

Nanostructures Replicated by Polymer Molding

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INTRODUCTION

This article discusses materials and techniques used to generate polymer replicas of nanostructures by molding, embossing, and printing. Nanostructures are defined as those that have lateral dimensions of less than 100 nm. The effect of spatially confining materials to these dimensions gives rise to physical, electronic, mechanical, magnetic, and optical properties, e.g., quantum behavior,^[1,2] superparamagnetism,^[3] depressed melting point,^[4,5] and increased hardness,^[6,7] that differ, at times significantly, from those of microstructures and macrostructures.

The fabrication and characterization of nanostructures are important for applications in optics,^[8] computation,^[9] data storage,^[10,11] specialty materials,^[7] and biology.^[12] Most processes for producing electrically, magnetically, and optically functional devices containing nanostructures include four basic steps: 1) fabrication of a “master” (i.e., a substrate from which replicas are formed); 2) replication of the master; 3) transfer of the replica into a functional material (e.g., semiconductor or metal); and 4) registration of the pattern of a master (the same as or different than the one used originally) with that of the replica for multilayer structures. This article focuses on the polymers and the molding techniques useful for the second step of this process.

OVERVIEW

Why Replication of Nanostructures into Polymers?

Replication of nanostructures into photosensitive polymers by photolithography is routine in fundamental and applied research and in commercial manufacturing.^[13] The process replicates features from a photomask that is prepared by a serial lithographic technique such as electron-beam lithography,^[14,15] focused-ion milling,^[16–18] or scanning probe lithography.^[19–21] The fabrication of masters by these techniques is slow (~ 10 hr/cm²) because each feature in the mask is drawn individually. The lateral

dimensions of the structures that can be patterned by photolithography are limited by the wavelength of the illumination source; state-of-the-art, 157-nm sources can fabricate features as small as 50 nm.^[22] The techniques for making masters and for sub-100-nm photolithography require specialized, expensive equipment; such equipment is readily accessible in industry, but is not commonly available in academic research laboratories.

Advantages and Disadvantages of Replication of Nanostructures into Polymers

Replication of nanostructures by the molding of polymers shares the attractive feature of photolithography (that is, it can replicate all the features on a master in one step), but with a much lower limit, in principle, for the lateral dimensions of features (~ 1 nm) than that for photolithography. This limit is set by the size of the molecules in the replica. The molding of polymers has four advantages over photolithography: 1) the techniques can replicate nanostructures over large areas (> 1 m²); 2) the dimensions of the features replicated into polymers are not distorted by problems common to photolithographic techniques (e.g., variations in focus, intensity, and exposure dose); 3) the materials and the facilities necessary are inexpensive and readily accessible; and 4) the process may be compatible with low-cost manufacturing processes (e.g., roll-to-roll processing).

The replication of nanostructures by molding in polymers has seen only limited commercial applications to date. Replication of sub-10-nm features is still difficult to obtain reproducibly over large areas because of lateral collapse of the features in the polymeric replica. Defect densities are currently too high for use in most high-performance electronic devices; no defects must be observed over an area of several square centimeters for commercial applications. The process of replication does not reduce the dimensions of features; that is, the dimensions of the features defined in the master must be the same as those desired in the replica. This characteristic differs from photolithography where dimensions in a mask can be reduced optically.

POLYMER MATERIALS AND PROPERTIES FOR USE IN REPLICAS

Table 1 summarizes some of the types of polymers used to replicate masters by molding and the properties relevant to molding. Two properties that influence the quality of a polymer replica are the coefficient of thermal expansion of the master and the polymer and the dimensional change in the polymer during curing. The dimensions of features defined in masters or replicas made of polymers with large coefficients of thermal expansion can be distorted by changes in the temperature. The polymer replica also can shrink during curing because of evaporation of solvents, cross-linking of the polymer, and/or thermal expansion of the polymer (for heat-based curing).^[23] These processes can also yield replicas with distorted features.

Some processes of replication reshape thin films of polymers by softening them at elevated temperatures; the temperature at which the polymer softens is the glass transition temperature (T_g). Low glass transition temperatures (i.e., $45^\circ\text{C} < T_g < 150^\circ\text{C}$) can minimize distortions of the critical dimensions of the features because of thermal expansion of the master during heating and thermal contraction of the replica during cooling. Temperatures within this range also make the process compatible with a wide range of substrate materials (e.g., polymers and low-melt glasses).

Mechanical instabilities in the polymers can lead to vertical and lateral collapse of the features in the replica. The elasticity or the tensile modulus of the material used to make the replica determines the importance of these distortions. They are significant for nanostructures defined in polymers that have a low tensile modulus (<2 MPa), and they limit the minimum dimension (>300 nm) and the minimum aspect ratio (0.4; height/width) of the features these polymers (e.g., derivatives of polydimethylsiloxane (PDMS) such as 184-PDMS and s-PDMS) can replicate.^[24–26] A number of groups have developed formulations of PDMS (e.g., *h*-PDMS and *hv*-PDMS) that have a medium to high elastic modulus (4–10 MPa).^[23,27,28] These formulations of PDMS are particularly useful for the replication of nanostructures, as they can replicate features with lateral dimensions as small as 30 nm and with vertical dimensions as small as 2 nm.^[27,29]

The process removing a rigid replica from a rigid master can damage the fragile nanostructures defined on each surface. The physical toughness of the polymer is an indication of how much stress it can tolerate before cracking. The potential for damage to the features in the master and in the replica decreases when using a polymer with a tensile strength of >0.1 MPa (e.g., PDMS) as the material for the replica. Polymers with a high toughness tend to have a low tensile modulus.

Table 1 Properties of polymers used commonly in replication

| | Tensile modulus (MPa) | Toughness (MPa) | Surface free energy (dyn/cm ²) | Coefficient of linear thermal expansion (ppm/°C) | Glass transition temperature (°C) | Method of curing | Commercially available |
|---------------------------------|------------------------|----------------------|--|--|-----------------------------------|------------------|------------------------|
| Poly(dimethyl siloxane) (PDMS) | | | | | | | |
| 184-PDMS ^a | 1.8 ^[23] | 4.77 ^[23] | 21.6 | 260–310 ^b | N/A | Heat | Yes |
| <i>h</i> -PDMS ^[27] | 8.2 ^[23] | 0.02 ^[23] | ~20 | 450 ^[27] | N/A | Heat | No |
| <i>hv</i> -PDMS ^[23] | 3.4 ^[23] | 0.13 ^[23] | ~20 | 300 ^[23] | N/A | UV-light | No |
| s-PDMS ^c | 0.6 ^[23] | 0.41 ^[23] | ~20 | — | N/A | UV-light | Yes |
| Poly(methyl methacrylate) | 2200–3100 ^d | 195 ^d | 36.5 | 50–90 ^d | 85–105°C ^c | N/A | Yes |
| Poly(vinylchloride) | 2400–4100 ^d | 65 | 39 | 50–100 ^d | 75–105°C ^c | N/A | Yes |
| Poly(styrene) | 2300–3300 ^d | 36.52 ^d | 33 | 50–83 ^d | 74–100°C ^c | N/A | Yes |
| Poly(urethane) | 20–70 ^e | 75–80 ^e | 28–30 | 30–60 | N/A | UV-light | Yes |
| Novalac | ~6000–9000 | ~100–110 | 43.6 | 30–50 | ~120°C ^c | N/A | Yes |
| Photoresist | | | | | | | |

^aSylgard 184 available from Dow Corning.

^bDow Corning technical data sheet for Sylgard 184.

^cRMS-033 available from Gelest.

^dModern Plastics Encyclopedia 1999, p B158 to B216.

^eNorland Optical Adhesives technical data sheets.



The surface free energy of the polymer is a parameter that determines the ease of release of the polymer replica from the master and thus the damage to the replicated nanostructures during this process. PDMS is a useful material for use in replicas because it has a low surface free energy (~ 21.6 dyn/cm).^[30] After molding, the surface energy of PDMS replica can be lowered further to ~ 12 dyn/cm by coating the surface with a fluoro-silane;^[31,32] this process makes the surface properties of the stamp similar to poly(tetrafluoroethylene) (Teflon®).

TECHNIQUES FOR THE REPLICATION OF NANOSTRUCTURES BY THE MOLDING OF POLYMERS

Replica Molding

Replica molding is a technique used routinely to fabricate macroscale and microscale objects, e.g., compact disks, digital versatile disks (DVD), holograms, and plastic parts, by molding a polymer against ceramic, metallic, or rigid plastic masters (Fig. 1). Typically, the surface of the master is modified chemically to lower its surface free energy by coating it with a fluorinated molecule or polymer; this layer facilitates the separation of the master from the replica after molding. Damage to the nanostructures defined in the master and/or the replica occurs most commonly during this separation. The use of elastomeric polymers in replica molding helps to minimize damage to the nanostructures, especially in the replica, during separation because of the toughness and elasticity of the polymers. An example of replica molding into PDMS is the replication of rings of photoresist into a composite polymer made of a thin layer ($40\text{ }\mu\text{m}$) of *h*-PDMS and a thick layer ($>1\text{ mm}$) of 184 PDMS (Fig. 2).

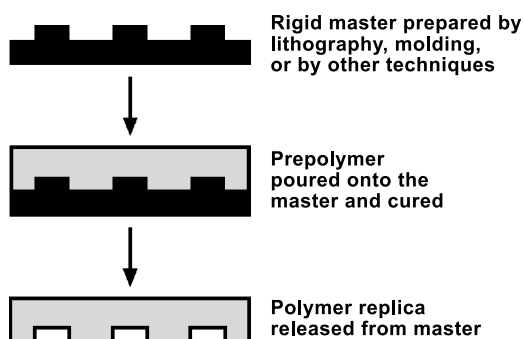


Fig. 1 Scheme for replica molding. (View this art in color at www.dekker.com.)

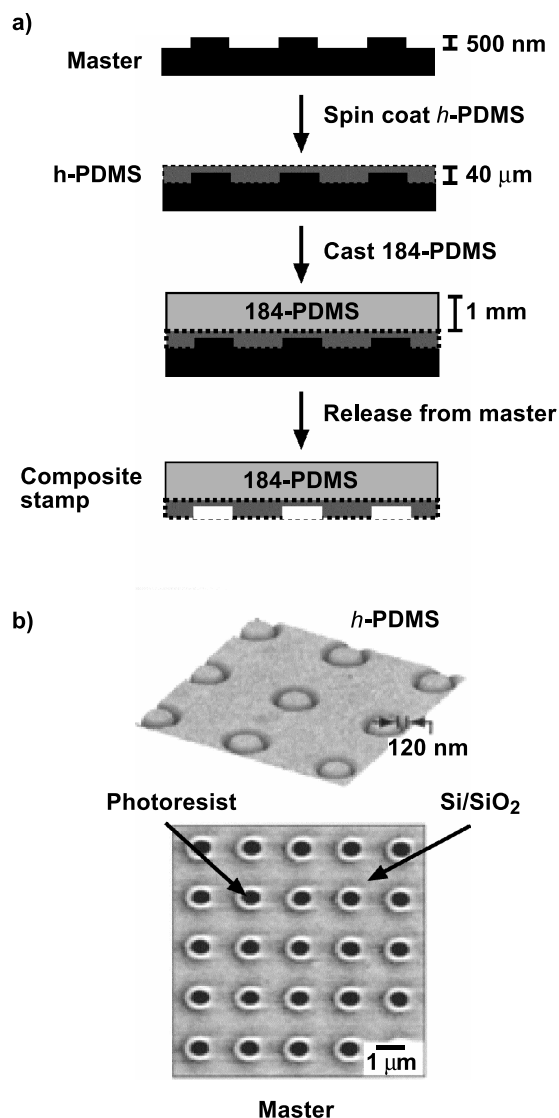


Fig. 2 a) Scheme for replica molding a master into a *h*-PDMS/184 PDMS composite polymer. b) An atomic force micrograph of the replica (top) and a scanning electron micrograph of the master (bottom). The scheme and images in (b) are reproduced with permission from the American Chemical Society. (From Ref. [28].) (View this art in color at www.dekker.com.)

The composite PDMS structure can replicate sub-100-nm features by molding and can be removed easily from a master without damaging the nanostructures on either surface.^[27,28]

Soft Lithography

Soft lithography is a suite of techniques that use a PDMS-based stamp—prepared by replica molding—as the master



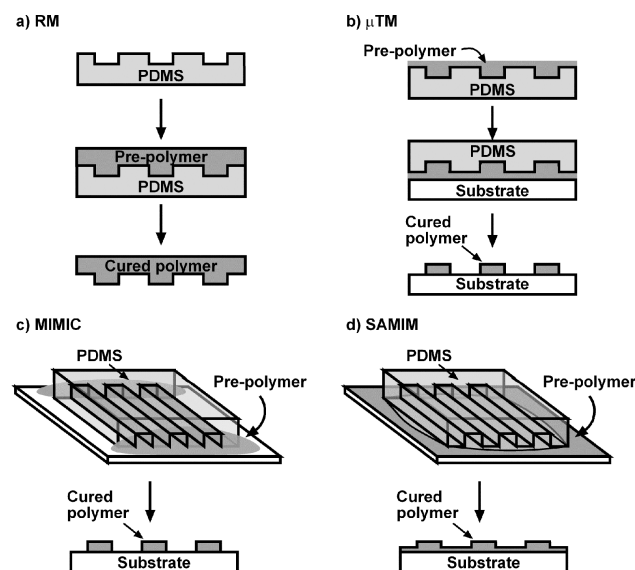


Fig. 3 Schematic illustrations of the procedures used in the corresponding soft lithographic techniques. (View this art in color at www.dekker.com.)

(Fig. 3).^[13,31,32] Replica molding (RM),^[33] microtransfer molding (μ TM),^[34] micromolding in capillaries (MIMIC),^[35] and solvent-assisted micromolding (SAMIM)^[36] are four soft-lithographic techniques that replicate features by the molding of polymers. For many of these techniques, the inherent low surface free energy of PDMS is enough to permit the stamp to be separated from the replica without the need of a release layer.

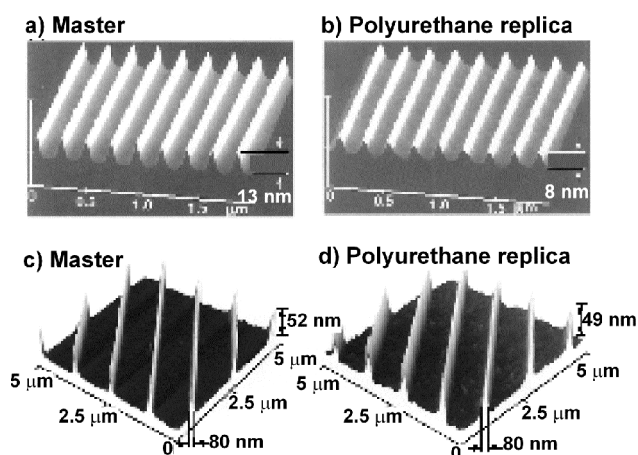


Fig. 4 Atomic force micrographs of (a) a chrome master and (b) a polyurethane replica of the master produced by replica molding. The images in this figure are reproduced with permission from *Advanced Materials*. (From Ref. [33].)

Replica molding

The soft lithographic version of replica molding uses a PDMS stamp as the master instead of a rigid material (Fig. 3a). Fig. 4 shows the replica molding of nanostructures into an UV-curable polyurethane. The PDMS stamp can be used repeatedly; no measurable difference in feature quality is observed after successive replication into polyurethane more than 20 times from the same stamp.

Microtransfer molding

Microtransfer molding prepares a replica by first filling the recessed regions of the stamp with a curable prepolymer (Fig. 3b). The excess prepolymer is scraped from the surface of the stamp using a thin slab of PDMS; this scraping process does not remove the excess polymer completely, and, often, a thin film of excess polymer remains on the replica. The filled stamp is placed onto a rigid substrate under slight pressure. The prepolymer is cured by the appropriate technique, and the mold is removed manually. This technique is well suited for UV-curable materials because the PDMS stamp is optically transparent above ~ 290 nm.

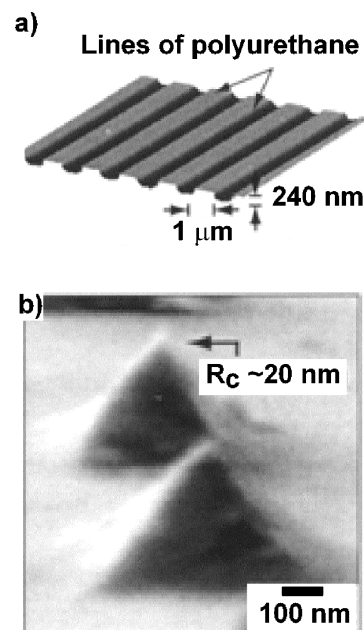


Fig. 5 (a) Atomic force micrograph of lines of photoresist patterned by MIMIC. (b) Scanning electron micrograph of Novalac photoresist patterned by SAMIM. The images are reproduced with permission from *The American Chemical Society*. (From Ref. [28].)



Micromolding in capillaries

Micromolding in capillaries uses capillarity to fill channels in a PDMS stamp with a photocurable or thermally curable polymer (Fig. 3c). A PDMS-based stamp is placed in conformal contact with a surface. The stamp is topographically patterned with a series of channels that extend from one end of the stamp to the other. A drop of liquid prepolymer placed at one end of the stamp fills the channels by capillarity. The polymer is cured once the entire channel network is filled. The replication of nanochannels in a 184-PDMS stamp is difficult because the channels tend to collapse when the stamp is placed in contact with a surface.^[28] Composite stamps of *h*-PDMS and 184-PDMS overcome this limitation and can be used to replicate features with critical dimensions below 300 nm (Fig. 5a). Unlike μ TM, this technique does not produce an excess polymer film on the replica.

Solvent-assisted micromolding

Solvent-assisted micromolding is similar operationally to traditional embossing techniques, but it uses solvent to reshape a polymer rather than elevated temperatures, and it uses an elastomeric stamp instead of a rigid master (Fig. 3d). Elastomeric stamps are especially useful in embossing because the stamp conforms to the surface of the polymer and contacts uniformly over large areas. The stamp is wet with a solvent for the polymer that is to be molded and placed in contact with a thin film of this polymer. The solvent is allowed to evaporate, and the stamp is removed to reveal the replica in the polymer. Air bubbles and voids in the replica as a result of poor evaporation of the solvent before removal of the stamp are not observed because the stamp is gas-permeable. This process has been demonstrated for a number of polymers including: Novalac photoresists, poly(styrene), poly(methyl-methacrylate), cellulose acetate, poly(vinyl chloride), and precursors to conjugated organic polymers.^[36] An example of nanostructures prepared by this technique is in Fig. 5b. The molded structure can also act as its own optical element for further size reduction of the features.^[37]

Advantages and disadvantages of soft lithography

The advantages of soft lithography are that: 1) it uses inexpensive materials and equipment; 2) it can replicate over large areas and on nonplanar surfaces; 3) it uses stamps that are compatible with a large number of polymers; and 4) it uses stamps that are gas-permeable. The disadvantages are that: 1) the PDMS molds are not compatible with many organic solvents or high temperatures; 2) the softness of PDMS can cause distortions in molded

structures; 3) the use of PDMS-based stamps requires careful temperature control because of the high coefficient of thermal expansion; that is, small changes in temperature can change the dimensions of the nanostructures; and 4) the registration of multilayer patterns is difficult.

Imprint Lithographies

Step-and-flash imprint lithography (developed by Willson et al.^[38–41]) and nanoimprint lithography (developed by Chou et al.^[42–44]) are two forms of imprint lithography that are used for the replication of nanostructures into polymers. Both techniques work by placing a topographically patterned, rigid master in contact with a formable material coated on a rigid surface. The rigid master is prepared by photolithographic replication of the features into a polymer that is coated on a rigid substrate (e.g., quartz and silicon). The structures are transferred into the substrate by etching.

Step-and-flash imprint lithography

Step-and-flash imprint lithography uses a low-viscosity, photocurable polymer as the material for the replica (Fig. 6)^[41] The low viscosity of the polymer eliminates the need for high temperatures and pressures. A quartz master is placed in contact with the photocurable polymer under slight pressure. Flood illumination through the backside of the master cures the polymer replica. The

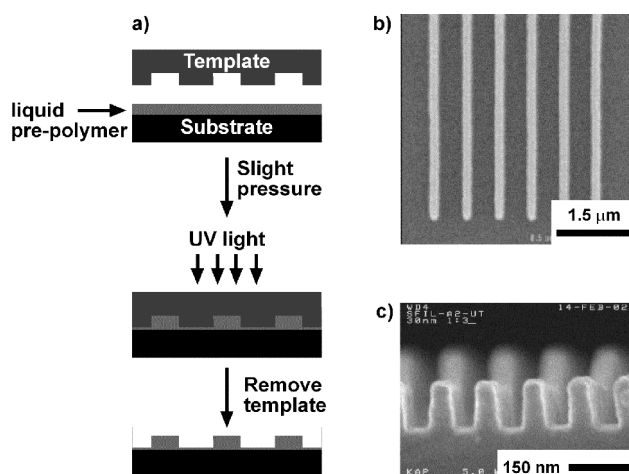


Fig. 6 a) Schematic illustration of step-and-flash imprint lithography. b) Scanning electron micrograph of lines of polymer on a silicon substrate patterned by the technique. c) Scanning electron micrograph of the cross-section of the lines in (b). The images in (b) and (c) are reproduced with permission from *Proceedings of the SPIE*. (From Ref. [45]). (View this art in color at www.dekker.com.)



master is transparent to the wavelengths necessary to cure the polymer. Treatment of the surface of the master with a fluorosilane lowers its surface free energy and facilitates the removal of the master from the replica. The technique can replicate features with lateral dimensions greater than 30 nm and with aspect ratios as high as 8:1 (for 50-nm lines).^[41,45] Step-and-flash lithography is “self-cleaning” because particulates on the surface of the master are trapped in the replica during the curing process. Repeated use of a master actually lowers the density of defects in the replica.^[46]

The advantages of step-and-flash imprint lithography are that: 1) it is a room-temperature technique and is therefore not subject to thermal- or pressure-induced deformations of the nanostructures; 2) it is a rapid process (<5 min/cycle);^[40,47] and 3) it uses optically transparent masters that permit alignment of the replica with underlying features. The disadvantages are that: 1) the masters are more difficult to prepare than those used in soft lithography; 2) the replication of nonplanar masters is difficult;^[48] and 3) the technique is not good for the replication of isolated, recessed features in the master.^[41]

Nanoimprint lithography

Nanoimprint lithography differs from step-and-flash imprint lithography in that it reshapes a polymer at temperatures above its glass transition point, e.g., 90–100°C, and requires high pressures, e.g., 50–100 bar (Fig. 7).^[43,44] The high temperatures lower the viscosity of the polymer enough to fill the master uniformly. The replica and mold

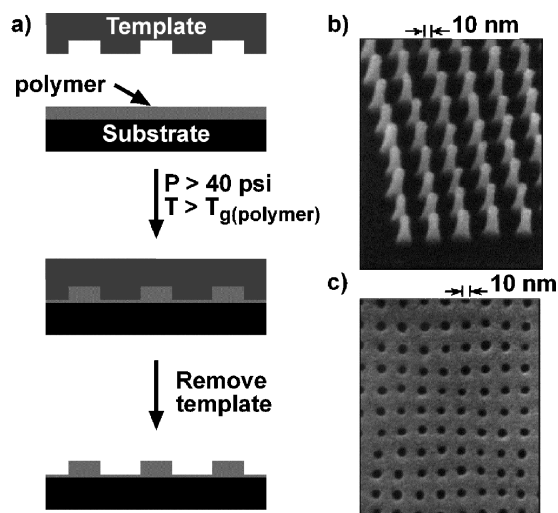


Fig. 7 a) Schematic illustration of the process used in nanoimprint lithography. b) Scanning electron micrograph of the SiO₂ master. c) Scanning electron micrograph of the polymer replica of the master in (b) made by nanoimprinting. The images in (b) and (c) are reproduced by permission of *MRS Bulletin*. (From Ref. [43].) (View this art in color at www.dekker.com.)

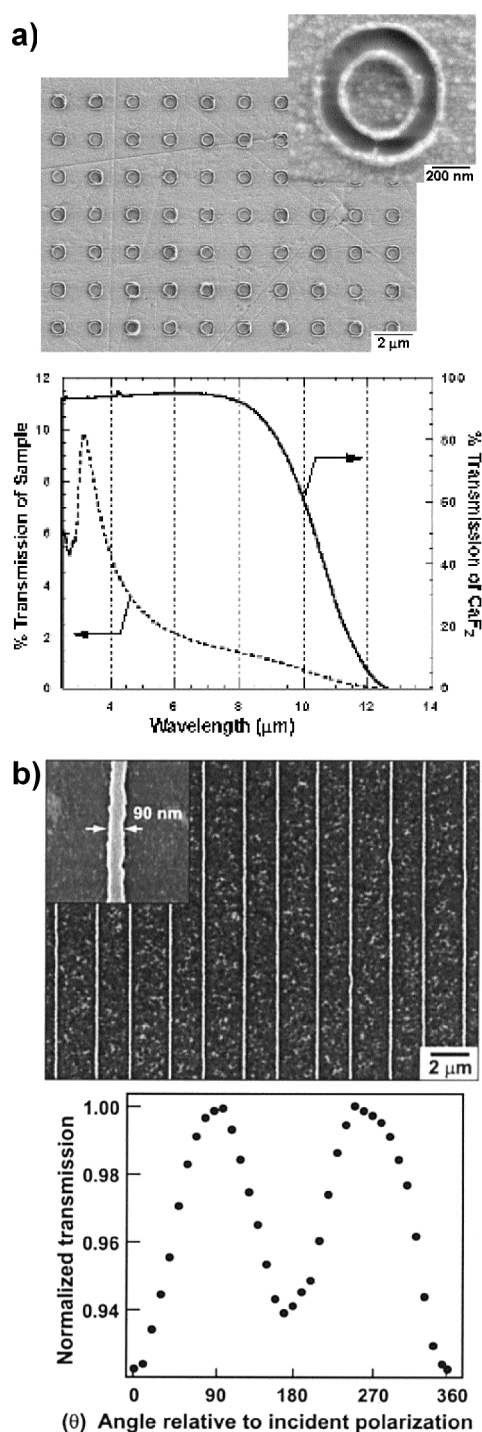


Fig. 8 a) Scanning electron micrograph of rings of nickel formed by lift-off of a photoresist patterned by phase-shifting photolithography and the corresponding transmission spectrum as a function of wavelength for the sample and the CaF₂ substrate. b) Lines of palladium formed by lift-off of photoresist patterned by phase-shifting photolithography and the corresponding plot of the intensity of the transmitted light as a function of angle of polarization. Figure (a) is reproduced with permission from *The Optical Society of America*. Figure (b) is reproduced with permission from *The American Chemical Society*. (From Ref. [28,62].)

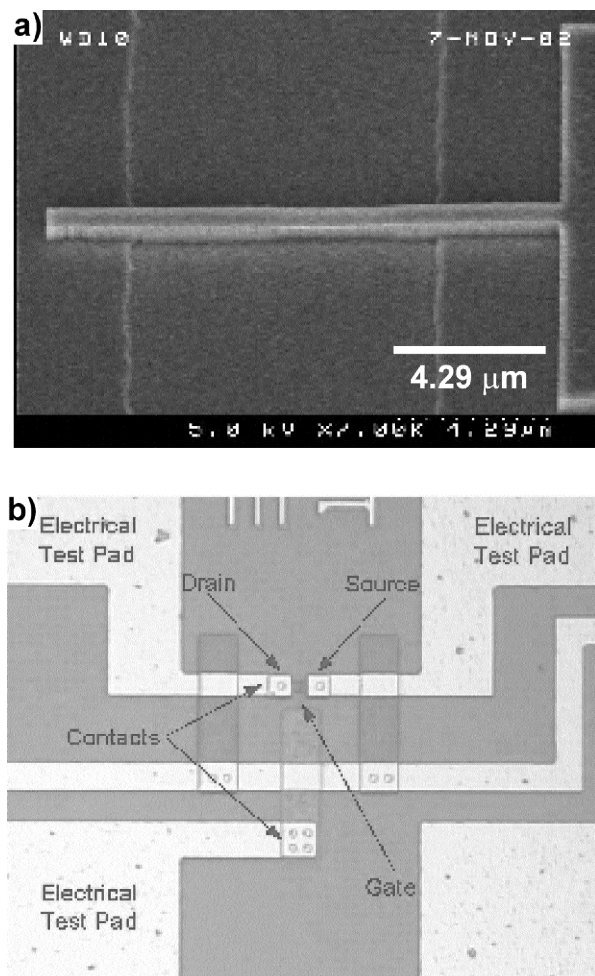


Fig. 9 a) Scanning electron micrograph of a polymer gate made by step-and-flash imprint lithography. b) Optical micrograph of the complete MOSFET device that incorporates the polymer gate in (a). The images are reproduced with permission from *Proceeding of the SPIE*. (From Ref. [77].) (View this art in color at www.dekker.com.)

are allowed to cool before separation. The technique can replicate nanostructures as small as 10 nm and aspect ratios as large as 10:1.^[43] Transparent masters can be used to permit multilevel registration of replicas. Nanoimprint lithography can be carried out in a sequential, step-by-step process similar to that of step-and-flash. The fidelity of replication of nanostructures with critical dimensions of less than 50 nm is poor over large areas because the polymer chains in the materials used in the replicas tend to relax and spread over distances of tens of nanometers.^[47] These factors can only be corrected by designing the original master to account for polymer shrinkage in the processing steps. Another disadvantage of nanoimprinting is that it requires 10–15 min per replication for the heating and cooling cycles; this interval is 3–5 times longer

than that necessary for the entire replication process for step-and-flash imprint lithography and some soft lithographic techniques.^[47]

Uses for Polymeric Replicas with Nanostructures

Replication of nanostructures into polymers is used to make electronic,^[49–59] optical,^[60–64] and mechanical^[65–69] devices. Single-layer, subwavelength, optical elements, e.g., frequency-selective surfaces (Fig. 8a), are one example of such a device fabricated by soft lithography.^[37,62,70,71] A master was replicated into Novalac photoresist by solvent-assisted micromolding. The replica acted as a photomask, and the edges of the raised features were transferred into the underlying photoresist upon exposure to UV-light. The PDMS replica prepared by standard replica molding was used to fabricate polarizers by a similar, phase-shifting lithography technique (Fig 8b).^[70] The PDMS replicas can also be used to replicate nanostructures into metals by microcontact printing. This process uses the PDMS replica as a stamp to print an organic molecule selectively onto a metal surface. This molecule acts as an etch resist and permits the selective etching of unprotected regions. This technique was used to fabricate polarizers,^[28] hydrogen-gas sensors,^[72] transistors,^[50,52] and microelectromechanical systems (MEMS) devices.^[69,73] The imprint lithographies use the polymer replica as an etch resist to transfer the pattern of the replica into a functional material. These techniques have been used to make photonic crystals,^[74] polarizers,^[75,76] photo-detectors,^[56] and transistors (Fig. 9).^[58,59,77]

CONCLUSION

Although replication will not replace the techniques used currently for the preparation of masters, it is extremely useful as a research tool for the rapid prototyping of devices using nanostructures. The combination of the two techniques could enable the fabrication of nanostructures to become routine and cost-effective. Polymeric replicas containing nanostructures may be most useful in the process of fabricating low-cost, low-to-medium performance optical and electronic devices (e.g., RF-ID tags, large area displays, optical filters, and polarizers). Efforts to improve the capabilities of replication will lead to the fabrication of new devices based on the unique properties of nanostructures.

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