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CHAPTER 122

Sub-Micrometer Patterning Using Soft Lithography

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Abstract

This chapter reviews the current state of soft lithography with a particular emphasis on the patterning of structures having lateral dimensions of below 1 µm. Soft lithography is generally perceived as an ensemble of techniques that collectively employ elastomeric polymers – mostly based on poly(dimethylsiloxane) (PDMS) – in the form of a mold, stamp or mask as the central element of a pattern-forming process. The virtue of these techniques is rapid prototyping during which the structural information from either of these elements is translated into multiple copies of a functional material. This chapter comprises a set of dedicated sections that outline principal patterning strategies, and highlight relatively recent developments in research which are illustrated with selected examples from the open literature.

Keywords

soft lithography • patterning • nanostructures • PDMS • molding • printing • edge effects

122.1 Introduction

The development of lithographic techniques that allow for controlling material properties at sub-micrometer length scales has become central to progress in many scientific and technological areas. In microelectronics, for example, optical lithography has enabled high-volume manufacturing of integrated circuits at ever increasing density, complexity, and performance [1–5]. This evolution has become possible in part through incremental changes towards shorter radiation wavelengths, high-index lens materials, advanced projection systems, and optimized resist formulations, pushing back the limits in resolution set by optical diffraction [3–5]. By using current state-of-the art step-and-repeat exposure tools it is possible, for example, to achieve a minimum transistor gate length of 20 nm and a dynamic random access memory (DRAM) periodicity (half-pitch) of 50 nm [5]. Scanning beams of high-energy particles comprising atoms, ions, and electrons also have evolved into robust and mature technologies which are being used for micro- and nanofabrication purposes [6, 7]. Each of these techniques can create arbitrary features at very high resolution (e.g., 5 nm and below), but their serial nature limits the scope of applications to selected, low-volume fabrication tasks. Any of these techniques relies on complex and expensive equipment, making them unpractical for research in common laboratory environments. Moreover, they are not well suited for applications in a number of emerging fields, such as biotechnology or plastic electronics, where sensitive materials being incompatible with resist and development procedures, curved or uneven substrates, and large-areas are of primary concern.

Soft lithography is an alternative concept to micro- and nanofabrication which offers plausible solutions to many of these challenges. From a methodological point of view, soft lithography promotes the concept of rapid prototyping – that is, the replication of an original pattern (commonly called master) into multiple copies at high turn-over times and at low cost [8]. The central component of the structure-forming process is an elastomeric polymer in the form of a patterned block, sheet, or layer (Figure 122.1), which can be used in a number of ways. For example, it can i) be employed as a mold or master for replicating bas-relief structures in polymeric materials, ii) serve as a stamp to transfer ink onto a substrate in a printing step, iii) provide a mask for near-field optical lithography, or iv) define a network of embedded microchannels to guide a solution along the surface of a substrate. Although all of these

approaches have a different emphasis of patterning, they collectively rely on the rubber-elastic properties of the polymer to achieve intimate, yet reversible contact with another surface, substrate or material. This characteristic feature then eventually helped conceive the term soft lithography in 1996 [9]. By current standards, however, the meaning of soft goes beyond the original nomenclature since this predicate can equally be applied to most of the materials that are to be patterned. In many cases, these are organic compounds (e.g., self-assembling molecules or polymers), biological species (e.g., proteins and cells) and, to some extent, thin metallic films, which are soft in the true sense of the word. Perhaps, properties such as sensitive or fragile are equally emphasized, but in a rather metaphorical manner. Moreover, soft patterning techniques generally proceed at relatively mild conditions, where high temperatures, extreme pressures or exposure to aggressive chemicals are commonly avoided. Here, soft may represent a synonym of this quality similar to as gentle or friendly would possibly be. There is no doubt that soft lithography enjoyed a great deal of popularity over the course of the past decade, and what once had been started by a handful of people at Harvard University has evolved into an enterprise of global dimension. With research in this field traditionally being strong in the United States, there is now an increasing presence of players in Europe and throughout Asia. The open literature also suggests that soft lithography has attracted interest across a broad range of scientific and technological areas, involving academic, government and industrial environments alike. The rapid and inexpensive manner to fabricate elastomeric stamps, molds and masters, along with experimentally unsophisticated, yet powerful patterning concepts are the major reasons for the success of this technology.

This chapter is intended to review the current state of soft lithography, with a particular emphasis on the patterning of structures having lateral dimensions of below 1 μm. The tremendous evolution that soft lithography experienced over the past couple of years makes it nearly impossible to cover all aspects of this topic in a single survey. This chapter therefore is focused on relatively recent developments in research which are illustrated with selected examples from the open literature. As such, the overview presented herein is largely complementary to other review articles that previously have been devoted to this field [8, 10–15]. The forthcoming sections are organized as follows. Section 122.2 covers general aspects of patterning using rubber-elastic polymers. This is followed by a description of techniques that rely on the use of elastomeric master molds for the replication of topographic structures in a

functional material (Section 122.3). Section 122.4 is focused on printing methods that involve elastomeric stamps to generate a pattern of ink on a substrate. Section 122.5 is devoted to techniques that employ topographic edges in a pattern transfer process. Section 122.6 concludes this chapter with some personal remark.

122.2 General Aspects of Patterning with Rubber-Elastic Polymers

Rubber-elastic polymers are instrumental to soft lithography as they enable conformal contact of a stamp, mold, or mask with another surface. To this end, poly(dimethylsiloxane) (PDMS) has been the backbone material for soft lithography since this commercial elastomer combines rubber-elastic flexibility with a number of advantageous characteristics, which include i) chemical inertness, ii) optical transparency (down to ~300 nm), iii) durability, and iv) permeability to organic solvents. Moreover, PDMS is nontoxic, making it suitable for applications that involve biological samples, such as living cells. While repeating units of dimethylsiloxane (–O–Si$(CH_3)_2$–) yield a surface with relatively low interfacial free energy (e.g., ~21.6 × 10^{-3} J m^{-2}), it is possible to tailor transport, wetting, and adhesion properties through a number of modification schemes, including exposure to oxygen plasma [16], deposition of thin films [17], or grafting of functional molecules [18–21]. PDMS comprises a three-dimensional polymer network which is formed through thermal curing of its liquid prepolymer components – that is, an elastomer base (e.g., a vinyl-terminated siloxane) and a cross-linking reagent (e.g., a hydrogen-terminated siloxane) – in the presence of a platinum catalyst. This process is commonly performed on a topographic master (see Section 122.3). Upon curing, the solidified material preserves the shape of the topographic features, yielding an accurate, yet inverse, replica of the master pattern. The chemical and structural constitution of the prepolymers (e.g., their molecular weight and chain length), the ratio of these components in the mixture, and the conditions of curing (e.g., temperature and time), combined, have a direct impact on the elastic properties of resultant material (e.g., Young's modulus, elongation at break etc.), determining the range of applications for which it may (or may not) be used. Most applications employ commercially available kits of Sylgard 184 (Dow Corning) at a ratio of 10:1 (w/w) elastomer base/cross-linker. Resultant polymer networks typically have a surface hardness of 50 (Shore A)

and a Young's modulus of 1 to 5 MPa. It is important to meet appropriate curing conditions (e.g., 60 °C for at least 12 h) to reduce the amount of low-molecular weight residues which can account for a source of contamination in subsequent lithographic steps as these compounds are easily transferred onto other surfaces. While rinsing of the stamp prior to its use generally helps removing unbound precursor compounds from the surface, more rigorous cleaning procedures would be required to extract residues from the bulk of the elastomer. According to Ratner and co-workers, it is necessary to wash PDMS with both polar (e.g., ethanol/water) and nonpolar solvents (e.g., hexanes) over extended periods of time to reduce contamination below the detection level [22]. It is equally possible to oxidize or otherwise modify the PDMS surface to prevent low-molecular weight constituents from migrating to the interface [23, 24].

Conformal contact occurs when a soft polymer adapts to the shape of another surface. Unlike stiff materials, elastomers are able to deform locally and globally, and, consequently, can tolerate a certain level of unevenness on a surface at both microscopic and macroscopic levels while still providing intimate contact without voids [25]. For planar surfaces, conformal contact typically initiates spontaneously, and propagation of the contact zones is governed entirely by interfacial adhesion forces. For substrates with elevated roughness, external pressure may be required to promote perfect adaptation. A notable advantage of PDMS is its relatively high permeability to gases at ambient conditions [26, 27], allowing small volumes of air being trapped in microscopic cavities to escape via diffusion through the bulk of the polymer. For pristine PDMS, conformal contact is reversible, and devices can be removed from a substrate without leaving notable residues on the surface. Although the use of elastomer formulations providing a relatively low Young's modulus and a high work of adhesion is advantageous for achieving conformal contact, mechanical stability of elastomeric features generally benefits from materials that have a sufficiently high modulus and a rather low work of adhesion. This contradiction is inherent to all soft patterning techniques and demands for optimization of material properties and processing conditions alike, as well as adjustment in design of elastomeric pattern-bearing elements.

Figure 122.2 illustrates common forms of deformation for micropatterned elastomeric features [28]. Sagging (or roof collapse) (Figure 122.2a) occurs when the fill factor of a pattern is low, leading to unwanted contact between a substrate and the recessed regions of a stamp [29]. It is possible to counterbalance this effect through the fabrication of hybrid stamps where a

relatively thin polymer layer is mounted on a backplane (e.g., a thin sheet of metal or glass) to provide long-range stability [30]. The implementation of proper support posts represents an alternative way to stabilize structures with low aspect ratios [25, 31]. Other forms of pattern distortion include buckling, broadening and pairing of features (Figures 122.2b–d, respectively). The development of harder material formulations providing a higher elastic modulus than Sylgard 184, such as *h*-PDMS [30, 32–34] or photocurable siloxanes [35] proved useful to overcome these constraints to a large extent. Surface tension and residual stress can lead to the appearance of pull-off effects during contact (Figure 122.2e) and the rounding of features that were originally designed to be sharp (Figure 122.2f). Moreover, the design of a mold may need to be adapted to compensate for shrinkage of a pattern upon release when a high level of long-range accuracy is to be achieved. Fracturing of features can occur during release of a stamp from a rigid mold or master due to high interfacial adhesion forces, especially when harder elastomer formulations are employed. For this reason, molds are often coated with an anti-sticking layer (e.g., Teflon® or a monolayer of a fluorinated silane) to reduce the risk of damage during separation. Swelling, finally, comes into play when a PDMS stamp or mold is exposed to an organic solvent that can easily diffuse into the bulk material.

The use of polymers based on other materials than siloxanes has also been explored. For example, block co-polymers (e.g., polystyrene in conjunction with butadiene or ethylene/butylene) seem promising to this end as they can fulfill many of the requirements for high-resolution soft lithography [36, 37]. A number of co-polymer formulations are superior to Sylgard 184 in terms of elastic modulus, which makes resultant replicas less susceptible to deformation and distortion. Moreover, elastomeric features formed from block co-polymers are less brittle and hence mechanically more robust than those obtained from *h*-PDMS. On the other hand, these materials necessitate the application of external pressure and higher temperatures (e.g., 150 to 200 ºC) in order to be shaped using imprint techniques, which demands for the availability of masters that are compatible with these processing conditions. The use of functional, photocurable polymers [38] provides another plausible route to high performance in replication of elastomeric features at sub-micrometer length scales.

122.3 Patterning Based on Molding

Molding is the process of duplicating topographic information in a functional material by solidifying its liquid precursor molecules on a master (Figure 122.3a) [39, 40]. In principle, a mold can be fabricated from both rigid and elastomeric materials, with the latter one being particularly useful for research and prototyping purposes. The use of an elastomeric mold is also advantageous for applications that involve harder polymer formulations or ceramic compounds with low flexibility which otherwise are difficult to separate from a rigid master without failure. Moreover, the inherent ability of elastomeric materials to be stretched, compressed, or otherwise deformed provides the possibility of replicating patterns against curved or uneven surfaces, which is nontrivial to achieve with a rigid template [39]. A master for replica molding is typically fabricated from a silicon wafer in conjunction with a thin layer of polymeric resist that is patterned using photolithographic methods or electron-beam writing. In a first replication step, a negative (inverse) pattern of the original design is drawn into PDMS by casting the liquid prepolymers onto the master followed by thermal treatment. Upon release, the PDMS mold is used for a second replication step, during which a liquid precursor component is solidified against its surface using either photo-induced or thermal curing processes, yielding a duplicate of the original master pattern. Figures 122.3b–d demonstrate the level of fidelity that can be achieved for the replication of sub-micrometer structures, even when features with high aspect ratios are the fabrication target. In principle, a proper PDMS mold can be used multiple times, depending on the materials that are involved in the replication process. Nonpolar and low-molecular weight monomers can penetrate PDMS easily, which may reduce the overall lifetime of the template. Polar or fluorinated precursor molecules, on the other hand, are less soluble in PDMS, which helps preserving the mold's integrity over a larger number of processing cycles. Replication against PDMS-based templates has been shown to be compatible with several organic polymers, including polyurethane (PU) [34, 39], polyimide [41], epoxy resin [42], and sol-gel materials [43]. Replication against elastomeric master molds has been shown to function over a broad range of length scales with features as small as ~30 nm being routinely achievable with *h*-PDMS. Using an elastomeric mold makes it possible to fabricate structures that are smaller than those on the master by mechanically bending or compressing the pattern prior to the replication process [39]. Features with dimensions in the lower nanometer range (e.g., 3 nm in

width and 1.5 nm in depth) have been faithfully revealed in successive replication cycles [34, 44]. An elegant approach to assess the limits in resolution achievable by replica molding has been suggested by Whitesides and co-workers who have used a partially fractured, single-crystalline silicon wafer as the master mold (Figure 122.4) [45]. As shown in Figure 122.4a, the fractured substrate provides a gradient in topography ranging from the micrometer scale to the atomic level. Replica molding using *h*-PDMS (Figure 122.4b) and PU (Figure 122.4c) preserved the morphological properties of this structure, making it possible to resolve a vertical deflection of 0.4 nm at the tip of the gradient (Figure 122.4d).

Microtransfer molding (μTM) [46] is an alternative technique that is used for the replication of topographic features on a substrate. As illustrated in Figure 122.5a, the mold is first covered with liquid prepolymers, followed by removal of excess material (e.g., through scraping) from the raised areas of the surface. The mold is then placed on a substrate and the prepolymer is cured while maintaining contact with the surface. Finally, the mold is peeled away to leave the replicated structure on the substrate. Using this method, it is possible to fabricate isolated and interconnected features on both planar and uneven substrates [46, 47–52]. Also, the process can be repeated multiple times to fabricate complex, three-dimensional structures in a layer-by-layer fashion [53–56]. The two-level grating structure shown in Figure 122.5b was obtained by electroplating of nickel in the void areas of a polymer scaffold that was fabricated by μTM. Structures generated in this way are particularly attractive for photonic applications [54–56]. With critical dimensions mostly being in the micrometer regime, the method has not yet prevailed as a general route for producing nanostructures. In fact, the limits in resolution that can be achieved by μTM remain to be determined. A major difficulty associated with this technique is to completely remove excess material from the raised surface of the mold. In practice, a thin residual film is often left behind, connecting the replicated features upon transfer. This film may prevent dissolution of the underlying surface and therefore needs to be removed by reactive ion etching when the replicated polymer features are to be employed as a resist in a wet-chemical etching process. It may be possible to limit or prevent the formation of a residue by using a mold with appropriate surface chemistry that promotes dewetting of the prepolymer from the raised features of the pattern.

Solvent-assisted micromolding (SAMIM) [57] uses a solvent to soften a polymer film so that it can be structured with an elastomeric mold (Figure 122.5c). In this way, the polymer is

processed at ambient conditions and without exposure to elevated temperatures, reducing the risk of degradation which makes the process compatible with fragile and sensitive components. Upon wetting of the mold by the solvent, it is brought in contact with the polymer layer which conforms to the surface of the elastomeric features. While the solvent dissipates through the bulk of the PDMS, the polymer film hardens, thereby preserving an imprint of the molds' topography. There are several conditions that a solvent needs to fulfill in order to be effective for this technique. An ideal solvent should rapidly dissolve or swell the polymer but not the PDMS mold. Also, it should have a relatively high vapor pressure to limit the time for excess solvent to evaporate. Alcohols (e.g., ethanol, methanol and isopropanol) or acetone are commonly employed, while solvents with a low vapor pressure, including ethylene glycol or dimethyl sulfoxide are less suitable for this technique. Nonpolar solvents, such as toluene, are impractical for use in SAMIM since they swell PDMS, thereby distorting the mold and compromising conformal contact with the polymer film. As for µTM, SAMIM generally results in a thin residual film between isolated features upon replication. SAMIM has been demonstrated for a number of polymers and organic precursor materials, including polystyrene, cellulose acetate, and Novolac photoresist [58–63]. Thanks its mild processing conditions, SAMIM proved suitable for the fabrication of polymer-based distributed feedback lasers [60] and organic light-emitting diodes [58].

Micromolding in capillaries (MIMIC) [64] is another technique for creating isolated structures on surfaces (Figure 122.3d). In MIMIC, a PDMS mold is brought in contact with a substrate, during which the relief features define a network of embedded microchannels. These channels can then be filled from macroscopic entry points with a low-viscosity prepolymer or a solution of functional material using capillary action. Once completed, the injected material is solidified by evaporation of the solvent as well as through photo or thermal curing processes. Removal of the PDMS mold leaves a replica of the channel network on the surface. Structures produced by MIMIC differ from those obtained by µTM and SAMIM in the sense that no layer of excess polymer interconnects the replica. Depending on the configuration of the mold, it is possible to produce structures of variable size and thickness in a single step. The technique has been shown to be compatible with a broad range of materials, including organic molecules [65–67], prepolymers [68], colloidal particles [69, 70], and biological macromolecules [71, 72]. Sub-micrometer patterning, however, is challenging since resistance to flow increases at smaller

scales, which makes it difficult for liquid to fill the capillaries, especially over long distances. Although is generally possible to support flow behavior through the application of vacuum [73], elevated temperature [74] or external electric fields, the increase in complexity associated with these methods renders MIMIC less attractive for nanofabrication purposes than competing technologies.

122.4 Patterning Based on Printing

Printing generally involves a stamp with bas relief structures that is brought in contact with a substrate to generate a pattern of ink. Printing, therefore, is an inherently additive process, even though the meaning of ink has become quite flexible and can include a broad range of compounds and materials. In a typical printing process, all features are transferred simultaneously over the entire area of the surface that is in contact with the stamp. The dimensions of the printed pattern are determined by the size of the raised features on the stamp: they can range from several millimeters to below 100 nm, and are typically reproduced at a 1:1 ratio. Microcontact printing (μCP) [8, 11, 75] has become a method of choice for patterning self-assembled monolayers (SAMs) of alkanethiols on gold [21, 76–78] and on other coinage metals, including silver [79, 80], copper [81, 82], palladium [83, 84], and platinum [85]. This application takes advantage of the high affinity of the sulfur moiety for noble metals, leading to rapid adsorption of molecules under the formation of a covalent and thermodynamically stable metal-sulfur bond. Noncovalent interaction of long alkyl chains (mostly based on van der Waal's forces), in addition, promotes organization of the molecules into a dense and well-ordered monolayer, in which chains are extended away from the surface, often in an all-trans conformation [86]. High-resolution μCP is recommended to be performed with thin-film stamps, comprising a thin and flexible backplane to support features that are formed from *h*-PDMS formulations (Figure 122.6a). Inking of a stamp with alkanethiols is commonly achieved by wetting the surface with a solution of dissolved molecules followed by drying. It is also possible to expose the stamp to vaporized ink using a spray gun. The use of an ink pad constitutes an alternative method [77] which localizes uptake of ink molecules by the raised features of the stamp. The absence of solvent, in addition, limits swelling of the elastomer which is beneficial

for high-resolution patterning. Nonpolar molecules, such as *n*-alkanethiols, are soluble in PDMS and, provided they are given enough time, diffuse into the bulk of the stamp [87]. Polar thiols (e.g., terminated with a carboxylic acid group), on the other hand, have limited solubility in PDMS, making behavior of these molecules on the stamp less predictable [88]. Inking and printing of polar molecules [21, 88, 89] generally benefits from hydrophilization of the stamp as it improves wettability and thus uniformity of resultant patterns. When placed onto a gold substrate, the stamp commonly remains in contact for several seconds before it is removed. Successful printing generally relies on mastering a number of parameters, which include the concentration of thiols in the ink (and thus on the stamp), the duration of contact and the pressure applied to the stamp [76, 90]. It is possible to use similar protocols to the patterning of other monolayer-forming molecules, such as aliphatic silanes on silicon or glass [91] and alkanephosphonic acids on metal oxides [92, 93]. Although being just a few nanometers in thickness, SAMs provide a means of altering effectively interfacial phenomena, such as wetting, nucleation, or adhesion. The use of ω-modified alkanethiols, in addition, makes it possible to introduce functionality to a surface in a chemically well-defined manner. Microcontact-printed SAMs can be employed as resists to create patterns in thin metal films by wet chemical etching (Figure 122.6a) [21, 76, 77, 79, 82]. The quality (e.g., contrast and resolution) of resultant metal structures largely depends on i) the characteristics of the SAM-forming molecules (e.g., their chain length, the nature of their head group etc.), ii) the density of defects in the printed SAM, iii) the morphology of the metal film (e.g., its thickness, roughness and grain size), and iv) the selectivity of the etch system. SAMs formed from hydrophobic, long-chain alkanethiols, such as 1-hexadecanethiol (HDT) or 1-eicosanethiol (ECT), are generally preferable for this application. While SAM-based resists proved to be compatible with a number of etch systems [86], they remain sensitive to disorder and defects at the molecular level. These drawbacks can be overcome to some extent by adding amphiphilic, defect-healing molecules to the etch bath or by employing complex-forming polymers as etchants [82]. The use of ω-functionalized alkanethiols in conjunction with grafting-on strategies to amplify the barrier properties of a monolayer may represent another plausible strategy to this end [94, 95]. While structures in the range of 200 nm can be produced in a reliable fashion (Figure 122.6b), this approach encounters limitations at length scales below 100 nm, mainly due to molecular diffusion and the granularity of the metal substrate [96].

Beyond SAM-forming molecules, μCP has been shown to work for a variety of other ink/substrate systems. A first class of ink is of organic nature. In this case, successful transfer is largely determined by molecular constitution along with surface properties of the substrate, and can involve covalent attachment of reactants, electrostatic interaction of charged species, differences in wettability between stamp and substrate, van der Vaals forces between hydrocarbon chains, and nonspecific adsorption. Successful printing has been demonstrated with a variety of compounds, ranging from small reactive molecules, to dendrimers and polymers [97–100]. The most compelling application is probably the patterning of bio-macromolecules such as proteins. For example, Delamarche and co-workers have explored the printing of protein features ranging from micrometer lengths scales to the single-molecule level [101]. These authors also developed an elegant extension of the conventional printing scheme by inking a planar stamp with a uniform layer of proteins and removing proteins from unwanted regions upon contact with a sacrificial template (Figure 122.7a) [102]. This approach provides flexibility in the design of the final array which is unparalleled by standard stamp configurations (Figure 122.7b). In this way, it is equally possible to pattern multiple types of proteins using sequential print and incubation steps with the same stamp. Inorganic species constitute another class of ink. For example, printing of ionic catalysts proved useful to induce selective metallization [103] or patterned growth of carbon nanotubes on insulating substrates [104, 105]. Finally, there are a number of demonstrations that involve colloidal particles as the ink. Patterns of ordered and dense films can be achieved when Langmuir-Blodgett films of nanoparticles are employed to ink the stamp [106, 107]. Conversely, it is also possible to position individual nanoparticles on a substrate. As shown in Figure 122.8a, the stamp can serve as a template which allows particles to occupy predefined topographical features during dewetting of the solution [108]. During transfer, the position of each particle is retained with high precision (Figure 122.8b), although pretreatment of the surface (e.g., with a polymer layer) and elevated temperature are necessary to mediate the transfer.

The development of printing techniques in which liquid ink is exchanged for one that is solid and dry at ambient conditions has been actively pursued in recent years. Motivation in exploring this approach was spurred in part by the possibility to i) overcome irregularities in pattern definition due to diffusion and disorder at the molecular level, ii) create three-dimensional structures, and iii) extent the range of functional materials that can be patterned

using soft lithography. In contrast to printing molecular species, transfer of solid objects is purely governed by differences in adhesion. Using surface chemistry, it is possible to design interfacial glue and release layers on both substrate and stamp, respectively. Nanotransfer printing (nTP) [109–114] – a variant of μCP that has been developed by Rogers and co-workers – involves coating of a topographic stamp with a thin film of metal, which is released as a continuous layer or in the form of individual features when brought in contact with a proper substrate. Interfacial chemistries that have been used to this end include covalent bonding of coinage metals via thiol-terminated SAMs as well as condensation of hydroxyl-terminated oxides [109]. Cold welding of two metal layers [111, 113] is an option that has also been pursued. Structures fabricated by nTP have been employed as components in organic thin film transistors, capacitors and electrostatic lenses. It is also possible to pick up thin films from a donor substrate followed by transfer to an appropriate receiver using a patterned or planar stamp as an intermediate vehicle [115, 116]. Decal transfer lithography (DTL) is a technique that involves printing of PDMS microstructures, which can be achieved through fracture of PDMS features [117] or by selective release of a thin film of PDMS being cast onto a stamp [118].

122.5 Patterning Based on Edge Effects

This patterning strategy comprises a number of techniques that are centered on the use of edges to define the features of a pattern. From a methodological point of view, they emphasize the virtue of size reduction – that is, the translation of a larger structure into a smaller one. Edge lithography therefore is essentially a top-down approach, even though several techniques comprise elements of bottom-up fabrication to an almost equal extent. This section describes three edge-lithographic approaches – photolithography with phase-shift masks, edge-spreading lithography (ESL), and the formation of thin metallic edges on stamps – which employ elastomeric patterning elements. A general and more comprehensive overview of edge lithography can be found elsewhere [119].

Phase-shift photolithography is a convenient and generally applicable route to the fabrication of nanostructures beyond the optical diffraction limit. This technique uses a topographic phase mask to mediate exposure of a thin film of photoresist to UV light [120–129].

A typical mask comprises relief structures with dimensions comparable to the wavelength of the light used for illumination (Figure 122.9a). The depth D of the features is related to the radiation wavelength λ by $D = \lambda/2(n-1)$, where n is the index of refraction of the material from which the mask was produced. Light passing through the mask is modulated in intensity at the vertical edges, thereby altering exposure of the underlying resist film. This effect is maximized when the transmitted light is shifted by odd numbers of π radians. In this case, light intensity near the surface drops to zero at the edges of relief, which induces the formation of dark-line features in the resist layer. As a result, ridges are generated in a positive-tone photoresist upon development, whereas trenches are obtained in the same areas when a negative-tone resist is used. Scattering of light at phase boundaries yields a modulated intensity distribution with coexisting bright- and dark-line features that vary in amplitude and periodicity. As the transmitted light directly affects the thickness of the photoresist film after development, the morphology of the forming resist structures is strongly dependent on exposure time. To this end, features generated by photolithography with elastomeric phase-shift masks are typically 30 to 100 nm in width [33, 120]. In order for a mask to be useful in phase-shift optical lithography, it has to be transparent to UV light and must be brought as close as possible to the surface of the resist layer. As for conventional photolithography, development of the resist features is typically followed by pattern transfer into a functional material using subsequent etch or deposition steps. In this way, Rogers and co-workers have fabricated metal features for use as optical polarizer or gate structures in organic transistors [120, 123]. Xia and co-workers have demonstrated that it is possible to produce freestanding single-crystal silicon rings, rods, and wires with lateral dimensions as small as 40 nm using this approach (Figure 122.9b) [124]. These authors employed a silicon-on-insulator (SOI) wafer for pattern transfer via RIE, which was followed by oxidation of the silicon, and lift-off using HF. Dissolution of the oxide layer around the silicon further reduced the dimensions of the features that were formed initially. Odom and co-workers have shown that trenches generated by phase-shift photolithography can be used to direct the assembly of semiconductor quantum dots (Figure 122.9c) [130], and the growth of ZnO nanowires (NWs) into ordered arrays [131]. More recently, Rogers and co-workers have demonstrated the fabrication of 3D nanostructures, which derive from a rather complex intensity distribution within the bulk of a relatively thick photoresist layer (Figure 122.9d) [127, 128].

Resultant structures have been implemented into channels of microfluidic devices where they served as passive, nanoporous filters [127] or as mixing elements [128].

Edge-spreading lithography (ESL) [132–135] is suitable for the patterning of alkanethiol monolayers on coinage metals at sub-micrometer length scales. This technique relies on two key features: a mesoscopic relief structure on the metal substrate and reactive spreading. The relief structure has dual functions as it mediates the transport of alkanethiol molecules from a planar PDMS stamp to a gold surface and determines the shape of the emerging SAM. For example, when a 2D array of silica beads is used as the guide, the circular footprint of each bead produces a pattern of monolayer rings with hexagonal arrangement. Reactive spreading [136, 137] is the extension of a SAM across a metal surface; it occurs when an excess of unbound thiol molecules and an unoccupied area on the surface into which the SAM can expand are both available. Lateral force microscopy (LFM) [138] revealed that monolayer rings of high contrast and accuracy can be formed from a number of thiols. For example, when *n*-octadecanethiol (ODT) is used, resultant monolayer rings appear dark due to the relatively weak interaction between the non-polar molecules and the polar surface of the silicon nitride tip that was used for the measurement (Figure 122.10a). It is possible to transfer the printed array into the supporting gold substrate via selective wet etching using the SAM as a resist (Figure 122.10b). ESL further allows for the patterning of multiple SAMs terminated with a variety of functional groups in the form of concentric rings using successive printing steps on the same substrate [135]. Figure 122.10c shows the result of such a process with 16-mercaptohexadecanoic acid (MHA), 12-hydroxyundecanethiol (HDDT), and ODT. It should be noted that the width of each segment in these rings can be tuned by variation of ink concentration and printing time, and that these thiols could be printed in any order. Concentric rings comprising distinct portions as small as 30 nm have been achieved using this approach. Concentric gold rings can be fabricated via selective etching when a less protective amine monolayer is sandwiched between two ring segments of thiolate SAMs [135]. Rings formed from mixtures of MHA and ODT show a gradual change in composition from the inside to the outside, which is a result of differences in the velocity of the two components to reach the gold surface. The steepness of the gradient can be tuned to some extent by varying the ratio of the two components in the solution used to ink the stamp [136]. Patterns comprising structures other than a hexagonal array of rings can be generated when silica beads are replaced with polymeric resist features of appropriate shape and geometry [134].

Polymers being compatible with this approach include AZ 1512 photoresist, polyimide (PI), and poly(methylmethacrylate) (PMMA). While ESL generally results in a uniform outline of a photoresist pattern, it is possible to confine SAM formation by exchanging the planar stamp with a patterned one. One example to this approach is illustrated in Figure 122.10d, where ESL is performed with a set of parallel resist lines on gold and a stamp bearing a simple test pattern. It is apparent from Figure 122.10e that gold wires formed only in those regions where the resist was in contact with the raised features on the stamp. The ends of these wires are tapered which indicates a gradient in concentration due to diffusion of the thiol molecules on the surface of the resist features.

A third edge lithographic approach is centered on the formation of thin metallic edges on a patterned stamp. This approach was demonstrated by Whitesides and co-workers who collimated the deposition of a thin metal film onto a topographically patterned PDMS stamp followed by its selective removal from the top regions of the raised features via transfer to a proper substrate (Figure 122.11a) [139]. Conceptually, this method borrows from principles of nTP (see Section 122.4), using interfacial chemistries that promote transfer of a metal film from PDMS to an adhesive surface. This can be achieved, for example, through condensation of hydroxyl-terminated titanium oxide with a freshly plasma-oxidized PDMS slab. While being connected to a conductive metal film, resultant edges can be used as nanoscale electrodes to generate patterns of charge in a thin dielectric film supported on a solid substrate using electrical microcontact printing (e-μCP) [140] (Figure 122.11b). It has been shown that patterns of both positive and negative charge can be generated in a number of polymeric and inorganic dielectric materials using this approach. Characterization of embedded potentials using Kelvin probe force microscopy (KFM) [141] revealed a typical width of 300 nm for metal films that are 10 to 40 nm in thickness, as exemplified by the image in Figure 122.11c.

122.6 Conclusion and Outlook

Soft lithographic methods based on molding, printing and edge effects are effective tools for fabricating sub-micrometer structures rapidly and without the need of resorting to elaborative and cost-intensive equipment. The strength of these techniques, both individually and combined,

lies in their capacity to produce multiple copies of an original pattern, many of which are difficult or impossible to realize using other technologies. In addition, soft lithographic methods are compatible with a diverse range of materials, including organic, inorganic and biological species alike. Many of the structures produced by soft lithography proved functional in a number of ways: depending on their size, morphology and composition, they have been used as nanoelectrodes, optical elements, or catalytic sites for chemical reactions, among others. Although several techniques provide access to structures with lateral dimensions extending well below 100 nm, the resolution of features remains determined by experimental details and the materials involved in a particular patterning process. For example, literature data suggests 30 nm as the current limit in feature size for pattern transfer based on both printing and edge lithographic methods when performed under optimized conditions, whereas replica molding seems suitable for patterning at the lower nanometer regime. The ultimate resolution that may be achievable with elastomeric polymers will likely be dependent on the ability to confine structural information at the level of an individual polymer chain or segments of it. Material properties at this particular size regime are therefore becoming the focus of considerable efforts in both fundamental research and development. On the other hand, soft lithography is not per se a nanolithographic technique, and many of its main applications (e.g., in cell biology or microfluidics) involve features that are substantially larger than 1 μm without the need for precision at the nanometer scale. Work related to the low-resolution aspects of soft lithography was, however, not within the scope of this review. Although a number of operations in soft lithography are readily scalable and may be performed in automated manner using commercial or custom-made equipment, it is not obvious whether they always can evolve into robust and efficient fabrication schemes for production purposes. The rubber-elastic nature of the polymers involved in the key processing steps accounts for an obstacle of primary importance in this context. For example, features made from PDMS remain susceptible to variability and distortion, which limits the scope of possible applications to areas that can tolerate a certain degree of imperfection. It is also challenging to align an elastomeric mold, stamp or mask with high accuracy to perform multiple lithographic steps on the same substrate, especially over large areas. Finally, PDMS and several other elastomers are sensitive to organic solvents and cannot withstand very high temperatures. It is generally accepted that soft lithography does not compete with optical lithography, which continues to strive as the mainstream technology for high-

throughput production of integrated circuits. It is rather obvious that soft lithography has strengthened its place as enabling technology in basic and applied research, proof-of-concept demonstration, and prototyping, where it is typically employed in a complementary fashion to standard micro- and nanofabrication schemes. As such, many of the techniques described in this chapter have stimulated significant advances in a broad range of areas, including surface chemistry, condensed matter physics and microbiology, among others, and it is more than likely that fascinating discoveries will continue to emerge as a result of their implication for years to come.

Dedicated to Prof. U.-W. Grummt (formerly at Friedrich-Schiller-Universität Jena) in retroactive recognition of his 65th birthday.

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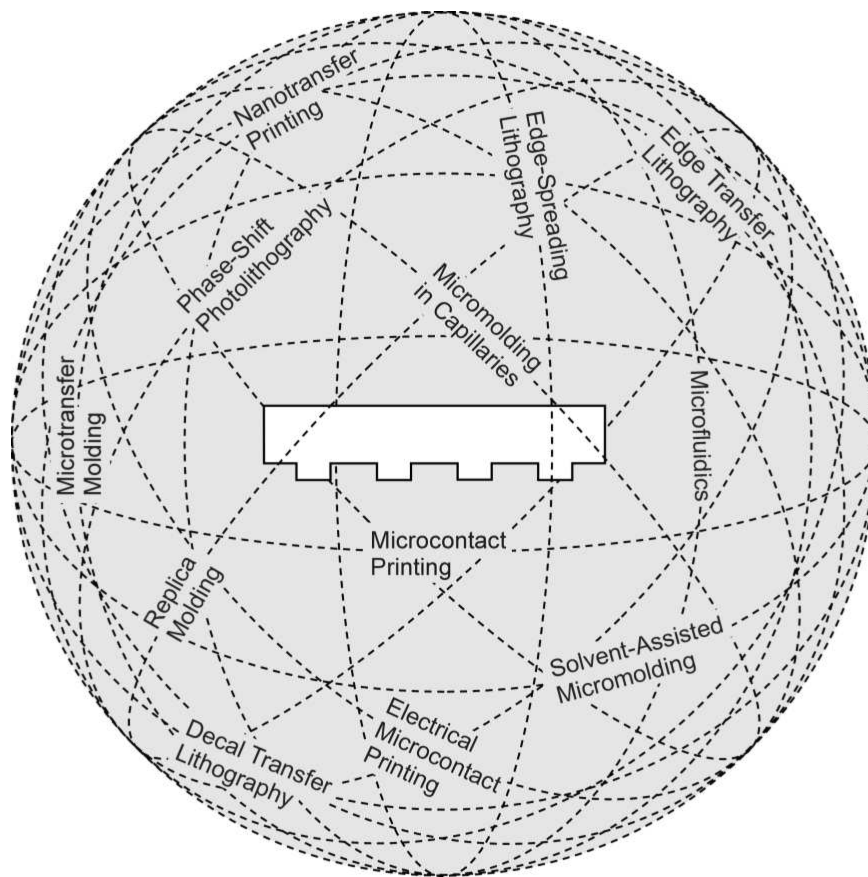

Figure 122.1 Soft lithography – a universe of possibilities that is centered on the use of a soft, elastomeric patterning element.

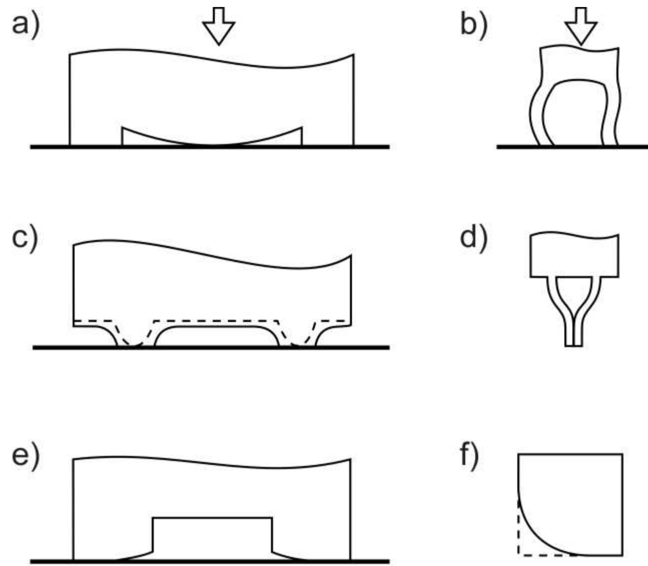

Figure 122.2 Deformation of elastomeric features in soft lithography. Common forms include a) sagging, b) buckling, c) broadening, d) pairing, e) pull-off, and (f) rounding.

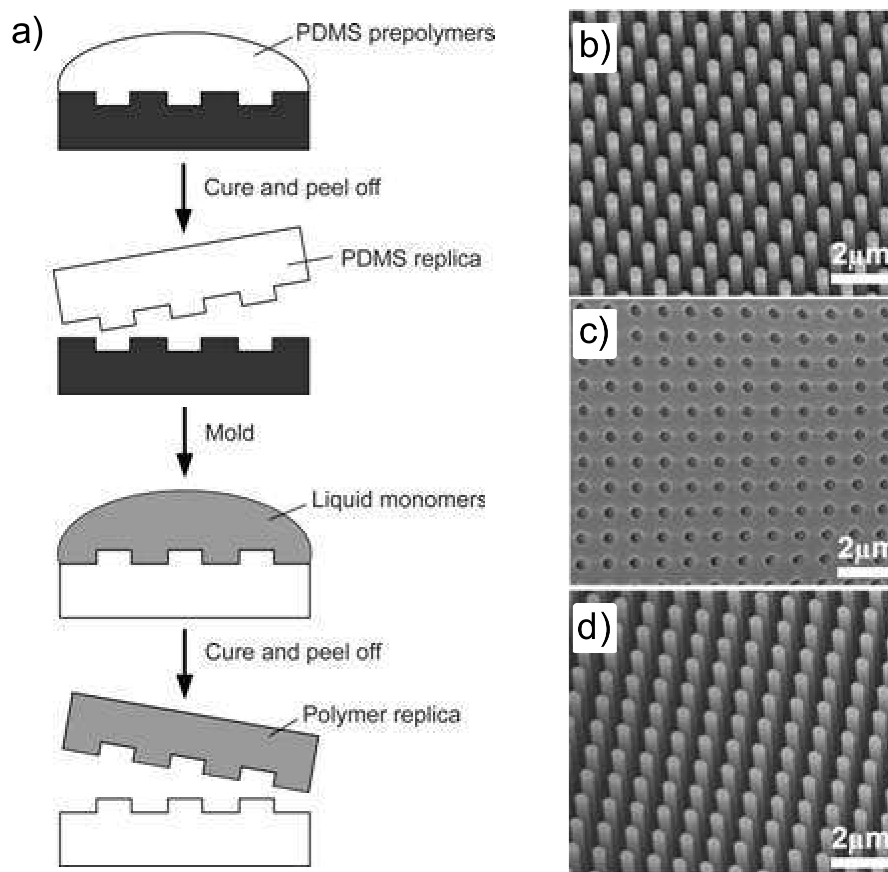

Figure 122.3 Pattern transfer based on replica molding. a) A master pattern is first replicated in PDMS, followed by duplication in a functional polymer. b–d) Scanning electron micrographs of nanopillars at different processing steps of replica molding. b) Silicon pillars on the master. c) Corresponding PDMS replica. d) Epoxy nanopillars replicated from the PDMS mold. Each pillar has a depth of 9 µm and a diameter of 500 nm. (Reprinted with permission from [42], copyright 2006, American Chemical Society.)

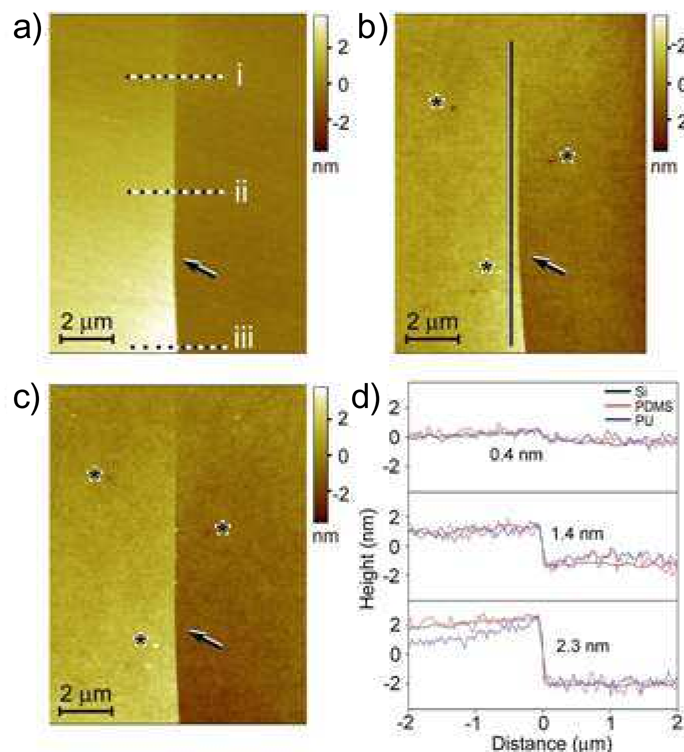

Figure 122.4 Probing the limits in resolution for replica molding of polymer features. a) Atomic force microscope (AFM) image of a crack in a silicon wafer. b) AFM image of a PDMS replica of the same crack. The image has been inverted in contrast and flipped horizontally so that it can be directly compared to the master. The vertical line serves as a guide to the eye to show the kink in the crack. c) AFM image of a PU replica produced with the PDMS mold. In a–c), the arrows indicate the point of inflection that has been used to ensure proper alignment of the scans. d) Line scan cross sections of the crack in the silicon master and in the polymer replicas taken at the locations that are indicated by the dashed lines in a), showing a smooth decrease in step height with approach to the crack tip. (Reprinted with permission from [45], copyright 2005, American Chemical Society.)

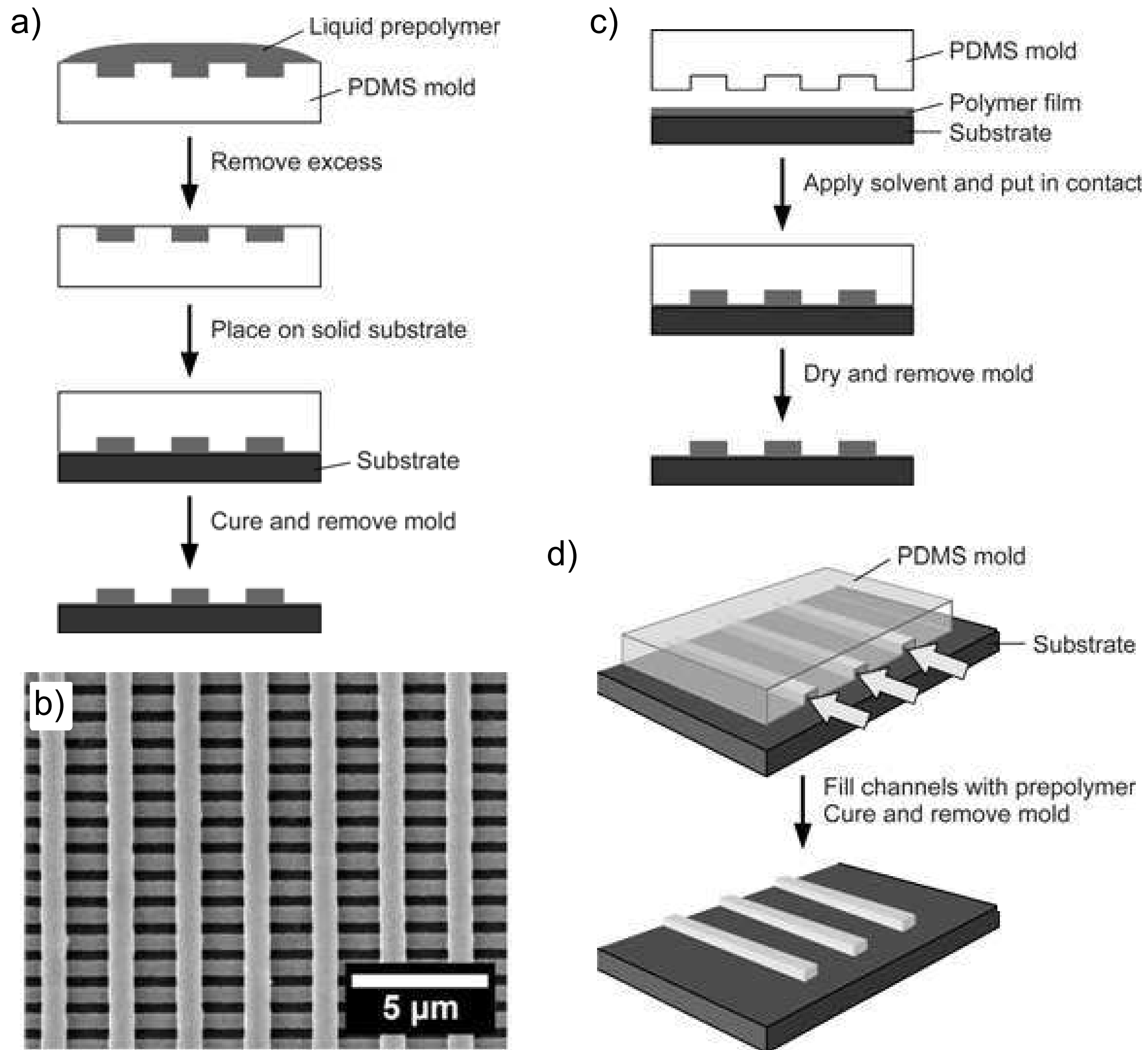

Figure 122.5 Microfabrication using various forms of molding. a) In µTM, the recessed areas of an elastomeric mold are filled with a prepolymer which is then transferred onto a substrate. b) Scanning electron micrograph of a thermal emitter fabricated by µTM of a polymer template followed by backfilling with nickel using electroplating. The polymer scaffold was removed upon completion of the metal deposition process. (Reprinted with permission from [56], copyright 2008, Optical Society of America.) c) SAMIM uses a solvent to mediate the patterning of a polymer layer. d) In MIMIC, a liquid prepolymer fills the recessed regions of a mold while being in contact with a substrate.

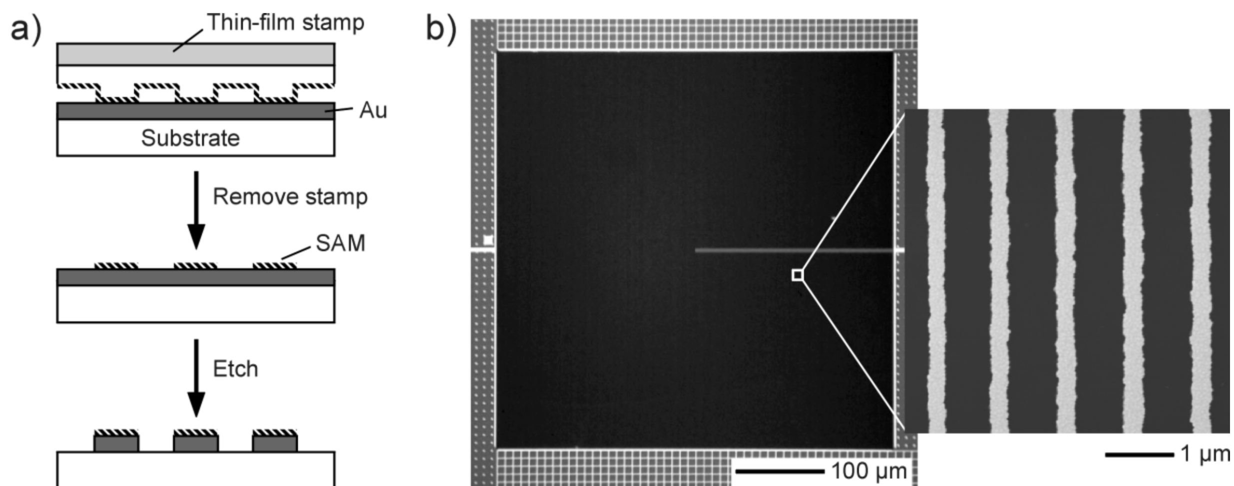

Figure 122.6 High-resolution µCP with alkanethiols on gold. a) A thin-film stamp supported on a flexible glass backplane is inked, dried and placed onto a gold substrate to localize the formation of a SAM in the regions of contact. The SAM can then be used as a resist to protect the underlying gold in a wet etching process. b) Optical micrograph and AFM inset of a gold nanowire array consisting of 400 individual wires (each being ~240 nm in width) spaced by 1 µm. The array was produced by using ECT as the ink and Fe^{3+}/thiourea as the etch system. (Reprinted with permission from [31], copyright 2003, American Chemical Society.)

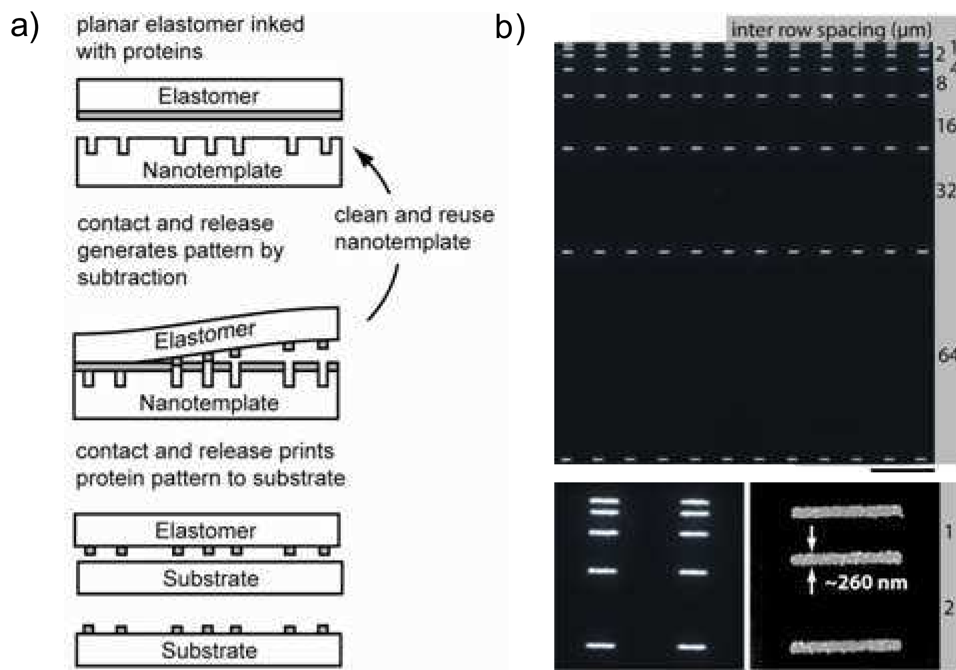

Figure 122.7 Formation of protein patterns using µCP in conjunction with a nanotemplate. a) A planar elastomeric stamp is inked with a monolayer of proteins, and brought in contact with a nanotemplate. Upon release, proteins are subtracted selectively from the surface, and the pattern of proteins remaining on the stamp is transferred onto a target substrate. b) Fluorescence micrographs and AFM image of a printed line array with a variable inter-row spacing. The average width of each line is 260 nm. Scale bars correspond to 20, 10 and 2 µm, respectively. (Reprinted with permission from [102], copyright 2007, Wiley-VCH.)

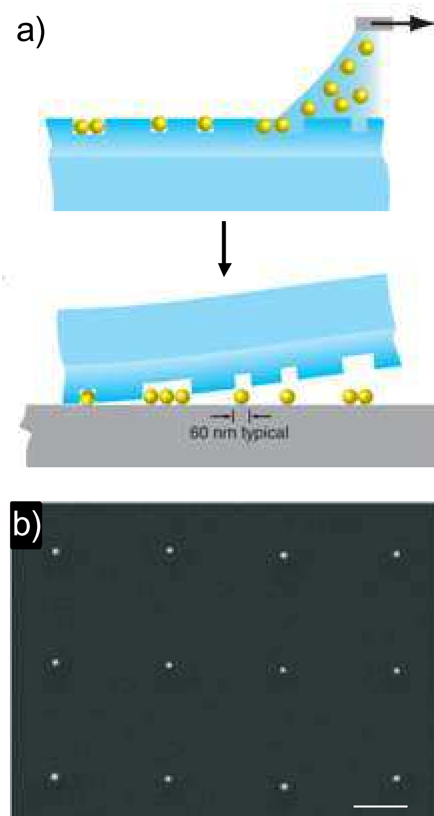

Figure 122.8 High-resolution particle printing. a) Self-assembly mediates the arrangement of particles on the stamp, whose positions are retained during transfer onto a substrate. b) Scanning electron micrograph of gold nanoparticles (60 nm in diameter) printed with a periodicity of 1 μm on a silicon substrate. The scale bar denotes 500 nm. (Reprinted with permission from [108], copyright 2007, Nature Publishing Group.)

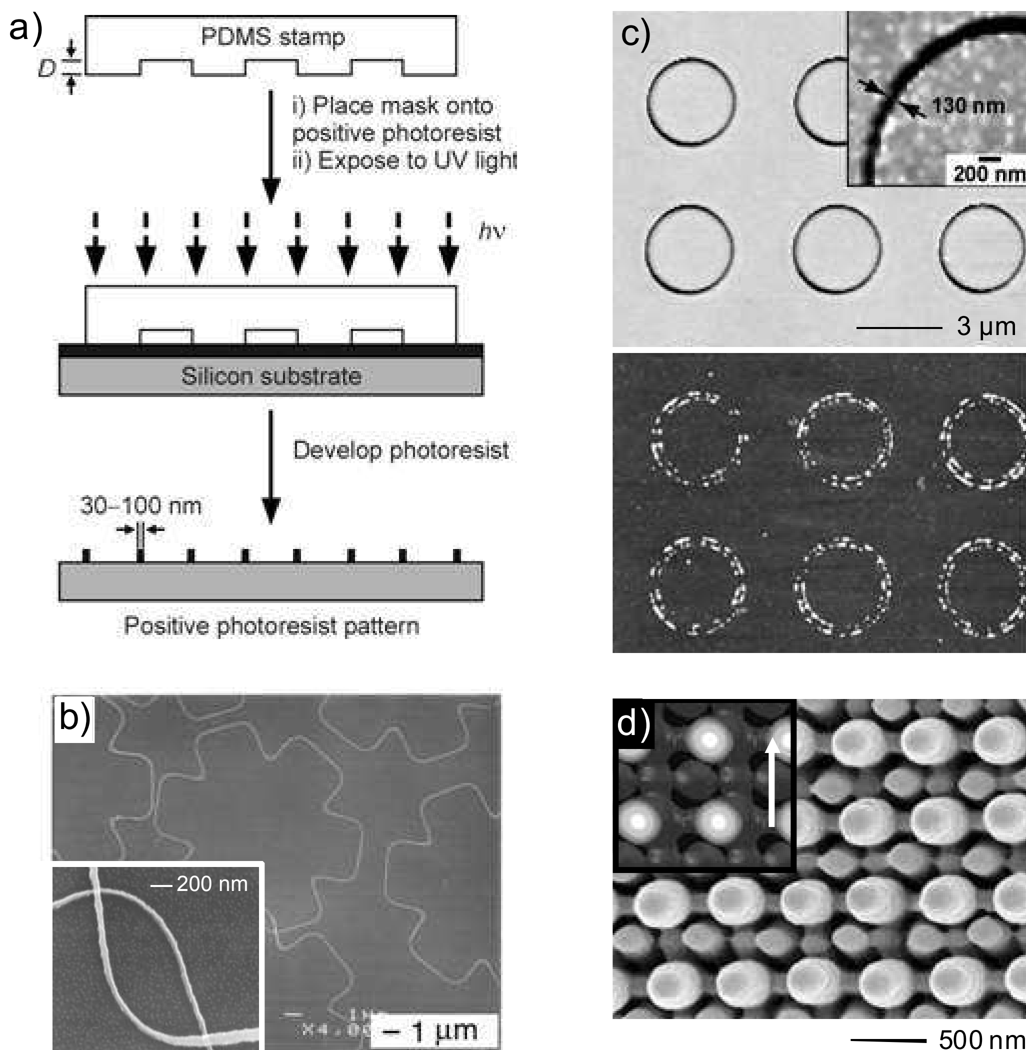

Figure 122.9 Near-field optical lithography with a conformal phase-shift mask. a) The mask comprises topographical features with a depth *D* that is similar to the wavelength of the light used for illumination. Upon exposure and subsequent development, dark line features are obtained in a positive-tone photoresist, which correspond to the edges of relief. The width of the features is typically in the range of 30 to 100 nm. (Reprinted with permission from [119], copyright 2008, John Wiley & Sons.) b) Scanning electron micrograph of a silicon nanowire pattern that was produced by near-field optical lithography followed by pattern transfer using RIE, oxidation of silicon in air at 850 °C for 1 h, and lift-off in a solution of HF. The width of the wires varies from 80 to 120 nm. (Reprinted with permission from [124], copyright 2000,

Wiley-VCH.) c) AFM images of circular trenches in a negative-tone photoresist (upper panel) and quantum dots (CdSe/ZnS) arranged in ring format (lower panel) using the patterned photoresist as a template. Line widths can be as narrow as 100 nm and the height of the quantum dot structures varies between 15 and 50 nm. (Reprinted with permission from [130], copyright 2004, Wiley-VCH.) d) Scanning electron micrograph (top view) of a 3D nanostructure fabricated in SU-8 using a conformal phase-shifting mask. The mask was fabricated in PDMS and had a square lattice of isolated relief features (circle) with a diameter of 375 nm, a relief depth of 420 nm, and a duty cycle of 35%. The thickness of the SU-8 layer was ~10 μm, and the tripled output (355 nm) of a Nd:YAG laser was used for exposure. The inset shows the corresponding computed optical intensity distribution and the arrow indicates the direction of polarization of the illuminating light. (Reprinted with permission from [127], copyright 2004, National Academy of Sciences of the USA.)

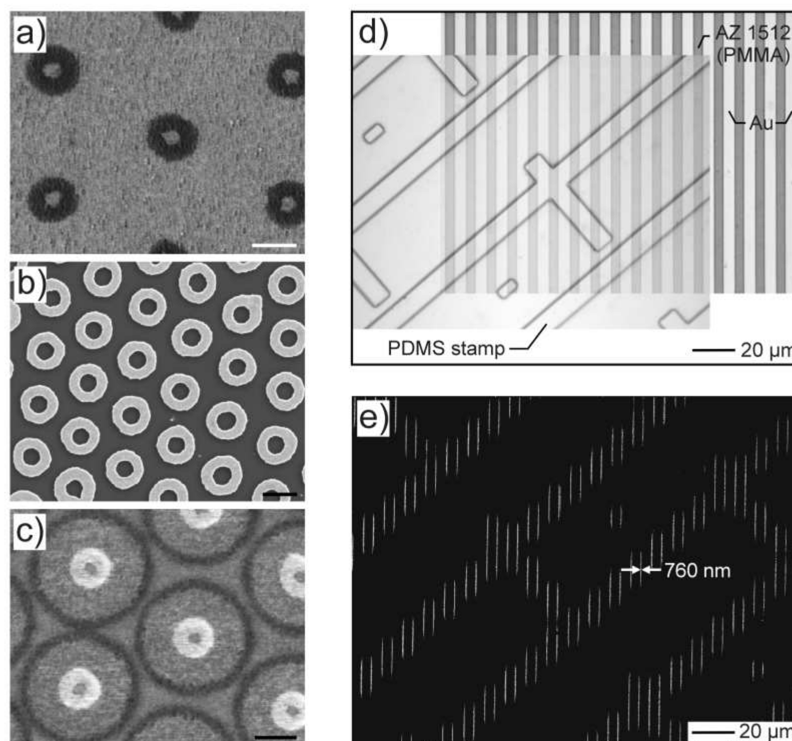

Figure 122.10 Examples of patterns generated by ESL. a) LFM image of ODT monolayer rings on a gold surface using silica beads (1.6 µm in diameter) as the guide. Scale bar: 500 nm. (Reprinted with permission from [119], copyright 2008, John Wiley & Sons.) b) Scanning electron micrograph of gold rings formed by selective wet etching using an ODT monolayer as resist. Scale bar: 1 µm. (Reprinted with permission from [119], copyright 2008, John Wiley & Sons.) c) LFM image of concentric SAM rings comprising MHA (bright), HDDT (grey), and ODT (dark) patterned by three successive ESL steps. Scale bar: 500 nm. (Reprinted with permission from [134], copyright 2005, Wiley-VCH.) d) Optical micrograph of a patterned stamp used for ESL in conjunction with resist lines (AZ 1512/PMMA) on a gold substrate. e) Scanning electron micrograph of resultant gold patterns. The SAM preserved the design of both stamp and resist lines during spreading. (Reprinted with permission from [133], copyright 2005, American Chemical Society.)

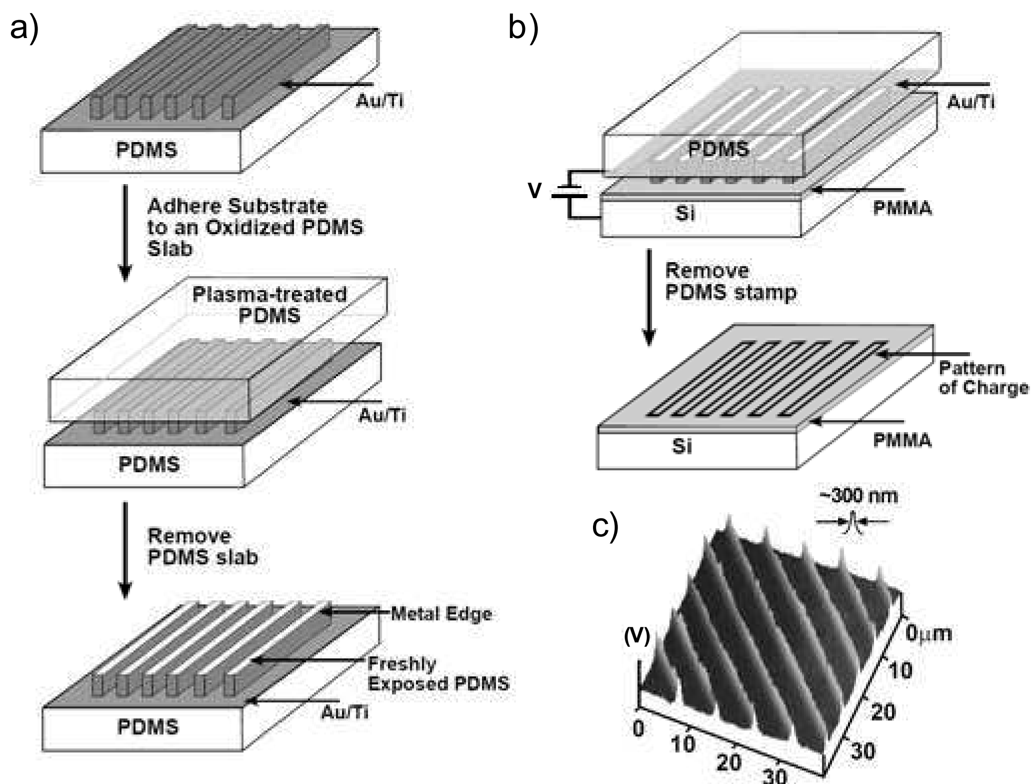

Figure 122.11 Formation and use of a patterned PDMS stamp comprising thin metallic edges. a) A patterned PDMS stamp is coated with a thin layer of gold and titanium, respectively, and brought into contact with a planer oxidized PDMS slab to remove the metal layer form the raised features of the stamp. b) Schematic illustration of patterning charge in a dielectric thin film using e-μCP. The shape of the pattern corresponds to the outline of the relief features on the stamp. c) KFM image of a charge pattern (positive surface potential) embedded in a layer of PMMA using e-μCP. (Reprinted with permission from [139], copyright 2005, Wiley-VCH.)