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Electrochemistry and soft lithography: A route to 3-D microstructures

The technology is being developed to make functional machines more compact and cost-effective. The use of microelectromechanical systems offers a way to produce microscopic, 3-D metallic components for compact functional machines.

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Machines are an important part of our lives. We rely on them for just about everything. Take a look around you; we are surrounded by machines—automobiles, airplanes, CD players, toaster ovens, pumps, lawnmowers, watches. These machines are all 3-D, contain metal parts, and are relatively large. We have processes for making the necessary metal components—casting, rolling, forging, stamping, grinding, milling, and cutting—and for assembling them—bolting, riveting, gluing, and welding—into structures with the required form and function. Making large machines is a highly developed science.

One of the broad trends in technology is to make structures smaller. Microelectronics, for example, is the science of making small electrical systems. The equivalent of a computer that would have occupied a large room in the early 1950s today fits into a wristwatch (*1*). A spin-off from microelectronics, microelectromechanical systems (MEMS), is the science of making small, functional machines. MEMS require the microscopic analogues of familiar mechanical components (motors, gears, pumps) designed to integrate with microelectronic circuitry. In other areas, we also need microscopic, 3-D metallic components: for example, in biomedicine (stents and metallic prostheses), in defense systems (small air vehicles, sensors to detect chemical and biological weapons), and in portable consumer products (power supplies, personal stereo equipment).

The techniques used for building metal structures at the macro level do not scale down easily to the micro level. It is hard to imagine riveting or investment casting at the micrometer scale! Electrochemistry is a technique that scales down well. Electroforming (electrodeposition and electromachining) can also be used at the macrolevel; for example, shaped mandrels and 3-D metal parts (*2*). Microelectrochemistry will play an important role in making small metallic components and joining them together to form functional 3-D structures (*3*, *4*). Microelectrodeposition has the potential to become the micrometer-scale equivalent of sheet forming, casting, forging, and welding. Our approach to making functional 3-D microstructures has been to combine microelectrodeposition with a suite of techniques we have developed and that we refer to collectively as "soft lithography".

Conventional approaches to 3-D microfabrication

Conventional solutions to the problem of microfabrication of 3-D functional devices, in part for historical reasons, have built on the techniques that were developed to produce microelectronics. Central to most processes is the

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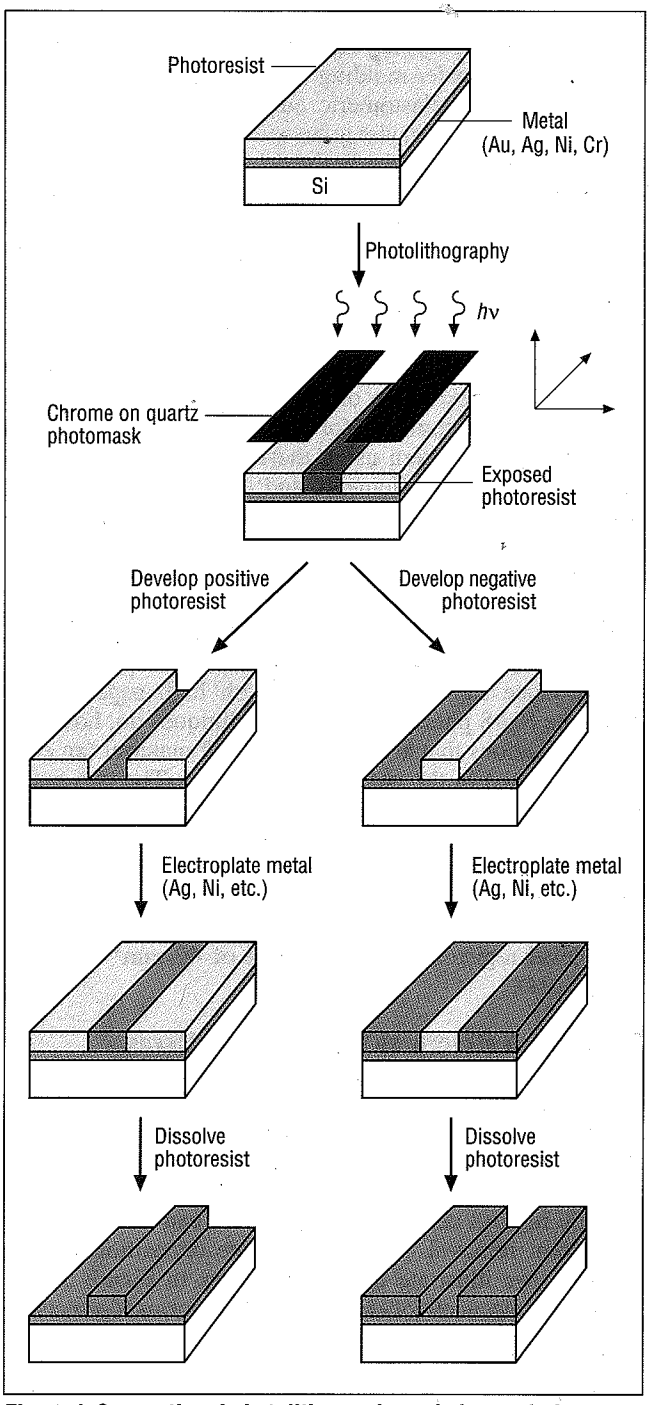

Figure 1. **Conventional photolithography and electroplating using positive and negative photoresists.** A layer of photoresist spin coated onto a substrate is exposed to UV light through an amplitude photomask. Exposure to light chemically alters the resist: Positive resist becomes soluble in the developing solution; negative resist becomes further cross-linked and insoluble in the developing solution. After developing, the conductive substrate is placed as the cathode in an electroplating bath, and metal deposits are placed into the mold defined by the resist. In a final step, the photoresist is removed and leaves behind a metallic microstructure.

use of photolithography in the pattern transfer step (*5*). A substrate, typically a silicon wafer (Figure 1) that has been coated with a thin layer of a photosensitive polymer (photoresist) is exposed to light through a rigid, physical mask that has clear and opaque features; these features can be as small as 0.18 μm (*4*). When the resist is exposed, it is chemically altered. It either becomes more soluble than the unexposed resist (positive resist) or becomes cross-linked and hence less soluble than the unexposed resist (negative resist) (*4*, *5*). A positive or negative pattern develops in the photoresist when the substrate is placed into a developing solution.

To use this process to make metallic structures, a conductive surface serves as the substrate for photolithography; the patterned photoresist functions as a mold that directs the deposition of metal when the substrate is in contact with the cathode in an electroplating bath. In a final step, dissolution of the photoresist, followed by etching the substrate, releases a free-standing structure. This complete process is referred to either as through-mask electroplating (*3*) or as *lithographie, galvanoformung, abformung* (LIGA) (*6*) if X-rays from a collimated synchrotron source are used in the pattern transfer step. By using LIGA, structures as tall as several millimeters can be easily produced. The need for a synchrotron source, however, limits the widespread use of this process.

Recently, a negative epoxy resist, SU-8, has been developed that requires only UV light for exposure but can be used to produce features in films as thick as several mm (*7*). It is sometimes referred to as the "poor man's" LIGA. Through-mask electroplating can make functional metallic microstructures with high-aspect ratios: thin-film magnetic read–write heads (*8*); X-ray lithography masks (*9*); bubble memory devices (*9*); thin-film chip carriers (*3*); and components for MEMS, such as nickel turbine rotors, magnetic microactuators, microgears, microvalves and pumps, capacitive accelerometers, and microtransformers (*5*).

The pattern transfer step, however, limits the kinds of substrates that can be patterned by lithography. The mask used in this step typically consists of features in chrome on a flat quartz plate (for photolithography) or gold features supported on a thin support (for X-ray lithography). To ensure the transfer of features without loss of resolution, the substrate must be either in contact with or in the image plane of the mask. If the substrate is not planar, problems arise with depth of focus, and there is a loss of resolution in the features.

Two ingenious methods have been developed to form pseudo-3-D microstructures, that is, planar structures with contoured surfaces. The first method uses a layer of photosensitive gelatin to direct electrodeposition that has been contoured by performing grayscale lithography on it (*10*). The second method uses self-shorting, electrically isolated metal structures that become joined during the isotropic electroplating step (*11*). The fabrication of fully 3-D microstructures with variation in z-direction is a challenge. Most frequently, this variation is introduced by building up structures layer by layer.

Alternatively, structures with large variations in the z-direction are

- carved, by using laser micromachining, from a solid object (*12*);
- formed by a "writing" technique, using a localized electrochemical deposition method (*13*), or a laser-induced chemical vapor deposition method that can deposit metals in spatially well-defined locations (*14*);
- or made by unconventional lithography either using an elaborate apparatus that allows rotation of a fiber during

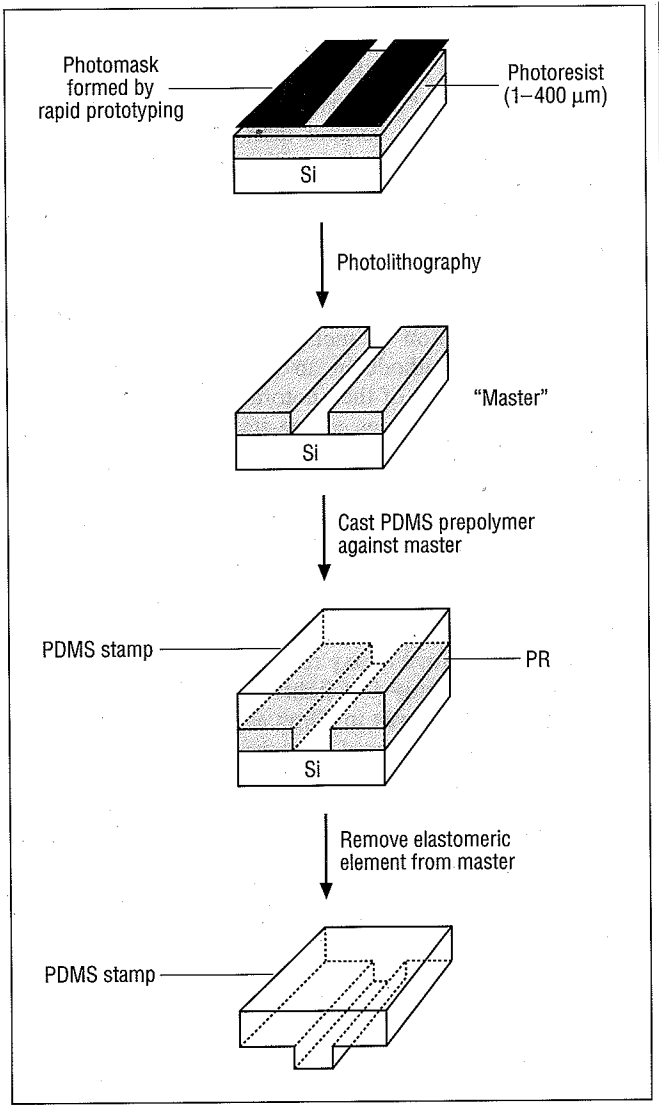

Figure 2. **Rapid prototyping and the fabrication of elastomeric elements.** A "master" is typically formed by performing photolithography using a flexible photomask produced by rapid prototyping. Casting a prepolymer of polydimethylsiloxane (PDMS) against the master formed an elastomeric element. After the elastomer was removed from the master, the elastomeric element was used as a stamp for microcontact printing, as a mold for micromolding in capillaries, or for microtransfer molding.

e-beam writing (*15*) or a lathe that rotates a cylindrical structure during an X-ray exposure (*16*).

All of these methods are, however, limited because each is a serial process and is operationally complex and expensive.

Unconventional approaches to 3-D microfabrication

Soft lithography combined with microelectrochemistry can be used to produce metallic microstructures. Soft lithography comprises a set of techniques that uses an elastomeric or flexible element in the pattern transfer step (*17*). This element permits the formation of high-resolution features in metal or photoresist (on a conductive substrate) that can then be used to form metallic 3-D structures. In the pattern transfer step, the elastomeric element either acts as a stamp to transfer an ink to a substrate via microcontact printing (*18*, *19*) or as a mold to control the patterning of a polymer via micromolding in capillaries (*20*) or microtransfer molding (*21*). Figure 2 illustrates the fabrication of an elastomeric element (*18*). We cast and cure a prepolymer against a "master" that usually consists of features in photoresist defined by photolithography on a silicon wafer. The master can be any structure having 3-D relief. The fabrication procedure is facilitated by using a rapid prototyping technique that we have developed (*22*). A pattern is designed using a CAD program and then printed onto transparencies using a commercial, laser-assisted image-setting system. The smallest features that can be formed by this method are 20 μm, a dimension limited by the resolution of the printer. We use the transparencies as photomasks for the photolithographic step. The photoresist pattern using these masks can be used to produce elastomeric elements and can function as molds for through-mask electroplating. In general, rapid prototyping allows the cycle from an idea to a metallic microstructure to be reduced to <24 h.

Soft lithography has many advantages. This simple, quick, and inexpensive technique makes it possible to pattern nonplanar substrates, generate by rapid prototyping, and produce stamps and molds with high aspect ratios using the SU-8 photoresist. These techniques do, however, have limitations that arise because a soft material (an elastomer) is used in the pattern transfer step: The two major problems are distortion of features and the resulting difficulties in registration of multiple layers. We have begun to address these problems by using rigid backings on the molded elastomers to reduce the distortions to <500 nm over an area of 0.25 cm^2 (*23*), and we have improved three-level registration over an area of 40 mm^2 to within 12 μm (*24*).

Making 3-D structures from planar patterns

Microcontact printing (μCP) is a soft lithographic technique that can produce metal features at the 1–100-μm scale routinely and high-resolution patterns at the submicrometer scale with greater effort (*18*, *19*, *25*). An elastomeric element (Figure 2) transfers an "ink" or "paint" to specific regions on a substrate. The ink can be used either to prevent removal (*18*) or to initiate deposition (*26*) of material; we illustrate both possibilities in Figure 3. The use of hexadecanethiol (HDT) as an ink forms a protective self-assembled monolayer (SAM) on silver or gold; the SAM serves as a resist against etching and can produce isolated metallic structures (*18*). A suspension of palladium colloids used as an ink will initiate deposition of metal when placed in an electroless plating bath (*26*). When μCP is followed by an electroplating or electroless deposition step, the thin, patterned metal films or layers of colloids formed in the printing step are transformed into structurally sound, free-standing metallic structures. We have used several strategies that involve electrodeposition to transform planar metallic structures, produced by μCP, into 3-D microstructures (Figure 4, p. 22).

Many simple 3-D structures consist of 2-D components that are simply connected in specific orientations; for example, a cube consists of six squares joined at right angles to one another along their edges. A cube can also be unfolded onto a plane. A simple approach to 3-D fabrication that we have explored is to print the 2-D components of a 3-D structure or the 2-D projection of a

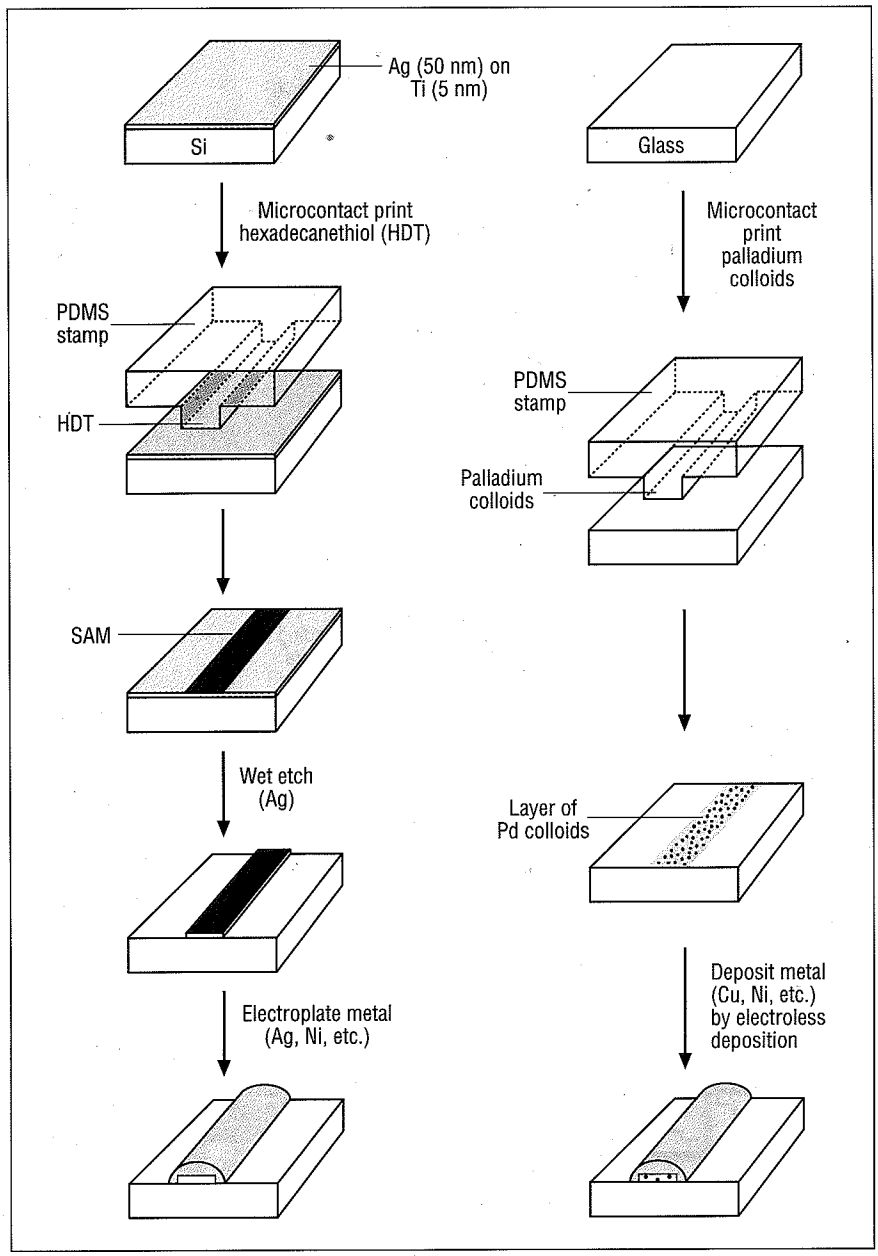

***Figure 3.* Producing metallic microstructures via microcontact printing with electrodeposition or electroless deposition.** Left: Using an ethanolic solution of hexadecanethiol (HDT) as an ink—a few nanometers thick—on a PDMS stamp, we printed a patterned self-assembled monolayer (SAM) on silver. After wet-chemical etching of the underivatized silver, we electroplated metal onto the thin, patterned metal layer. Right: Using a suspension of palladium colloids as an ink, we printed a pattern of palladium colloids onto a glass substrate. The layer of activated colloids then initiated electroless deposition of metal.

3-D structure with a set of tabs and slots onto a planar substrate. After electroplating the 2-D structures and releasing them from the substrate, we can either join the pieces together (*27*), or we can fold the projection back into a 3-D structure (holding it together initially with tabs and slots) (*28*). Once assembled, we use electrodeposition to cover the joined regions (and the rest of the structure) with metal. Thus, we are able to weld the structure together and give it structural rigidity. At smaller scales, assembly by hand becomes increasingly difficult, and we are exploring other approaches to 2-D and 3-D fabrication that do not rely on manipulating individual components by hand or that rely on self-assembly.

Another approach to making 3-D structures from 2-D patterns is to deform the 2-D structure itself by applying an out-of-plane strain to it. Again, the electroplating is important for solving this problem because it makes it possible to perform high-strain deformations on structures. If the structures are too thin, they will crack when strained. Electroplating increases the thickness of the structures and, if small cracks develop in the structure when strain is applied, electroplating can also repair these defects.

By introducing components that deform in a controlled manner into a structure the shape of the final structure is predetermined. Examples of deformable components are hinges (thinner sections of metal) that can bend and zig-zag sections that can straighten under tension.

Figure 4 also shows two collapsible square-based pyramids formed in silver by first microcontact printing hexadecanethiol in the pattern shown, followed by wet-chemical etching to remove underivatized silver (*28*). Electrodeposition of silver onto the pattern increased its thickness and ensured that it was self-supporting when released from the substrate. Additional electroplating made the structure more rigid. Arrays of all of these 3-D micro-

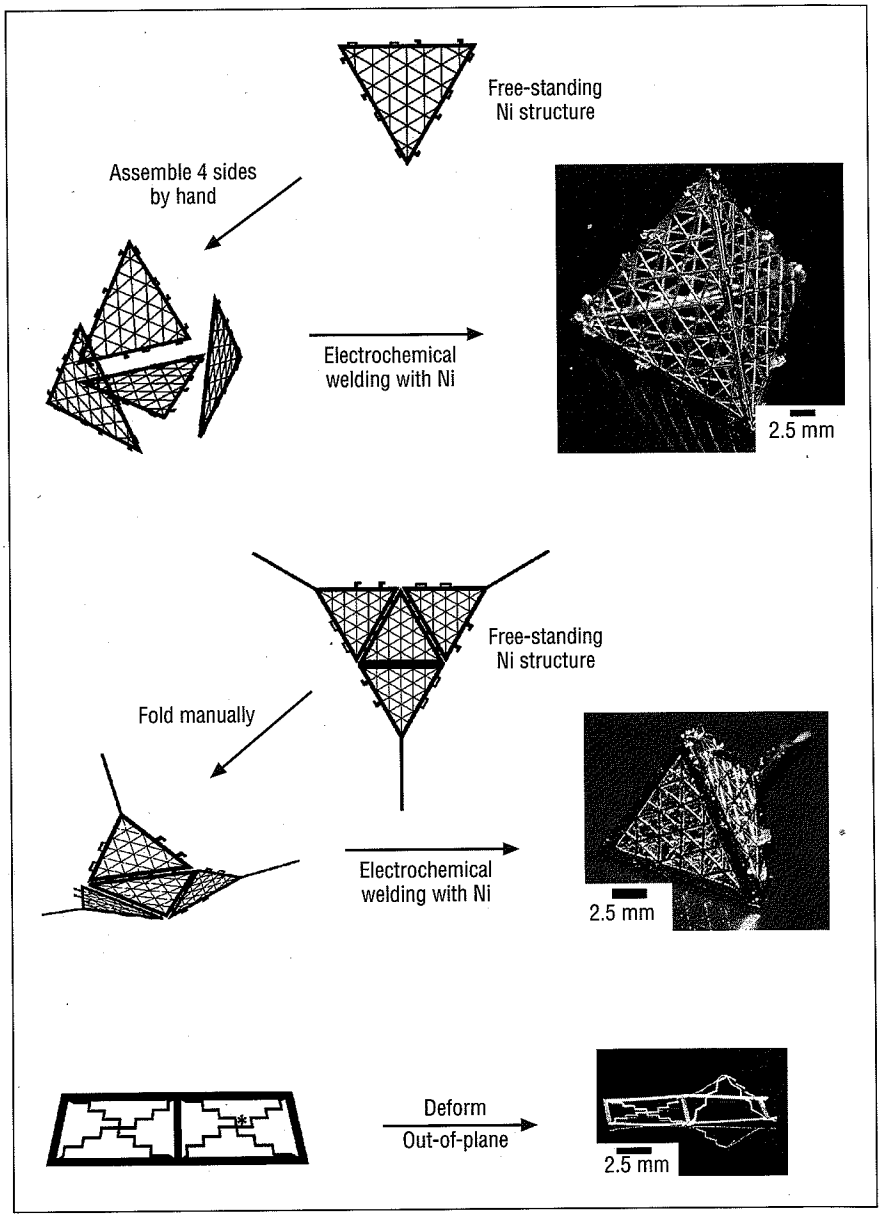

Figure 4. **Images of 3-D microstructures formed from planar patterns printed by μCP and then electroplated together.** A tetrahedron formed by printing four triangular pieces with tabs and slots, electroplating nickel to solidify it, and then slotting pieces together by hand and electroplating the structure with nickel to join it. A tetrahedron formed by folding up manually a free-standing planar projection of it and then electrochemically welding it together using nickel. A square-based pyramid formed by an out-of-plane deformation of a collapsed, 2-D structure. By pulling the crossing point of the two zigzag lines (marked *) out of the plane of the square support, the zigzag wires straightened and a square-based pyramid resulted.

structures may find applications as structural components in MEMS that require structural integrity and lightweight components (e.g., small air vehicles).

Although μCP, followed by electroplating, produces structures with sloped sidewalls, it (and other soft lithographic techniques) has several advantages over through-mask electroplating.

- It can be used with nonplanar substrates and has been used to transform 2-D patterns into 3-D structures.
- It uses only an elastomeric stamp in the pattern transfer step, so routine access to a cleanroom facility is not necessary.
- A single stamp can be used many times, whereas the photoresist molds for through-mask electroplating typically can be used only once.

Producing cylindrical microstructures

One of the advantages of soft lithography is that it can be used to transfer patterns to nonplanar substrates. When coupled with electrodeposition, this advantage makes it possible to form complete 3-D structures. In the case of μCP (Figure 5), the elastomeric nature of the stamp allows patterning on cylindrical substrates: we can simply roll the substrate across the surface of the stamp (*29*). When using a flexible mask (formed by rapid prototyping), we can bend the mask around the surface of the capillary and use it to do photolithography (Figure 5). When used in conjunction with microelectrodeposition, these methods produce metallic, cylindrical structures (*28*, *30*, *31*).

Printing on large substrates can often be done by hand and aligned by eye. To print micrometer-sized features onto small structures requires more accuracy. To control the pressure applied during printing, the rate of printing, and the relative orientation of the stamp and the cylindrical substrate being printed, we have used a simple set of translation and rotation stages (Figure 6, p. 24) (*32*). By changing the angle at which we roll the substrate across a stamp bearing an array of parallel lines, we can

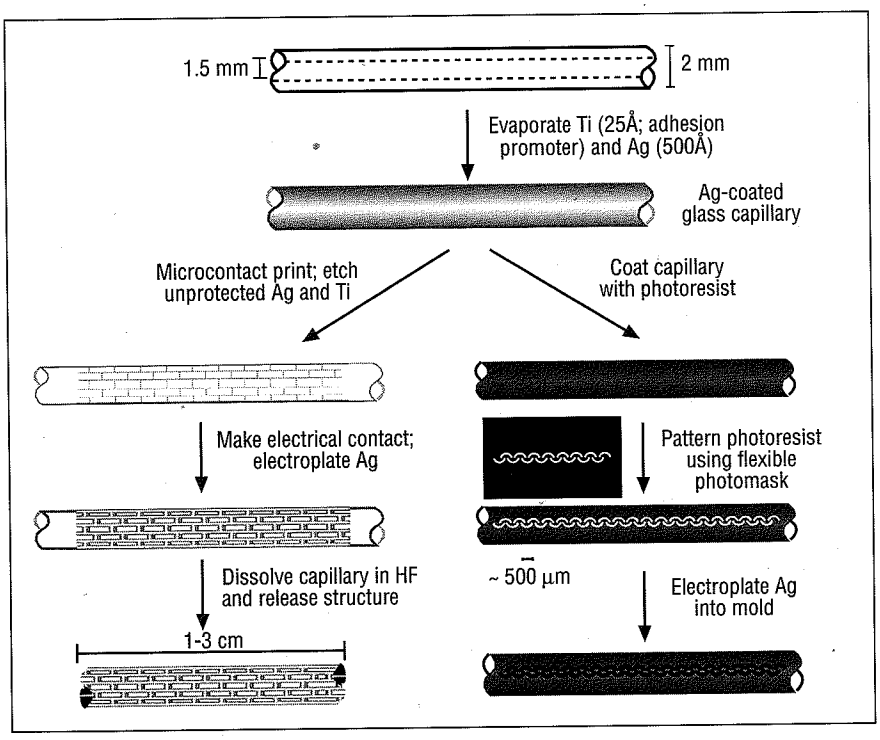

***Figure 5.* Scheme illustrating the use of soft lithographic techniques and electrodeposition to pattern cylindrical substrates.** We deposited a layer of silver (50 nm) around the outside of a glass capillary (~2 mm diam) coated with a layer of titanium (25 Å; adhesion promoter). Using μCP, we printed SAM onto the silver with an elastomeric stamp and then removed the unprotected silver and titanium by wet-chemical etching. After electroplating silver to make the structure self-supporting, we dissolved the capillary in hydrofluoric acid (49%) to release the free-standing structure. Figures 7–9 show structures produced by this technique. We also coated the capillary with a layer of photoresist, and then patterned it by exposing it to UV light through a flexible photomask. After developing the resist, we electroplated silver into the mold. Figure 10 shows a structure produced by this method.

choose to print bands, coils, stripes, or arbitrary patterns on the capillary. The printing apparatus allows us to set the angle between the stamp and cylindrical substrate to better than 0.1°; for capillaries <125 μm, it should be possible to reduce the widths of wires to <3 μm and still control the angle exactly enough to produce, for example, continuous spirals (*33*).

Creating functional metallic 3-D microstructures

In many instances, full function would be introduced most easily into microsystems by using nonplanar and 3-D structures. A lack of suitable patterning technique has frustrated the fabrication of these structures. Often, alternative, less optimal, planar configurations are used for which conventional patterning techniques suffice. We discuss several applications for which 3-D microstructures are the best solution to a problem; until now, most solutions have been planar.

In-fiber gratings. In-fiber gratings formed in optical fibers have many applications in optical communications. They are used, for example, as wavelength-sensitive mirrors, filters, and strain and temperature sensors (*34*). An optical fiber consists of a core (~3 μm diam) with a high index of refraction, a lower index cladding layer (~125 μm diam), and usually a protective polymer jacket (total diam, ~300 μm) that increases the flexibility of the fiber and protects it from damage. The difference in index of refraction between the core and cladding allows light to propagate only in the core. A fiber grating is created by introducing a periodic variation (period ~0.5–200 μm) in the index of refraction along the length of the core of an optical fiber over tens of millimeters. This modulation changes how light propagates through the fiber. For example, a grating can cause the reflection of a small range of wavelengths of light back along the fiber while allowing others to pass through unaffected (Bragg grating), or it can result in the attenuation of light over a wider range of wavelengths. By varying the period of the grating, the desired response is achieved. The change in index of refraction is small ($\Delta n \sim 10^{-4}\%$) and can be induced by exposing the core to UV light (*35*). The modulation in the index of refraction is usually introduced either by exposing the fiber to the interference pattern created by two crossed-UV laser beams (for short-period gratings) (*36*) or by exposure of the fiber through a rigid amplitude (chrome on quartz) or phase mask (for long-period gratings) (*37*).

Using crossed beams to pattern has some limitations. The optical instabilities of the laser can cause the angle between the beams to vary and the mechanical instabilities of the system can result in movement of the fiber relative to the interference pattern during exposures. When amplitude or phase masks are used, the stability of the laser is less important because the pattern in UV light is defined by the mask itself, but the issue of the motion of the fiber relative to the mask remains. These problems limit exposure times and can prevent the fabrication of high-resolution gratings. We have addressed this problem by integrating a mask directly with a fiber.

To produce in-fiber gratings we generated an opaque photomask on the exterior of a fiber (Figure 7, top, p. 25) (*32*). We printed bands of palladium colloids onto the exterior of an optical fiber by using a stamp with parallel lines (width, ~250 μm, spaced by ~250 μm). The colloids initiated the deposition of copper metal when we placed the printed fiber into an electroless copper-plating bath (*26*). After ~1 μm of copper was deposited, the bands were opaque. In this case, electroless deposition of metal was necessary because the discrete colloidal particles that were present in bands around the exterior of the fiber were not electrically connected. Because we printed the colloids directly onto the glass fiber, we did not need to deposit a layer of metal onto the exterior of the substrate.

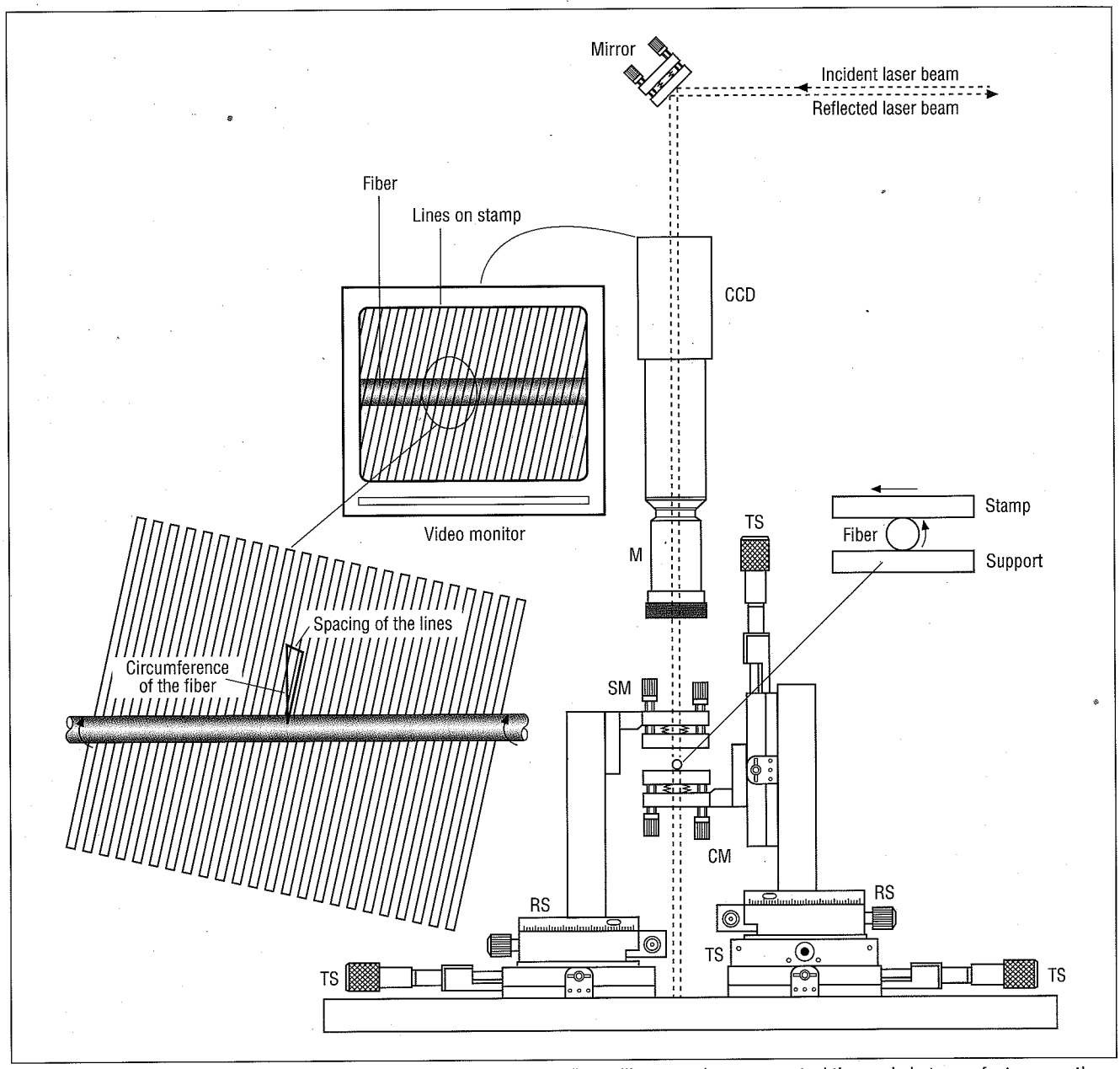

Figure 6. **Apparatus used to perform μCP on curved substrates.** The figure illustrates how we control the angle between features on the mount for the stamp (SM) and the mount for the capillary (CM). Rotation stages (RS) allow control over the relative orientation of the fiber and the stamp to within 0.1°, and translation stages (TS) allow control over the stamping time, area, and pressure. Adjustable stages support the stamp and the capillary, and their alignment parallel to the bench is ensured by the laser. A microscope (M) connected to a charge-coupled detector (CCD) camera and video allows the printing to be monitored.

The middle diagram in Figure 7 illustrates the apparatus used to pattern the core of the optical fiber. The performance of the long-period grating formed using these photomasks is illustrated in the bottom image of Figure 7. The performance is comparable to a grating produced with an amplitude mask (*37*). By printing a photomask directly onto the exterior of the fiber, we eliminate problems that result from the motion of the fiber relative to the mask or interference pattern during an exposure and allow long exposure times. A simple UV lamp, rather than a UV laser, is all that is needed for an exposure.

Microcoils for microfluidics and MEMS. In miniaturized electromechanical systems, wires with high current-carrying capacity are critical for functionality and are easily created in two dimensions. Microcoils with diameters <100 μm are needed for many applications, such as read–write heads for magnetic data storage (*38*), sensors for measuring magnetic fields (*39–42*), and excitation and detection coils for NMR. In some cases, the fabrication of microcoils has been avoided by working with planar coils, but this geometry is not ideal. A planar coil occupies more area than the equivalent 3-D coil and is more difficult to integrate into, for example, a microfluidic–microanalytical system. Using microelectrochemistry coupled with μCP, we have produced electrically conducting microcoils (Figure 8, p. 26) and have

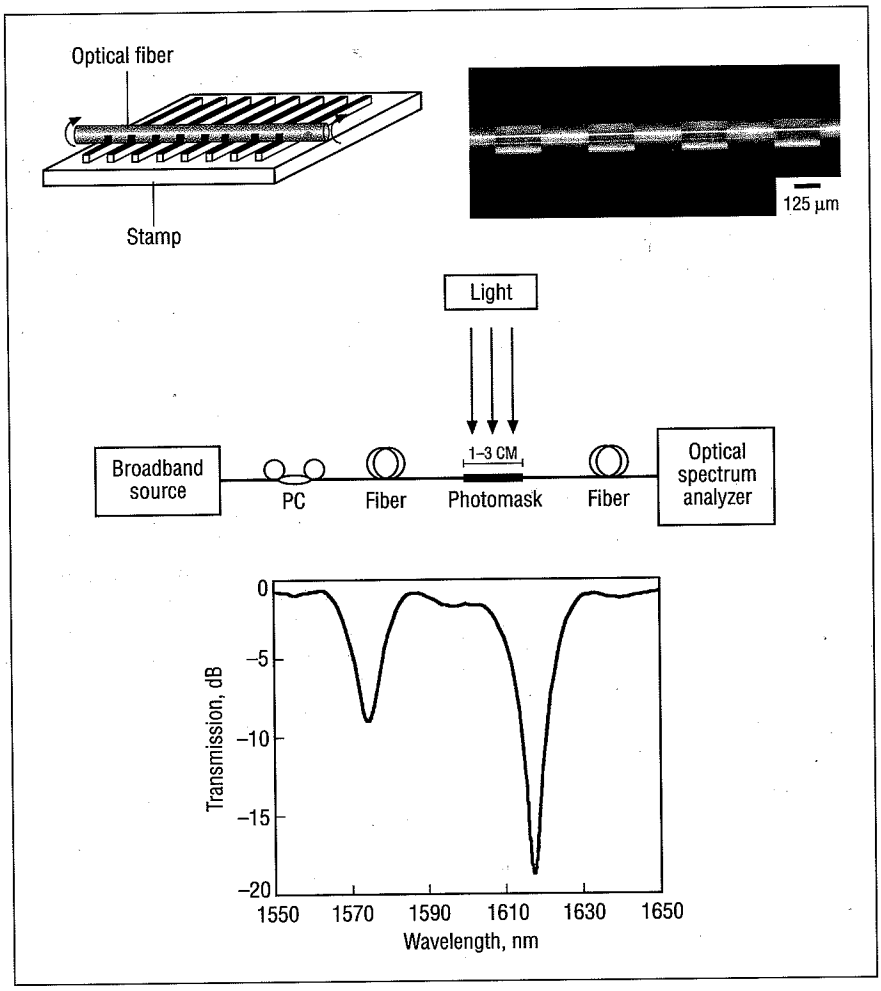

***Figure 7.* In-fiber gratings generated by using photomasks.** We formed the photomasks by printing colloids on optical fibers followed by electroless deposition. Top: Image of copper bands on an optical fiber. Middle: Apparatus for producing in-fiber gratings. Exposure of the opaque copper bands to UV light generated a grating structure in the core of the fiber. Bottom: The development of the grating was monitored via a long-period amplitude grating (2.5 cm long; 500-μm period) as a function of optical wavelength. The fiber, which had been loaded with hydrogen, required an exposure of only 7 min.

used them in two different microsystems. Here, electroplating increases the cross-sectional area of the thin (~500 Å) patterns of metal coils formed on cylindrical substrates and transforms them into wires with high conductivity. We form the coils by printing with HDT on silver and then wet-chemical etching the unprotected silver.

Sweedler and co-workers demonstrated that microcoils (50 μm diam) wound around the exterior of a microcapillary (357 μm o.d.; 75 μm i.d.) could serve as the excitation and detection coils in an NMR system and could be used to obtain spectra for nanoliter volumes of material (*43*). The signal-to-noise ratio per mole of analyte in this system was increased by >100 times over that of a conventional 5-mm spinning-tube probe. Using microcoils for NMR enables spectra to be obtained on mass-limited samples. Also, because the sample is contained in a microcapillary, it should be possible to incorporate this detection scheme as part of a fully integrated microfluidic or microanalytic system.

The required coils for this application were formed by winding the wires by hand around the capillary. This procedure is slow and limits the geometric formation of the wires. In collaboration with Sweedler, we showed that "printed" wires could be used for this application (*45*). We formed the coils by μCP with HDT on a silver-coated microcapillary using a stamp with parallel lines, followed by wet-chemical etching of the unprotected metal. Our printing press (Figure 6) allowed us to control the relative angle between the microcapillary and the stamp so that in a single rotation of the capillary, a full spiral of HDT was printed. We used electroplating to increase the conductivity of the coils (length ~1.6 mm; dc resistance ~16 Ω), so they were conducting at the frequency (300 MHz) used in acquiring the NMR spectra. A representative spectrum of ethylbenzene acquired using these coils is shown in the top of Figure 8.

The printed coils had a signal-to-noise ratio 15 times better than that obtained with a conventional 5-mm spinning-tube probe. This improvement was not as high as for the wound microcoils. The printed coil had a higher dc resistance than the wound coil (~8 times greater) that resulted either because of a smaller cross-section for the wire or a higher resistivity of the electrodeposited copper. There may also have been a contribution from the silver epoxy connections. Possible advantages of printing coils over wound microcoils, however, are that we can print coils much smaller than can be wound and that this capability might make it possible to measure smaller volumes of samples. The geometries and patterns of printed coils could also be tailored to improve sensitivity and line shape.

In the field of MEMS, electrically conducting coils can be used as micropositioners, microactuators, microinductors, microtransformers, and sensors. These structures are

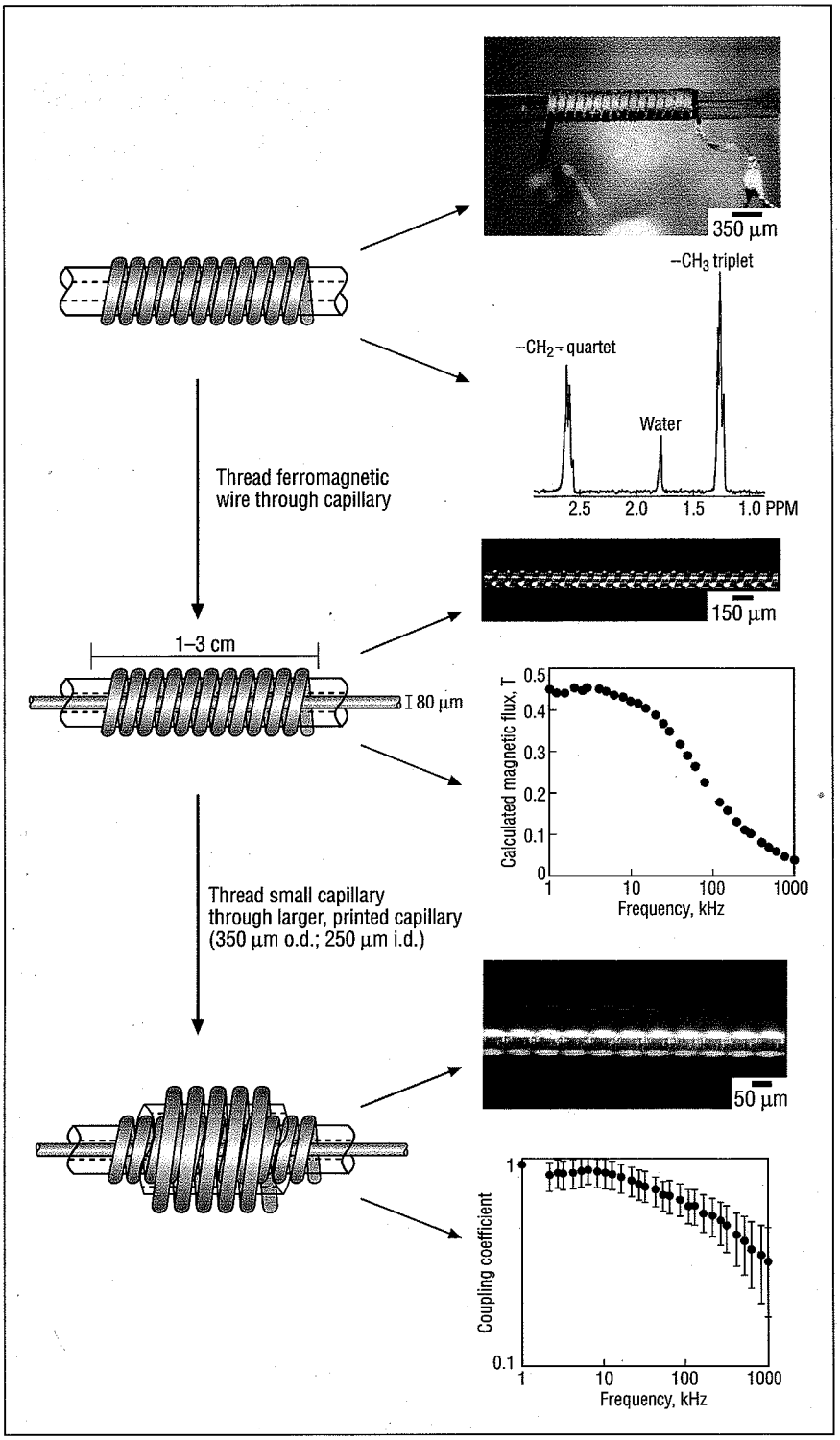

Figure 8. **The use of microcoils formed by electroplating and microcontact printing.** The images of (top) microcoils for NMR on nanoliter volumes; (middle) microelectromagnets; and (bottom) microtransformer are shown with their performance.

important as components in more complex microsystems; for example, to produce small electrical power supplies, small magnetic devices are needed (*46*).

It is difficult to make 3-D coils by methods based on conventional photolithography. We have used microcoils formed by μCP and electrodeposition to form microinductors (Figure 8, middle) (*33*) and microtransformers (Figure 8, bottom) (*47*). To produce the microinductors, we printed and electroplated coils (25–150-μm wide) on capillaries (as small as 150 μm o.d.; 100 μm i.d.). A ferromagnetic wire threaded through the bore of the capillary increased the relative permeability of the core. The measured inductances were consistent with the behavior of a simple inductor. The inductance showed a linear dependence on length and on the square of the number of turns per unit length. Figure 8, middle, shows the magnetic flux density (calculated from the inductances) for a typical microinductor. The maximum flux density was as high as 0.4 T. These microstructures are microelectromagnets; by varying the current applied to them,

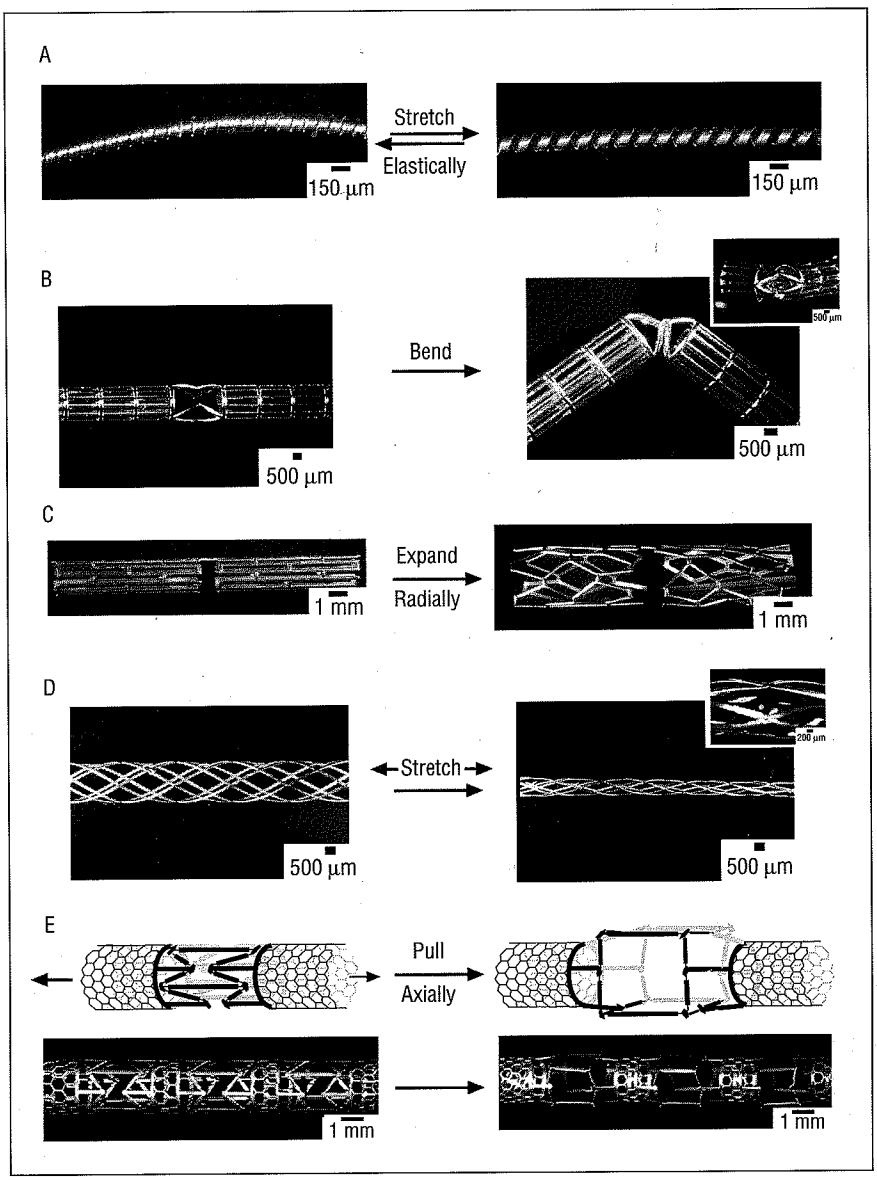

Figure 9. **Free-standing, 3-D microstructures.** We formed microstructures by printing a pattern of HDT onto a silver-coated glass capillary (~2 mm diam) using an elastomeric stamp, etching the unpatterned silver, electrodepositing the silver, and then dissolving the glass capillary. Final structures were produced by (**A**) releasing microcoils to produce microsprings; (**B**) bending at joints; (**C**) radial expansion (stents); (**D**) stretching axially (stretchable tube); and (**E**) axial deformation.

we can change the generated magnetic field. This property should allow these structures to be used as magnetic actuators for mechanical components.

The microtransformer (*47*) was made simply by threading one capillary printed with coils and containing ferromagnetic wire inside of a larger capillary (250 μm i.d.; 350 μm o.d.), which was also patterned with a microcoil (Figure 8, bottom). The coupling coefficient measured for these coils showed that they were almost perfectly coupled up to frequencies of 20 kHz (a number determined mainly by the properties of the ferromagnetic wire). Just as transformers are important components in macroscopic electrical systems, microtransformers are needed in microelectrical systems to vary the voltage-to-current ratio without power losses.

Deformable metal patterns and repairs after high-strain deformation. Using electrochemistry to increase the conductivity of structures formed by printing also has the effect of increasing the rigidity of the microstructures. By electroplating and then removing the underlying substrate, we transformed thin-metal patterns into self-supporting metallic structures. In the case of the microcoils fabricated on glass, by dissolving the glass in hydrofluoric acid, we can produce microsprings (Figure 9A). These springs can be completely deformed elastically (*30*).

We are not, however, limited to printing parallel lines onto cylinders to produce coils or bands. Using rapid prototyping, we can easily design arbitrary structures and then transform them into stamps that can be can used to print on cylinders. For an appropriately designed free-standing cylindrical mesh, the application of a force will cause its controlled deformation and transformation into a 3-D structure that could not have been printed directly. We illustrate structures formed by several deformations: bending, radial expansion, axial stretching, and axial deformation.

Bending. Without a joint or hinge, a free-standing, lightweight, cylindrical mesh will collapse when bent. With appropriate joints, the location and orientation of bending can be manually controlled, and collapse of the cylinder can be avoided (Figure 9B); for example, two diamond-

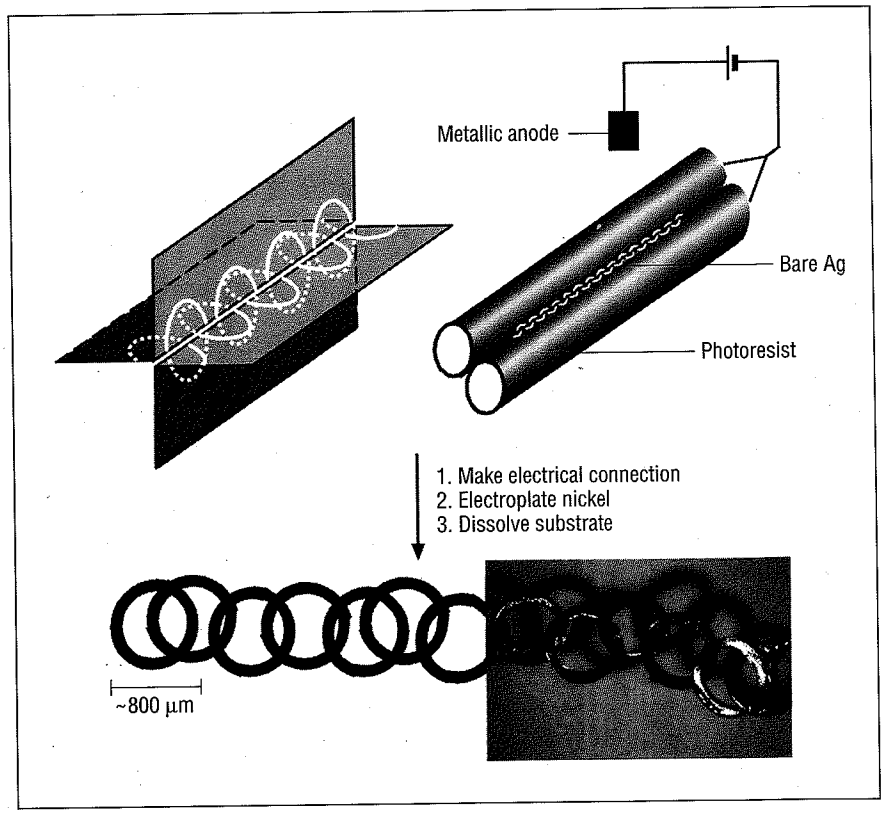

***Figure 10.* Fabrication of a chain.** To create a nickel chain, we used a flexible mask, electroplated the nickel, and dissolved the substrate.

shaped structures placed on opposite sides of the circumference of the capillary function as joints (*28*). By deforming the joint manually by moving the two vertices of one diamond (not directly connected to the rigid sections) out, relative to the axis of the capillary, we caused the other two vertices (and the attached rigid sections) to move together. The diamond on the outside of the joint deformed slightly in the opposite sense.

Radial expansion (stent). Objects similar in design to the structure shown in Figure 9C are used in balloon angioplasty as coronary stents (*48*, *49*). Stents act effectively as "scaffolding" for the arteries. They are inserted into a clogged artery with a deflated microballoon in their core and are then expanded by inflating the balloon in situ. After they have been expanded, the balloon is removed and the stents remain in place to keep the artery open. Using a stamp in the design of a Palmaz–Schatz coronary stent, we printed HDT onto a metal-coated glass tube. After etching the underivatized metal and electroplating metal to strengthen the structure, we dissolved the capillary to produce the free-standing microstructure (~2 mm diam) (*30*). A microballoon provided the necessary radial force to expand its structure up to 2.5 times the original diameter (Figure 9C, right).

Axial stretching. Figure 9D shows a cylindrical mesh (~2 mm diam) with a diagonal pattern formed using microcontact printing and electroplating. When we deformed this structure axially by up to 120%, we reduced the diameter of the structure by ~50%. Rather than bending at the intersection of wires (which are relatively reinforced) under strain, the wires themselves bent (see inset).

Axial deformation. The hinges shown in Figure 9B demonstrate the formation of noncylindrically symmetrical structures; however, each transformation was performed individually by hand with tweezers—an approach that will not easily scale down to tens of micrometers! We have developed a different approach that should be miniaturizable because it uses a macroscopic force distributed over a set of microscopic, deformable elements. The structure contains rigid sections that transduce the applied force and hinged joints (i.e., thinner wires at the joints) that are designed to bend in a controlled manner under tension. Once the cylindrical structure (Figure 9E) has been released from the substrate, applying a macroscopic, axial force transforms it into a 3-D microstructure with noncylindrical symmetry (Figure 9E) (*31*).

Electrodeposition as a micrometer tool for welding. When working in the flatland to which standard photolithography is confined, making 3-D structures is difficult and making structures with more complex topographies is almost impossible. For example, in a single plane, it is not possible to link three rings together to produce an interlinked chain without disrupting the structure of each ring. At the intersection of two planes, however, we can envision such a chain (Figure 10).

Instead of using two intersecting planes, we can also use the edges of two square rods or two cylinders touching along a tangent line; these structures are all topologically equivalent. Using two substrates to do the fabrication means that they can be patterned individually using soft lithography and then brought together and welded into a continuous structure in a final step. The key to this problem is the final step—finding a method by which to join structures on the two substrates.

Microelectrochemistry is essential for this type of fabrication; it acts as a tool for micrometer-scale welding. As

seen in Figure 4, when two or more electrically conductive structures are held close during electroplating, the structures come into contact and weld together as the metal plates. Discrete structures on different substrates become joined to produce more complex structures. We have shown this concept using a flexible mask (Figure 5) to pattern a pair of capillaries; using electrochemistry as a welding tool (Figure 10), we produced a freely jointed chain (*31*).

Future directions

Making small, functioning machines requires methods for fabricating and joining small components in three dimensions. Although photolithography is good for planar structures, it is not practical for curved or 3-D structures. We believe that the ability to produce 3-D structures is central to introducing fully functional microstructures. By analogy, at the macroscale, a single panel used to form the door of a car might, in principle, be cut from a planar sheet of metal, but, in practice, a fully operational car is built by assembling many intricate 3-D components in a well-defined arrangement!

Microelectrochemistry, in conjunction with soft lithography, can produce 3-D microstructures with shapes sufficiently complex that it would be difficult or impossible to produce them by other methods. Microelectrodeposition is important for structures we have made:

- It gives rigidity to thin metal structures.
- It provides the cross-section necessary to carry current.
- It permits the fabrication of structures that deform gracefully and that can be repaired after deformation.
- It joins structures.

Electrodeposition is a chemical skill and, when coupled with a technique for pattern transfer, it provides us with control over the physical dimensions and the mechanical properties of the microstructures we make. Many metals and conducting polymers can be deposited electrochemically. By varying the material deposited, we gain flexibility in determining the properties of the final structure. By appropriate selection of the deposited material, the microstructure can be magnetic or nonmagnetic; superconducting or conducting; malleable or brittle; stiff or flexible; porous or solid (by using an appropriate pattern); or can be bimetallic (for the purpose of actuation).

In addition to the constraints imposed by practical fabrication, consumers (the public, industry, and the military) continue to demand smaller, faster systems with longer lifetimes, lower power consumption, and lower environmental impact. The structures we have produced are functional and have applications as components in MEMS (structural components, microsolenoids, microtransformers, microsprings), microfluidic systems (microcoil NMR), and biomedical systems (stents). Other components—for example, the expanding cube and the linked chain—were made to illustrate the capabilities of our techniques; similarly constructed objects could, in principle, function as structural supports or housings for MEMS.

With the flexibility in the properties of materials that electrodeposition offers, we envision many other applications and devices for which microelectrochemistry will be important. In the long term, these and other electrochemically based techniques will make it possible to manufacture portable sensors and fully integrated microanalytical systems that can be used in hospitals, in the field, and at home. These mobile devices, and others such as cell phones and personal digital assistants, all require power to function, and electrochemistry may provide a means for producing lightweight power supplies for them. Existing systems may be improved by components or devices produced by microelectrochemical fabrication, for example, sensors in automobiles and airplanes and mechanisms in CD players. Lightweight, open metallic meshes may be suitable for structural components of the types used in the aerospace industry.

A final but important consideration when making small structures is the cost—it must be kept affordable to ensure continued consumer demand. The techniques demonstrated here are potentially low cost, could be used to pattern large areas, and could be automated to give a high throughput. The sizes of structures are limited, at this stage, by the rapid prototyping technique used to produce the flexible masks and stamps. By using photolithography or e-beam writing to produce masters, we should be able to make structures with dimensions <1 μm.

For more information

For general discussions, see *Scientific American. The Solid State Century* (Scientific American, Inc.: New York, 1998; Special Issue Vol. 8), or *Scientific American* **1995**, *273*, 146–167.

For technical descriptions, see Kovacs, G.T.A. *Micromachined Transducers Sourcebook* (McGraw-Hill: New York, 1998), or Madou, M. *Fundamentals of Microfabrication* (CRC Press: Boca Raton, FL, 1997).

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"What's this I hear about your praying for a raise? You know I don't stand for anybody going over my head!"