 892.
(39) Melosh, N. A.; Boukai, A.; Diana, F.; Gerardot, B.; Badolato, A.; Petroff, P. M.; Heath, J. R. *Science* **2003**, *300*, 112.
(40) Xu, Q.; Gates, B.; Whitesides, G. M. *J. Am. Chem. Soc.* **2004**, *126*, 1332.
(41) Gates, B. D.; Xu, Q.; Thalladi, V. R.; Cao, T.; Knickerbocker, T.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2780.
(42) Toh, K. K. H.; Dao, G.; Singh, R.; Gaw, H. *Proc. SPIE-Int. Soc. Opt. Eng.* **1991**, *1496*, 27.
(43) Zach, M. P.; Ng, K. H.; Penner, R. M. *Science* **2000**, *290*, 2120.
(44) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.
(45) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; John Wiley & Sons: New York, 1995.
(46) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3349.
(47) Boncheva, M.; Bruzewicz, D. A.; Whitesides, G. M. *Pure Appl. Chem.* **2003**, *75*, 621.
(48) Yang, P.; Deng, T.; Zhao, D.; Feng, P.; Pine, D.; Chmelka, B. F.; Whitesides, G. M.; Stucky, G. D. *Science* **1998**, *282*, 2244.
(49) Yin, Y. D.; Lu, Y.; Gates, B.; Xia, Y. N. *J. Am. Chem. Soc.* **2001**, *123*, 8718.
(50) Ozin, G. A.; Yang, S. M. *Adv. Funct. Mater.* **2001**, *11*, 95.
(51) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103.
(52) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Science* **1993**, *262*, 218.
(53) Wilder, K.; Soh, H. T.; Atalar, A.; Quate, C. F. *Rev. Sci. Instrum.* **1999**, *70*, 2822.
(54) Geissler, M.; Xia, Y. *Adv. Mater.* **2004**, *16*, 1249.
(55) Stewart, M. D.; Patterson, K.; Somervell, M. H.; Willson, C. G. *J. Phys. Org. Chem.* **2000**, *13*, 767.
(56) Willson, C. G.; Trinque, B. C. *J. Photopolym. Sci. Technol.* **2003**, *16*, 621.
(57) Ito, H. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3863.
(58) ASML (http://www.asml.com/).
(59) Switkes, M.; Kunz, R. R.; Rothschild, M.; Sinta, R. F.; Yeung, M.; Baek, S. Y. *J. Vac. Sci. Technol. B* **2003**, *21*, 2794.
(60) Mulkens, J.; Flagello, D. G.; Streefkerk, B.; Graeupner, P. *J. Microlith. Microfab. Microsys.* **2004**, *3*, 104.
(61) Owa, S.; Nagasaka, H. *J. Microlith. Microfab. Microsys.* **2004**, *3*, 97.
(62) Hoffnagle, J. A.; Hinsberg, W. D.; Sanchez, M.; Houle, F. A. *J. Vac. Sci. Technol. B* **1999**, *17*, 3306.
(63) Owa, S.; Nagasaka, H.; Ishii, Y.; Hirakawa, O.; Yamamoto, T. *Solid State Technol.* **2004**, *47*, 43.
(64) Switkes, M.; Rothschild, M. *J. Vac. Sci. Technol. B* **2001**, *19*, 2353.
(65) Savile Bradbury, B. B. *Introduction to Light Microscopy*; BIOS Scientific Publishers Ltd: Oxford, U.K., 1998.
(66) Burnett, J. H.; Kaplan, S. G. *J. Microlith. Microfab. Microsys.* **2004**, *3*, 68.
(67) Goethals, A. M.; Bisschop, P. D.; Hermans, J.; Jonckheere, R.; Van Roey, F.; Van den Heuvel, D.; Eliat, A.; Ronse, K. *J. Photopolym. Sci. Technol.* **2003**, *16*, 549.
(68) Mulkens, J.; McClay, J.; Tirri, B.; Brunotte, M.; Mecking, B.; Jasper, H. *Proc. SPIE−Int. Soc. Opt. Micro.* **2003**, *5040*, 753.
(69) Cerrina, F.; Bollepalli, S.; Khan, M.; Solak, H.; Li, W.; He, D. *Microelectron. Eng.* **2000**, *53*, 13.
(70) Brainard, R. L.; Cobb, J.; Cutler, C. A. *J. Photopolym. Sci. Technol.* **2003**, *16*, 401.
(71) Golovkina, V. N.; Nealey, P. F.; Cerrina, F.; Taylor, J. W.; Solak, H. H.; David, C.; Gobrecht, J. *J. Vac. Sci. Technol. B* **2004**, *22*, 99.
(72) Talin, A. A.; Cardinale, G. F.; Wallow, T. I.; Dentinger, P.; Pathak, S.; Chinn, D.; Folk, D. R. *J. Vac. Sci. Technol. B* **2004**, *22*, 781.
(73) Toriumi, M.; Ishikawa, T.; Kodani, T.; Koh, M.; Moriya, T.; Yamashita, T.; Araki, T.; Aoyama, H.; Yamazaki, T.; Furukawa, T.; Itani, T. *J. Vac. Sci. Technol. B* **2004**, *22*, 27.
(74) Li, Y.; Ota, K.; Murakami, K. *J. Vac. Sci. Technol. B* **2003**, *21*, 127.
(75) Stulen, R. *Proc. Electrochem. Soc.* **1997**, *97−3*, 515.
(76) Larruquert, J. I.; Keski-Kuha, R. A. M. *Appl. Opt.* **2002**, *41*, 5398.
(77) Montcalm, C.; Grabner, R. F.; Hudyma, R. M.; Schmidt, M. A.; Spiller, E.; Walton, C. C.; Wedowski, M.; Folta, J. A. *Appl. Opt.* **2002**, *41*, 3262.
(78) Zaidi, S. H.; Brueck, S. R. J. *J. Vac. Sci. Technol. B* **1993**, *11*, 658.
(79) Bozler, C. O.; Harris, C. T.; Rabe, S.; Rathman, D. D.; Hollis, M. A.; Smith, H. I. *J. Vac. Sci. Technol. B* **1994**, *12*, 629.
(80) Hoffnagle, J. A.; Hinsberg, W. D.; Houle, F. A.; Sanchez, M. I. *J. Photopolym. Sci. Technol.* **2003**, *16*, 373.
(81) Huang, W.-S.; He, W.; Li, W.; Moreau, W. M.; Lang, R.; Medeiros, D. R.; Petrillo, K. E.; Mahorowala, A. P.; Angelopoulos, M.; Deverich, C.; Huang, C.; Rabidoux, P. A. *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *5130*, 58.
(82) Yasin, S.; Hasko, D. G.; Ahmed, H. *Appl. Phys. Lett.* **2001**, *78*, 2760.
(83) Hu, W.; Sarveswaran, K.; Lieberman, M.; Bernstein, G. H. *J. Vac. Sci. Technol. B* **2004**, *22*, 1711.
(84) Gamo, K. *Microelectron. Eng.* **1996**, *32*, 159.
(85) Morita, T.; Kometani, R.; Watanabe, K.; Kanda, K.; Haruyama, Y.; Hoshino, T.; Kondo, K.; Kaito, T.; Ichihashi, T.; Fujita, J.-i.; Ishida, M.; Ochiai, Y.; Tajima, T.; Matsui, S. *J. Vac. Sci. Technol. B* **2003**, *21*, 2737.
(86) Prewett, P. D.; Gentili, M.; Maggiora, R.; Mastrogiacomo, L.; Watson, J. G.; Turner, G. S.; Brown, G. W.; Plumb, D.; Leonard, Q.; Cerrina, F. *Microelectron. Eng.* **1992**, *17*, 249.
(87) Blauner, P. G.; Ro, J. S.; Butt, Y.; Thompson, C. V.; Melngailis, J. *Mater. Res. Soc. Symp. Proc.* **1989**, *129*, 483.
(88) Kubena, R. L. *Mater. Res. Soc. Symp. Proc.* **1993**, *279*, 567.
(89) Xia, Y.; McClelland, J. J.; Gupta, R.; Qin, D.; Zhao, X. M.; Sohn, L. L.; Celotta, R. J.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 147.
(90) Zhao, X. M.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 837.

(91) Kim, E.; Xia, Y.; Whitesides, G. M. *Nature* **1995**, *376*, 581.
(92) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Appl. Phys. Lett.* **1995**, *67*, 3114.
(93) Kim, E.; Xia, Y.; Zhao, X. M.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 651.
(94) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem., Int. Ed.* **1989**, *101*, 1475.
(95) Kikuchi, A.; Coulter, J. P.; Angstadt, D. C. *J. Inject. Mold. Technol.* **2002**, *6*, 91.
(96) Schift, H.; David, C.; Gobrecht, J.; D'Amore, A.; Simoneta, D.; Kaiser, W.; Gabriel, M. *J. Vac. Sci. Technol. B* **2000**, *18*, 3564.
(97) Schift, H.; David, C.; Gabriel, M.; Gobrecht, J.; Heyderman, L. J.; Kaiser, W.; Koppel, S.; Scandella, L. *Microelectron. Eng.* **2000**, *53*, 171.
(98) Schift, H.; Heyderman, L. J.; Gobrecht, J. *Chimia* **2003**, *56*, 543.
(99) Gadegaard, N.; Mosler, S.; Larsen, N. B. *Macromol. Mater. Eng.* **2003**, *288*, 76.
(100) Janucki, J.; Owsik, J. *Opt. Commun.* **2003**, *228*, 63.
(101) Colburn, W. S. *J. Imag. Sci. Technol.* **1997**, *41*, 443.
(102) Zhang, W.; Chou, S. Y. *Appl. Phys. Lett.* **2003**, *83*, 1632.
(103) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *J. Vac. Sci. Technol. B* **1996**, *14*, 4129.
(104) Smith, B. J.; Stacey, N. A.; Donnelly, J. P.; Onsongo, D. M.; Bailey, T. C.; Mackay, C. J.; Resnick, D. J.; Dauksher, W. J.; Mancini, D. P.; Nordquist, K. J.; Sreenivasan, S. V.; Banerjee, S. K.; Ekerdt, J. G.; Willson, C. G. *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *5037*, 1029.
(105) Colburn, M.; Grot, A.; Amistoso, M. N.; Choi, B. J.; Bailey, T. C.; Ekerdt, J. G.; Sreenivasan, S. V.; Hollenhorst, J.; Willson, C. G. *Proc. SPIE-Int. Soc. Opt. Eng.* **2000**, *3997*, 453.
(106) Chou, S. Y.; Keimel, C.; Gu, J. *Nature* **2002**, *417*, 835.
(107) Chou, S. Y.; Krauss, P. R. *Microelectron. Eng.* **1997**, *35*, 237.
(108) Resnick, D. J.; Mancini, D.; Dauksher, W. J.; Nordquist, K.; Bailey, T. C.; Johnson, S.; Sreenivasan, S. V.; Ekerdt, J. G.; Willson, C. G. *Microelectron. Eng.* **2003**, *69*, 412.
(109) Resnick, D. J.; Dauksher, W. J.; Mancini, D. P.; Nordquist, K. J.; Ainley, E. S.; Gehoski, K. A.; Baker, J. H.; Bailey, T. C.; Choi, B. J.; Johnson, S.; Sreenivasan, S. V.; Ekerdt, J. G.; Willson, C. G. *Proc. SPIE-Int. Soc. Opt. Eng.* **2002**, *4688*, 205.
(110) Resnick, D. J.; Dauksher, W. J.; Mancini, D.; Nordquist, K. J.; Ainley, E.; Gehoski, K.; Baker, J. H.; Bailey, T. C.; Choi, B. J.; Johnson, S.; Sreenivasan, S. V.; Ekerdt, J. G.; Willson, C. G. *J. Microlith. Microfab. Microsys.* **2002**, *1*, 284.
(111) Johnson, S. C.; Bailey, T. C.; Dickey, M. D.; Smith, B. J.; Kim, E. K.; Jamieson, A. T.; Stacey, N. A.; Ekerdt, J. G.; Willson, C. G.; Mancini, D. P.; Dauksher, W. J.; Nordquist, K. J.; Resnick, D. J. *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *5037*, 197.
(112) Resnick, D. J.; Dauksher, W. J.; Mancini, D. P.; Nordquist, K. J.; Bailey, T. C.; Johnson, S. C.; Stacey, N. A.; Ekerdt, J. G.; Willson, C. G.; Sreenivasan, S. V.; Schumaker, N. E. *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *5037*, 12.
(113) Jung, G. Y.; Ganapathiappan, S.; Ohlberg, D. A. A.; Olynick, D. L.; Chen, Y.; Tong, W. M.; Williams, R. S. *Nano Lett.* **2004**, *4*, 1225.
(114) Scheer, H. C.; Schulz, H.; Hoffmann, T.; Sotomayor Torres, C. M. *J. Vac. Sci. Technol. B* **1998**, *16*, 3917.
(115) Scheer, H. C.; Schulz, H. *Microelectron. Eng.* **2001**, *56*, 311.
(116) McMackin, I. *Proc. SPIE-Int. Soc. Opt. Eng.* **2004**, *5347*, 232.
(117) Ruchhoeft, P.; Colburn, M.; Choi, B.; Nounu, H.; Johnson, S.; Bailey, T.; Darmle, S.; Stewart, M.; Ekerdt, J.; Sreenivasan, S. V.; Wolfe, J. C.; Willson, C. G. *J. Vac. Sci. Technol. B* **1999**, *17*, 2965.
(118) Colburn, M.; Grot, A.; Choi, B. J.; Amistoso, M.; Bailey, T.; Sreenivasan, S. V.; Ekerdt, J. G.; Grant Willson, C. *J. Vac. Sci. Technol. B* **2001**, *19*, 2162.
(119) Stewart, M. D.; Johnson, S. C.; Sreenivasan, S. V.; Willson, C. G. *J. Microlithogr., Microfabr., Microsyst.* **2005**, *4*, in press.
(120) Roos, N.; Luxbacher, T.; Glinsner, T.; Pfeiffer, K.; Schulz, H.; Scheer, H.-C. *Proc. SPIE-Int. Soc. Opt. Eng.* **2001**, *4343*, 427.
(121) Tan, H.; Gilbertson, A.; Chou, S. Y. *J. Vac. Sci. Technol. B* **1998**, *16*, 3926.
(122) Haatainen, T.; Ahopelto, J. *Phys. Scr.* **2003**, *67*, 357.
(123) Austin, M. D.; Ge, H.; Wu, W.; Li, M.; Yu, Z.; Wasserman, D.; Lyon, S. A.; Chou, S. Y. *Appl. Phys. Lett.* **2004**, *84*, 5299.
(124) Ansari, K.; van Kan, J. A.; Bettiol, A. A.; Watt, F. *Appl. Phys. Lett.* **2004**, *85*, 476.
(125) Hoff, J. D.; Cheng, L.-J.; Meyhoefer, E.; Guo, L. J.; Hunt, A. J. *Nano Lett.* **2004**, *4*, 853.
(126) Li, H.-W.; Huck, W. T. S. *Nano Lett.* **2004**, *4*, 1633.
(127) Behl, M.; Seekamp, J.; Zankovych, S.; Torres, C. M. S.; Zentel, R.; Ahopelto, J. *Adv. Mater.* **2002**, *14*, 588.
(128) Makela, T.; Haatainen, T.; Ahopelto, J.; Isotalo, H. *J. Vac. Sci. Technol. B* **2001**, *19*, 487.
(129) Finder, C.; Beck, M.; Seekamp, J.; Pfeiffer, K.; Carlberg, P.; Maximov, I.; Reuther, F.; Sarwe, E. L.; Zankovych, S.; Ahopelto, J.; Montelius, L.; Mayer, C.; Sotomayor Torres, C. M. *Microelectron. Eng.* **2003**, *67*–*68*, 623.
(130) Sotomayor Torres, C. M.; Zankovych, S.; Seekamp, J.; Kam, A. P.; Clavijo Cedeno, C.; Hoffmann, T.; Ahopelto, J.; Reuther, F.; Pfeiffer, K.; Bleidiessel, G.; Gruetzner, G.; Maximov, M. V.; Heidari, B. *Mater. Sci. Eng., C* **2003**, *23*, 23.
(131) Li, M.; Wang, J.; Zhuang, L.; Chou, S. Y. *Appl. Phys. Lett.* **2000**, *76*, 673.
(132) Xia, Q.; Keimel, C.; Ge, H.; Yu, Z.; Wu, W.; Chou, S. Y. *Appl. Phys. Lett.* **2003**, *83*, 4417.
(133) Grigaliunas, V.; Tamulevicius, S.; Tomasiunas, R.; Kopustinskas, V.; Guobiene, A.; Jucius, D. *Thin Solid Films* **2004**, *453*–*454*, 13.
(134) McAlpine, M. C.; Friedman, R. S.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 443.
(135) Khang, D.-Y.; Yoon, H.; Lee, H. H. *Adv. Mater.* **2001**, *13*, 749.
(136) Otto, M.; Bender, M.; Hadam, B.; Spangenberg, B.; Kurz, H. *Microelectron. Eng.* **2001**, *57*–*58*, 361.
(137) Schulz, H.; Wissen, M.; Scheer, H. C. *Microelectron. Eng.* **2003**, *67*–*68*, 657.
(138) Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002.
(139) Fichet, G.; Stutzmann, N.; Muir, B. V. O.; Huck, W. T. S. *Adv. Mater.* **2002**, *14*, 47.
(140) Trimbach, D.; Feldman, K.; Spencer, N. D.; Broer, D. J.; Bastiaansen, C. W. M. *Langmuir* **2003**, *19*, 10957.
(141) Tsibouklis, J.; Nevell, T. G. *Adv. Mater.* **2003**, *15*, 647.
(142) Rolland, J. P.; Van Dam, R. M.; Schorzman, D. A.; Quake, S. R.; DeSimone, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 2322.
(143) Rolland, J. P.; Hagberg, E. C.; Denison, G. M.; Carter, K. R.; De Simone, J. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5796.
(144) Csucs, G.; Kuenzler, T.; Feldman, K.; Robin, F.; Spencer, N. D. *Langmuir* **2003**, *19*, 6104.
(145) Choi, S. J.; Yook, P. J.; Baek, S. J.; Kim, T. W.; Lee, H. H. *J. Am. Chem. Soc.* **2004**, *126*, 7744.
(146) Khang, D.-Y.; Lee, H. H. *Langmuir* **2004**, *20*, 2445.
(147) Lee, J. N.; Park, C.; Whitesides, G. M. *Anal. Chem.* **2003**, *75*, 6544.
(148) DowCorning (http://www.dowcorning.com/).
(149) Gelest (http://www.gelest.com).
(150) Childs, W. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 13583.
(151) Childs, W. R.; Nuzzo, R. G. *Adv. Mater.* **2004**, *16*, 1323.
(152) Clarson, S. J.; Semlyen, J. A. *Siloxane polymers*; Prentice Hall: Englewood Cliffs, NJ, 1993.
(153) Perutz, S.; Wang, J.; Kramer, E. J.; Ober, C. K.; Ellis, K. *Macromolecules* **1998**, *31*, 4272.
(154) Chaudhury, M. K.; Whitesides, G. M. *Langmuir* **1991**, *7*, 1013.
(155) Kim, C.-J.; Kim, J. Y.; Sridharan, B. *Sens. Actuators A* **1998**, *64*, 17.
(156) Delamarche, E.; Schmid, H.; Michel, B.; Biebuyck, H. *Adv. Mater.* **1997**, *9*, 741.
(157) Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *J. Vac. Sci. Technol. B* **1998**, *16*, 88.
(158) Hui, C. Y.; Jagota, A.; Lin, Y. Y.; Kramer, E. J. *Langmuir* **2002**, *18*, 1394.
(159) Odom, T. W.; Love, J. C.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. *Langmuir* **2002**, *18*, 5314.
(160) Bietsch, A.; Michel, B. *J. Appl. Phys.* **2000**, *88*, 4310.
(161) Schmid, H.; Michel, B. *Macromolecules* **2000**, *33*, 3042.
(162) Odom, T. W.; Thalladi, V. R.; Love, J. C.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 12112.
(163) Gates, B. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 14986.
(164) Choi, K. M.; Rogers, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 4060.
(165) Xia, Y.; Whitesides, G. M. *Polym. Mater. Sci. Eng.* **1997**, *77*, 596.
(166) Deng, Z.; Mao, C. *Langmuir* **2004**, *20*, 8078.
(167) Kim, D. H.; Lin, Z.; Kim, H.-C.; Jeong, U.; Russell, T. P. *Adv. Mater.* **2003**, *15*, 811.
(168) Hua, F.; Sun, Y.; Gaur, A.; Meitl, M.; Bilhaut, L.; Rotkina, L.; Wang, J. F.; Geil, P.; Shim, M.; Rogers, J. A.; Shim, A. *Nano Lett.* **2004**, *4*, 2467.
(169) Xu, Q.; Mayers, B.; Lahav, M.; Vezenov, D. V.; Whitesides, G. M. *J. Am. Chem. Soc.* **2005**, *127*, in press.
(170) Dujardin, E.; Ebbesen, T. W.; Hiura, H.; Tanigaki, K. *Science* **1994**, *265*, 1850.
(171) Martin, C. R. *Science* **1994**, *266*, 1961.
(172) Jeon, N. L.; Choi, I. S.; Xu, B.; Whitesides, G. M. *Adv. Mater.* **1999**, *11*, 946.
(173) Pisignano, D.; Sariconi, E.; Mazzeo, M.; Gigli, G.; Cingolani, R. *Adv. Mater.* **2002**, *14*, 1565.
(174) Zhao, X. M.; Xia, Y. N.; Whitesides, G. M. *J. Mater. Chem.* **1997**, *7*, 1069.
(175) LaFratta, C. N.; Baldacchini, T.; Farrer, R. A.; Fourkas, J. T.; Teich, M. C.; Saleh, B. E. A.; Naughton, M. J. *J. Phys. Chem. B* **2004**, *108*, 11256.
(176) Leung, W. Y.; Kang, H.; Constant, K.; Cann, D.; Kim, C. H.; Biswas, R.; Sigalas, M. M.; Ho, K. M. *J. Appl. Phys.* **2003**, *93*, 5866.
(177) Rogers, J. A.; Bao, Z.; Dhar, L. *Appl. Phys. Lett.* **1998**, *73*, 294.
(178) Lawrence, J. R.; Turnbull, G. A.; Samuel, I. D. W. *Appl. Phys. Lett.* **2003**, *82*, 4023.
(179) Kim, Y. S.; Park, J.; Lee, H. H. *Appl. Phys. Lett.* **2002**, *81*, 1011.
(180) Duineveld, P. C.; Lilja, M.; Johansson, T.; Inganaes, O. *Langmuir* **2002**, *18*, 9554.

(181) Israelachvili, J. N. *Intermolecular and Surface Forces*; McGraw-Hill Publishing Co.: Tokyo, Japan, 1991.
(182) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
(183) Abdo, A. Y.; Zheng, L.; Wei, A.; Mikkelson, A.; Nellis, G.; Engelstad, R. L.; Lovell, E. G. *Microelectron. Eng.* **2004**, *73*−*74*, 161.
(184) Rogers, J. A.; Bao, Z.; Meier, M.; Dodabalapur, A.; Schueller, O. J. A.; Whitesides, G. M. *Synth. Met.* **2000**, *115*, 5.
(185) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.
(186) Xia, Y.; Zhao, X.-M.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 2332.
(187) Kumar, A.; Abbott, N. L.; Biebuyck, H. A.; Kim, E.; Whitesides, G. M. *Acc. Chem. Res.* **1995**, *28*, 219.
(188) Wilbur, J. L.; Kumar, A.; Kim, E.; Whitesides, G. M. *Adv. Mater.* **1994**, *6*, 600.
(189) Delamarche, E.; Geissler, M.; Wolf, H.; Michel, B. *J. Am. Chem. Soc.* **2002**, *124*, 3834.
(190) Love, J. C.; Wolfe, D. B.; Chabinyc, M. L.; Paul, K. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 1576.
(191) Koide, Y.; Such, M. W.; Basu, R.; Evmenenko, G.; Cui, J.; Dutta, P.; Hersam, M. C.; Marks, T. J. *Langmuir* **2003**, *19*, 86.
(192) Geissler, M.; Wolf, H.; Stutz, R.; Delamarche, E.; Grummt, U.-W.; Michel, B.; Bietsch, A. *Langmuir* **2003**, *19*, 6301.
(193) Geissler, M.; Schmid, H.; Bietsch, A.; Michel, B.; Delamarche, E. *Langmuir* **2002**, *18*, 2374.
(194) Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3274.
(195) Biebuyck, H. A.; Larsen, N. B.; Delamarche, E.; Michel, B. *IBM J. Res. Dev.* **1997**, *41*, 159.
(196) Li, S. P.; Natali, M.; Lebib, A.; Pepin, A.; Chen, Y.; Xu, Y. B. *J. Magn. Magn. Mater.* **2002**, *241*, 447.
(197) Rogers, J. A.; Baldwin, K.; Bao, Z.; Dodabalapur, A.; Raju, V. R.; Ewing, J.; Amundson, K. *Mater. Res. Soc. Symp. Proc.* **2001**, *660*, JJ7 1/1.
(198) Xia, Y.; Qin, D.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 1015.
(199) Tien, J.; Terfort, A.; Whitesides, G. M. *Langmuir* **1997**, *13*, 5349.
(200) Rogers, J. A.; Jackman, R. J.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 475.
(201) Jackman, R. J.; Wilbur, J. L.; Whitesides, G. M. *Science* **1995**, *269*, 664.
(202) Delamarche, E.; Donzel, C.; Kamounah, F. S.; Wolf, H.; Geissler, M.; Stutz, R.; Schmidt-Winkel, P.; Michel, B.; Mathieu, H. J.; Schaumburg, K. *Langmuir* **2003**, *19*, 8749.
(203) Donzel, C.; Geissler, M.; Bernard, A.; Wolf, H.; Michel, B.; Hilborn, J.; Delamarche, E. *Adv. Mater.* **2001**, *13*, 1164.
(204) Hyun, J.; Ma, H.; Zhang, Z.; Beebe, T. P., Jr.; Chilkoti, A. *Adv. Mater.* **2003**, *15*, 576.
(205) Kunzler, J. F.; Salamone, J. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2003**, *44*, 215.
(206) Lange, S. A.; Benes, V.; Kern, D. P.; Hoerber, J. K. H.; Bernard, A. *Anal. Chem.* **2004**, *76*, 1641.
(207) Bernard, A.; Renault, J. P.; Michel, B.; Bosshard, H. R.; Delamarche, E. *Adv. Mater.* **2000**, *12*, 1067.
(208) Bernard, A.; Delamarche, E.; Schmid, H.; Michel, B.; Bosshard, H. R.; Biebuyck, H. *Langmuir* **1998**, *14*, 2225.
(209) James, C. D.; Davis, R. C.; Kam, L.; Craighead, H. G.; Isaacson, M.; Turner, J. N.; Shain, W. *Langmuir* **1998**, *14*, 741.
(210) Branch, D. W.; Corey, J. M.; Weyhenmeyer, J. A.; Brewer, G. J.; Wheeler, B. C. *Med. Biol. Eng. Comput.* **1998**, *36*, 135.
(211) Csucs, G.; Michel, R.; Lussi Jost, W.; Textor, M.; Danuser, G. *Biomaterials* **2003**, *24*, 1713.
(212) Renault, J. P.; Bernard, A.; Juncker, D.; Michel, B.; Bosshard, H. R.; Delamarche, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 2320.
(213) Bernard, A.; Fitzli, D.; Sonderegger, P.; Delamarche, E.; Michel, B.; Bosshard, H. R.; Biebuyck, H. *Nat. Biotech.* **2001**, *19*, 866.
(214) Hidber, P. C.; Helbig, W.; Kim, E.; Whitesides, G. M. *Langmuir* **1996**, *12*, 1375.
(215) Santhanam, V.; Liu, J.; Agarwal, R.; Andres, R. P. *Langmuir* **2003**, *19*, 7881.
(216) Shin, H. S.; Yang, H. J.; Jung, Y. M.; Kim, S. B. *Vib. Spectrosc.* **2002**, *29*, 79.
(217) Cherniavskaya, O.; Adzic, A.; Knutson, C.; Gross, B. J.; Zang, L.; Liu, R.; Adams, D. M. *Langmuir* **2002**, *18*, 7029.
(218) Choi, D.-G.; Yu, H. K.; Yang, S.-M. *Mater. Sci. Eng., C* **2004**, *C24*, 213.
(219) Wang, M.; Braun, H.-G.; Kratzmuller, T.; Meyer, E. *Adv. Mater.* **2001**, *13*, 1312.
(220) Li, H.-W.; Muir, B. V. O.; Fichet, G.; Huck, W. T. S. *Langmuir* **2003**, *19*, 1963.
(221) Jacobs, H. O.; Whitesides, G. M. *Science* **2001**, *291*, 1763.
(222) Loo, Y.-L.; Hsu, J. W. P.; Willett, R. L.; Baldwin, K. W.; West, K. W.; Rogers, J. A. *J. Vac. Sci. Technol. B* **2002**, *20*, 2853.
(223) Wolfe, D. B.; Love, J. C.; Gates, B. D.; Whitesides, G. M.; Conroy, R. S.; Prentiss, M. *Appl. Phys. Lett.* **2004**, *84*, 1623.
(224) Jacobs, H. O.; Campbell, S. A.; Steward, M. G. *Adv. Mater.* **2002**, *14*, 1553.
(225) Jacobs, H. O.; Stemmer, A. *Surf. Interface Anal.* **1999**, *27*, 361.
(226) Wiles, J. A.; Grzybowski, B. A.; Winkleman, A.; Whitesides, G. M. *Anal. Chem.* **2003**, *75*, 4859.
(227) Grzybowski, B. A.; Winkleman, A.; Wiles, J. A.; Brumer, Y.; Whitesides, G. M. *Nat. Mater.* **2003**, *2*, 241.
(228) Ferreira, G. F. L.; Figueiredo, M. T. *IEEE Trans. Electron. Insul.* **1992**, *27*, 719.
(229) Mesquida, P.; Stemmer, A. *Adv. Mater.* **2001**, *13*, 1395.
(230) Stemmer, A.; Mesquida, P.; Naujoks, N. *Chimia* **2003**, *56*, 573.
(231) Mesquida, P.; Knapp, H. F.; Stemmer, A. *Surf. Interface Anal.* **2002**, *33*, 159.
(232) Barry, C. R.; Lwin, N. Z.; Zheng, W.; Jacobs, H. O. *Appl. Phys. Lett.* **2003**, *83*, 5527.
(233) Barry, C. R.; Steward, M. G.; Lwin, N. Z.; Jacobs, H. O. *Nanotechnology* **2003**, *14*, 1057.
(234) Loo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 7654.
(235) Loo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *Appl. Phys. Lett.* **2002**, *81*, 562.
(236) Zaumseil, J.; Meitl, M. A.; Hsu, J. W. P.; Acharya, B. R.; Baldwin, K. W.; Loo, Y.-L.; Rogers, J. A. *Nano Lett.* **2003**, *3*, 1223.
(237) Schmid, H.; Wolf, H.; Allenspach, R.; Riel, H.; Karg, S.; Michel, B.; Delamarche, E. *Adv. Funct. Mater.* **2003**, *13*, 145.
(238) Kim, C.; Shtein, M.; Forrest, S. R. *Appl. Phys. Lett.* **2002**, *80*, 4051.
(239) Wang, Z.; Yuan, J.; Zhang, J.; Xing, R.; Yan, D.; Han, Y. *Adv. Mater.* **2003**, *15*, 1009.
(240) Schaper, C. D. *Nano Lett.* **2003**, *3*, 1305.
(241) Jeon, S.; Menard, E.; Park, J.-U.; Maria, J.; Meitl, M.; Zaumseil, J.; Rogers, J. A. *Adv. Mater.* **2004**, *16*, 1369.
(242) Menard, E.; Bilhaut, L.; Zaumseil, J.; Rogers, J. A. *Langmuir* **2004**, *20*, 6871.
(243) Lasky, J. B. *Appl. Phys. Lett.* **1986**, *48*, 78.
(244) Tong, Q. Y. *Mater. Sci. Eng., B* **2001**, *B87*, 323.
(245) Helt, J. M.; Drain, C. M.; Batteas, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 628.
(246) Loo, Y.-L.; Lang, D. V.; Rogers, J. A.; Hsu, J. W. P. *Nano Lett.* **2003**, *3*, 913.
(247) Jackman, R. J.; Duffy, D. C.; Cherniavskaya, O.; Whitesides, G. M. *Langmuir* **1999**, *15*, 2973.
(248) Jackman, R. J.; Duffy, D. C.; Ostuni, E.; Willmore, N. D.; Whitesides, G. M. *Anal. Chem.* **1998**, *70*, 2280.
(249) Li, H.; Kang, D.-J.; Blamire, M. G.; Huck, W. T. S. *Nano Lett.* **2002**, *2*, 347.
(250) Hong, S.; Mirkin, C. A. *Science* **2000**, *288*, 1808.
(251) Hong, S.; Zhu, J.; Mirkin, C. A. *Science* **1999**, *286*, 523.
(252) Ryu, K. S.; Wang, X.; Shaikh, K.; Bullen, D.; Goluch, E.; Zou, J.; Liu, C.; Mirkin, C. A. *Appl. Phys. Lett.* **2004**, *85*, 136.
(253) Lee, K.-B.; Lim, J.-H.; Mirkin, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 5588.
(254) Smith, J. C.; Lee, K.-B.; Wang, Q.; Finn, M. G.; Johnson, J. E.; Mrksich, M.; Mirkin, C. A. *Nano Lett.* **2003**, *3*, 883.
(255) Lee, K.-B.; Kim, E.-Y.; Mirkin, C. A.; Wolinsky, S. M. *Nano Lett.* **2004**, *4*, 1869.
(256) Nam, J.-M.; Han, S. W.; Lee, K.-B.; Liu, X.; Ratner, M. A.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1246.
(257) Zhang, H.; Mirkin, C. A. *Chem. Mater.* **2004**, *16*, 1480.
(258) Zhang, H.; Chung, S.-W.; Mirkin, C. A. *Nano Lett.* **2003**, *3*, 43.
(259) Rozhok, S.; Piner, R.; Mirkin, C. A. *J. Phys. Chem. B* **2003**, *107*, 751.
(260) Schwartz, P. V. *Langmuir* **2001**, *17*, 5971.
(261) Schwartz, P. V. *Langmuir* **2002**, *18*, 4041.
(262) Jang, J.; Schatz, G. C.; Ratner, M. A. *Phys. Rev. Lett.* **2004**, *92*, 08550401.
(263) Jang, J.; Schatz, G. C.; Ratner, M. A. *Phys. Rev. Lett.* **2003**, *90*, 15610401.
(264) Jang, J.; Hong, S.; Schatz, G. C.; Ratner, M. A. *J. Chem. Phys.* **2001**, *115*, 2721.
(265) Liu, J.-F.; Cruchon-Dupeyrat, S.; Garno, J. C.; Frommer, J.; Liu, G.-Y. *Nano Lett.* **2002**, *2*, 937.
(266) Liu, G.-Y.; Xu, S.; Qian, Y. *Acc. Chem. Res.* **2000**, *33*, 457.
(267) Rolandi, M.; Suez, I.; Dai, H.; Frechet, J. M. J. *Nano Lett.* **2004**, *4*, 889.
(268) Garno, J. C.; Yang, Y.; Amro, N. A.; Cruchon-Dupeyrat, S.; Chen, S.; Liu, G.-Y. *Nano Lett.* **2003**, *3*, 389.
(269) Carpick, R. W.; Salmeron, M. *Chem. Rev.* **1997**, *97*, 1163.
(270) Porter, L. A., Jr.; Ribbe, A. E.; Buriak, J. M. *Nano Lett.* **2003**, *3*, 1043.
(271) Bouzehouane, K.; Fusil, S.; Bibes, M.; Carrey, J.; Blon, T.; Du, M. L.; Seneor, P.; Cros, V.; Vila, L. *Nano Lett.* **2003**, *3*, 1599.
(272) Dagata, J. A.; Schneir, J.; Harary, H. H.; Evans, C. J.; Postek, M. T.; Bennett, J. *Appl. Phys. Lett.* **1990**, *56*, 2001.
(273) Snow, E. S.; Campbell, P. M.; McMarr, P. J. *Appl. Phys. Lett.* **1993**, *63*, 749.
(274) Snow, E. S.; Campbell, P. M. *Appl. Phys. Lett.* **1994**, *64*, 1932.
(275) Day, H. C.; Allee, D. R. *Appl. Phys. Lett.* **1993**, *62*, 2691.
(276) Song, H. J.; Rack, M. J.; Abugharbieh, K.; Lee, S. Y.; Khan, V.; Ferry, D. K.; Allee, D. R. *J. Vac. Sci. Technol. B* **1994**, *12*, 3720.
(277) Gwo, S.; Yeh, C. L.; Chen, P. F.; Chou, Y. C.; Chen, T. T.; Chao, T. S.; Hu, S. F.; Huang, T. Y. *Appl. Phys. Lett.* **1999**, *74*, 1090.

(278) Dai, H.; Franklin, N.; Han, J. *Appl. Phys. Lett.* **1998**, *73*, 1508.
(279) Liu, S.; Maoz, R.; Schmid, G.; Sagiv, J. *Nano Lett.* **2002**, *2*, 1055.
(280) Maoz, R.; Frydman, E.; Cohen, S. R.; Sagiv, J. *Adv. Mater.* **2000**, *12*, 725.
(281) Sun, S.; Leggett, G. J. *Nano Lett.* **2002**, *2*, 1223.
(282) Sun, S.; Chong, K. S. L.; Leggett, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 2414.
(283) Sun, S.; Leggett, G. J. *Nano Lett.* **2004**, *4*, 1381.
(284) Vettiger, P.; Brugger, J.; Despont, M.; Drechsler, U.; Durig, U.; Haberle, W.; Lutwyche, M.; Rothuizen, H.; Stutz, R.; Widmer, R.; Binnig, G. *Microelectron. Eng.* **1999**, *46*, 11.
(285) Vettiger, P.; Despont, M.; Drechsler, U.; Durig, U.; Haberle, W.; Lutwyche, M. I.; Rothuizen, H. E.; Stutz, R.; Widmer, R.; Binnig, G. K. *IBM J. Res. Dev.* **2000**, *44*, 323.
(286) Vettiger, P.; Binnig, G. *Sci. Am.* **2003**, *1*, 47.
(287) Bullen, D.; Chung, S.-W.; Wang, X.; Zou, J.; Mirkin, C. A.; Liu, C. *Appl. Phys. Lett.* **2004**, *84*, 789.
(288) Zhang, M.; Bullen, D.; Chung, S.-W.; Hong, S.; Ryu, K. S.; Fan, Z.; Mirkin, C. A.; Liu, C. *Nanotechnology* **2002**, *13*, 212.
(289) Minne, S. C.; Flueckiger, P.; Soh, H. T.; Quate, C. F. *J. Vac. Sci. Technol. B* **1995**, *13*, 1380.
(290) Despont, M.; Brugger, J.; Drechsler, U.; Durig, U.; Haberle, W.; Lutwyche, M.; Rothuizen, H.; Stutz, R.; Widmer, R.; Rohrer, H.; Binnig, G.; Vettiger, P. *Technical Digest 12th IEEE Int'l Micro Electro Mechanical Systems Conf. "MEMS '99"*, Orlando, FL, 1999, p 564.
(291) Black, A. J.; Paul, K. E.; Aizenberg, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 8356.
(292) Rogers, J. A.; Paul, K. E.; Jackman, R. J.; Whitesides, G. M. *Appl. Phys. Lett.* **1997**, *70*, 2658.
(293) Fasol, G. *Science* **1998**, *280*, 545.
(294) Nichols, R. J.; Kolb, D. M.; Behm, R. J. *J. Electroanal. Chem. Interface Electrochem.* **1991**, *313*, 109.
(295) Himpsel, F. J.; Ortega, J. E. *Phys. Rev. B* **1994**, *50*, 4992.
(296) Himpsel, F. J.; Jung, T.; Kirakosian, A.; Lin, J. L.; Petrovykh, D. Y.; Rauscher, H.; Viernow, J. *MRS Bull.* **1999**, *24*, 20.
(297) Dekoster, J.; Degroote, B.; Pattyn, H.; Langouche, G.; Vantomme, A.; Degroote, S. *Appl. Phys. Lett.* **1999**, *75*, 938.
(298) Love, J. C.; Paul, K. E.; Whitesides, G. M. *Adv. Mater.* **2001**, *13*, 604.
(299) Mundschau, M.; Bauer, E.; Telieps, W.; Swiech, W. *J. Appl. Phys.* **1989**, *65*, 4747.
(300) Jung, T.; Mo, Y. W.; Himpsel, F. J. *Phys. Rev. Lett.* **1995**, *74*, 1641.
(301) de la Figuera, J.; Huerta-Garnica, M. A.; Prieto, J. E.; Ocal, C.; Miranda, R. *Appl. Phys. Lett.* **1995**, *66*, 1006.
(302) Jung, T.; Schlittler, R.; Gimzewski, J. K.; Himpsel, F. J. *Appl. Phys. A* **1995**, *61*, 467.
(303) Gambardella, P.; Blanc, M.; Brune, H.; Kuhnke, K.; Kern, K. *Phys. Rev. B* **2000**, *61*, 2254.
(304) Morin, S.; Lachenwitzer, A.; Magnussen, O. M.; Behm, R. J. *Phys. Rev. Lett.* **1999**, *83*, 5066.
(305) Petrovykh, D. Y.; Himpsel, F. J.; Jung, T. *Surf. Sci.* **1998**, *407*, 189.
(306) Hahn, E.; Schief, H.; Marsico, V.; Fricke, A.; Kern, K. *Phys. Rev. Lett.* **1994**, *72*, 3378.
(307) Otero, R.; Rosei, F.; Naitoh, Y.; Jiang, P.; Thostrup, P.; Gourdon, A.; Laegsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. *Nano Lett.* **2004**, *4*, 75.
(308) Penner, R. M. *J. Phys. Chem. B* **2002**, *106*, 3339.
(309) Walter, E. C.; Murray, B. J.; Favier, F.; Kaltenpoth, G.; Grunze, M.; Penner, R. M. *J. Phys. Chem. B* **2002**, *106*, 11407.
(310) Favier, F.; Walter, E. C.; Zach, M. P.; Benter, T.; Penner, R. M. *Science* **2001**, *293*, 2227.
(311) Menke, E. J.; Li, Q.; Penner, R. M. *Nano Lett.* **2004**, *4*, 2009.
(312) Li, Q.; Olson, J. B.; Penner, R. M. *Chem. Mater.* **2004**, *16*, 3402.
(313) Li, Q.; Newberg, J. T.; Walter, E. C.; Hemminger, J. C.; Penner, R. M. *Nano Lett.* **2004**, *4*, 277.
(314) Murray, B. J.; Walter, E. C.; Penner, R. M. *Nano Lett.* **2004**, *4*, 665.
(315) Walter, E. C.; Favier, F.; Penner, R. M. *Anal. Chem.* **2002**, *74*, 1546.
(316) Kaltenpoth, G.; Schnabel, P.; Menke, E.; Walter, E. C.; Grunze, M.; Penner, R. M. *Anal. Chem.* **2003**, *75*, 4756.
(317) Sundar, V. C.; Aizenberg, J. *Appl. Phys. Lett.* **2003**, *83*, 2259.
(318) Yang, H.; Love, J. C.; Arias, F.; Whitesides, G. M. *Chem. Mater.* **2002**, *14*, 1385.
(319) Prober, D. E.; Feuer, M. D.; Giordano, N. *Appl. Phys. Lett.* **1980**, *37*, 94.
(320) Tas, N. R.; Berenschot, J. W.; Mela, P.; Jansen, H. V.; Elwenspoek, M.; van den Berg, A. *Nano Lett.* **2002**, *2*, 1031.
(321) Choi, Y.-K.; Zhu, J.; Grunes, J.; Bokor, J.; Somorjai, G. A. *J. Phys. Chem. B* **2003**, *107*, 3340.
(322) Greyson, E. C.; Babayan, Y.; Odom, T. W. *Adv. Mater.* **2004**, *16*, 1348.
(323) Rogers, J. A.; Paul, K. E.; Jackman, R. J.; Whitesides, G. M. *J. Vac. Sci. Technol. B* **1998**, *16*, 59.
(324) Li, Z.-Y.; Yin, Y.; Xia, Y. *Appl. Phys. Lett.* **2001**, *78*, 2431.
(325) Maria, J.; Jeon, S.; Rogers, J. A. *J. Photochem. Photobiol., A* **2004**, *166*, 149.
(326) Yin, Y.; Gates, B.; Xia, Y. *Adv. Mater.* **2000**, *12*, 1426.
(327) Rogers, J. A.; Dodabalapur, A.; Bao, Z.; Katz, H. E. *Appl. Phys. Lett.* **1999**, *75*, 1010.
(328) Paul, K. E.; Zhu, C.; Love, J. C.; Whitesides, G. M. *Appl. Opt.* **2001**, *40*, 4557.
(329) Aizenberg, J.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Appl. Opt.* **1998**, *37*, 2145.
(330) Babayan, Y.; Barton, J. E.; Greyson, E. C.; Odom, T. W. *Adv. Mater.* **2004**, *16*, 1341.
(331) Crowell, J. E. *J. Vac. Sci. Technol. A* **2003**, *21*, S88.
(332) Rossnagel, S. M. *J. Vac. Sci. Technol. A* **2003**, *21*, S74.
(333) Fasol, G.; Runge, K. *Appl. Phys. Lett.* **1997**, *70*, 2467.
(334) Chopra, N.; Kichambare, P. D.; Andrews, R.; Hinds, B. J. *Nano Lett.* **2002**, *2*, 1177.
(335) Morris, R. B.; Franta, D. J.; White, H. S. *J. Phys. Chem.* **1987**, *91*, 3559.
(336) Stormer, H. L.; Baldwin, K. W.; Pfeiffer, L. N.; West, K. W. *Appl. Phys. Lett.* **1991**, *59*, 1111.
(337) Natelson, D.; Willett, R. L.; West, K. W.; Pfeiffer, L. N. *Appl. Phys. Lett.* **2000**, *77*, 1991.
(338) Artemyev, M.; Moeller, B.; Woggon, U. *Nano Lett.* **2003**, *3*, 509.
(339) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
(340) Chakraborty, A. K.; Golumbfskie, A. J. *Annu. Rev. Phys. Chem.* **2001**, *52*, 537.
(341) De Wild, M.; Berner, S.; Suzuki, H.; Ramoino, L.; Baratoff, A.; Jung, T. A. In *Molecular Electronics III*; New York Academy of Sciences: New York, 2003; Vol. 1006.
(342) Muchado, V. G.; Baxter, P. N. W.; Lehn, J. M. *J. Braz. Chem. Soc.* **2001**, *12*, 431.
(343) Pileni, M. P.; Lalatonne, Y.; Ingert, D.; Lisiecki, I.; Courty, A. *Faraday Discuss.* **2004**, *125*, 251.
(344) Whitesides, G. M.; Boncheva, M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4769.
(345) Fasolka, M. J.; Mayes, A. M. *Annu. Rev. Mater. Res.* **2001**, *31*, 323.
(346) Krausch, G.; Magerle, R. *Adv. Mater.* **2002**, *14*, 1579.
(347) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.
(348) Sun, S. H.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989.
(349) Li, L. S.; Walda, J.; Manna, L.; Alivisatos, A. P. *Nano Lett.* **2002**, *2*, 557.
(350) Jeoung, E.; Galow, T. H.; Schotter, J.; Bal, M.; Ursache, A.; Tuominen, M. T.; Stafford, C. M.; Russell, T. P.; Rotello, V. M. *Langmuir* **2001**, *17*, 6396.
(351) McFarland, A. D.; Van Duyne, R. P. *Nano Lett.* **2003**, *3*, 1057.
(352) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153.
(353) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89.
(354) Gale, P. A. *Philos. Trans. R. Soc. A* **2000**, *358*, 431.
(355) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975.
(356) Seeman, N. C. *Chem. Biol.* **2003**, *10*, 1151.
(357) Zimmerman, S. C.; Lawless, L. J. In *Dendrimers IV*; Springer-Verlag: Berlin, 2001; Vol. 217.
(358) Shu, D.; Moll, W.-D.; Deng, Z.; Mao, C.; Guo, P. *Nano Lett.* **2004**, *4*, 1717.
(359) Liu, D.; Wang, M.; Deng, Z.; Walulu, R.; Mao, C. *J. Am. Chem. Soc.* **2004**, *126*, 2324.
(360) Deng, Z.; Mao, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 4068.
(361) Yang, J.; Mayer, M.; Kriebel, J. K.; Garstecki, P.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1555.
(362) Knez, M.; Sumser, M.; Bittner, A. M.; Wege, C.; Jeske, H.; Martin, T. P.; Kern, K. *Adv. Funct. Mater.* **2004**, *14*, 116.
(363) Knez, M.; Bittner, A. M.; Boes, F.; Wege, C.; Jeske, H.; Maiss, E.; Kern, K. *Nano Lett.* **2003**, *3*, 1079.
(364) Deng, Z. X.; Mao, C. D. *Nano Lett.* **2003**, *3*, 1545.
(365) Yan, H.; Park, S. H.; Finkelstein, G.; Reif, J. H.; LaBean, T. H. *Science* **2003**, *301*, 1882.
(366) Kim, S. O.; Solak, H. H.; Stoykovich, M. P.; Ferrier, N. J.; de Pablo, J. J.; Nealey, P. F. *Nature* **2003**, *424*, 411.
(367) Shin, K.; Leach, K.; Goldbach, J.; Kim, D.; Jho, J.; Tuominen, M.; Hawker, C.; Russell, T. *Nano Lett.* **2002**, *2*, 933.
(368) Thurn-Albrecht, T.; Steiner, R.; DeRouchey, J.; Stafford, C.; Huang, E.; Bal, M.; Tuominen, M.; Hawker, C.; Russell, T. *Adv. Mater.* **2000**, *12*, 787.
(369) von Werne, T. A.; Germack, D. S.; Hagberg, E. C.; Sheares, V. V.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3831.
(370) Edwards, E. W.; Montague, M. F.; Solak, H. H.; Hawker, C. J.; Nealey, P. F. *Adv. Mater.* **2004**, *16*, 1315.
(371) Sundrani, D.; Darling, S. B.; Sibener, S. J. *Nano Lett.* **2004**, *4*, 273.
(372) Sundrani, D.; Darling, S. B.; Sibener, S. J. *Langmuir* **2004**, *20*, 5091.
(373) Decher, G. *Science* **1997**, *277*, 1232.
(374) Hammond, P. T. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 430.
(375) Clark, S.; Handy, E.; Rubner, M.; Hammond, P. *Adv. Mater.* **1999**, *11*, 1031.

(376) Afsharrad, T.; Bailey, A. I.; Luckham, P. F.; Macnaughtan, W.; Chapman, D. *Colloids Surf.* **1987**, *25*, 263.
(377) Campas, M.; O'Sullivan, C. *Anal. Lett.* **2003**, *36*, 2551.
(378) Hammond, P. T. *Adv. Mater.* **2004**, *16*, 1271.
(379) Caruso, F. *Adv. Mater.* **2001**, *13*, 11.
(380) Caruso, F.; Schuler, C.; Kurth, D. G. *Chem. Mater.* **1999**, *11*, 3394.
(381) Schneider, G.; Decher, G. *Nano Lett.* **2004**, *4*, 1833.
(382) Shchukin, D. G.; Sukhorukov, G. B. *Adv. Mater.* **2004**, *16*, 671.
(383) Shchukin, D. G.; Shutava, T.; Shchukina, E.; Sukhorukov, G. B.; Lvov, Y. M. *Chem. Mater.* **2004**, *16*, 3446.
(384) Caruso, F. In *Colloid Chemistry II*; Springer-Verlag: Berlin, 2003; Vol. 227.
(385) Wang, D. Y.; Mohwald, H. *J. Mater. Chem.* **2004**, *14*, 459.
(386) Pham, T.; Jackson, J. B.; Halas, N. J.; Lee, T. R. *Langmuir* **2002**, *18*, 4915.
(387) Yin, Y.; Lu, Y.; Gates, B.; Xia, Y. *Chem. Mater.* **2001**, *13*, 1146.
(388) Barton, J. E.; Odom, T. W. *Nano Lett.* **2004**, *4*, 1525.
(389) Harnack, O.; Pacholski, C.; Weller, H.; Yasuda, A.; Wessels, J. M. *Nano Lett.* **2003**, *3*, 1097.
(390) Love, J. C.; Urbach, A. R.; Prentiss, M. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 12696.
(391) Gourdon, D.; Yasa, M.; Alig, A. R. G.; Li, Y.; Safinya, C. R.; Israelachvili, J. N. *Adv. Funct. Mater.* **2004**, *14*, 238.
(392) Nagle, L.; Ryan, D.; Cobbe, S.; Fitzmaurice, D. *Nano Lett.* **2003**, *3*, 51.
(393) Nagle, L.; Fitzmaurice, D. *Adv. Mater.* **2003**, *15*, 933.
(394) Yin, Y.; Lu, Y.; Gates, B.; Xia, Y. *J. Am. Chem. Soc.* **2001**, *123*, 8718.
(395) Hutchinson, T. O.; Liu, Y.-P.; Kiely, C.; Kiely, C. J.; Brust, M. *Adv. Mater.* **2001**, *13*, 1800.
(396) Lu, N.; Chen, X.; Molenda, D.; Naber, A.; Fuchs, H.; Talapin, D. V.; Weller, H.; Mueller, J.; Lupton, J. M.; Feldmann, J.; Rogach, A. L.; Chi, L. *Nano Lett.* **2004**, *4*, 885.
(397) Xia, D.; Brueck, S. R. J. *Nano Lett.* **2004**, *4*, 1295.
(398) Xia, D.; Biswas, A.; Li, D.; Brueck, S.-R. J. *Adv. Mater.* **2004**, *16*, 1427.
(399) Yang, X.; Liu, C.; Ahner, J.; Yu, J.; Klemmer, T.; Johns, E.; Weller, D. *J. Vac. Sci. Technol. B* **2004**, *22*, 31.
(400) Cui, Y.; Bjork, M. T.; Liddle, J. A.; Sonnichsen, C.; Boussert, B.; Alivisatos, A. P. *Nano Lett.* **2004**, *4*, 1093.
(401) Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, *15*, 353.
(402) Huang, Y.; Duan, X. F.; Wei, Q. Q.; Lieber, C. M. *Science* **2001**, *291*, 630.
(403) Smith, P. A.; Nordquist, C. D.; Jackson, T. N.; Mayer, T. S.; Martin, B. R.; Mbindyo, J.; Mallouk, T. E. *Appl. Phys. Lett.* **2000**, *77*, 1399.
(404) Lieber, C. M. Personal communication.
(405) Srinivasan, U.; Liepmann, D.; Howe, R. *J. Microelectromech. Sys.* **2001**, *10*, 17.
(406) Srinivasan, U.; Helmbrecht, M.; Rembe, C.; Muller, R.; Howe, R. *IEEE J. Sel. Top. Quantum* **2002**, *8*, 4.
(407) Snyder, E.; Chideme, J.; Craig, G. *Jpn. J. Appl. Phys.* **2002**, *41*, 4366.
(408) Rogers, J. A.; Bao, Z.; Baldwin, K.; Dodabalapur, A.; Crone, B.; Raju, V. R.; Kuck, V.; Katz, H.; Amundson, K.; Ewing, J.; Drzaic, P. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 4835.
(409) Rogers, J. A.; Bao, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3327.
(410) Anfinsen, C. B. *Science* **1973**, *181*, 223.
(411) Grzybowski, B. A.; Radkowski, M.; Campbell, C. J.; Lee, J. N.; Whitesides, G. M. *Appl. Phys. Lett.* **2004**, *84*, 1798.
(412) Conn, M. M.; Rebek, J. *Curr. Opin. Struct. Biol.* **1994**, *4*, 629.
(413) Moore, G. E. *Electron. Lett.* **1965**, *38*, April 19.
(414) Schellekens, J.; DBurdinski, D.; Saalmink, M.; Beenhakkers, M.; Gelinck, G.; Decre, M. M. J. *Mater. Res. Soc. Symp. Proc.* **2004**, *EXS-2*, M2.9.
(415) Schellekens, J.; DBurdinski, D.; Saalmink, M.; Beenhakkers, M.; Gelinck, G.; Decre, M. M. J. *Mater. Res. Soc. Symp. Proc.* **2004**, *EXS-2*, M4.9.

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