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Unconventional Methods for Fabricating and Patterning Nanostructures

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1. Introduction

Fascinating (and sometimes technologically important) phenomena occur in systems that have a spatial dimension comparable to that of a fundamental physical, chemical, or biological process. Some of the most interesting examples—ballistic movement of an electron in a semiconductor,[1] near- and far-field diffraction of visible light,[2] diffusion of an active species close to an electrode,[3] excitation of a collective resonance by light,[4] attachment or spreading of a eukaryotic cell[5−7]—can be observed in structures that have dimensions larger than macromolecules (∼2−20 nm) but smaller than or equal to eukaryotic cells (∼1−50 μm). Structures with these dimensions are often referred to as meso-scale systems or "mesosystems".[8,9] Because mesosystems bridge the molecular and the macroscopic world, fabrication and study of these systems have become active areas of research in physics, materials science, and increasingly in chemistry and biology. Nanosystems—systems that we define as having features or characteristic lengths between 1 and 100 nm—exhibit particularly peculiar and interesting characteristics: quantized excitation,[10,11] Coulomb blockade,[12] single-electron tunneling (SET),[13] and metal−insulator transition.[14] These phenomena occur in structures small enough for quantum mechanical effects to dominate. Other interesting physical processes that can be observed in similar structures—for example, near-field optical behavior[15,16] and interaction of light with photonic band-gap crystals[17]—represent nanoscopic manifestations of processes that have more familiar macroscopic analogues (in these two cases, interaction of microwave radiation with antennas or apertures[18] and operation of microwave band-gap structures[19]). The fundamental study of phenomena that occur in structures having dimensions in the 1−100 nm regime has already evolved into a new field of research that is sometimes referred to as nanoscience.[20−23]

In addition to their uses in nanoscience, nanostructures are central to the development of a number of existing and emerging technologies. The ability to fabricate on the nanometer scale guarantees a continuation in the miniaturization of functional devices. In microelectronics, "smaller" has always meant better—more components per chip, faster response, lower cost, lower power consumption, and higher performance.[24−26] The miniaturization and production of microelectronic chips has, in recent years, been guided by a road map issued by the Semiconductor Industry Association (SIA). The current SIA road map forecasts a steady downward trend in the minimum feature size of DRAMs from ∼250 nm today to ∼70 nm in the year 2010.[27] Miniaturization may also be the trend in a range of other technologies. There are active efforts, for example, to develop magnetic storage media having elements with dimensions as small as ∼100 nm,[28] compact disks (CDs) with pit sizes of <50 nm (to be read by scanning

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probe devices),[29] and nanometer-sized sensors or nanoelectromechanical systems (NEMS).[30] The ability to fabricate on the nanometer scale also allows for technologies that rely on physical principles (for example, quantum size effects) that cannot be exploited or are absent in macroscopic or microscopic structures. Revolutionary devices such as arrays of quantum dot lasers,[31] quantum cascade lasers,[32] single-electron transistors,[33] and arrays of nanometer-sized magnets[34] are appearing rapidly in prototype forms in research labs. Organic self-assembled monolayers have been used as a gate insulator in a nano-field effect transistors.[35]

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There are also applications of nanostructures in areas that have not, so far, been seriously explored. For example, ultrasmall sensors or electrodes might be used to communicate with cells and to form the basis for minimally invasive diagnostic systems;[36] nanoscale chemical reactors and analytical probes could make the study of individual molecules routine;[37] and arrays of very large numbers of nanometer-scale systems could open the door to the study of statistical phenomena such as nucleation.

In almost all applications of nanostructures, fabrication represents the first and one of the most significant challenges to their realization. This review outlines a range of techniques that are, in principle, suitable for the fabrication of structures for applications in nanoscience and nanotechnology. The focus of the review is on new methods for replication of nanostructures based on printing, molding, or embossing,[38] and on methods that involve relatively inexpensive forms of near-field photolithography[39] or that use molecular self-assembly[40]—rather than on extensions of projection photolithography (using ei-

ther EUV or X-ray photons) and electron- or ion-beam lithography[41]—for three reasons. First, we believe that these methods are less developed than conventional photo-, electron-, or ion-beam lithography and, hence, offer more opportunity for innovation. Second, there is more chemical and materials content to these methods, and they are more relevant to the interests of a chemical audience. Third, X-ray or EUV photolithography, e-beam, and focused ion-beam writing are technologies that are now well into advanced engineering development, and although there are important chemical/materials opportunities in all of them (for example, in developing advanced resists, in production and maintenance of masks, and in new materials for functional components of nanostructures), it will, in practice, be difficult for chemistry or materials science to influence significantly the outcome of these programs.

We define techniques for nanofabrication as those capable of generating structures with at least one lateral dimension between 1 and 100 nm;[42] we will, however, also discuss a limited number of methods that, so far, have only been demonstrated at the ~200 nm scale but that we judge to have the potential to be improved to ≤100 nm. We devote the most attention to systems that can draw arbitrary or semiarbitrary patterns but we also outline ideas, like those based on self-assembly,[40] that may lead to useful regular arrays or that may be parts of systems capable of forming complex patterns. In general, we do not deal with structures such as zeolites (which have nanometer-scale dimensions[43] but limited potential for patterning) and only touch on structures such as carbon nanotubes (which have intensely interesting properties but which can, at present, only be grown, cut, and assembled, rather than patterned). Also, although many thin film structures, such as Langmuir–Blodgett (LB) films,[44] self-assembled monolayers (SAMs),[45,46] and evaporated thin films have nanometer thicknesses and subnanometer internal structures, these films only represent structure out of the plane of the substrate. This review deals only with in-plane nanostructures.

We broadly divide the problem of fabrication of nanostructures (or nanolithography) into two separate parts: *writing* and *replication*.[42,47] Writing and replication are usually different kinds of processes with different characteristics, and they also emphasize different aspects of nanofabrication. They both connect to the idea of a *master*: that is, a structure that provides or encodes a pattern to be replicated in multiple copies. *Writing* nanostructures or "making masters" is usually done by serial techniques such as writing with a focused beam of electrons or ions. *Replication* of nanostructures is a process of pattern transfer in which the information—for example, the shape, morphology, structure, and pattern—present on a master is transferred to a functional material in a single step, rapidly, inexpensively, and with high fidelity. Most techniques used for writing nanostructures de novo are either too slow or too expensive to be used for mass production. Replication of a master should provide an economical and convenient route to multiple copies of the nanostructures written on the master. A combination of high-precision writing of masters with low-cost replication of these masters seems to provide the most practical protocol for nanomanufacturing: high-resolution, high-cost fabrication techniques can be used to make masters in one set of materials; these structures can then be replicated in a low-cost process in other materials. The cost of the master can be an insignificant part of the overall cost structure if it is used to make many replicas.

We begin this review with an overview of strategies that have been explored for fabricating patterned nanostructures. We then describe these strategies in detail in four sections: (i) current technologies with broad flexibility in patterning; (ii) new methods that have the potential for broad flexibility in patterning; (iii) techniques for making regular or simple patterns; and (iv) new concepts not yet demonstrated for nanometer-scale patterning but with long-term potential in nanotechnology.

2. Strategies for Fabricating Patterned Nanostructures

Table 1 summarizes strategies that have been explored for fabricating patterned nanostructures. These strategies include (i) lithography with photons, particles, and scanning probes; (ii) replication against masters (or molds) via physical contact; (iii) self-assembly; (iv) templated deposition; and (v) size reduction. Because many of these methods have only emerged recently, most of their characteristics—fidelity, resolution, density of errors, speed, and cost—are only vaguely known. We therefore emphasize their demonstrated performance (that is, feature size and flexibility in materials that can be patterned) and comment on their intrinsic limits (that is, limits that originate in the physics and chemistry on which they are based). In some cases, we highlight approaches that may circumvent shortcomings associated with the current forms of these techniques.

2.1. Lithography with Photons, Particles, and Scanning Probes

Photolithographic methods all share the same operational principle:[48,49] exposure of an appropriate material to electromagnetic radiation (UV, DUV, EUV, or X-ray) introduces a latent image (usually a difference in solubility) into the material as a result of a set of chemical changes in its molecular structure; this latent image is subsequently developed into relief structures through etching. Methods based on writing with particles (electrons or ions) usually accomplish the same task using a scanned beam or projected image of energetic particles rather than photons. Exposure is usually patterned either by interposing a mask between the source of radiation (or particles) and the material or by scanning a focused spot of the source across the surface of the material. When masks are used, the lithographic process yields a replica (perhaps reduced in size) of the pattern on the mask. With scanning probes, a sharp tip induces local change in a resist or causes local deposition. Methods that involve scanning or

Table 1. Strategies and Intrinsic Limitations

pattern formation using[a]	basis for intrinsic limitations	strategies to circumvent the limitations
photons		
UV, DUV, EUV, and X-rays	diffraction	contact mode, near-field exposure
	depth of focus	nonlinear photoresists
particles		
electrons and ions	electrostatic interactions	neutral atoms
	writing is serial	projection
	small field of writing	arrays of sources
neutral atoms	de Broglie wavelength	
machining		
AFM, STM, NSOM, and electrochemical	writing is serial	arrays of probes
	small field of writing	
physical contact	van der Waals forces	
printing, molding, and embossing	speed of capillary filling	low-viscosity solutions
	adhesion of mold and replica	surface modification
self-assembly	control over order, domain size, and density of defects	
surfactant systems		
block copolymers		
crystallization of proteins and colloids		
deposition	low flexibility in patterning and fabrication of masks or templates	
cleaved edge overgrowth		
shadowed evaporation		
size reduction		
glass drawing	low flexibility in patterning; reproducibility	
compression of elastomeric masters or molds		
controlled reactive spreading		
edge-based technologies		
near-field phase-shifting photolithography	diffraction	
topographically directed photolithography	diffraction	
topographically directed etching		

[a] Abbreviations: UV (ultraviolet), DUV (deep ultraviolet), EUV (extreme ultraviolet); AFM (atomic force microscope); STM (scanning tunneling microscope); and NSOM (near-field scanning optical microscope).

writing can generate arbitrary patterns and therefore be used for master writing.

Pattern Formation Using Photons. Photons have been used for many years to induce chemical reactions in photographic materials[50] or resist polymers.[51] The lithographic technology—photolithography—based on this process uses a mask or aperture to localize the photochemistry spatially; it is an invaluable tool for microfabrication in a broad range of applications in science and technology and one of the most widely used and highly developed of all technologies now practiced.[48] Although a scanned aperture (or a stationary aperture and a scanned sample) can be used to write arbitrary patterns, the predominant use of photolithography is to replicate a pattern on a mask into a layer of photoresist. In this case, the image of the mask is reduced (usually by a factor of 4) and projected onto the resist with an optical system (projection mode photolithography) or the mask is placed in physical contact with the resist (contact mode photolithography). Most fabrication in the integrated circuit (IC) industry uses projection-mode lithography; feature sizes of 250 nm with 248 nm UV light are common for fabrication in microelectronics.

The resolution of photolithography increases as the wavelength of the light used for exposure decreases. With 193 nm light from an ArF excimer laser and synthetic fused silica (or calcium fluoride) lenses, projection photolithography may yield a reliable (and perhaps economical) solution to patterning features as small as ~150 nm.[52−54] Similar systems based on transmission optics with exposure wavelengths below 193 nm are difficult to construct, however, because of the lack of transparent materials suitable for lenses at these short wavelengths. One of the several technical challenges to extending photolithographic methods into the sub-100-nm range is, therefore, the development of reflection optics or stencil masks that can be used with very short wavelengths (for example, EUV with $\lambda \approx 0.2-100$ nm or soft X-rays with $\lambda \approx 0.2-40$ nm).[55,56] Although lithography was demonstrated with soft EUV and X-rays many years ago, fabricating the masks and optics capable of supporting a robust, economical method still provides significant unsolved challenges.[57] Other, equally significant, problems include repairing the mask, limiting damage and distortion of the mask on exposure to high fluxes of energetic radiation, and achieving the registration required for multilevel fabrication. Controlling the capital cost of new facilities is also a key economic problem.

In addition to advances in the physics and engineering of new light sources and projection optics, clever designs for the chemistries of the photoresist have been critical to the success of photolithography. Chemically amplified resists[51,58] and those based on surface silylation and dry development,[59] for example, have remarkably improved the speed of patterning and the fidelity of the transfer of patterns of intensity into the resist. Materials for antireflective coatings have been useful as well.[49] Also, when operated in the linear response regime, photoresists can be used to image distributions of intensity[60,61] and can guide the optical design of new types of photolithographic systems. By exploiting the nonlinear response of

conventional resists, it is even possible to produce patterns that have features smaller than or geometries different from those present in the linear optical image.[62,63] Special classes of nonlinear resists, such as those based on two-photon absorption, are specifically designed to produce well-defined nonlinearities that can be used to increase the resolution.[64] Although these nonlinear resists are not applicable to general tasks in nanopatterning (for example, they cannot generate densely packed features), they may be important for specialized applications. Other key technologies in IC processing such as reactive ion etching (RIE),[65] lift-off,[48] deposition,[48] ion implantation,[66] and planarization of wafers[67] also contain important chemical and materials components that could, potentially, be improved to deliver or facilitate patterning of features below 100 nm.

Pattern Formation Using Particles. Energetic particles—electrons, ions, and electrically neutral metastable atoms—can also be used to form patterns with nanometer resolution in appropriate resist films; these approaches are attractive, in part, because the de Broglie wavelengths of these particles are sufficiently short (<0.1 nm) that they minimize the effects of diffraction that currently limit many photolithographic approaches. These methods can provide resolution higher than that required by the IC industry for the foreseeable future.[42] For example, resolution of ~10 nm, which was achieved more than 20 years ago with e-beam writing,[68] comfortably exceeds the lithographic requirements necessary for the 50-nm technology projected for the year 2012.[27] Conventional lithography with focused beams of electrons or ions is, however, performed serially and is slow. For example, typical electron-beam patterning of a 4-in. wafer that has a high density of features requires ~1 h.[69] One means to increase the speed is to use stencil masks[70] and projection optics to expose large areas at once.[71] These approaches appear promising: 80-nm features can now be routinely produced using a 4× reduction projection system for electrons.[69] It may also be possible to use large arrays of particle beams from single[72] or multiple sources[73] to allow multiple serial writing processes to happen simultaneously. Even if these new approaches do not yield high-throughput solutions, it is certain that conventional lithography with focused beams of electrons and ions will remain indispensable tools for generating and repairing masks or masters with nanometer features for the foreseeable future.

Neutral metastable atoms can also be used for particle-based lithography. Neutral atoms are attractive partly because they do not electrostatically interact with one another. Their neutrality requires, however, development of new types of optics based on light forces if they are to be used with projection systems. Initial results are encouraging: features as small as ~50 nm have been fabricated in a single step over large areas with stencil masks,[74,75] and ~70-nm features have been produced using directed deposition with light force lenses.[76,77]

Pattern Formation Using Scanning Probes. Scanning probe lithography (SPL) encompasses techniques that use small (<50 nm) tips scanned near the surface of a sample in the configuration of scanning tunneling microscopes (STMs),[78] atomic force microscopes (AFMs),[79] scanning electrochemical microscopes (SECM),[80] or near-field scanning optical microscopes (NSOMs).[15] Although scanning probes were originally designed to provide high-resolution images of surfaces, their lithographic capability was demonstrated in a set of experiments with an STM, just five years after the first STM images were recorded.[81] In that work, a large electrical bias applied between a tungsten tip and a germanium surface caused transfer of a single atom from the tip to the surface. Since then, STMs, AFMs, SCEMs, and NSOMs have been used in many different ways to perform sophisticated lithography; several examples are described in a subsequent section.

Advantages of SPL methods include resolution that, for AFM and STM methods, approaches the atomic level, the ability to generate features with nearly arbitrary geometries, and the capability to pattern over surface topography that deviates significantly from planarity.[82] These methods are serial techniques, however, and have writing speeds that are typically limited by the mechanical resonances of the tips and the piezoelectric elements that maintain constant separation between the tips and the sample. Research is underway to increase the speed of these methods by incorporating integrated arrays of tips that can write in parallel by using new designs for tips[83,84] and by incorporating piezoelectric elements that have high resonance frequencies.[82,85] Unless these approaches yield a huge increase in speed, it is likely that SPL methods will be better suited for formation of masters than for replication.

2.2. Replication against Masters by Methods Based on Physical Contact

The limitations to the use of projection photolithography with transmission optics to generate features with dimensions <100 nm (the so-called "100 nm-barrier") *may* have opened the door to new technologies. Although photolithography has circumvented many limitations during its development and certainly cannot be neglected for nanofabrication, the limitations that it now faces are based on the physics of diffraction and of interactions of high-energy photons with matter and may be harder to overcome. As a result, it is now worth considering nonphotolithographic methods for pattern transfer. Some promising nonphotolithographic methods for nanofabrication include printing,[86] molding,[87] and embossing.[88] In fact, replica molding (or cast molding) with a UV (or thermally) curable precursor material and embossing (or imprinting) with a rigid master have already been widely used in industry to manufacture microstructures and some nanostructures: examples include diffraction gratings, holograms, and compact disks (CDs); these systems require replication of features with a fidelity ranging from ~200 nm to 10 μm.[2,87,88] In these techniques, the resolution is mainly determined by van der Waals interactions, by wetting, by kinetic factors such as filling of the capillaries on the surface of a master, and by the properties of materials (for example, changes in dimensions with

changes in temperature or pressure, with wear, and on passing through phase transitions). They are not limited by optical diffraction. In research applications, replication techniques based on physical contact can now produce complex three-dimensional structures with features as small as a few nanometers, a resolution that would be extremely difficult to achieve using photolithography.[47,89−91] Replica molding down to the molecular level (molecular imprinting) has also been reported, but we feel that the interpretation of these results is still ambiguous.[92,93]

2.3. Pattern Formation Using Self-Assembly

One family of radically different approaches to fabrication of nanostructures is based on self-assembly.[23] The concept of self-assembly originates from biological processes such as the folding of polypeptide chains into functional proteins and chains of RNA into functional t-RNAs,[94] the formation of the DNA double helix,[95] and the formation of cell membranes from phospholipids.[96] In self-assembly, subunits (molecules or meso-scale objects) spontaneously organize and aggregate into stable, well-defined structures based on noncovalent interactions. The information that guides the assembly is coded in the characteristics (for example, topographies, shapes, surface functionalities, and electrical potentials) of the subunits, and the final structure is reached by equilibrating to the form of the lowest free energy. Because the final self-assembled structures are close to or at thermodynamic equilibrium, they tend to reject defects.[23,40] Self-assembly is the route followed in biological systems for the formation of the cell and its components. These structures are enormously complex and very small, and their formation in biological systems suggests that self-assembly may provide a route to certain types of patterned nanostructures.

A variety of strategies for self-assembly have been demonstrated and employed to fabricate two- and three-dimensional structures with dimensions ranging from molecular, through mesoscopic, to macroscopic sizes.[97] Examples of these structures include self-assembled monolayers,[45,98] structures (micelles, liposomes) derived from aggregated surfactant molecules,[99] phase-separated block copolymers,[100,101] crystallized proteins[102] or colloidal particles,[103] and aggregated meso-scale objects.[104] Self-assembly is now being examined extensively for patterning at scales >1 μm, and applications are moving to smaller dimensions. Demonstrations, including microcontact printing of self-assembled monolayers,[105] reactive ion etching with thin films of block copolymers as masks,[106] and synthesis of mesoporous materials with aggregates of surfactants as templates,[107,108] illustrate the capability and feasibility of self-assembly as a strategy for fabricating nanostructures. The development of these methods into practical routes to useful patterned nanostructures still requires great ingenuity. In microcontact printing (μCP), for example, the formation of defects, the distortion of patterns, the dimensional stability of the stamps, and registration must be understood and controlled.

2.4. Pattern Formation Using Controlled Deposition

Features with nanometer sizes can also be generated using various methods of controlled deposition. In addition to deposition induced by focused laser beams[109,110] and focused ion beams (FIB),[111] cleaved edge overgrowth (CEO)[112,113] and shadowed evaporation[114] represent two attractive methods that fall into this category.

Cleaved edge overgrowth is a technique based on molecular-beam epitaxy (MBE).[112,113] It takes advantage of the high accuracy of MBE in controlling the thickness of deposited superlattices. After cleavage, the cross-section of a multilayer film prepared by MBE offers nanometer-wide templates for the growth of other materials or for the fabrication of simple patterns of quantum structures of semiconductors. This technique has molecular-scale resolution but is limited in the types of patterns that it can produce. Although it is most commonly used and has highest resolution with MBE films, the same basic approach is also certainly suitable for use with films grown using other techniques.

In shadowed evaporation,[114] a stencil mask is fabricated directly on, but raised slightly above, the surface of the sample; this mask forms shadows when the sample is exposed to a flux of atoms or molecules. The shadows may be produced by depositing the material to be patterned at an angle or by fabricating the mask with an overhang. Removal of the mask after deposition leaves a pattern defined both by the mask and the method of deposition. The gray scale that occurs at the edges enables formation of features with smooth gradients in thickness;[115] these types of features are difficult to fabricate using other methods. When MBE is used with carefully selected conditions, patterns can be formed that are not simple geometrical images of the shadows. In these cases, self-organization of deposited crystalline material yields features that can be sharper and smaller than those on the mask;[116] 100-nm crystalline features with tip radii as small as 10 nm have been demonstrated.[117] If the flux is incident on the sample at an angle, features in the pattern can be much smaller than those in the mask.[114,118] Early work demonstrated a factor of 5 reduction in feature size with this technique.[114] The method has been extended to glancing angle deposition on corrugated surfaces;[119,120] features as small as 15 nm were generated in this way.[120,121] Shadowed evaporation techniques occupy an important niche in the fabrication of certain types of nanostructures, but they are limited in the types of patterns that they can produce. They cannot form, for example, densely packed features with sizes significantly smaller than those in the masks.

2.5. Size Reduction

While it has been expensive or difficult to fabricate structures directly at the nanometer scale, a number of procedures have been developed that reduce the size of features that can be routinely produced by conventional microlithographic techniques. These

procedures demonstrate a cost-effective strategy for the fabrication of certain types of nanostructures that does not require access to high-resolution lithographic techniques. The most commonly used approaches for size reduction are based on physically isotropic deformation or shrinkage of amorphous materials[122−127] and chemically anisotropic etching of single crystals.[128,129]

In isotropic deformation (for example, drawing of glass fibers[122−124] or compression of poly(dimethyl siloxane) (PDMS) molds[125−127]), size reduction in one (or two) direction(s) is obtained at the expense of an increase in dimension in the other two (or one) dimensions. The mechanical deformation can be made reversible by using an elastomeric material.[125−127] This reversibility yields an attractive capability—the feature size can be continuously reduced and iteratively adjusted by controlling the extent of deformation. The deficiency of methods based on mechanical deformations is that they depend on uniform distortion in the material; the level of uniformity necessary at the <100-nm scale may be difficult to achieve.

In anisotropic etching (for example, etching of Si-(100) in an aqueous KOH solution),[128,129] the lateral dimension(s) between trenches decreases in a controlled way as the etching proceeds. By controlling the etching time, the feature size can be continuously reduced. This technique is probably most useful for generating simple patterns of nanostructures and in most cases must be combined with other techniques.

3. Current Technologies with Broad Flexibility in Patterning

The desire for features with sizes smaller than 100 nm in microelectronics and the interest in nanoscience motivates the development of photolithographic methods based on nanometer-wavelength electromagnetic radiation and lithographic techniques that use particles with de Broglie wavelengths in the range of angstroms.[42,130] Table 2 compares current UV photolithography with advanced lithographic technologies (short-wavelength photolithography and beam-writing methods). All of these techniques have broad flexibility in patterning and are capable of generating structures with lateral dimensions in the range of a few nanometers to a few hundred micrometers.[42,49,130] This section discusses some aspects of these methods with emphasis on photolithography and e-beam writing.

Table 2. Current Technologies with Broad Flexibility in Patterning[a]

using	writing	replication	refs
photons			
UV	no	yes	48, 49, 131
DUV	no	yes	27, 49, 131
EUV	no	yes	55, 56
X-ray	no	yes	55, 56, 131
particles			
focused electrons	yes	no	42, 49, 69, 136
focused ions	yes	no	49, 111, 142

[a] In this table, yes means this technique is practical for writing or replication of features of ≤100 nm; no means this technique cannot practically be so used.

Photolithography. As discussed in a previous section, photolithography is usually carried out using one of two different schemes: contact (or proximity) printing or projection printing.[48] In contact printing, the photomask is in physical contact with, or in close proximity to, the resist film. The minimum feature size that can be obtained by this process is primarily determined by diffraction that occurs as light passes through the gap between the mask and the resist. Even with the use of elaborate vacuum systems to pull the mask and substrate together, it is still difficult in practice to reduce the gap between a conventional rigid mask and a rigid, flat substrate to less than ∼1 μm over large areas. As a result, the resolution of contact mode photolithography is typically 0.5−0.8 μm when UV light (360−460 nm) is used. Contact-mode photolithography is not seriously considered as a generally useful technique because the required mechanical contact can damage fragile structures on the mask or the sample, the features on the mask must be as small as those generated in the resist, and slight unwanted lateral motion of the mask when it is pulled against the mask makes accurate alignment to existing features difficult.

In projection printing, a system of lenses placed between the mask and the resist film projects a high-quality, demagnified (usually by a factor of 4) image of the mask onto the resist. With this approach, the features on the resist can be significantly smaller than those on the mask, contact with the sample is not required, and alignment or registration can be relatively straightforward. Essentially all integrated circuits are manufactured by projection photolithography, using equipment known as a step-and-repeat machine (or stepper).[38] The theoretical resolution (R) of an optical system for projection printing is limited by Rayleigh diffraction (eq 1)[131] where λ is the wavelength of the illuminating light, NA is the numerical aperture of the lens system, and k_1 is a constant that depends on the imaging technology and process control but typically must be >0.7 for adequate production yield. This equation indicates that

$$R = k_1\lambda/\mathrm{NA} \tag{1}$$

improvements in optical resolution can be achieved either by increasing the numerical aperture or by reducing the wavelength of the illuminating light. For the purposes of this review, we assume that the numerical aperture cannot be increased beyond ∼1, a value that, at least for small areas, can be approached now. Reducing λ, then, has historically represented a promising route to achieving significant decreases in R. This inference is consistent with experience in the microelectronics industry: production of 250-nm structures is achieved with wavelengths of 248 nm (KrF excimer laser), and sub-150-nm features (due in the year 2001) are generally, but not universally, thought to require 193-nm radiation (ArF excimer laser).[41]

In addition to the resolution, the spatial depth over which the image of the mask is faithfully produced (the depth of focus, DOF) is an important quantity; increasing this value to acceptable levels poses a technical challenge for projection photolithography.

The DOF is related to the wavelength and the numerical aperture by eq 2

$$\mathrm{DOF} = 0.5k_2\lambda/\mathrm{NA}^2 \qquad (2)$$

where k_2 is a constant that depends on the aberrations of the imaging system and tends to be in the range of 1−2. In practical terms, there is significant blurring and distortion of the image for distances beyond the DOF from the image plane. At a minimum, the image must not degrade over distances ±0.5 μm from the image plane (i.e., DOF = 1 μm) in order to have the projected image stay in focus throughout the thickness of films of photoresists that are typically used. In practice, it is useful to have a DOF larger than 1 μm in order to have some insensitivity to slight variations in the thickness of the resist or the position of the surface of the substrate.

To lower the NA or to increase the DOF, it is necessary to decrease λ to maintain the resolution. Since changing λ is usually not easy, schemes that increase the DOF and R through a reduction in k_1 and/or an increase in k_2 are attractive. Strategies for achieving this result include the use of phase-shifting masks,[132] off-axis illumination,[133] optical proximity correction,[134] and chemically amplified photoresists.[51,58] Many of these methods are extremely useful, and clever implementation of combinations of these techniques or development of new ones may allow for continued increases in resolution without changes in wavelength. One process uses advanced phase-shifting masks and optical proximity correction with 248-nm light to fabricate features as small as 100 nm.[135] It is somewhat clearer that, in principle, large increases in resolution can be achieved with similarly large decreases in the wavelengths of the illuminating sources. Unfortunately, few materials are suitable for lenses that are transparent at wavelengths below ∼200 nm. Even though fused silica will likely be used for 193 nm lithography, this material becomes increasingly absorbing below 200 nm. While there are now substantial efforts to develop grades of silica that are more transparent and less susceptible to photodamage than those currently available, new materials such as CaF_2 or a switch to reflective optics may be required for future generations of photolithographic systems.

X-ray Lithography. X-ray lithography (XRL) represents the short-wavelength limit of what is currently being explored for photon-based approaches to lithography.[55,56,130] Two types of schemes have been demonstrated for XRL: soft X-ray (or EUV) projection lithography that uses reflective optics[55,56] and proximity XRL with wavelengths near 1 nm.[130] Although routine fabrication of structures as small as ∼30 nm has been demonstrated by proximity XRL, the implementation of this technique for IC production is slowed by the lack of a commercially feasible way to produce the required masks and by the absence of suitable optics to project or reduce the image of the mask. In addition, reproducibly placing the mask in close proximity to (∼10 mm) but out of physical contact with the substrate can be challenging.

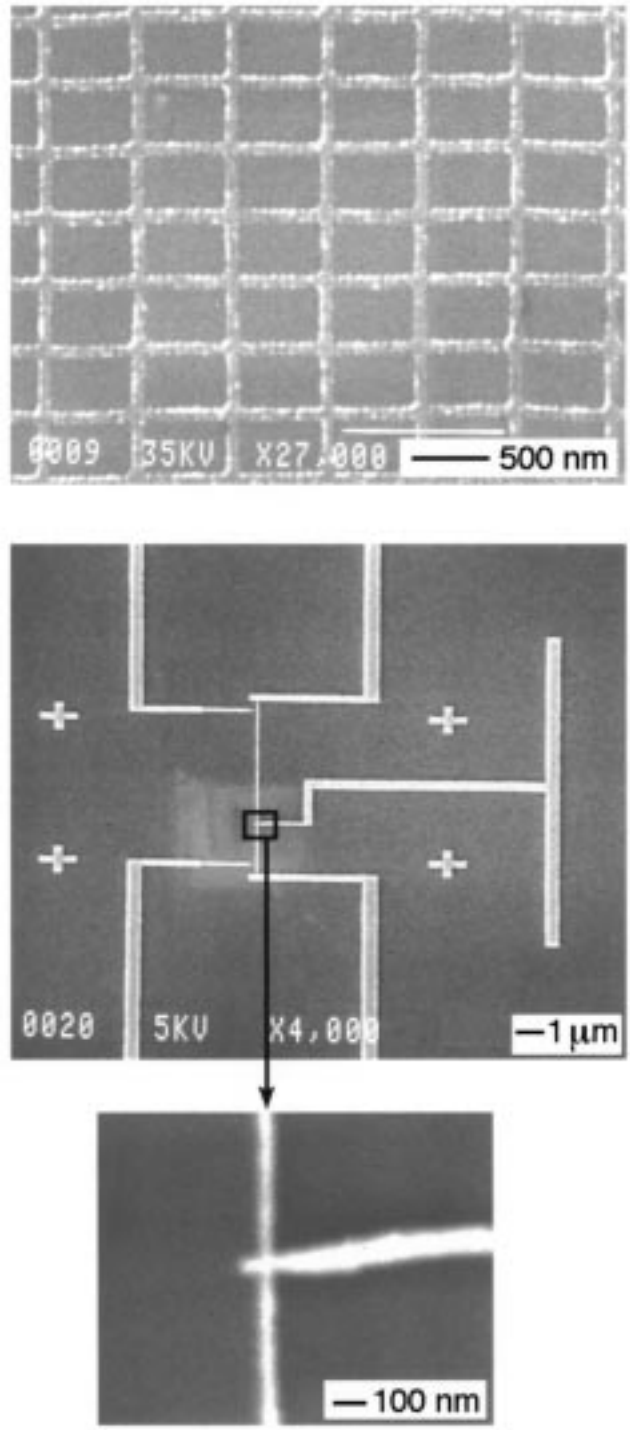

Figure 1. SEM images of nanostructures of gold that were fabricated using e-beam writing in thin films of PMMA resist, followed by evaporation of gold and lift-off (courtesy of Prof. Lydia Sohn of Princeton University).

Electron-Beam Lithography. Focused electron beams, beyond observing samples as in scanning electron microscopy (SEM) or transmission electron microscopy (TEM), can also be used to form patterned nanostructures in an electron-sensitive resist film.[69,136] In typical e-beam lithography, a tightly focused beam of electrons scans across the surface of a layer of resist, such as poly(methyl methacrylate) (PMMA).[137] Interaction of the electron beam with the resist causes local changes in its solubility, and in the case of PMMA, the electrons induce local chain scission

Table 3. New Technologies with Broad Flexibility in Patterning[a]

pattern formation using	writing	replication	refs
physical contact			
nanomachining (STM, AFM, NSOM, and electrochemical methods)	yes	no	144−159
soft lithography (μCP, MIMIC, μTM, REM, and SAMIM)	no	yes	38, 161
embossing/imprinting	no	yes	88, 91, 194
photons			
near-field phase-shifting photolithography	no[b]	yes	39, 201, 203
topographically directed photolithography	no[b]	yes	204
deposition			
topographically directed etching	no[b]	yes	205
particles			
metastable atom lithography	no	yes	209, 210
size reduction			
glass drawing	yes	no	122−124
compression of elastomeric mold	yes	yes	125−127
shadowed evaporation	yes	no	114−116
controlled reactive spreading	yes	no	191

[a] In this table, yes means this technique is practical for writing or replication of features of ≤100 nm; no means this technique cannot practically be so used. [b] With possible specialized exceptions.

and formation of micropores that causes the material to be soluble in a developer that consists of methylisobutyl ketone and 2-propanol.[48] The short wavelength associated with high-energy electron beams (for example, ~0.005 nm for 50 keV electrons) gives e-beam writing an extremely high resolution capability; 0.5-nm focused spots were possible very early in the development of this technique,[138] and high-brightness spots with diameters as small as 0.25 nm are now possible.[139,140] For e-beam lithography, the resolution is mainly determined by the scattering of primary and secondary electrons in the resist film and the substrate. Patterns with features as small as ~50 nm can be routinely generated by e-beam writing.[141] By using thin (10−100 nm) membranes as substrates to minimize the scattering problem, structures as fine as ~2 nm have been obtained.[42] Figure 1 shows SEM images of nanostructures of gold fabricated using e-beam writing in PMMA film, followed by evaporation of gold and lift-off.

Conventional direct-write e-beam technology is a sequential process that exposes a film of resist in a serial fashion; it is impractical for mass production because of the lengthy writing time (approximately 1 h) per wafer (4 in.).[69] Electron beam writers, therefore, tend to be used mostly to produce photomasks in optical lithography or to produce small numbers of nanostructures for research purposes. It is also widely used in certain niche applications where optical lithography simply fails: fabrication of high-frequency GaAs field-effect transistor (FET) devices that requires resolution down to ~100 nm and manufacturing of relatively low-volume products such as application-specific integrated circuits (ASIC).[49] Electron-beam projection techniques, such as SCALPEL (scattering with angular limitation projection electron lithography), that have the resolution approaching direct-write systems and the parallelism of projection lithographic systems are very promising and are now being intensely developed for mass production of patterned nanostructures.[69]

Focused Ion Beam Lithography. Focused ion beam (FIB) lithography is another attractive tool for writing nanostructures.[49,111] Features as small as ~6 nm have been fabricated using a 50 kV Ga^+ two-lens system.[142] FIB lithography is also a serial technique, but it has at least two advantages over electron-beam lithography: (i) FIB has a higher (approximately 2 orders of magnitude) resist exposure sensitivity than focused electron beam and (ii) FIB has negligible ion scattering in the resist and very low backscattering from the substrate. The damage to samples induced by high-energy ions is a major problem for FIB. Nevertheless, FIB is likely to remain useful for generation of patterned nanostructures in resist films, patterned implantation, repair of defects in photo- and X-ray masks, inspection in IC processes, failure analysis, and surface characterization (for example, in secondary ion mass spectroscopy, SIMS).[111,143]

4. New Methods with the Potential for Broad Flexibility in Patterning

The enormous expense of the advanced lithographic techniques discussed in section 3 is perhaps one of their most significant disadvantages.[42] Thus, the development of cost-effective methods that are capable of writing or replicating nanostructures in a wide range of materials represents one of the greatest technical challenges now facing nanofabrication. The precise meaning of "cost-effective" depends on the application. For successful, high-throughput fabrication facilities such as those used in manufacturing microprocessors and memories, it may be possible to recover high operating costs but the projected capital costs ($1−10 billion per facility) are daunting; for consumer markets with short product lifetimes and low margin, both capital and operating costs must be controlled. A range of techniques for nanofabrication that may have economics superior to those now used have been recently demonstrated, and those with broad flexibility in patterning are summarized in Table 3 and described in detail below.

4.1. Nanomachining with Scanning Probes

The demonstrated ability of the scanning probe microscope (for example, STM, AFM, NSOM, and SECM) to image and modify surfaces with atomic resolution suggests opportunities for their use in

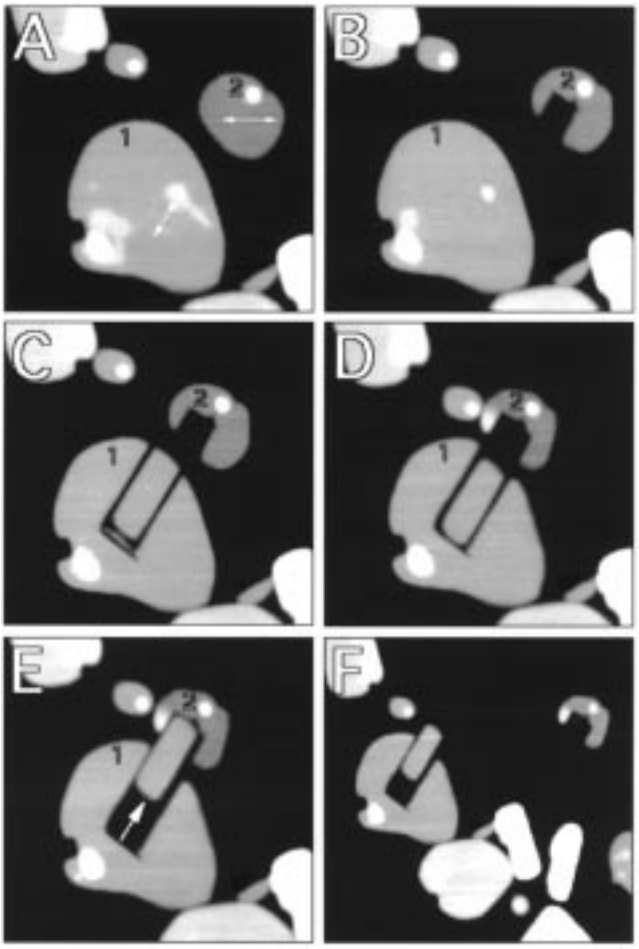

Figure 2. AFM images of selected steps in the fabrication of a nanostructure (containing three interlocking pieces) by AFM lithography and manipulation (courtesy of Prof. Charles Lieber of Harvard University).[146,159] (A) Initial positions of two MoO_3 nanocrystals, crystal 1 and crystal 2 (the preferred sliding directions are indicating by two-headed arrows). (B) A 52-nm notch was defined in crystal 2 by nanomachining. (C) A 58-nm free rectangle (latch) was machined in crystal 1, and crystal 2 was translated toward crystal 1. (D) Crystal 2 was translated to align the notch with the latch. (E) The latch was moved into the notch of crystal 2. (F) The latch was broken after a force of 41 nN was applied to the latch axis. Reprinted with permission from *Science* **1996**, *272*, 1158. Copyright 1996, American Association for the Advancement of Science.

generating nanostructures and nanodevices.[79,144] Atomic force microscopy has been the most widely used technique; typical approaches include the use of an AFM tip to scratch nanostructure in soft materials,[145,146] to expose thin films of resist,[147,148] to induce and/or enhance oxidation of H-terminated Si(100),[149] to change the headgroups or packing density of organic monolayers catalytically,[150] and to "write" 30-nm patterns of alkanethiols on gold.[151] STM tips have been used to alter the structure or order of organic monolayers,[152] to oxidize hydrogen-terminated silicon,[78,153] to induce phase transition in a solid material,[154] and to manipulate atoms or molecules.[155,156] Other uses of scanning probes include an NSOM tip to expose photoresist films[15,157,158] and an SECM tip to deposit metals.[80] Figure 2 shows AFM images of a nanostructure that has been machined in a thin film of MoO_3.[146,159] The AFM tip was also used to manipulate and transfer this carved nanostructure.

The smallest features that have been fabricated using SPM lithography are only a few tenths of a nanometer in dimension.[155] The system based on H-terminated Si(100) is most important for applications in microelectronics since almost all silicon devices are fabricated from this type of wafer. Quate et al. have used this approach to fabricate the first working device with an AFM—a functional MOSFET.[160] More recently, SPM lithography in H−Si(100) has been used by a number of groups to fabricate quantum devices such as single-electron transistors (SETs) and metal-oxide junctions.[79,149]

Despite enormous advances in this area, the use of SPM lithography in IC manufacturing remains to be developed seriously. Like e-beam writing, SPM lithography is a serial process and its slow speed will likely limit its use only to master writing. Unlike lithography with electrons, there is no equivalent to projection printing with SPMs. The only obvious route to increase the speed of SPM methods is to build arrays of probes to make this technique semiparallel.[82,83] MacDonald et al. have fabricated structures that contain thousands of STM tips.[84] Although these approaches may increase the throughput of SPM lithography, they will also increase significantly its complexity and cost.

4.2. Soft Lithography

Soft lithography (Figure 3) is the collective name for a set of lithographic techniques—replica molding (REM), microcontact printing (μCP), micromolding in capillaries (MIMIC), microtransfer molding (μTM), solvent-assisted micromolding (SAMIM), and near-field conformal photolithography using an elastomeric phase-shifting mask—that has been developed as an alternative to photolithography and a replication technology for micro- and nanofabrication.[38,39,161] These techniques use a patterned elastomer (usually PDMS) as the mold, stamp, or mask to generate or transfer the pattern. Soft lithography offers immediate advantages over photolithography and other conventional microfabrication techniques for applications in which patterning of nonplanar substrates, unusual materials, or large area patterning are the major concerns. It is especially promising for microfabrication of relatively simple, single-layer structures for uses in cell culture, as sensors, as microanalytical systems, in MEMS, and in applied optics. The initial success of soft lithography indicates that it has the potential to become an important addition to the field of micro- and nanofabrication. Because two recent review articles have been devoted to soft lithography,[38,161] this section will concentrate on soft lithographic techniques that have been demonstrated at the ≤100-nm scale.

Replica Molding (REM). The capability and feasibility of replica molding can be greatly enhanced by incorporating elastomeric materials into the procedure, albeit at some cost in reproducibility (Figure 3A).[127,163] In REM, an elastomer (for example, PDMS) is cast against a rigid master and the elastomeric replica is subsequently used as a mold against which

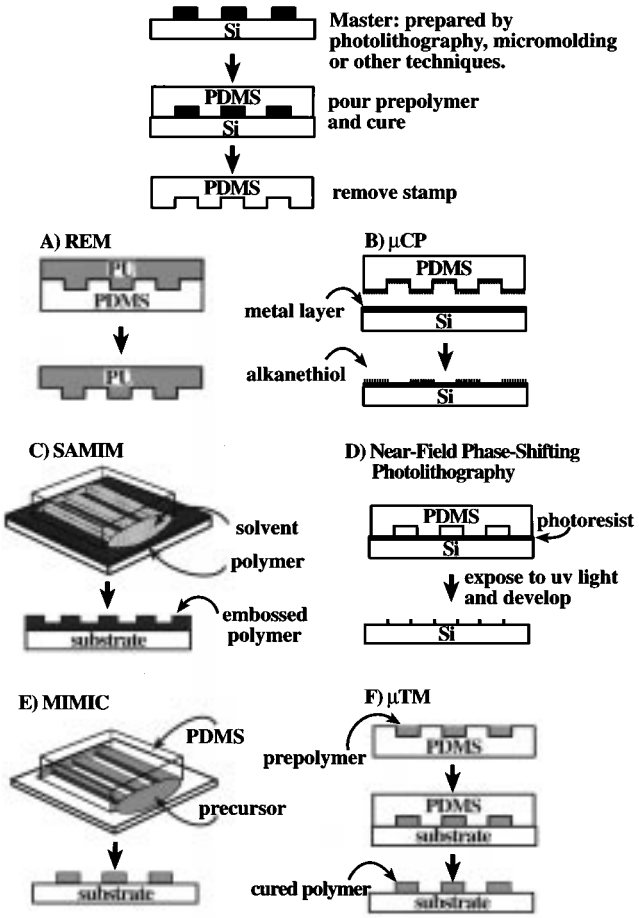

Figure 3. Schematic procedures describing soft lithographic methods[38,161] and near-field phase-shifting photolithography.[38,162]

new replicas are produced in organic polymers. The introduction of elastomers into replica molding makes it easier to preserve small, fragile structures on the original master; the low surface energy (~21.6 dyn/cm) of PDMS, in particular, also allows the replica to be separated from the mold easily.[164] An elastomeric mold also offers the opportunity to manipulate the size and shape of structures on the mold by mechanical or thermal deformation. For example, we have been able to reduce the lateral dimension of nanostructures from ~50 to ~30 nm by replica molding against a PDMS mold which is compressed mechanically.[47]

Figure 4 illustrates the use of REM to generate patterned nanostructures. Figure 4A shows an AFM image of chromium nanostructures on a master that was fabricated using light guiding to pattern the deposition of chromium atoms.[165] Figure 4B shows an AFM image of a polyurethane (PU) replica that was prepared from a PDMS mold cast from this chromium master.[47] Although this process used replica molding twice, the vertical dimension of the chromium nanostructures was reproduced with an accuracy of better than 5 nm over a substantial area (~1 mm^2). Figure 4C shows an AFM image of gold nanostructures on another master (fabricated by Lydia Sohn at Princeton University using a combination of e-beam writing in PMMA, gold evaporation, and lift-off). Figure 4D shows an AFM image of nanostructures in polyurethane generated by replica molding against a PDMS mold cast from this second master. Using this procedure, we have successively produced more than 20 copies of PU nanostructures from a single master; these polymer nanostructures are indistinguishable from each other.

This work based on replica molding against an elastomeric mold has demonstrated a practical protocol for nanomanufacturing: that is, production of multiple copies of indistinguishable nanostructures from a single master, rapidly and economically.[47] The challenge for the future in considering this technique for use in microelectronics or optics is to transfer the structural information present in the polymer into electrical or optical materials, to control distortions in the dimensions of the master and the replicas on

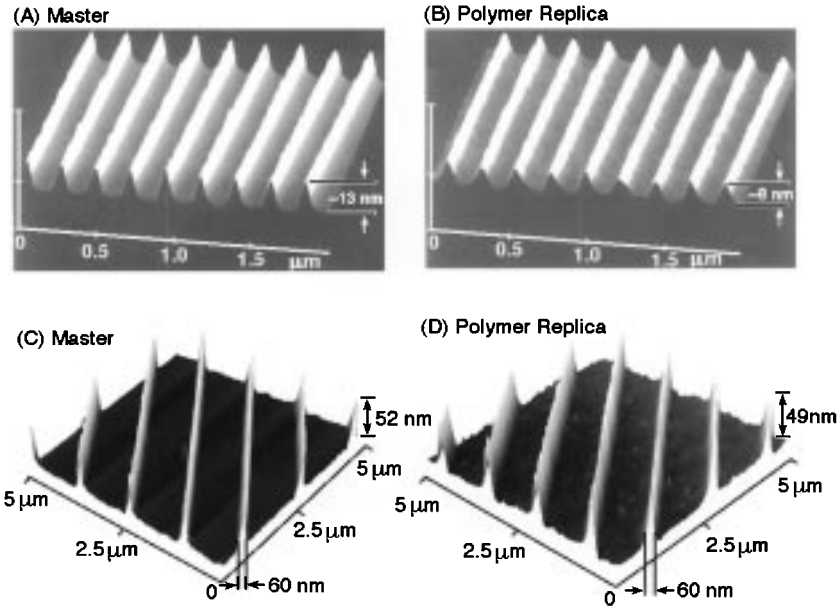

Figure 4. (A,B) AFM images of chromium nanostructures on a master, and a polyurethane replica prepared from a PDMS mold cast from this master. (C,D) AFM images of gold nanostructures on another master, and a polyurethane replica produced from different a PDMS mold cast from this master.[47]

casting and curing the polymers and during use, and to develop schemes that allow the registration required for multilevel fabrication.

Microcontact Printing (μCP). Microcontact printing was mainly developed with self-assembled monolayers (SAMs) of alkanethiolates on gold and silver.[105,166] The procedure for carrying out μCP in these systems is remarkably simple (Figure 3B): an elastomeric PDMS stamp, inked with an appropriate solution of alkanethiol, is brought into contact with the surface of a substrate to transfer the ink molecules to those regions of the substrate that contact the stamp. The success of μCP relies on the conformal contact between the stamp and the surface of the substrate, on the rapid (less than 1 sec!) formation of highly ordered monolayers as a result of self-assembly,[167] and on the autophobicity of the SAM, which effectively blocks the reactive spreading of the ink across the surface.[168] Microcontact printing is an additive process that minimizes waste of starting materials. It is intrinsically parallel: patterned SAMs can be formed over relatively large areas (~50 cm^2) in a single impression.[169] It is also applicable to curved substrates and, hence, is useful in some kinds of 3-D fabrication,[170−172] although the formation of patterned SAMs is at present, intrinsically a 2-D process. It can also be used on inner surfaces that are not accessible to any plausible projection lithographic scheme.[169]

Microcontact printing has been used with a number of systems including SAMs of alkanethiolates on gold,[173] silver,[166] and copper;[174,175] SAMs of alkylsiloxanes on HO-terminated surfaces;[176−183] and SAMs of RPO_3H_2 on aluminum.[184] Of these, alkanethiolates on gold and silver presently give the highest resolution patterning; most other systems have been demonstrated only at scales >1 μm. Microcontact printing can routinely form patterns of alkanethiolate SAMs on gold and silver with in-plane dimensions at the scale of ~500 nm and with some difficulty with dimensions <100 nm.[185]

The patterned SAMs can be used either as resists in selective wet etching[186] or as templates in selective deposition[177−179,181,183] to form patterned structures of a variety of materials: metals, silicon, liquids (by dipping or condensation from the vapor), organic polymers (by dipping or polymerization of monomer), and even biological species.[187] Figure 5 shows SEM images of nanostructures of gold and silver that were fabricated using μCP, followed by selective wet etching. Lateral force microscopy (LFM) shows that patterned SAMs of hexadecanethiolate on gold have an edge roughness that is less than ~50 nm.[188] These results indicate that μCP has the capability to produce structures with lateral dimensions <100 nm. We believe that the edge resolution of nanostructures in coinage metals fabricated by a combination of μCP and wet etching is largely determined by the grain size of the metal films, the etching process, or a combination of these factors. The smallest features fabricated with a combination of μCP of SAMs and wet etching are trenches in gold that are ~35-nm wide and separated by ~350 nm (Figure 5B).[185] The minimum feature size that can be achieved by μCP

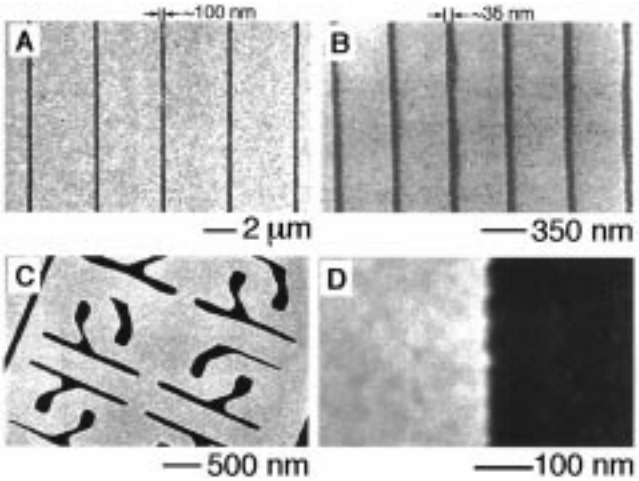

Figure 5. SEM images of nanostructures of gold (A,B) and silver (C,D) fabricated using μCP with hexadecanethiol, followed by selective wet etching. (A) An array of ~100-nm trenches fabricated in gold by μCP with controlled reactive spreading of hexadecanethiol under water.[191] (B) Array of ~35-nm trenches fabricated in gold by μCP with hexadecanethiol (courtesy of Dr. Hans Biebuyck of IBM).[185] (C,D) Patterned structures in silver with feature sizes of ~200 nm fabricated by μCP with hexadecanethiol.[166]

has still not been completely defined, and continuing systematic study on the mechanical properties of the stamp and of interactions between the stamp, the ink, and the substrate will be useful for the optimization of μCP for use in the <100-nm regime.[98,189]

Solvent-Assisted Micromolding. Solvent-assisted micromolding (SAMIM) shares operational principles with embossing, except that SAMIM uses a solvent instead of temperature to "soften" the polymeric material and an elastomeric PDMS mold rather than a rigid one to emboss relief structures into the surface of a substrate.[190] In SAMIM (Figure 3C), a PDMS mold is wetted with a good solvent for the polymer to be embossed and brought into contact with the surface of that polymer. The solvent is selected to dissolve (or "soften") the substrate without affecting the PDMS mold. After the solvent dissipates and/or evaporates, the mold is removed and a patterned relief structure complementary to that on the surface of the mold remains. This structure forms by molding the thin layer of fluid (probably, gellike) material generated by interaction of the polymer and the solvent.

SAMIM has been used with a wide variety of organic polymers: polystyrene, PMMA, Novalac photoresists, poly(vinyl chloride), cellulose acetate, and precursors to conjugated organic polymers.[190,192] Its only requirement is for a relatively volatile solvent that dissolves the substrate and wets (but does not significantly swell) the surface of the PDMS mold. Other materials can also be added into the solvent; these materials are then incorporated into the resulting relief structures. SAMIM is capable of replicating complex quasi 3-D relief structures over relatively large areas in a single step. Figure 6 shows AFM images of nanostructures that we have generated using SAMIM: parallel lines ~60-nm wide and ~50-nm high formed in a thin film of photoresist. These features rest on top of a thin underlying film of the

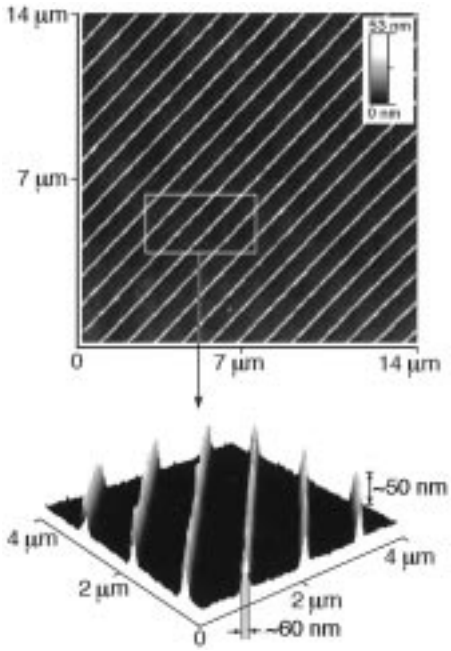

Figure 6. AFM images of polymeric nanostructures fabricated using SAMIM in a thin (~0.4 mm thick) film of Microposit 1805 spin-coated on Si/SiO_2.[190] Reprinted by permission from *Adv. Mater.* **1997**, *9* (8), 651−654. Copyright 1997, Wiley-VCH Verlag GmbH.

polymer; similar underlying films are also often formed in replica molding and in embossing. If necessary, this thin film can be removed by reactive ion etching (RIE) in an O_2 plasma without excessive damage to the surface topography that represents the pattern.

An important characteristic of SAMIM is that it is "self-cleaning". Dust particles on the surface of the stamp tend to remain in the molded polymer. Each cycle of use therefore cleans the mold and limits the influence of adventitious particulates to one cycle of replication. The extent to which the surface of the mold is eventually wetted by and damaged by the polymer being molded remains to be established.

4.3. Embossing with Rigid Masters

Conventional embossing uses a rigid master (for example, a master made of nickel or SiO_2) to imprint relief structures into a thermoplastic polymer (for example, polycarbonate or PMMA) that has been thermally softened.[2,88] It is a simple, reliable, cost-effective, and high-throughput process and is the standard for manufacturing replicas of holograms, diffraction gratings, and compact disks (CDs).[2,88] Recently, this technique has been reexamined as a method for producing nanometer-sized structures of semiconductors, metals, and other materials commonly used in microelectronic circuitry or information storage.[91,193] Chou et al. have used embossing with a Si/SiO_2 master to generate features in silicon with lateral dimensions as small as ~25 nm.[91] It is remarkable that such nanostructures can be generated over areas as large as 3 cm^2,[194] given the fact that it is nontrivial to bring two rigid substrates into conformal contact (for example, one cannot reproducibly achieve zero gaps in contact-mode photolithography) and then separate them while a thin film of polymer remains between them. Using this technique, Chou et al. have fabricated prototype functional devices such as silicon field-effect transistors (FETs).[195] More recently, they and other groups have explored this technique as a potential method for producing binary structures for high-density information storage, including arrays of nanometer-sized bars of cobalt or nickel for quantized magnetic disks and nanometer-sized pits in polymer films for optical disks.[196] The initial success of this technique indicates that it may be worthwhile to reexamine other existing microlithographic techniques for their potential in nanofabrication.

Embossing shares with SAMIM the characteristic that it is self-cleaning. Release of the polymer being embossed from the master, damage to the master while it is under pressure, and the importance of distortions in the embossed structures due to thermal cycling during molding all remain to be defined.

4.4. Near-Field Phase-Shifting Photolithography

The resolution in projection photolithography is fundamentally limited by the wavelength of the light used for exposure and by the numerical aperture of the imaging optics.[48] Contact-mode photolithography with an amplitude mask, on the other hand, has a resolution that can be made exceedingly high without changing the wavelength by simply reducing the size of the gap between the mask and by minimizing the thickness of the resist. Projection and contact techniques have different dependence on wavelength in part because the former does not allow the photoresist to interact with evanescent waves, which are nonpropagating electromagnetic modes that can modulate the intensity at spatial frequencies higher than the diffraction limit allows. These waves are confined to a narrow region near the mask and cannot propagate through imaging optics in projection systems. Approximate calculations of the near field show that for a slit with a width of $\lambda/2$, the intensity in the evanescent modes (which, for this situation, is slightly less than the intensity in the propagating modes at zero separation from the mask) decays by a factor of ~10 over a distance of $\sim\lambda/4$ from the mask, where λ is the wavelength of the light evaluated in the medium into which it propagates as it passes through the mask.[197]

On the basis of NSOM imaging results, better than $\lambda/10$ should be achievable with contact photolithography and even smaller features should be possible if highly nonlinear resists are used.[15] Even elaborate vacuum systems, however, cannot pull a rigid or semiflexible mask close enough (even separations less than ~1 μm can be difficult to achieve) to the resist over large areas to take advantage of the full potential of near-field optics, because dust on the resist or the mask, nonuniformities in the thickness of the resist, or bowing of the mask or the substrate that supports the resist prevent the necessary positioning. NSOM photolithography avoids this problem through the use of narrow, subwavelength sources of light that can be scanned within ~10 nm of the surface of the resist.[15] Unfortunately, this technique, like other

scanning probe methods, has the drawback that patterning must occur in a serial fashion.

There have been several attempts to design specialized masks for eliminating the mask-resist gap in large area contact-mode photolithography.[198,199] Until recently, such masks have all been based on thin layers of rigid materials that can be bent and pulled close to the sample by applying external forces. These methods yielded encouraging initial results: the smallest features generated in the first experiments were ~400 nm, and since then, features as small as ~100 nm have been achieved.[200] In all of these methods, however, patterning over large areas was difficult and external forces were required to bring the mask and the resist into contact. As a result, many of the disadvantages of conventional contact photolithography—potential damage to mask and sample (resulting from contact, shear, and adhesion) and susceptibility to dust and other contaminants—remain.

A different approach to conformal near-field photolithography uses masks constructed from "soft" organic elastomeric polymers.[39,128,162] These soft masks spontaneously and nondestructively come into conformal, atomic-level contact with layers of photoresist over areas that can exceed several hundred square centimeters without the need for external force. They completely eliminate the gap between projecting regions of the mask and the resist; atomic-level contact allows for exposure of the resist directly in the near field of the mask. Dust or other nonuniformities only locally frustrate contact. The masks are essentially insensitive to modest degrees of bowing or warping of the substrate and can even be applied to curved surfaces.

We have used elastomeric binary phase-shifting masks with conventional photoresists and polychromatic, incoherent light from low-cost ultraviolet lamps to produce ~90-nm features over large areas on flat surfaces and on the surfaces of cylindrical lenses.[39,162] By optimizing the construction of the masks, we generated lines as narrow as 50 nm.[60,61] Figure 7 shows representative results. This resolution corresponds approximately to $\lambda_r/5$, where λ_r is the wavelength of the light used for exposure evaluated in the photoresist; it significantly exceeds the diffraction limit in air. Since the exposure of the top surface of the resist happens directly in the near field of the mask, we believe that features even smaller than 50 nm will be possible. It is likely that the resolution can be improved by reducing the wavelength of the light, the thickness of the resist, the thickness of the modulating component (in our initial work, the surface relief) of the masks, by increasing the index of refraction of the resist, by using surface-sensitive resists, or by a combination of these approaches.

With simple binary phase masks, it is possible to generate a wide variety of patterns that consist of lines with fixed width; producing lines with variable widths or other types of features was difficult. Schmid et al. have since described the addition of amplitude modulating components derived from thin layers of gold to elastomeric phase masks[201] or using feature

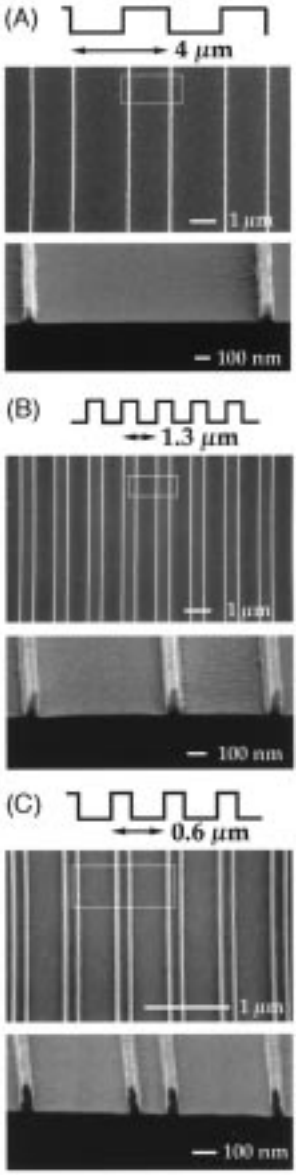

Figure 7. SEM images of lines in positive photoresist formed by near-field phase-shifting photolithography using a PDMS mask with 500-nm deep relief. The periodicity of the mask relief decreases from A to C.[39,60,61,162]

sizes on the mask that are equal to or smaller than the wavelength of the light used for exposure.[202] This construction yields masks that have more flexibility in patterning than those based purely on phase modulation: in particular, lines and other more complex features with a wide range of sizes are possible.

We believe that there are two primary limitations inherent to methods based on near-field photolithography with an elastomeric mask: distortions that can arise from lateral deformation of the elastomer when it comes into conformal contact with the resist and vertical deformations that can cause sagging of the recessed regions of the masks.[203] With the masks that are used now, lateral distortions are on the order of, or less than, 1 μm over areas of ~1 cm^2. Stiffer elastomers and perhaps active control of the deformations of the masks may enable reductions in these distortions. Stiff elastomeric materials and thin elastomeric amplitude masks will also minimize or

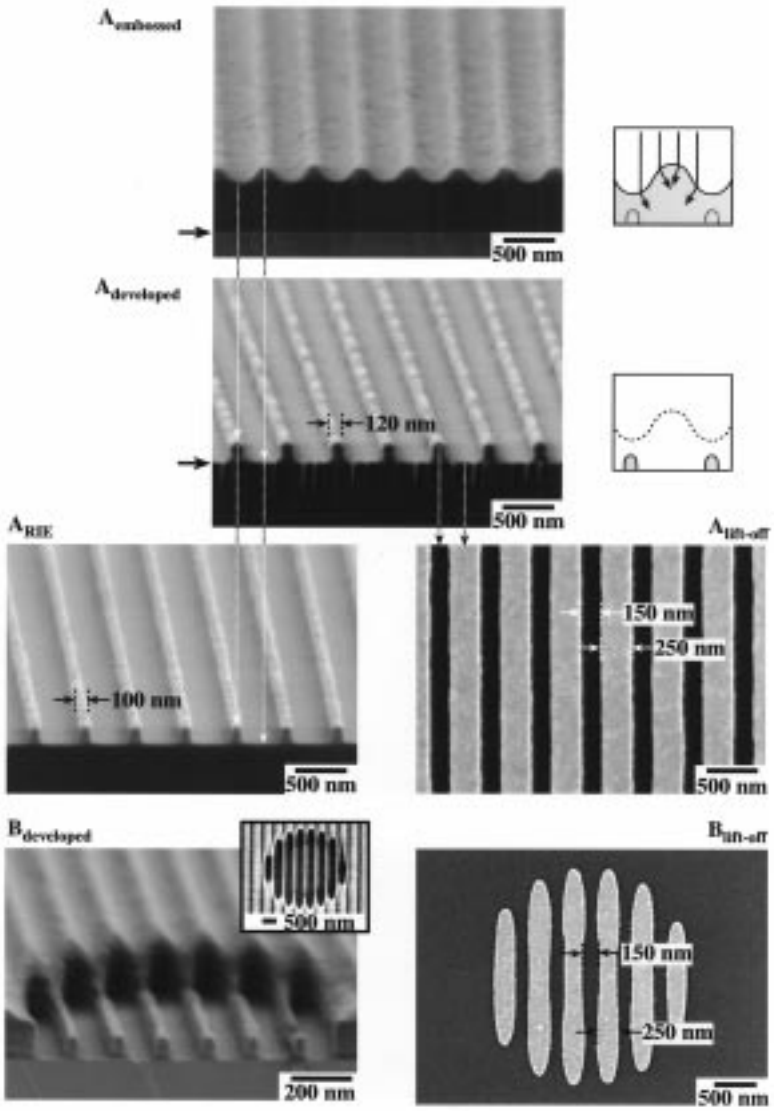

Figure 8. SEM images of nanostructures generated by topographically directed photolithography ($\lambda = 350-440$ nm).[204] Dashed arrows show where the features originate. ($A_{embossed}$) Grating embossed on a 0.48-μm photoresist film with a 2400 lines/mm holographic grating; ($A_{developed}$) exposed for 2.75 s and developed for 1 min. The drawings suggest the exposure process schematically. The photoresist pattern was then transferred into silicon (A_{RIE}) by RIE and gold ($A_{lift-off}$) by lift-off. ($B_{developed}$) Embossed 2400 lines/mm holographic grating was covered with an amplitude mask of 3-μm circles separated by 11 μm and exposed for 1.85 s. ($B_{lift-off}$) The resulting pattern was transferred into gold by lift-off. Reprinted with permission from *Appl. Phys. Lett.* **1998**, *73*, 2893−2895. Copyright 1998, American Institute of Physics.

eliminate adverse effects of sagging. Even without further improvement, we believe that these techniques will be valuable for a range of applications that require rapid, low-cost nanopatterning over large areas. They currently provide one of the easiest experimental routes to nanostructures that can have a wide range of possible geometries.

4.5. Topographically Directed Photolithography

The patterned structure of photoresist generated by SAMIM has been used in a photolithographic technique we call topographically directed photolithography (TOP).[204] In this method, a topographically patterned layer of photoresist (for example, an array of lenses or rectangular gratings) directs UV light inside the resist layer in the optical near field, during exposure. Development gives complex features with feature sizes from ∼50 to ∼200 nm over large areas. It uses no mask in the conventional sense, and although it is a photolithographic technique, it circumvents many of the limitations of both conventional far-field lithography and near-field photolithography. Figure 8 shows SEM images of nanofeatures generated by this procedure. Subsequent process such as RIE or lift-off can transfer the pattern into other materials.

4.6. Topographically Directed Etching

This technique uses a topographically patterned surface to generate a pattern corresponding to the edges of the original pattern. It is, therefore, a technique similar to pure phase-shifting photolithography in the types of patterns it can generate: the *edges* of the original pattern become the pattern after the transfer step.[205] In this technique (Figure 9), a layer of metal (gold or silver in the first demonstration) is deposited on a substrate and this initial layer is then patterned with metal islands, in the same or

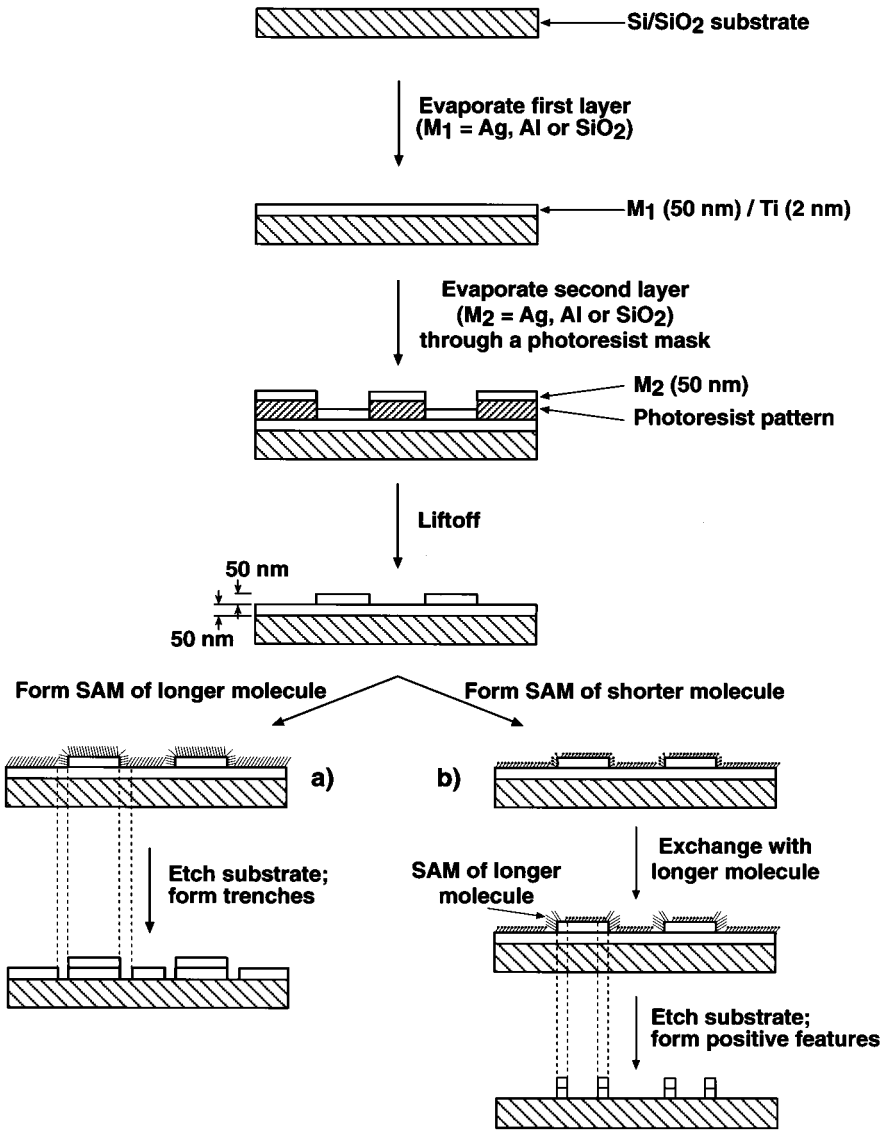

Figure 9. Schematic description of topographically directed etching.[205]

a different metal, by lift-off or a through-mask deposition. Exposure of the topographically patterned metal layer to a thiol generates a SAM that is disordered at the edges of the metal islands. The disordered regions etch selectively; the resulting features are the outline of the patterned island. The size of the etched region is controlled by the etching time; trenches obtained by a 10-s etch are ~50-nm wide (Figure 10). Exchange in the disordered region with a thiol of a longer chain length followed by etching gives the inverse pattern as the area with shorter chain thiols are etched first.

4.7. Lithography with Neutral Metastable Atoms

The development of optics for neutral atomic beams[206−208] has enabled lithography to be carried out with an alternative exposure source—neutral metastable atoms.[209,210] The use of neutral atoms offers two advantages relative to methods based on high-energy electrons or ions: (i) neutral atoms with low kinetic energies cause less damage to the mask than do high-energy charged particles; (ii) neutral atoms do not interact (over typical distances) electrostatically, and (iii) electrostatic interactions do not limit the resolution. The use of patterned beams of neutral metastable atoms was originally demonstrated with SAMs of alkanethiolates on gold[209] and later extended to other systems.[210,211] In patterning SAMs on gold, the substrate is exposed to a beam of neutral metastable atoms (Ar* or Cs*) through a physical mask that is usually placed on the surface of the substrate.[74,75,209] The release of energy from the metastable atoms induces sufficient damage to the unmasked areas of the monolayer to make them susceptible to etching. As a result, the gold under the damaged SAM can be removed by a wet etchant.

The electronic energy released from the neutral metastable atoms can also be used to decompose hydrocarbon vapors and deposit an etch-resistant carbonaceous film of unknown composition on the exposed regions of the surface (a form of so-called "contamination lithography").[77,210] Figure 11 shows SEM images of nanostructures that have been fabricated by lithography with neutral metastable atoms. The smallest structures that have been fabricated are arrays of holes in gold that are ~70 nm in

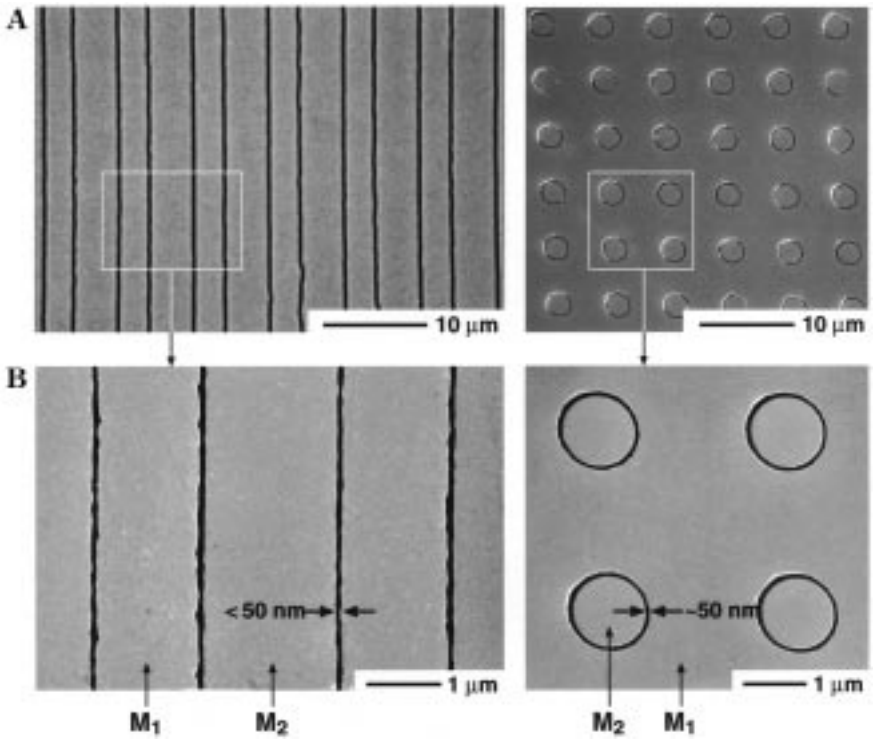

Figure 10. SEM images of nanostructures fabricated by topographically directed etching.[205] Selective etching of the micropatterned substrates—2 μm wide lines (left) and a square array of circles with 1.5 μm diameter (right)—fabricated by depositing silver (50 nm) on an silver film through a layer of patterned photoresist, followed by lift-off. (A) Low-magnification SEM, showing the homogeneity of the pattern. (B) Trenches (~50-nm wide) in the metal substrates fabricated by etching for 10 s. Reprinted by permission from *Nature* **1998**, *394*, 868−871. Copyright 1998, Macmillan Magazines Ltd.

lateral dimensions.[74] A disadvantage of the use of proximal stencil masks is that 1:1 imaging is required (for example, a 10-nm line requires a 10-nm slit) and small gaps are necessary (a <5-μm gap is required for <7-nm features) to prevent diffraction. Methods that rely on light to quench parts of a neutral metastable beam and those that use optical interference patterns for lenses to guide deposition of atoms on surfaces have the drawback that the densities of the features that can be formed in a single step are limited by the optical wavelength (unless, of course, the pattern of light is modulated during an exposure). Neutral-atom lithography will probably require development of appropriate stencil masks or projection optics before it becomes a practically attractive method; the use of optical forces provides a promising approach for constructing the atom optical elements that may be necessary.[77,212]

4.8. Approaches to Size Reduction

A number of strategies are capable of reducing the feature size of a test pattern from 1 to 10 μm to ≤200 nm. Tonucci et al. have fabricated glass membranes with hexagonal arrays of channels as small as ~30 nm in diameter by repeatedly drawing a bundle of glass fibers (consisting of an etchable glass core surrounded by a sheath of a different, etch-resistant glass) with a starting diameter of >1 μm.[122] The nanochannel membrane fabricated from the cross section of the bundle can be further used as a mask in metal evaporation or as a mold in replica molding to fabricate nanostructure of other materials.[213] Birks et al. have fabricated photonic band-gap optical fibers using a similar procedure.[123] Xia et al. have generated structures of 100−200 nm in size by mechanically manipulating the elastomeric stamp (or mold) used in microcontact printing or replica molding.[124,126,127] Figure 12 shows a typical example in which the feature size has been reduced from ~2 μm to ~200 nm by two cycles of replica molding of polyurethane against a mechanically compressed PDMS mold. Other approaches relying on size reduction from an original pattern have also been explored as potential routes to nanostructures, including μCP with controlled reactive spreading (Figure 5A)[191] and μCP or photolithography with a PDMS block cast from V-shaped microtrenches etched in a Si(100) substrate.[125,128] Although these methods may lack the characteristics required for registration in device fabrication, they offer an easy access to simple patterns of nanostructures that are directly useful in making sensors, arrays of nanoelectrodes, and diffraction gratings.

5. Techniques for Making Regular or Simple Patterns

A number of techniques (Table 4) have been demonstrated for making regular or simple patterns of nanostructures such as parallel lines and arrays of holes or posts. These simple structures can be directly used as diffraction gratings, arrays of nanoelectrodes, and arrays of quantum dots. These techniques may also be valuable when combined with other more general techniques for pattern formation.

Interference or Holographic Lithography. The interference pattern generated by two mutually

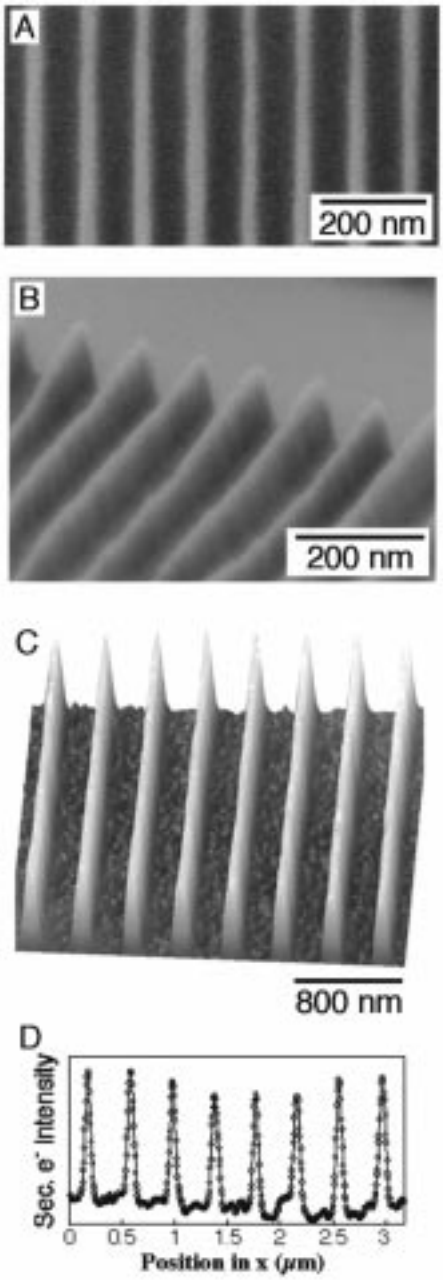

Figure 11. Patterned nanostructures fabricated by metastable atom lithography (courtesy of Prof. Mara Prentiss of Harvard University).[74−77] (A) SEM image of features (white) etched in Si(110) by RIE. Features were patterned by contamination lithography using metastable argon atoms passed through a Si_3N_4 mask in contact with the surface. (B) Features viewed at a 75° angle; they have an aspect ratio greater than 2:1. (C) AFM image of the pattern etched into a Si(110) substrate. Features were patterned using metastable argon atoms passing through a standing wave. They are 12-nm tall and extended over and area of ~0.5 mm^2. (D) Average line profiles of SEM images used to determine the width of the features. Analysis of the secondary electron intensity versus position indicates that the FWHM of the lines is 65 ± 5 nm. A and B reprinted with permission from *J. Vac. Sci. Technol. B* **1998**, *16*, 1155−1160. Copyright 1998, American Vacuum Society.

coherent laser beams can be recorded in a thin film of photoresist.[2,214−216] After development, an array of parallel lines is created in the resist film and the spacing between the lines is $\lambda/2n \sin(\theta/2)$, where λ is the wavelength of the laser, n is the refractive index

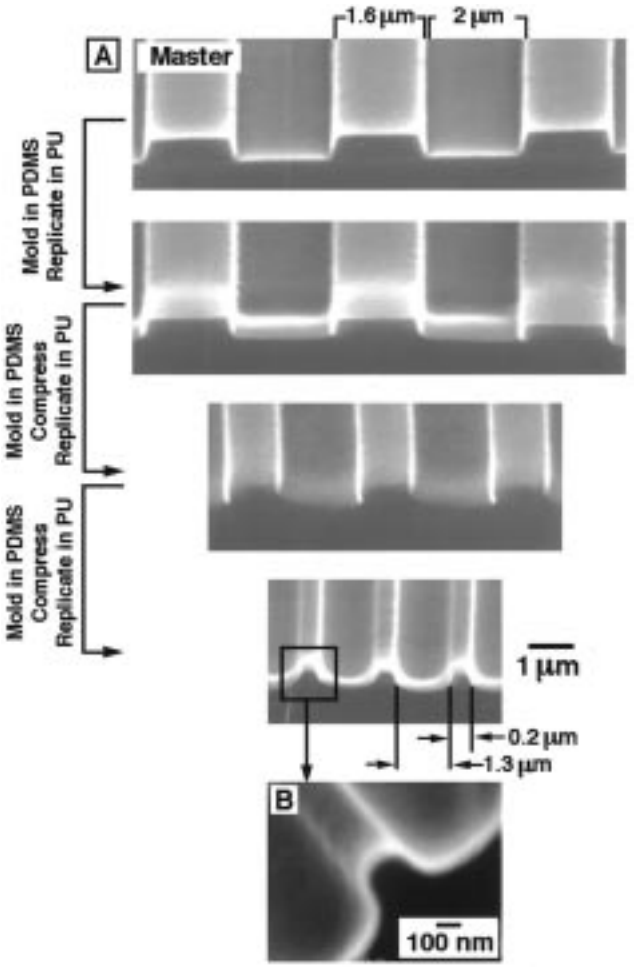

Figure 12. Cross-sectional SEMs of the original master (generated in a photoresist film coated on a silicon wafer using photolithography) and the polyurethane replicas generated after different cycles of replication in PDMS, compression, and replication in polyurethane.[126,127]

of the photoresist, and θ is the angle of intersection of the beams. The pattern in the resist film can be further transferred into underlying substrates such as SiO_2, Si_3N_4, and silicon by RIE. This method is widely used in industry to manufacture holographic diffraction gratings and antireflection coatings. By exposure of the photoresist to the interference pattern twice (orthogonally to each other), 2-D arrays of posts can be fabricated,[217] and this procedure is a possible approach to manufacturing field-emission displays (FEDs).[218] Figure 13 shows the AFM image of an array of 200-nm posts in Si_3N_4 that was fabricated by holographic lithography using an argon-ion laser (λ = 351 nm), followed by RIE.[219]

Complex patterns can be formed by intersecting more than two laser beams or by using multiple sequential exposures. The use of interference patterns produced through the use of multiple diffraction gratings[220,221] increases the flexibility of holographic patterning. In these cases, the period of the holographically defined grating structure is equal to one-half of the period of a single diffraction grating divided by the number of gratings.[221] Gratings with periods as small as ~100 nm have been fabricated using this method. Imaging interferometric lithography uses multiple offset exposures or multiple

Table 4. Techniques for Making Regular or Simple Nanoscale Patterns[a]

pattern formation using	writing	replication	refs
photons			
holographic lithography	yes	yes	214−221
deposition			
laser-focused deposition	yes	no	165, 223, 224
cleaved edge overgrowth	yes	no	113, 259, 260
self-assembly			
crystallization of proteins, colloids, and microspheres	yes	no	226−242
microphase separation of block copolymers	yes	no	106, 246−251
other			
anodic oxidation of aluminum	yes	no	252−257

[a] In this table, yes means this technique is practical for writing or replication of features of ≤100 nm; no means this technique cannot practically be so used.

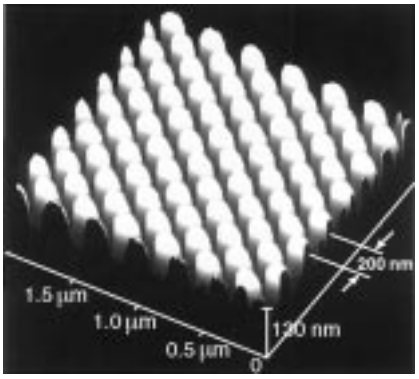

Figure 13. AFM image of Si_3N_4 nanostructures fabricated using holographic lithography,[219] followed by wet etching of photoresist and RIE of Si_3N_4 (the sample was provided by Prof. Henry Smith of MIT, and the AFM image was taken by Dr. Jabez McClelland of NIST).

mutually incoherent laser sources in a single exposure to generate interference and is theoretically able to achieve feature sizes of $\lambda/4$ while retaining the ability to make complex patterns.[222]

Laser-Focused Deposition. The interference pattern produced by the intersection of two or more laser beams can focus certain neutral atoms (for example, chromium or aluminum) into patterns as they deposit onto a surface.[165,223,224] For two beams, counterpropagating parallel to the surface on which deposition occurs, each node of the optical standing wave acts as a cylindrical lens. Atoms passing through the standing wave are focused into a series of parallel lines (Figure 4A) with a period equal to half the wavelength of the laser. A two-dimensional standing wave formed by crossing more than two laser beams has been used to focus chromium or aluminum atoms into an array of posts on the surface of a substrate.[225] Prentiss et al. have also used this technique to focus metastable Ar* atoms that can be used for patterned deposition of ultrathin resists.[77]

Crystallization of Proteins, Colloids, and Microspheres. Many methods are capable of forming two-dimensional crystals of spherical or quasi-spherical particles: proteins,[102,226−231] colloidal particles,[232] and polymer latexes.[106,233−237] The hexagonal-close-packed structures formed from spherical particles with diameters in the range of 300 nm to 4 μm have been used as physical masks, in conjunction with metal evaporation, to form patterned arrays of nanoscale metal islands.[238−243] The lateral dimensions of metal islands and the spacing between them can be precisely controlled by using spherical particles with different sizes. This method is remarkable for its simplicity and for its capability to form nanostructures over a wide range of sizes: the smallest spacing and pitch that have been attained simultaneously are ~50 and ~300 nm.[236] New procedures that can produce defect-free 2-D crystals over relatively large areas are still needed. Nanostructures generated by current procedures may be useful, for example, in fabricating arrays of nanoelectrodes, quantum dot arrays, and photovoltaic cells. They may also find applications as photonic band-gap materials.[244]

Microphase Separation of Block Copolymers. Block copolymers having the correct dimensions for their blocks develop domain patterns at equilibrium: these patterns reflect the repulsions and attractions of the monomer units for one another and the constraints imposed by their covalent connections.[100,101,245] For example, poly(styrene-*block*-isoprene), a block copolymer consisting of two chemically distinct ends, can exhibit a wide range of microphase-separated morphologies: spherical microdomains, cylindrical microdomains, and lamellar structures.[246,247] The relative lengths of the two monomer units, their interactions with each other, and the character of the boundary surfaces primarily determine the geometry of the phase-separated state. The domains of block copolymer in a coated thin film can also be guided into arbitrary structures by patterning the surface of the substrate with monolayers with different interfacial energies.[248] Because different monomers have different resistance to etching in RIE,[106] a spin-coated film of block polymer can be used as mask to transfer the domain pattern in the polymer film into the underlying substrate. Arrays of posts or holes with dimensions less than 20 nm have been successfully fabricated in Si_3N_4 using this procedure. The phase-separated polymers can also be used to guide the growth or deposition of materials such as gold.[249] Means for controlling the geometry of the phase-separated patterns, such as those based on electric fields, for example, appear to be promising but will require further development.[250,251]

Anodic Oxidation of Aluminum Films. Anodic oxidation of aluminum films in an acidic solution generates an array of hexagonally packed columnar holes in the film.[252] This procedure has long been applied in commercial production of alumina membranes used for separation. Pore densities as high as 10^{11} per cm^2 can be achieved. The size of pores can

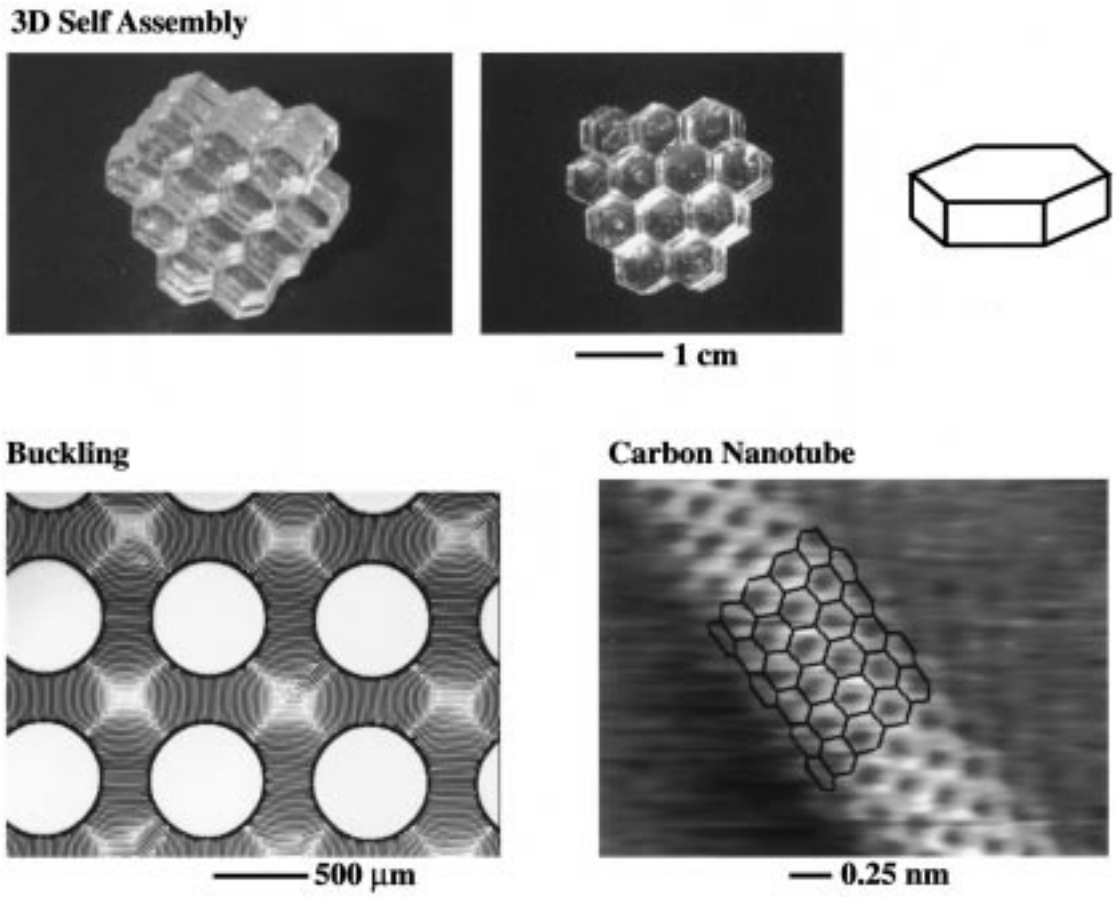

Figure 14. Illustration of new concepts that are potentially useful in nanopatterning: meso-scale three-dimensional self-assembly of polyurethane plates;[264] buckling of a PDMS surface patterned in bas relief with 600-μm circles,[265] and a STM image (courtesy of Prof. Charles Lieber of Harvard University) of a single-walled carbon nanotube.[266]

be precisely controlled in the range of 5−200 nm by changing electrolyte composition, applied voltage, and temperature. A one-dimensional array of holes (with a high aspect ratio) was also fabricated by anodic oxidation of an evaporated thin film of aluminum sandwiched between two solid substrates.[253] This kind of membrane has been extensively explored (largely by Martin and co-workers) as a template to synthesize nanostructures of a wide range of functional materials.[89,254−257]

Cleaved Edge Overgrowth (CEO). As described previously in this review, CEO takes advantage of multilayer structures grown by molecular-beam epitaxy (MBE).[113,258] It has been employed to fabricate atomically precise structures such as quantum wires and quantum dots. In this technique, a superlattice structure consisting, for example, of alternating layers of AlGaAs and GaAs is made by MBE.[112] The sample is then remounted in the growth chamber in an orthogonal direction to the original mounting and cleaved through the thickness of the multilayer structure in situ to produce an atomically clean surface. MBE or electrochemical deposition is then used to grow epitaxial layers on selected regions of the exposed surface. Conventional forms of lithography have also been used to pattern this cleaved surface. This approach enables the formation of intersecting quantum wells with atomic- or angstrom-level control of the thickness in two directions.[258] Devices such as quantum wire lasers formed from the intersection of ∼7-nm wide quantum wells have been fabricated with this method.[259,260] More recently, quantum dot structures have been formed at step edges on the cleaved surface of GaAs[261] and through a 2-fold cleaving method.[262] For the fabrication of many types of quantum structures, CEO yields more uniform structures than electron-beam or optical lithography or selective area deposition, because CEO incorporates the uniformity and precision of MBE.[112,263] CEO is, however, limited to those structures that can be fabricated along the natural cleavage directions of a substrate and along lattice planes on which MBE growth occurs easily.[113] Also, the structures must be built up from intersecting planes of material.

6. New Concepts, Not Yet Demonstrated for 100-nm-Scale Patterning

The challenges to generating broadly useful techniques for fabricating on nanometer length scales have led to the development of radically different approaches (Figure 14). Most of these methods have been developed at the μm or mm scale and need to be scaled down to the <100-nm scale. Some of them have been demonstrated for generating nanostructures but have not yet been adapted for patterning surfaces.

Meso-Scale Self-Assembly (MESA). The concepts of molecular self-assembly have been extended to the directed self-assembly of meso-scale (100 μm

to 5 mm sized) objects.[104,264,267,268] The assembly of hexagonal PDMS plates at the water-perfluorodecalin (PFD) interface, driven by capillary forces, is an example.[104,267] By controlling the hydrophilicity of the sides of these plates, they can be directed into arrays having a range of structures. MESA is able to generate a substantial range of structures and is a promising technique for precision microassembly.

Whether it will be practical to use capillary forces to assemble nanostructures is presently unclear. Nagayama has used capillary forces (at the receding edge of a meniscus) to assemble nanospheres;[234] there is, therefore, some hope that these interactions might be useful (albeit in a different context than that used by Bowden et al.[104]) in nanostructure assembly. Other forces have also been used to make regular assemblies of <100 nm-scale objects: the examples of Grier and Murray[236]—based on combinations of Coulombic interactions and more complex self-polarization—indicate that if capillary forces fail, it is possible to consider other types of interactions. The work of both Mirkin et al.[269] and Alivisatos et al.,[270] for example, show how DNA can be used to assemble arrays of gold colloids as small as a few nanometers. Other promising interactions that could be used to direct assembly of nanoparticles include magnetic and electrical fields: Ferrofluids and electrorheological fluids containing nanoscopic particles can be aligned into ordered structures in a magnetic[271] or electric field.[272] Both are currently being investigated in wide ranging applications: for example, ferrofluids have been shown to be useful in nanomotors and generators.[273] A key, unsolved problem in this area is the development of flexible methods for making small (<100 nm) objects with a substantial degree of control over their shapes and the character of their individual faces.

Buckling. When a block of PDMS is heated, it expands. If the surface is heated briefly with an oxygen plasma (to introduce a thin SiO_2-like layer) or coated with a thin film of gold by e-beam evaporation and then allowed to cool, the difference in coefficients of thermal expansion of the bulk PDMS and the relatively incompressible surface layer places that layer under compressive stress.[265] The stress is relieved by formation of uniform buckles in the surface. On a flat, uniform surface, these surface waves form highly irregular patterns. If, however, the PDMS surface is embossed, the bas-relief pattern causes ordering in the surface waves. Highly regular structures with periodicity of <1 μm have been produced.

The spontaneous formation of small ordered structures (the surface waves) under the influence of a larger template (the bas relief) is a process that could be useful if the period of the waves could be reduced by a factor of 10−100 from those observed in current examples. The phenomenon of spontaneous ordering through formation of surface waves has been analyzed theoretically, and the materials properties required to achieve waves with shorter wavelengths are understood.

Assembly Using Optical Tweezers. Forces generated by refraction of a tightly focused laser beam passing through an interface between two media with different indices of refraction can be used to manipulate micrometer-sized particles and assemble them into 3-D arrays. Burns et al. used 1−5 laser beams passing through a glass sample cell to organize particles (with a range of compositions: polystyrene beads, titanium dioxide colloids, and biological cells) and generated what they termed "optical matter": systems held together by the interaction of oscillating electromagnetic fields with matter, rather than by the Coulombic interactions of electrons with nuclei.[274] The periodicities are governed by the wavelength of light used (λ = 514 nm) and the angle of the intersecting beams. This method of crystallizing particles is capable of generating complex (albeit periodic) patterns. It can also be used to hold particles in place while the liquid carrying the particles is cured into a solid, for example. Structures formed in this manner may be useful for three-dimensional photonic band-gap crystals.[244] Optical tweezers have also been considered as a tool to assemble nanometer-scale parts or to make connections to self-assembled structures in a nanosystem.

Growth of Buckyballs and Nanotubes. New forms of carbon nanostructures—buckyballs and nanotubes[266,275−277]—are an important new class of materials, in part because they can be either semiconductors or metallic conductors.[266,277] They can also be converted into nanorods of other functional materials such as ceramics by reacting with different chemical reagents.[278] In principle, single-wall, conductive graphitic nanotubes are probably nearly ideal quantum wires: they are environmentally stable, defect-free, and intrinsically conductive. Unfortunately, as-prepared carbon nanotubes are usually tangled mats, and although it is now possible to cut them, separate them, and manipulate them individually, it is presently difficult to envision making large, ordered, connected structures with them.[279] The future application of carbon nanotubes in practical device fabrication will probably depend on the invention of some new way of growing them (or equivalent structures) in the desired patterns.[280] Although buckyballs have been assembled into a nanometer-sized abacus on a copper substrate using an STM tip, carbon nanotubes will probably be more useful than buckyballs in fabrication of nanodevices.[281]

7. Conclusions

Physics and electrical engineering now depend on the fabrication of structures with dimensions less than 100 nm to generate tools and devices for many areas of research. Materials science, chemistry, and biology are beginning to require similar capabilities in fabrication. Research in all of these fields will advance the fundamental understanding of systems with dimensions less than 100 nm; it will also create new technologies to support commercial applications of nanoscopic structures.

The largest, most obvious, but not necessarily most realizable opportunities for nanostructures are in electronics, where smaller sizes have historically allowed the production of denser, faster circuits and where the ability to produce nanostructures may lead to new types of devices that operate on quantum

mechanical principles. For true nanosized devices, however, serious problems in circuit design will have to be solved before complex, high-speed integrated circuits can be fabricated. The problem is not just a problem in fabrication of individual small-scale devices; the interactions between these devices, the dissipation of the heat that they generate, and the design of circuits incorporating large numbers of devices differing significantly and unavoidably in their performance are all problems that will also have to be managed.

Examples of applications for nanostructures in areas outside of electronics may include, for instance, ultrasmall mechanical and chemical sensors based on nanoelectromechanical systems and nanoelectrodes, optical elements with nanometer dimensions for photonic band-gap structures or near-field storage devices, and structures for use in cell biology that will have the ability to sense and manipulate phenomena that occur at scales smaller than organelles. These applications, together with a fundamental interest in nanoscience, provide compelling motivation for research into techniques for nanofabrication.

We divide the task of fabricating complex nanostructures into four parts: (i) preparing the masters; (ii) replicating these masters into patterns of sacrificial or functional materials; (iii) transferring the replicated patterns of sacrificial materials into patterns of functional materials; and (iv) registering and aligning patterns to existing features. Conventional scanning electron-beam lithography is now the most widely used technique for generating the masters used in microelectronics (that is, the first task). Although there are certainly opportunities for improving this technique and for establishing other methods that have similar or superior capabilities, we believe that electron-beam lithography, in basically its current form, can provide an acceptable solution to generating masters with feature sizes less than 50 nm and that it will remain an indispensable tool for this purpose. We also believe that the third task—transforming structural into functional patterns—represents a relatively minor challenge for most applications, since many of the established methods—lift-off, patterned etching or ion implantation, and shadowed evaporation—do not depend strongly on feature size. Although registration (the fourth task) is a significant challenge, its solution will likely rely on clever engineering rather than on new chemistry or chemical methods (although self-assembly may ultimately make self-registration possible in some systems).

Rapid, reliable replication of features near or below ~100 nm, on the other hand, is currently both a significantly unsolved problem and one in which we believe innovation in chemical and physical methods can introduce fundamentally new techniques. It seems likely that whatever technologies are used for fabrication in the region below 100 nm will not represent simple engineering extensions of conventional photolithography, although sophisticated enhancements may play a role. There may exist, therefore, an opportunity to introduce new ideas in replication of micro- and nanostructures that is unique in the 50-year history of this field of technology. This review has focused, therefore, mainly on techniques for replication of master structures having nanoscale features into sacrificial or functional materials.

Characteristics present in an ideal method for replication would include low operating and capital cost, flexibility in the materials that can be used, fidelity in the replication, ability to pattern on nonplanar surfaces, low density of defects, high speed and parallel operation, and capability for fabrication in three dimensions. Because all of these characteristics may never be present in a single method, it may be necessary to combine techniques in ways that exploit their various advantages and to design strategies for fabrication that use different methods for different parts of the structure.

Historically, photolithography has been the dominant technique for replication since the origin of fabrication of microelectronic systems; it satisfies many of these requirements, and it has been used for every generation of technology in microelectronics. Photolithography will probably continue to provide an attractive solution to replication at scales down to, perhaps, 70 nm by using 193 nm (or 157 nm) light and/or performance-enhancing techniques such as phase-shifting masks, off-axis illumination, optical proximity correction, or photoresists based on top surface imaging with silylation and dry development. Several companies in the microelectronics industry can now fabricate working devices such as microprocessors and memory cells with features as small as 80 nm using deep uv (248, 193 nm) photolithography, phase shifting masks, and optical proximity correction.[286] Projection photolithography using transmission optics seems, however, to be reaching a point—set by the physics of diffraction and the properties of materials—where it may no longer be the most effective method of fabricating small structures. Lithographic methods based on proximity mode exposure with X-rays and projection systems that use EUV radiation, electrons, or ions are now being aggressively developed for replication at resolutions (<100 nm) that are very challenging to achieve with conventional projection-mode photolithography. These techniques are currently in an engineering development phase; each already has the demonstrated capability to replicate patterns with features less than 100 nm over large areas in a parallel fashion. Although it is not yet clear which of these techniques (if any) will ultimately emerge as an acceptable approach, projection electron-beam lithography, in particular, appears to be promising because (i) it relies on electrons, whose usefulness in generating masters with features well below 100 nm is inarguable, and (ii) it uses projection optics, which allows features in the replicas to be much smaller (~4 times) than those on the mask.

This review focused on a number of exploratory techniques for replication of masters based on high-resolution printing, embossing, molding, and conformal near-field optics; it also touched on other techniques, including replication using arrays of scanning probes or beams of neutral atoms and topographically directed etching and photolithography. Approaches

based on physical contact, such as the soft lithographic techniques, are particularly attractive because they circumvent limitations due to diffraction, allow patterning on curved surfaces, and allow patterning a wide range of materials and materials precursors. These capabilities, which are absent from many other methods, have already enabled soft lithography to begin to establish niche applications in fabricating microfluidic analytical systems,[282,283] in constructing new types of active fiber-optic devices that use microstructures printed onto the surface of the fiber,[284] and in patterning surfaces presenting complex organic functional groups that direct the attachment and metabolism of mammalian cells.[6,7,285] Demonstrating direct compatibility with materials commonly used in microelectronics, controlling registration and distortion, and reducing the density of defects are areas in which all of these methods require further development before they can be competitive with the much more highly developed processes of conventional microelectronics.

Our experiences with soft lithography suggest that traditional metrics, such as feature size and distortion, have only limited value when applied to new techniques with unfamiliar characteristics that do not conform to these metrics. In fact, many future opportunities for microfabrication may exist not only in the development of fabrication techniques that improve speed, resolution, and distortions and in those that enable new processes such as purely additive fabrication of all-organic devices but also in the design of systems that have fundamentally new structures and capabilities (for example, 3-D memories and junctions between biological and electronic components).

Finally, we also included in this review several methods for fabrication of patterned structures based on self-assembly, templated growth, and size reduction that have only been demonstrated at sizes much larger than those of central concern in micro- and nanofabrication. We believe that these (and doubtless many other approaches) are promising directions for exploratory research in fabrication and precision assembly and that they embody new science that may develop into fundamentally new approaches to fabrication of small, patterned structures. In their current state of development, these techniques are potentially valuable only in niche applications or in those where they can be naturally integrated with other more general fabrication techniques, but their fundamental limits and their futures have not been defined. As with soft lithography, however, some of these techniques allow patterning of unconventional materials into structures that can be difficult or impossible to achieve with any standard approaches.

The rich range of technical opportunities in micro- and nanofabrication and the number of new approaches to small-scale fabrication combine to suggest a future where control of structure and function can be accomplished with a sophistication that we cannot presently imagine. The range of these new approaches is now making it possible for makers and users of very small structures to move beyond the familiar question, How can one use photoresist and silicon to make useful structures?, to a newer question, Since it is possible to pattern many materials into many geometries with <100 nm features, what new structures can we now make and what new functions can we now achieve?

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9. References

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