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Soft lithography is a set of techniques that extends and complements conventional photolithography by allowing curved surfaces to be patterned and enabling complex, nanoscale structures to be formed using a variety of materials in a relatively simple way

Soft lithography and microfabrication

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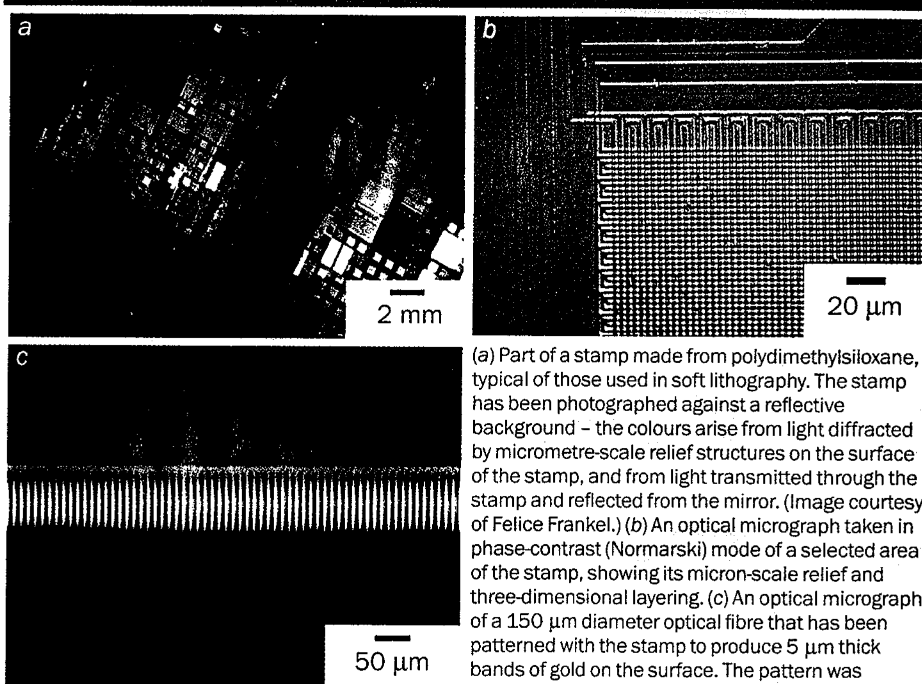
MINIATURIZATION is a central theme in technology. As the computer industry knows, smaller microelectronic devices have made computers faster, cheaper and more portable. These advances in microelectronics have also spawned a huge variety of other tiny devices. For example, micro-electro-mechanical systems are now being used in medicine as disposable blood-pressure sensors, and in the automotive industry as tiny accelerometers in airbags that protect drivers in crashes.

Microanalytical systems, which are like tiny chemistry labs on a chip, are also being developed. One firm, iSTAT Corporation, already sells a portable, battery-powered blood-analysis system that can be used to measure the concentration of gases in a patient's blood in a matter of minutes. All it requires is a few drops of blood. There are also micro-chemical reactors, micro-sensors and micro-optical systems. Indeed, the use of micro-optical systems for switching is increasing daily as communications companies rush to expand their fibre-optic networks.

1 Stamping on fibres



(*a*) Part of a stamp made from polydimethylsiloxane, typical of those used in soft lithography. The stamp has been photographed against a reflective background – the colours arise from light diffracted by micrometre-scale relief structures on the surface of the stamp, and from light transmitted through the stamp and reflected from the mirror. (Image courtesy of Felice Frankel.) (*b*) An optical micrograph taken in phase-contrast (Normarski) mode of a selected area of the stamp, showing its micron-scale relief and three-dimensional layering. (*c*) An optical micrograph of a 150 μm diameter optical fibre that has been patterned with the stamp to produce 5 μm thick bands of gold on the surface. The pattern was created using micro-contact printing.

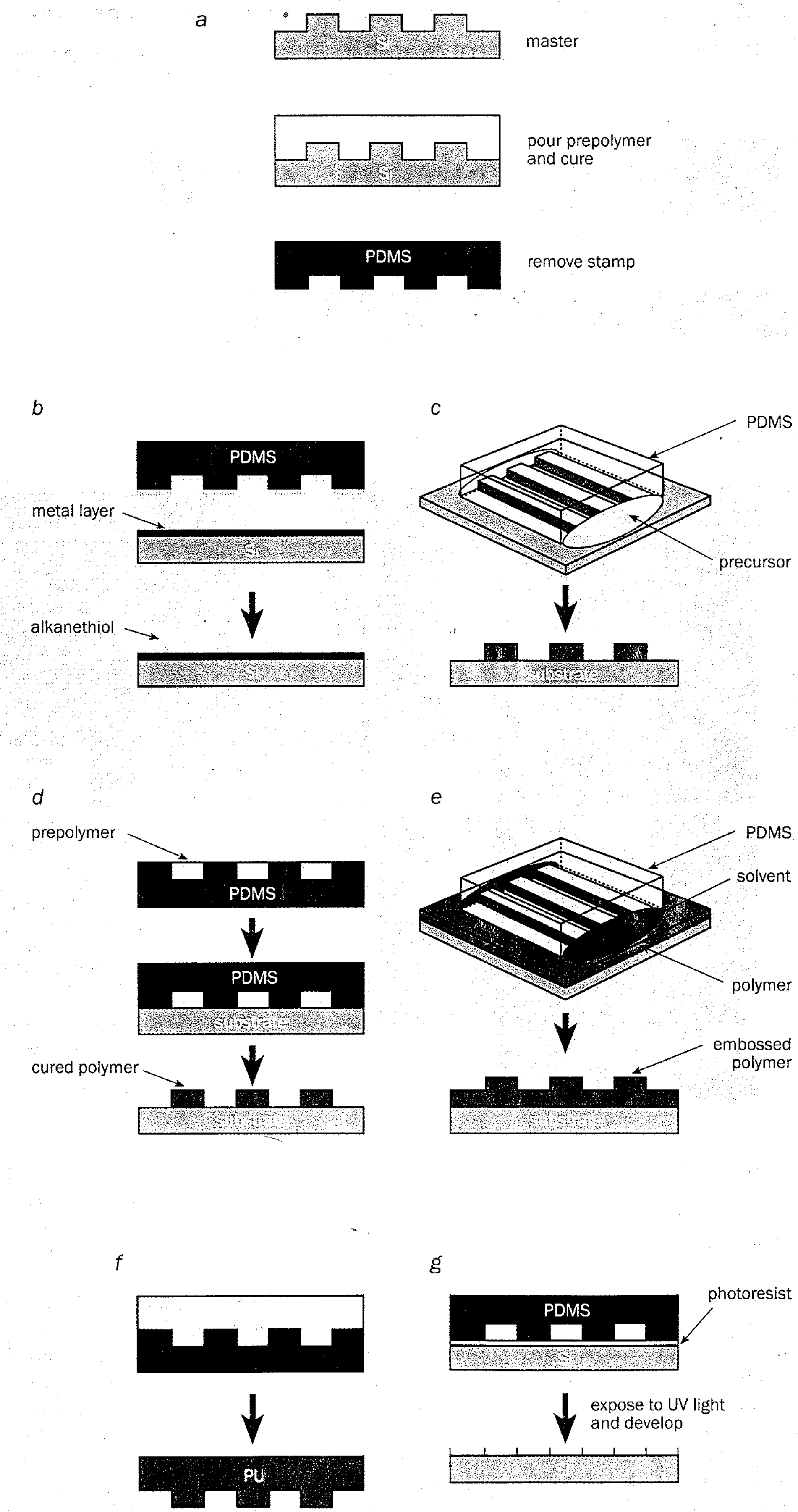
The common feature of all of these technologies is the need to fabricate small systems. Researchers have therefore drawn heavily on methods from microelectronics, in particular the enormously powerful technique of photolithography. In this method, a surface is covered with a light-sensitive photoresist and then exposed to ultraviolet light shone through a mask. The light alters the structure of the resist, and the areas of the resist exposed to the light can be washed away with chemicals, leaving just the pattern of the mask on the surface.

However, conventional photolithography has its drawbacks. It cannot generate features smaller than about 100 nm and can only form structures on flat surfaces. There is therefore no reason to think that photolithography will always be the best choice for new microfabrication technologies. Indeed, each of the devices mentioned above has distinct components, and the microfabrication techniques must be tailored to meet the relevant materials, feature sizes and costs of the device.

Classical photolithography will, of course, continue to be used for making planar microelectronic devices with feature sizes larger than 100 nm, but devices with features smaller than this will need new techniques. This need for new techniques in micro- and nano-fabrication prompted our group at Harvard University about ten years ago to start exploring methods that get round the limitations of photolithography. These methods are collectively known as "soft lithography".

Soft lithography currently consists of six different microfabrication techniques, although new techniques continue to

Techniques of soft lithography



Soft lithography - how it works

How to make a pattern-transfer element

(*a*) Pattern-transfer elements, which are usually made from polydimethylsiloxane (PDMS), are generated by pouring PDMS prepolymers onto a "master" made from silicon, allowing the monomers to cure to form the elastomer and then removing the master. The three-dimensional layering of the master is then faithfully reproduced in the element, also known as a stamp.

Micro-contact printing

(*b*) A PDMS replica cast from a master is used as a stamp. An "ink" – such as a solution of $CH_3(CH_2)_{15}SH$ in ethanol – is applied to the stamp using a cotton swab. The inked stamp is then placed by hand onto a metal-coated silicon substrate. The stamp conforms to surface and a self-assembled monolayer forms in the regions of contact between the stamp and the surface. After 10–20 s, the stamp is separated from the substrate, leaving the monolayer on the surface.

Micromoulding in capillaries

(*c*) A PDMS mould with an interconnected system of recessed channels on one face is placed on a substrate, which can be either planar or curved. This forms a network of capillaries. A drop of low-viscosity liquid prepolymer is then placed at one end of the channels and drawn into the capillaries by capillary action. The polymer is "cured" by heating or by exposing it to ultraviolet radiation to form a network within the PDMS channels. When the mould is removed, the polymeric structures are left supported on the substrate.

Microtransfer moulding

(*d*) In this technique, a small drop of liquid prepolymer is poured into a PDMS mould. After it has filled the relief structures, any excess polymer is wiped from the surface of the mould by hand. The filled mould is placed on the substrate and the prepolymer is "cured" by heating or irradiation. When the mould is separated from the substrate, the polymeric microstructures remain on the surface.

Solvent-assisted micromoulding (SAMIM)

(*e*) A thin film of polymer is first coated onto a planar or curved surface. A PDMS mould is then wetted with a liquid that is a good solvent for this polymer. When the mould is brought into contact with the substrate, the solvent dissolves (or swells) the polymer. The resulting fluid layer of dissolved polymer flows and conforms to the shape of the features on the mould. The mould is left until the solvent dissipates (after about 5 min) before being peeled away from the substrate.

Replica moulding

(*f*) A PDMS replica is coated with a polymeric precursor, such as polyurethane. After the polyurethane has been cured by heating or irradiation with ultraviolet light, it is separated from the mould, resulting in a polymeric replica of the original master.

Near-field contact-mode lithography

(*g*) A surface is covered with a photosensitive material or "photoresist" and a PDMS stamp is placed above it. The material is then exposed to ultraviolet light through a mask. After chemical development, features about 100 nm wide form at phase boundaries along the mask edges.

be developed and added. In each method, tiny patterns are created on the surface of a material using a "pattern-transfer element" or stamp that has a three-dimensional structure moulded onto its surface (figure 1*a*). These pattern-transfer elements are always made from an elastomer – a polymer network that deforms under the influence of a force and regains its shape when the force is released. This elasticity is why these techniques are called "soft" lithography.

Pattern-transfer elements

A pattern-transfer element is formed by pouring a liquid polymer onto a master, allowing the polymer chains to "cure" to form the elastomer and then removing the master (see box figure *a*). This ensures that the micron-scale relief and the three-dimensional layering of the master are faithfully reproduced in the elastomer copy. This replica can then be used as a stamp to transfer a chemical ink to a surface, as a mould to replicate surface features in organic polymers, or as a mask to produce nano-scale patterns in photoresists.

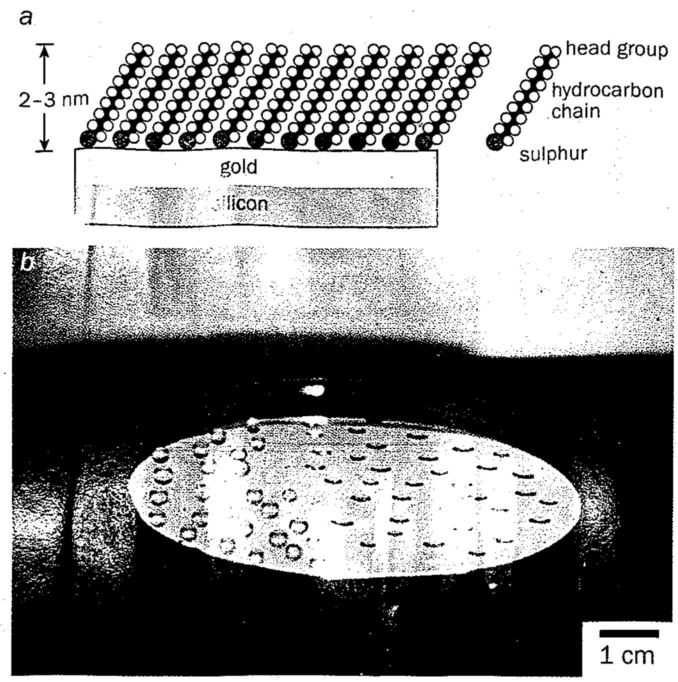
The advantages are that numerous replicas can be generated from a single master, and that each replica can be used more than once. Soft lithography is therefore a replication technique: it provides a cheap way of reproducing structures that would otherwise need to be formed with expensive techniques such as electron-beam writing and X-ray lithography. The masters themselves are produced using a variety of techniques, including photolithography, X-ray lithography, electron- or ion-beam writing and micromachining.

The material of choice for pattern-transfer elements is polydimethylsiloxane (PDMS) – a chemically inert and non-toxic organic polymer that is also durable, cheap and commercially available. There are several advantages to this material. PDMS does not adhere well to other materials, which means that it can be easily separated from delicate, moulded structures that have nanoscale or high-aspect-ratio features, thereby causing minimal damage to the replica or the master. Pattern-transfer elements made from PDMS are physically flexible, which means that they can reproduce patterns on curved as well as planar structures. PDMS also provides a way of processing materials that are incompatible with photolithography, and it can create features that are smaller than ultraviolet photolithography allows. Finally, PDMS can be used with many organic polymers and solvent systems, while its optical transparency means that it can be used with polymers that need to be cured with ultraviolet light, as a phase mask in near-field contact photolithography and as a functional component in optical systems.

Micro-contact printing on curved surfaces

One technique of soft lithography is micro-contact printing, which enables "self-assembled monolayers" to be formed with sub-micron resolution on a surface. In the self-assembling process, molecules spontaneously arrange themselves on a well defined surface to form a regular lattice, thereby minimizing their free energy. The self-assembled systems are usually close to thermal equilibrium and therefore tend to have few defects. They are also "self-healing", which means that the molecules can rearrange themselves to repair small defects that may appear in the lattice. Self-assembly is found widely in nature – for example, when water molecules form a rain-drop with a smooth, curved surface or when polypeptide chains fold into functional proteins.

2 Self-assembled monolayers

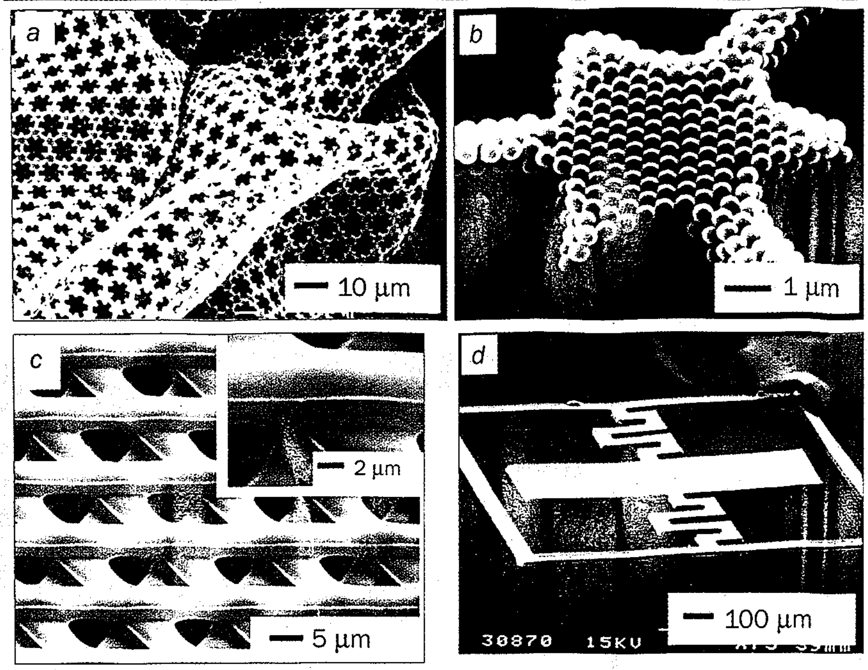


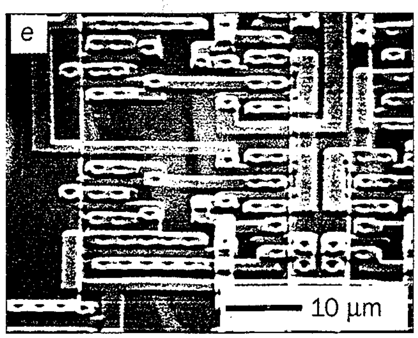
(*a*) A self-assembled monolayer of a functionalized alkanethiolate, $R(CH_2)_nS^-$, on gold. Modifying the organic functional group, R, controls the surface properties of the monolayer, while varying *n*, the number of CH_2 groups in the alkyl chain, changes the thickness of the monolayer. (*b*) The left-hand half of this gold-coated silicon wafer is covered with a self-assembled monolayer of $CH_3(CH_2)_{15}SH$, which is hydrophobic, while the right-hand half is covered with a $CO_2H(CH_2)_{15}SH$ monolayer, which is hydrophilic. It is easy to distinguish between the two halves: drops of water form beads on the hydrophobic surface but spread out on the hydrophilic surface. This demonstration shows how self-assembled monolayers can be made to tailor the properties of a surface in a specific way.

In micro-contact printing, an "ink" is applied to the surface of a pattern-transfer element. The inked stamp is then placed on a substrate and a self-assembled monolayer forms wherever the stamp touches the surface. When the stamp is removed, the monolayer is left on the surface (see box figure *b*). For example, the surface of a gold-coated silicon wafer can be exposed to a solution of an alkanethiol, $R(CH_2)_nSH$, in ethanol, where R is a functional group such as CH_3 or CO_2H. The sulphur atom bonds to the gold surface, forming a self-assembled monolayer of $R(CH_2)_nS^-$ (figure 2*a*). These crystals are usually 2–3 nm thick, and have many grain boundaries and defects due to steps in the surface of the gold. If the molecules have more than ten CH_2 groups, they form close-packed layers on the surface, presenting only the head group, R, to the environment. Varying R therefore provides a way of engineering the properties of the surface to produce particular chemical or physical properties. For example, if R is changed from CH_3 to CO_2H, the surface goes from being non-wetting (hydrophobic) to wetting (hydrophilic) (figure 2*b*).

Self-assembled monolayers can be used in a range of ways to transfer patterns using micro-contact printing. In particular, patterned monolayers can be transferred to highly curved surfaces, such as those of lenses and optical fibres – something that is completely impractical with conventional planar fabrication methods. For example, we have patterned a 150 μm diameter gold-coated optical fibre by rolling the fibre over a stamp that had parallel lines of a self-assembled monolayer

3 Products of soft lithography





(*a*) A scanning electron microscopy (SEM) image of a free-standing polyurethane grid made using the technique of micromoulding in capillaries (MIMIC). The polymeric microstructure was freed from the substrate on which it was formed by dissolving a sacrificial layer of SiO_2 (grown prior to MIMIC by heating the silicon wafer in air to 1100 °C for several hours) in an aqueous solution of hydrogen fluoride. (*b*) An SEM image of polystyrene beads crystallized from an aqueous dispersion inside capillaries that were formed and patterned using MIMIC. (c) An SEM image of a three-layer polyurethane grid fabricated in three steps using the technique of microtransfer moulding. (*d*) An SEM image of a glassy carbon deflector made using microtransfer moulding. The structure, which was formed from a furfuryl alcohol-phenol resin that was then heated at 1000 °C, is slightly buckled due to shrinkage and mass loss during heating. The structure is electrically conducting, and when electrostatically actuated, the central plate twists in and out of the plane of the supporting frame, along the axis of the spring-like, serpentine arms. (e) An SEM image of a microelectronic test pattern formed using the technique of solvent-assisted micromoulding (SAMIM) in a thin film of a Novolac polymer photoresist using ethanol as the solvent. The height variations replicated in the polymer show that this technique can be used to fabricate quasi-three-dimensional structures in a single step.

on its surface (figure 1*b*). The gold-coated fibre picks up the pattern from the stamp but those areas of gold that are not covered by the monolayer are removed by chemical etching. This generates a pattern of 5 µm wide parallel bands on the fibre (figure 1*c*). (Varying the angle at which the fibre is rolled relative to the pattern of lines on the stamp also enables micro-spirals rather than bands to be created.) We are currently using these banded films as masks to make in-fibre gratings, as microtransformers and microsolenoids, and as micro-coils for nuclear magnetic resonance experiments.

Microfabrication in unconventional materials

Another technique in soft lithography is micromoulding in capillaries, in which a PDMS stamp with an interconnected system of recessed channels on one face is placed on a substrate (see box figure *c*). This forms a network of capillaries, each of which is bounded on three sides by the features of the PDMS stamp and on the fourth by the substrate. A drop of low-viscosity polymeric or other fluid precursor is then placed at one end, and capillary action draws the fluid into the channels. The substrate is then dissolved, leaving an interconnected system of microstructures.

By chemically separating the cured polymer from the substrate, we have produced free-standing, polyurethane networks with this technique (figure 3*a*). Close-packed arrays of polystyrene spheres can also be formed by filling the channels with a suspension (figure 3*b*). As the fluid evaporates, the spheres become more concentrated and the polystyrene crystallizes out.

In the related technique of microtransfer moulding, monomers contained in the recesses of a PDMS mould are transferred directly to a substrate by bringing the patterned surface of the stamp into "conformal contact" with the surface to be patterned (see box figure *d*). This means that the compliant mould adapts its shape so that it comes into intimate contact with the surface. This technique allows a range of polymers to be patterned into discrete structures with feature sizes ranging from microns to millimetres. Indeed, the procedure can be repeated to build multiple layers of structure (figure 3*c*).

Microtransfer moulding is also useful for patterning other materials. For example, microstructures fabricated with a furfuryl alcohol-phenol copolymer – a polymer that is a precursor to carbon solids – can be heated at 1000 °C under an inert atmosphere to yield free-standing, glassy carbon microstructures (figure 3*d*). Such structures conduct electricity and could be used in displays or sensors that use micro-electromechanical systems.

Microstructures have also been fabricated in glasses by microtransfer moulding of "sol-gel precursors". A sol is a colloidal suspension of solid particles in a liquid. Cross-linking these colloidal particles creates a gel, which consists of a continuous solid skeleton of colloids enclosing a continuous liquid phase. When the gel is heated, its density increases, and eventually a solid ceramic is formed (figure 4).

Microembossing without pressure

In solvent-assisted micromoulding (SAMIM), a thin film of polymer is coated onto a planar or curved surface. A PDMS mould is then wetted with a liquid that is a "good" solvent for this polymer, which means that when the mould is brought into contact with the substrate, the solvent dissolves (or "swells") the polymer. The resulting fluid layer of dissolved polymer flows and conforms to the shape of the features on the mould. When the mould is peeled away from the substrate, one finds that the original relief pattern of the mould has been transferred to the polymer film (see box figure *e*).

We have used this technique to transfer the pattern of a test microelectronic circuit to a substrate – proving that we can fabricate quasi-three-dimensional structures in a single step (figure 3*e*). In fact, using field-emission scanning microscopy, we found that SAMIM can reproduce features as small as 50 nm. SAMIM has been used to pattern microstructures in common plastics like polystyrene and polymethylmethacrylate. It has also patterned materials like cellulose acetate, a natural polymer that can be spun into fibres and used in fabrics, as well as poly(acrylonitrile-butadiene-styrene), a rubber that is prized for its inability to swell when placed in contact with organic solvents.

Replicas smaller than 100 nm

Other soft lithographic techniques can pattern features smaller than 100 nm. Conventional semiconductor processing, in contrast, is currently limited to 250 nm. For example, in replica moulding, a PDMS replica of a master acts as a mould for reproducing features in a polymeric material (see box figure *f*). The replica is first coated with another polymer, such as polyurethane, which is then cured by heating or irradiation. The polyurethane is then separated from the mould. Since PDMS is an elastomer, it can be bent and compressed, which reduces the lateral dimensions of the features on its surface. For example, we have cast a PDMS mould from a master that had 50 nm wide gold ridges. When we bent the mould laterally, we found that this reduced the width of the grooves replicated from 50 nm to 30 nm.

We have also made topologically complex, optically functional surfaces using soft lithography. For example, we have made a "chirped diffraction grating" – one in which the periodicity of the lines changes smoothly with position on the surface – by first compressing a PDMS mould prepared from a normal grating and then using replica moulding.

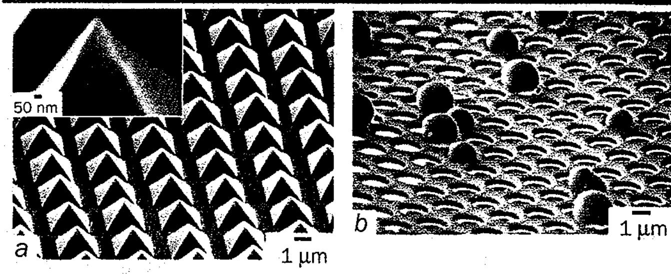
Embossing is a related technique that uses a rigid mould to imprint microstructures in "thermoplastics" – polymers that soften on heating. Various companies use this technique to manufacture compact discs by imprinting polycarbonate with nickel masters, and to make holograms by imprinting DuPont's SURPHEX™ photopolymer with masters made from fused quartz. Recently, Stephen Chou and co-workers at the University of Minnesota in the US have used a rigid mould to show that embossing can generate features as small as 25 nm. Researchers at Philips' Laboratory in Eindhoven in the Netherlands and at IBM's Zürich laboratory in Switzerland have also been active in this field.

Patterns smaller than 100 nm

As we have seen, conventional photolithography is a powerful technique, but it cannot generate features smaller than about 100 nm. It also has a limited depth of focus and can only be used to form structures on flat surfaces. "Near-field, phase-shift photolithography" gets round these problems. In this technique, a transparent mask with a nanometre-deep relief structure imbedded on its surface is placed in contact with the photosensitive substrate to be patterned (see box figure *g*). The depth of the features on the surface of the mask is chosen so that light passing through the recessed regions is shifted in phase by an odd multiple of π relative to the regions that are in contact with the substrate (figure 5*a*). This "phase-shift mask" therefore manipulates the phase – and hence the intensity – of the light to which the surface is exposed.

The abrupt change in the phase of the light at the edges of the recessed features, which are also known as "phase edges", causes the intensity of the transmitted light to decrease due to

4 Glassy microstructures



(*a*) A scanning electron microscopy (SEM) image of silicate glass moulded from a sol-gel precursor. The structure was annealed at 1100 °C. (*b*) An SEM image of a membrane of titanosilicate glass. The spheres are 2 µm diameter silica beads that were filtered from an aqueous suspension as it passed through the membrane and were added as a reference scale.

destructive interference. This produces a node in the intensity of transmitted light, leaving these narrowly defined areas of the photosensitive substrate unexposed. Using a quartz phase mask, this technique can produce feature sizes of about 100 nm in a photoresist. However, since features form only at a phase edge, producing nanometre-sized features with nanometre pitch requires features with a similar pitch on the mask.

In recent work, we have used a patterned, transparent PDMS stamp as a phase-shift mask. The elastomeric phase mask adapts its shape as it comes into intimate contact with the photoresist. At each phase edge, the node in intensity leaves the photoresist unexposed to light, so that when the surface is chemically etched, features with dimensions of 40–100 nm are produced. (The features themselves are separated by distances of microns, as this corresponds to the separation of the phases edges on the photomask.) We have used phase-shift photolithography to pattern an entire area of about 10 cm^2 contacted by a stamp, using a single exposure to ultraviolet light that lasted no more than one second (figures 5*b–d*).

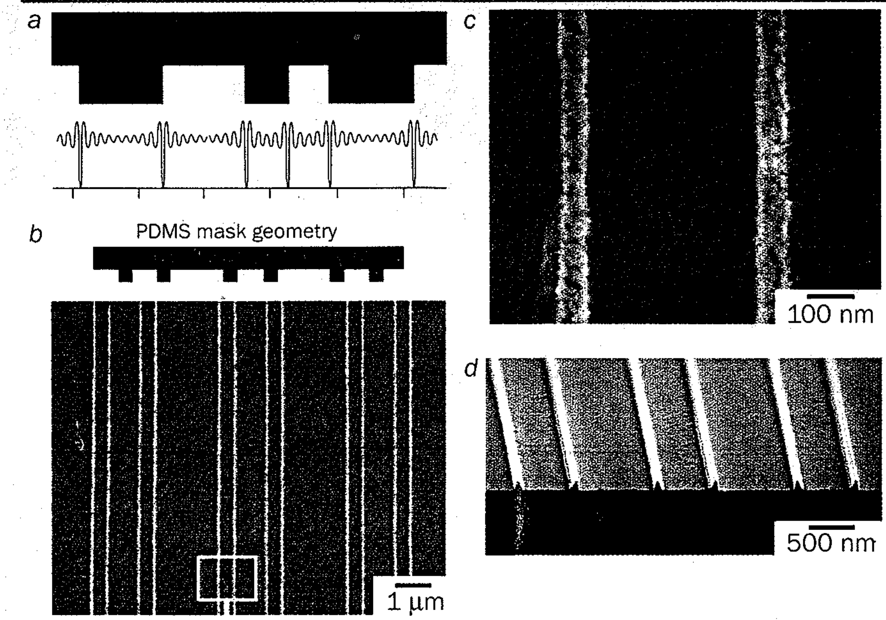
Near-field lithography avoids the diffraction and focusing problems of conventional photolithography because the elastomeric mask conforms to any irregularities on the surface. And since the phase mask is "soft", it reduces the damage to the substrate that can easily occur when a substrate comes into contact with a rigid phase mask. Using a thin (1 mm) elastomeric phase mask that can conform to a non-planar substrate, we have also generated features on curved substrates. We have subsequently transferred features into metals using standard fabrication techniques.

Challenges for soft lithography

Soft lithography overcomes certain limitations of photolithography, and provides new capabilities for micro- and nanofabrication. It can be used to make devices that are smaller than 100 nm, and can pattern curved surfaces and functional materials other than photoresists. It can also fabricate three-dimensional structures, and chemically modify surfaces.

Soft lithography is also compatible with the processes used to fabricate microelectronic devices. Although most work in this area has focused on single-layer structures, we have recently been able to fabricate more complex, multi-layer structures. For example, we have used the technique of micromoulding in capillaries to make high-electron-mobility transistors on a gallium arsenide/aluminium gallium arsenide heterostructure (see Hu *et al.* in further reading). The

5 Features smaller than 100 nm



(*a*) In near-field, phase-shift lithography, a transparent mask with a nanometre-deep relief structure on its surface is placed on a photosensitive substrate to be patterned. The depth of the features on the surface of this mask is chosen so that light passing through the recessed regions of the mask is shifted in phase by an odd multiple of π relative to the regions that are in contact with the substrate. Interference between phase-shifted and non-phase-shifted light produces a minimum in the intensity of transmitted light at the edge of each feature on the mask. (*b*) An SEM image of 50 nm features formed on a silicon/silicon dioxide surface by near-field, phase-shift photolithography using an aperiodic mask. (*c*) An SEM image of the same features taken at higher magnification. Light areas correspond to the photoresist; dark areas correspond to the silicon substrate. (*d*) An SEM image showing a side view of similar features formed by near-field lithography on silicon/silicon dioxide.

current–voltage characteristics of these devices were found to be similar to high-electron-mobility transistors made using conventional photolithography. Despite this success, we have not yet overcome some of the intrinsic limitations of this technique. In particular, a mould can distort and sag easily, and it is difficult to accurately position the mould on a substrate.

Indeed, the physical flexibility of a PDMS stamp is a disadvantage throughout soft lithography. Any distortion of the stamp distorts the pattern that it is transferring, and the best values for faithful pattern transfer are of the order of 1 μm. There are other problems as well. Defects may form because the stamp does not adhere properly to the substrate. Moulded structures may release poorly from the stamp. Bubbles may arise in the precursor and substrates may be contaminated with low-molecular-weight monomers in the stamp. These problems limit the quality of patterns that can be produced using soft lithography to a level that is well below what is needed to fabricate complex electronic devices. Nevertheless, it is more than adequate for many applications in microelectromechanical systems, optical components and microfluidic systems.

Photolithography will continue to be the dominant technique in the microfabrication of sophisticated semiconductor devices and systems for the foreseeable future. Emerging technologies may, however, take advantage of (or require) the unique characteristics of soft lithography. These techniques allow features bigger than 1 μm to be fabricated routinely in a normal laboratory, rather than in a clean room. Soft lithography is also simple to perform, making it attractive for laboratories that do not have routine access to microfabrication facilities or cannot afford standard photolithographic equipment.

At its current level of development, soft lithography is also useful for prototyping and fabricating research devices in which long-range order is not important, such as sensors, microelectrodes, patterns of conducting wires, diffraction gratings and micro-capillary electrophoresis systems. The fabrication of elementary microelectronic devices also seems practical. But for it to become a viable technology for microfabricating complex microelectronic devices, soft lithography must be substantially improved. In particular, it has to be able to transfer patterns more accurately, and must be integrated with existing processes that are used to produce microelectronic devices.

Thanks to soft lithography, it has now become straightforward to fabricate structures and devices in organic polymers, metals, glasses and ceramics. However, soft lithography could also be used to make all-organic circuits and hybrid electronic/biological systems. It may, for example, become possible to mould electronic circuitry in conducting and semiconducting polymers.

Such "additive fabrication", in which microelectronics and microsystems would be printed on a substrate like newsprint on paper, could significantly change the economics of the production of consumer microelectronic systems. To make a hybrid bioelectronic system, soft lithography would be used to pattern surfaces with materials that could allow cells to attach, grow and interconnect. This type of patterning is already technologically well advanced, and is an important step in guiding the interconnection of cellular and digital components. Future developments in soft lithography can only further enhance the capabilities of those scientists and engineers who are working in the nano-world.

Further reading

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