Microsolidics: Fabrication of Three-Dimensional Metallic Microstructures in Poly(dimethylsiloxane)**

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This Communication describes a method of fabricating complex metallic microstructures in 3D by injecting liquid solder into microfluidic channels, and allowing the solder to cool and solidify; after fabrication, the metallic structures can be flexed, bent, or twisted. This method of fabrication—which we call *microsolidics*—takes advantage of the techniques that were developed for fabricating microfluidic channels in poly(dimethylsiloxane) (PDMS) in 2D and 3D, uses surface chemistry to control the interfacial free energy of the metal–PDMS interface, and uses techniques based on microfluidics, but ultimately generates *solid* metal structures. This approach makes it possible to build flexible electronic circuits or connections between circuits, complex embedded or freestanding 3D metal microstructures, 3D electronic components, and hybrid electronic–microfluidic devices.

There are several techniques for making metal microstructures in 3D. Electroplating and electroless deposition are routinely used to construct microstructures with metallic layers several nanometers to several microns thick in 2D or 3D.[1–11] To generate solid replicas of 3D objects, several groups have developed a technique, referred to as "microcasting", to form metals in order to fabricate microparts (e.g., posts and gears) with features as small as 10 μm and aspect ratios as high as 10 from steel, zirconia, and alumina.[12,13] Techniques based on LIGA (Lithographie, Galvanoformung, und Abformung) produce even more complicated metallic objects by depositing a metal onto a molded polymer template that is subsequently removed to yield an open structure (such as a honeycomb arrangement of cells).[14,15] In principle, these approaches can be used to pattern metals of any thickness to produce features with an aspect ratio that is larger than that produced using electroplating.

Solder reflow is a standard technique in electronic packaging,[16,17] and has recently been combined with micromolding in channels to form custom-made solder pieces for batches of chips.[18] The technique has also been used to form 3D connections (e.g., bridging opposite sides of an electronic circuit board or substrate): Lauffer and co-workers and Ference and co-workers describe similar approaches to bridge electrical "islands" of metal by heating solid rods of solder "on chip"—the solder flows along trenches, holes, or metal strips (formed lithographically) and produces electrically conductive wires between the top and bottom surfaces of the substrate.[19,20]

A growing interest in flexible sensors and displays has fueled the development of polymer–metal composites. Research in this field includes composites of metal in PDMS with optical functions,[21] conductive PDMS–carbon nanotube composites,[22,23] substrates for surface-enhanced Raman spectroscopy,[24,25] spherically curved metal oxide semiconductor field-effect transistors,[26] and flexible gold–polymer nanocomposites as passive components.[27,28] In addition to materials with electrical functionality on curved or bendable surfaces, some groups have demonstrated stretchable electronics by patterning stiff materials on compliant polymer surfaces. The stiff interconnects include silicon wires fabricated by Khang et al.[29] and arrays of gold lines by Lacour et al.[30] that can withstand up to 12 % strain.

Although these methods for fabricating metal in 3D are useful in specific applications, many of them are limited or not applicable for general use. Fabrication of metal in 3D using electrodeposition and electroplating requires multiple lithography steps; this process is slow, costly, and the process is generally limited to patterning metals layer-by-layer on smooth, rigid substrates. LIGA and injection molding provide a useful, specialized approach to fabrication, but are limited by the cost of the equipment, high pressure (3–5 MPa for low-pressure powder-injection molding; higher for other techniques),[12] shrinking of the molded metal upon cooling (typically 15–22 %),[12] and the cost of materials for electroplating thick layers of highly conductive metals such as gold. Solder reflow is a useful method for forming electrical connections between metal features, but the technique requires patterning metal features prior to reflow, and cannot be easily applied to form intricate patterns in 3D. Polymer–metal composites show promise in the field of printable electronic devices.

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These materials, however, are generally poor electrical conductors and cannot be patterned thicker than several micrometers; this limitation restricts their use in structural applications or applications requiring high electrical current. These materials are also fabricated using a layer-by-layer lamination process that requires costly and time-intensive lithography steps. In all of these techniques, it is difficult to repair metal wires or structures that have been broken or fractured, and the metal structures cannot easily be integrated with microfluidic systems without alignment steps.

We have developed a technique for fabricating metallic microstructures in 3D by injecting molten solder into networks of microfluidic channels fabricated in PDMS (or, in principle, other polymers or materials) (Fig. 1a). The general procedure consists of five steps: i) fabrication of microfluidic channels embossed in PDMS using soft lithography and rapid prototyping;[31,32] ii) plasma oxidation and silanization of the inside surfaces of the microchannels with 3-mercaptopropyltrimethoxysilane (0.1 M solution in acetonitrile) to reduce their surface free energy and cause them to be wettable to the solders we use (Fig. 1b); iii) introduction of molten solder into the channels by applying a vacuum to draw metal into the channels—the walls of the silanized channels are rapidly wet by liquid solder; iv) cooling the channels to form solid metal microstructures; and v) forming the solder-filled system of channels into nonplanar topologies (if desired) by bending, twisting, rolling, or deforming. This last step—modifying the shape—works particularly well when the metal is encapsulated in thin (50–200 μm) layers of PDMS. Using this technique, we have fabricated metallic structures with lateral dimensions as small as 50 μm, and thicknesses of 10 μm–1 mm. This process makes it possible to fabricate structures that are difficult or time consuming to fabricate using other methods; specifically: i) planar metallic structures in PDMS that can be bent, twisted, coiled, knotted, rolled, or braided into 3D without breaking; and ii) complex metallic structures embedded in PDMS with 3D topologies such as a basket-weave pattern.

Table 1 lists the composition and physical properties of the twelve metals and alloys that we patterned into microsolidic structures. Although all twelve metals and alloys worked with our technique, the metal that we used for most of the microstructures described in this paper—In100, or 100 % In metal—has several characteristics that make it particularly useful: i) it has a low melting point (158 °C), which makes it easier to pattern than solders with higher melting points; ii) it is electrically conductive ($14.3 \times 10^6 \, \Omega^{-1} \, m^{-1}$, or ca. 24 % the conductivity of copper); iii) it has a low Brinell hardness (0.9 HB) compared to other metals (Sn = 5.3 HB, Bi = 7.0 HB, Cu = 65 HB) making it ductile in its solid form; and iv) it was empirically determined to be one of the better alloys for wetting PDMS that had been surface-oxidized and silanized. The alloy In52/Sn48, the eutectic composition of In and Sn, also wets surface-oxidized silanized PDMS well and has a low melting point (118 °C).[33]

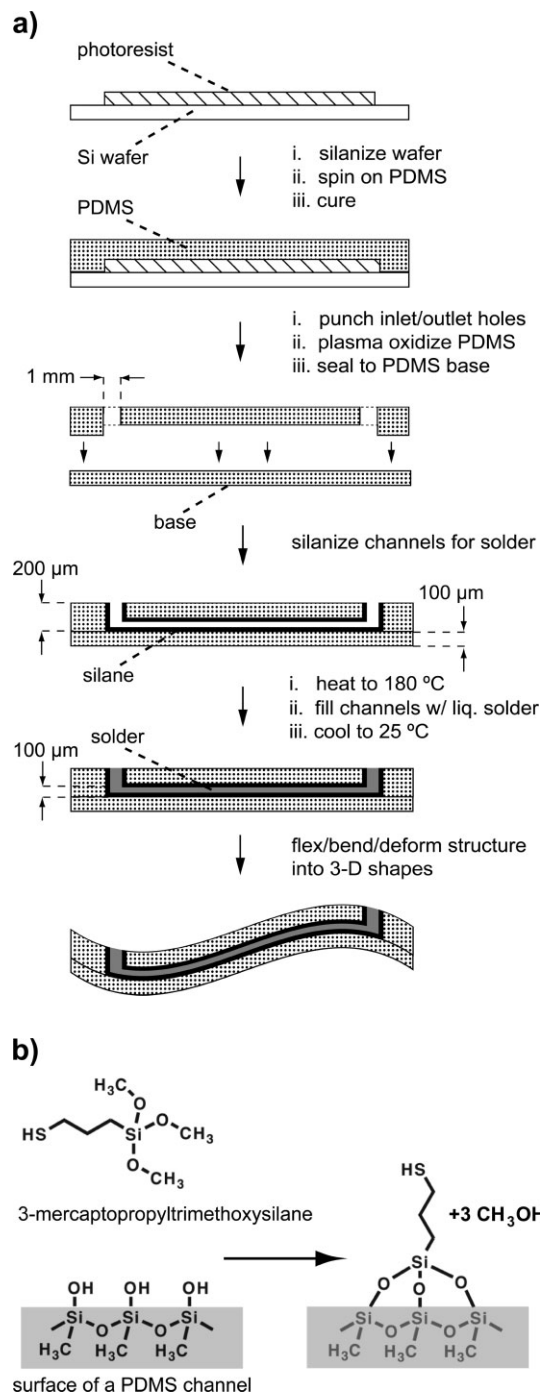We used the procedure summarized in Figure 1 to fabricate flexible metal wires embedded in PDMS. Figure 2a shows a

Figure 1. Fabrication of flexible metallic microstructures by injecting liquid solder into microfluidic channels. a) Fabrication of a wire 100 μm thick. Figure 2a shows a photograph of a completed device. b) Silanization of the interior surface of PDMS microchannels. PDMS recently (< 15 min) exposed to an oxygen plasma is rendered hydrophilic by the formation of hydroxyl groups on the surface. A solution of 3-mercaptopropyltrimethoxysilane reacts with the surface to form a surface presenting thiol groups; the organic groups lower the surface free energy of the PDMS, and the thiol groups make it wettable by liquid solder.

wire (100 % In, length = 5 cm, width = 50 μm, height = 80 μm) embedded in a layer of PDMS that was unmodified, coiled

Table 1. Properties of metals and alloys used in the formation of solder wires and microstructures. Values for In100, In97/Ag3, In80/Pb15/Ag5, In52/Sn48, In50/Pb50, In25/Sn75, Sn100, and Sn63/Pb37 were obtained from the supplier, AIM Specialty Inc. and from [16] and [30]. Values for LMA solders were obtained from the supplier, Small Parts, Inc. Alloys with a high composition of In were determined, empirically, to have the best wetting characteristics for PDMS. Structures containing alloys composed of Bi fractured more easily than structures containing alloys or metals of other compositions. For some alloys, the temperature at which the metal becomes liquid is not equal to the temperature at which the metal becomes a solid; for these alloys, the melting point is expressed as a range of temperature. n.p. = not provided.

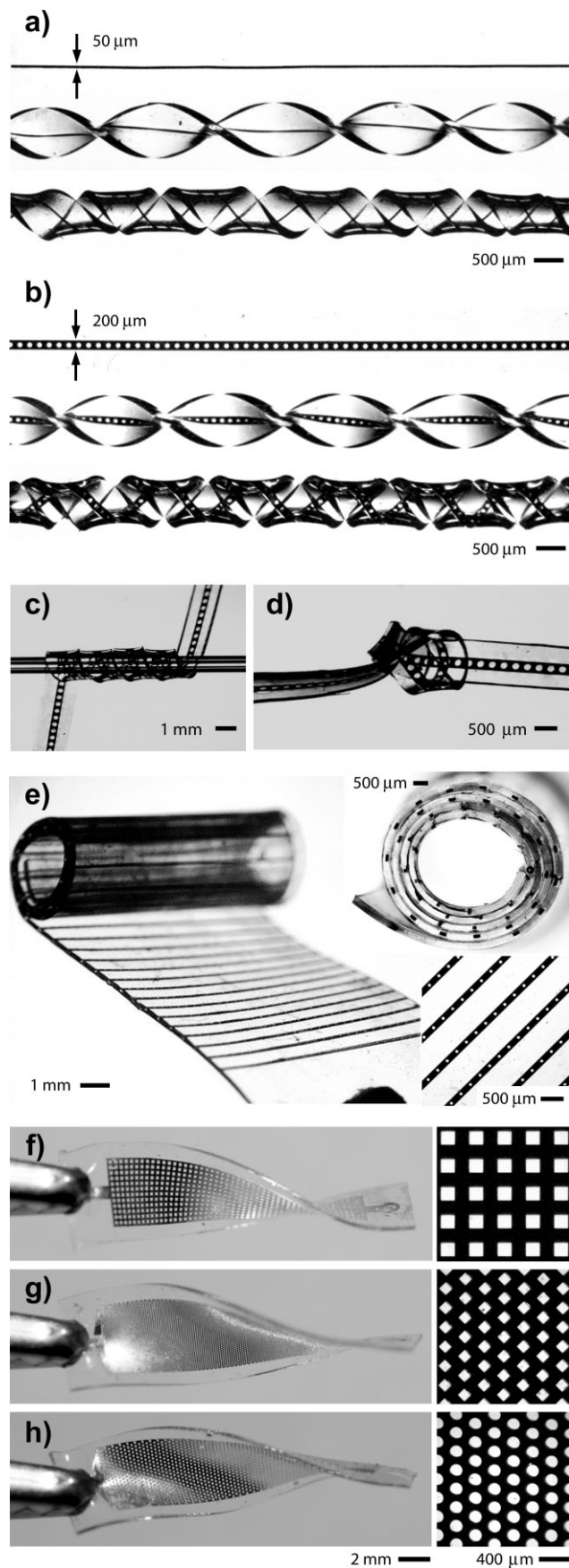| Solder	Melting point [°C]	Electrical conductivity $[\Omega \cdot m]^{-1}$	Brinell hardness [HB]	Retail price [US$ g^{-1}]	Composition [% of total weight]					
					In	Ag	Bi	Pb	Sn	Cd
In100	158	14.3×10^6	0.9	1.50	100.0	0.0	0.0	0.0	0.0	0.0
In97/Ag3	146	13.8×10^6	2.7	1.50	97.0	3.0	0.0	0.0	0.0	0.0
In80/Pb15/Ag5	142-149	5.0×10^6	n.p.	1.50	80.0	5.0	0.0	15.0	0.0	0.0
In52/Sn48	118	6.8×10^6	4.9	1.50	52.0	0.0	0.0	0.0	48.0	0.0
In50/Pb50	178-210	4.0×10^6	n.p.	1.95	50.0	0.0	0.0	50.0	0.0	0.0
In25/Pb75	250-264	n.p.	n.p.	1.50	25.0	0.0	0.0	75.0	0.0	0.0
Sn100	232	8.7×10^6	3.9	0.02	0.0	0.0	0.0	0.0	100.0	0.0
Sn63/Pb37	183	6.9×10^6	17.0	0.50	0.0	0.0	0.0	37.0	63.0	0.0
LMA-117	47	2.3×10^6	12.0	0.49	19.1	0.0	44.7	22.6	8.3	5.3
LMA-158	70	2.3×10^6	9.2	0.04	0.0	0.0	50.0	26.7	13.3	10.0
LMA-255	124	2.3×10^6	10.2	0.05	0.0	0.0	55.5	44.4	0.0	0.0
LMA-288	138	2.8×10^6	22.0	0.07	0.0	0.0	58.0	0.0	42.0	0.0

chamber (length = 2 cm, width = 5 mm, height = 80 μm) containing posts of PDMS (50–100 μm diameter) that had a circular, rectangular, or diamond cross section. After heating the microfluidic chambers, we applied a vacuum to their outlets; the chambers filled quickly with solder (< 1 s), and produced metallic gratings with unique patterns. After cooling, we twisted the solder–PDMS structures axially one half turn; the gratings held shape for > 1 h before the shape relaxed slowly. It was also possible to bend the gratings into other shapes (images not shown).

Breaks or defects in solder microstructures could be repaired or "healed" (Fig. 3). A metallic wire of composed of solder (In100) was fabricated between two layers of PDMS; the electrical resistance of the wire was 0.40 Ω. The device was bent to break the embedded wire; the resistance of the broken wire was effectively infinite. The device was heated to 180 °C for 5 min, and then exposed to an ultrasound bath for 1 s; sonication was a necessary step to reconnect the liquid metal in the microfluidic channel. Following this procedure, the resistance of the solder wire was 0.40 Ω. It was also possible to repair broken wires by heating and exposing the fractured region to an ultrasonic probe, or by heating and pressing on the wire with tweezers or a finger.

Microsolidics makes it possible to fabricate devices in 3D by using multilayer lithography. Figure 4a shows a magnified image of a solder microstructure in a basket-weave pattern. We constructed the pattern by aligning and bonding three layers of PDMS in which we had patterned microfluidic channels using the techniques of rapid prototyping (see Experimental section);[34] we injected solder into each microchannel of the pattern to complete the structure. For comparison, Figure 4b shows a structure composed of individual metal wires (fabricated using single-layer lithography) that we braided manually to form a complex structure with a topologically similar basket-weave pattern.

We released microsolidic structures from PDMS by dissolving the polymer in a 1.0 M solution of tetra-*n*-butyl ammonium fluoride (TBAF) in *N,N*-dimethylformamide (DMF) for 48 h; this process was particularly useful for freeing multilayer metallic structures that could not be released by simply peeling away the layer of PDMS (see Supporting Information). The use of DMF was critical—other solvents that we tested (e.g., ethyl acetate, acetone, and tetrahydrofuran) swelled the PDMS more rapidly than DMF and caused the embedded solder structures to buckle and break.[35] After extraction from PDMS, we coated freestanding solder microstructures with other metals (e.g., gold, copper, and nickel) by electroplating or electroless deposition. Figure 4c shows a basket-

(8 turns), and super-coiled (16 turns). It was also possible to fabricate wires that were super-super-coiled (32 turns, image not shown). Figure 2b shows a similar wire (length = 5 cm, width = 200 μm, height = 80 μm) embedded in PDMS in which the channel contained small PDMS posts (50 μm diameter); this latter example demonstrates that this technique can be used to fabricate wires or other structures with complex patterned features that are not easily fabricated using other methods. Both the patterned and unpatterned wires embedded in PDMS (300 μm thick) were held in a coiled shape using alligator clips; when the clips were released, the tension in the PDMS caused the wires to unwind back to their original shape. We observed that wires with a large cross section (20 000 μm^2) maintained their shape for a longer period of time after manipulation than wires with a smaller cross section (10 900 μm^2). It may be possible to control the mechanical properties of the embedded wires by modifying the cross-sectional area of the wires, the thickness of the polymer surrounding the wires, or the composition of the metal. After uncoiling, we tested the wires for electrical continuity using a multimeter and found that the wires were conductive. We also inspected the wires using a microscope; we found no fractures, cracks, or visible defects in the wires.

Wires fabricated using microsolidics could be flexed manually into a variety of shapes: they can be wrapped around a capillary tube (Fig. 2c), tied into a knot (Fig. 2d), and rolled into multilayer "jellyroll" structures (Fig. 2e). In the last example, we patterned wires (80 μm thick) in a thin (200 μm thick) layer of PDMS, and then rolled the structures up to form a 3D jellyroll.

Microsolidics could also be used to fabricate complex, flexible metallic gratings (Figs. 2f–h). We used the fabrication procedure described in Figure 1 to pattern solder in a PDMS

a)

↓ 50 µm

↑

500 µm ▬

b)

↓ 200 µm

↑

500 µm ▬

c)

1 mm ▬

d)

500 µm ▬

e)

500 µm

1 mm ▬

500 µm ▬

f)

g)

h)

2 mm ▬   400 µm ▬

weave structure embedded in PDMS; Figure 4d shows the same structure after release from the polymer and electroless deposition of a 1 µm thick layer of gold on the surface.

Microsolidics makes it possible to fabricate complex hybrid electronic–microfluidic devices. Figure 5a shows a photograph of a coil microheater embedded in PDMS. The device comprises a solder coil (In100, height = 80 µm, width = 800 µm, length = 12 cm) positioned axisymmetrically around a central microfluidic channel (height = 80 µm, width = 800 µm, length = 3 cm). The coil wraps (ten times) around a section of the microfluidic channel that is 1.6 cm long. We fabricated the device using a procedure similar to that used to fabricate the basket-weave microstructure shown in Figure 4a: three layers of PDMS containing microfluidic channels were aligned, bonded together, and mounted to a glass slide to form a multilayer network of microfluidic channels. The network was composed of two channels: a central microfluidic channel, and a "coil channel" that passed through all three microfluidic layers to surround the central channel. We injected solder into the coil channel and cooled the device to form the coil microheater (see Experimental section for details).

To characterize the microheater, we applied a series of electrical currents ($I = 0$–600 mA, at 100 mA intervals) through the wire while flowing deionized water through the central channel (flowrate, $Q = 100$ µL min^{-1}) (Fig. 5b); as the current passed through the solder coil increased, the temperature of the fluid passing through the microfluidic channel increased because of Joule heating. We applied electrical current to the wire and flowed fluid continuously for 5 min (to equilibrate) prior to measuring the temperature of the water; the temperature of the water in the microfluidic channel at steady state was recorded using an infrared camera.

In this work, we describe a technique for fabricating complex metallic microstructures by injecting liquid solder into microfluidic channels embossed in PDMS and solidifying the

Figure 2. Images of flexible metallic wires embedded in PDMS. a) A wire (length = 5 cm, width = 50 µm, height = 80 µm) embedded in PDMS: unmodified, coiled (8 turns), and super-coiled (16 turns); each end of the wire was attached to an alligator clip while we twisted it. It was also possible to fabricate wires that were super-super-coiled (32 turns, image not shown). b) A wire with holes (length = 5 cm, width = 200 µm, height = 80 µm) embedded in PDMS with circular posts (50 µm diameter) in the channel. c) A wire (length = 5 cm, width = 500 µm, height = 80 µm) wrapped around a glass capillary and d) tied into a knot. e) An array of patterned wires (length = 5 cm, width = 200 µm, height = 80 µm) rolled into a "jellyroll" structure; top right: a cross section of the jellyroll; bottom right: a magnified image of the array of wires. f–h) Flexible metallic gratings embedded in PDMS. Gratings were fabricated with holes having square, diamond, and circle geometries. The images at the right show a magnified view of the pattern using an optical microscope, with illumination of the grating from behind; the metal layer appears black. In each case, the metallic structures were 5 mm wide, 2 cm long, and 100 µm thick; the PDMS was 300 µm thick. The grating were twisted axially one half turn with a pair of tweezers and retained the twisted shaped for > 1 h before relaxing. In the images on the left, the objects are held in place with alligator clips.
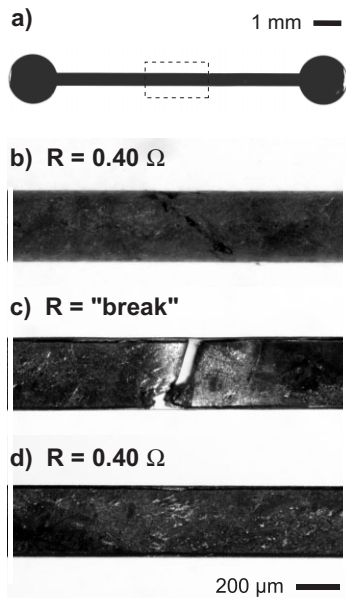
Figure 3. Heating solder microstructures to heal breaks. a) A solder wire (height = 80 μm, width = 500 μm, length = 5 mm) embedded in PDMS. b) A magnified image of the solder wire and its resistance. c) The solder wire after bending 180° and its resistance; a crack in the metal forms a visible discontinuity. d) The solder wire after heating to 180 °C for 5 min, exposing the device to an ultrasound bath for 1 s, and cooling to room temperature. It was also possible to heal wires by heating and exposing the fractured region to an ultrasonic probe, or by heating and pressing on the wire with tweezers or a finger.

Figure 4. Microsolidic structures with basket-weave patterns. a) A photograph of a metallic microstructure with a basket-weave pattern embedded in PDMS; the device was fabricated using multilayer lithography. The inset is a magnified image of the cross section of one of the wires. b) A photograph of microsolidic wires embedded in PDMS and manually braided into a basket-weave pattern; the wires contain small holes (100 μm in diameter). c) A photograph of a metallic structure with a basket-weave pattern embedded in PDMS. d) A magnified photograph of the metallic structure in (c) after dissolving the PDMS polymer in TBAF and electroless deposition of a 1 μm thick layer of gold on the surface.

solder. Microsolidics has several advantages over other techniques for fabricating metallic microstructures. The procedure is rapid and makes it possible to co-fabricate microfluidic channels and metallic features, each with arbitrary shape, in the same layer using one lithographic mask; this approach dramatically simplifies the process required for fabricating metallic wires, electrodes, electromagnets, or heating elements in close proximity (< 10 μm) to microfluidic channels.[36] Microsolidic structures can be "healed": that is, reflowing the solder in the device repairs cracks or defects in the continuity of the solder wires. Microsolidics is a relatively inexpensive way to fabricate ductile metallic microstructures with large cross-sectional area (up to 1 mm in diameter) on both smooth and textured surfaces; these "thick" structures can be fabricated using metals and alloys with high electrical conductivity (up to ca. 24 % of the conductivity of copper) to produce electrical connections that sustain high electrical current (> 1 A). Metal features can (with appropriate registration) traverse multiple layers of microfluidic channels. Unlike most large-scale methods for shaping metal into complex shapes, microsolidics is a relatively low-temperature technique carried out between 50–250 °C.

Microsolidics also has several limitations. The technique can only be used with specific metals and metal alloys that have a low melting point (generally < 300 °C) and affinity for materials such as oxidized silanized PDMS. These low-melt-
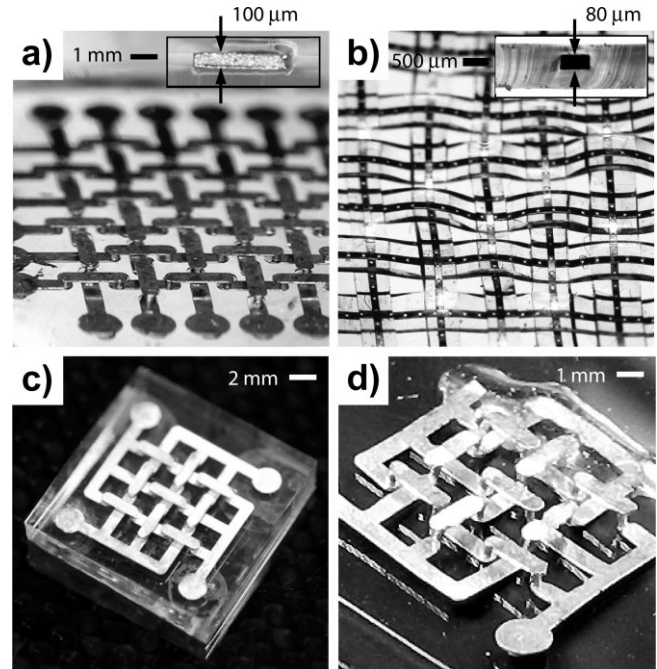
ing-point solders are typically more expensive than commonly used solders, and some (those containing Pb or Cd) are not biocompatible. In addition, the technique cannot be used to fill "dead-end" channels. If a user desires to create a straight metallic wire (e.g., an electrode) without inlets/outlets at either end, the wire must be fabricated as a loop. Lastly, it is currently difficult to use this process to fabricate wires with cross-sectional dimensions smaller than 10 μm; we are investigating new silanes, metals, and injection techniques that will make it possible to fabricate microsolidic structures with nanoscale dimensions.

We believe that this technique for fabricating microstructures in solder will be useful for making flexible electronic circuits, 3D electronic components, and hybrid electronic–microfluidic devices, including: i) low-power microfluidic heaters and temperature controllers; ii) radiofrequency or microwave antennas, or arrays of antennas; iii) microcoils for electrical inductors or transformers; iv) anodes for flexible or microscale batteries; v) magnetic-field generators;[36] vi) materials for controlling light in 3D microsystems; vii) multilayer metallic connections for integrated circuits; and viii) electrical components for flexible electronics.
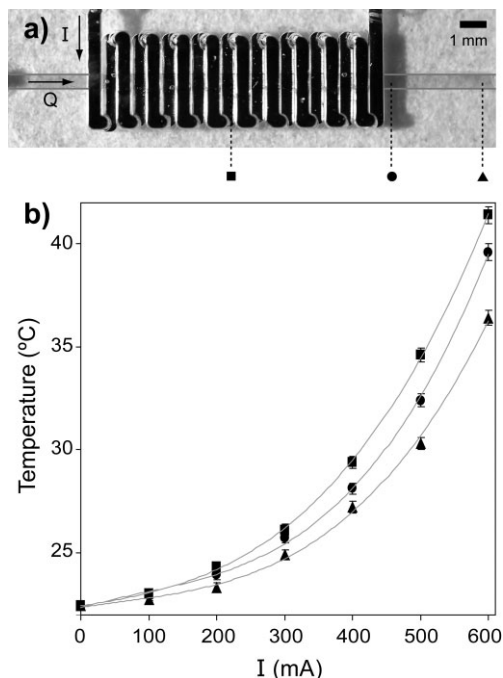
Figure 5. A coil microheater embedded in PDMS. a) Photograph of a solder coil positioned axisymmetrically around a central microfluidic channel; the channel was filled with dyed deionized water to make it easier to see; the exterior walls of the central microfluidic channel were highlighted for clarity. b) The temperature in the microfluidic channel at steady state as a function of the electrical current I through the coil with constant flow Q of deionized water through the microfluidic channel ($Q = 100 \, \mu L \, min^{-1}$); we applied the flow and the electrical current continuously for 5 min (for equilibration) prior to taking all measurements. The symbols (■) show the temperature of liquid in the microfluidic channel measured at the center of the microcoil. The symbols (●) show the temperature of liquid in the microfluidic channel measured at the end of the microcoil. The symbols (▲) show the temperature of liquid in the microfluidic channel measured 3 mm from the end of the microcoil. Error bars describe the range of temperature observed over five measurements at each applied current; lines connecting the data points are a guide to the eye.

Experimental

Fabrication of Microfluidic Channels: We fabricated microsolidic structures according to the procedure illustrated in Figure 1. Masters for the lower and upper layers of the network of microfluidic channels were fabricated in SU-8 photoresist (MicroChem, Inc.) on silicon wafers (in bas-relief) using a procedure that we have described previously [31,32]. The wafers were silanized by exposing them to a vapor of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane overnight. Freshly prepared PDMS (Sylgard 184, Dow Corning, Inc.) was spin-coated on the masters to a thickness of 200 μm, cured thermally (70 °C, 8 h), and peeled away. Inlet and outlet holes were punched in the PDMS layer containing the channels using a needle (16 Gauge = 1.65 mm diameter). We spin-coated a second layer of PDMS on a silanized silicon wafer to a thickness of 100 μm and cured it thermally (70 °C, 8 h). We exposed the two layers of PDMS—the second layer was still bound to the silicon wafer—to a plasma of oxygen for 1 min and brought them in contact to form a permanent seal [31].

Silanization of Microfluidic Channels: We placed a droplet of 3-mercaptopropyltrimethoxysilane in acetonitrile (0.1 M) at the inlets of each microfluidic channel within 15 min after exposure to the oxy-

gen plasma; capillary action filled the channels with the solution completely. We stored the device at 22 °C until the solution had emptied the channels (ca. 1 h; by some combination of evaporation from the ends of the channels and permeation into and through the PDMS). This process coated the inside surface of the channels with a silane; the silane decreased the free energy of the metal–PDMS interface of the channels and made it possible to wet the walls with liquid solder (Fig. 1b).

Injection of Liquid Solder: We placed the microfluidic device on a hotplate and placed a droplet (ca. 1 g) of molten solder at each inlet to the microfluidic channels; the hotplate was 20 °C higher than the melting temperature of the solder. The distribution of temperature in the device was observed using an infrared camera (Inframetrics Inc.); the temperature of the PDMS was approximately uniform with a maximal deviation of 15 % below the temperature of the hotplate. We applied a source of negative pressure (120 torr; 1 torr = 133.322 Pa) to the outlets of the microfluidic channels by connecting them to a house vacuum using a polypropylene tube with diameter (ca. 3 mm) greater than the diameter of the outlets (ca. 1 mm); the solder was pulled through the microfluidic channels rapidly (< 1 s). In most experiments, the solder filled the microfluidic channels completely; nonuniform wetting of the microfluidic channel was occasionally observed, but was rare. Several factors may contribute to nonuniform wetting: i) development of metallic dross—clumps caused by impurities—in the solder; ii) a nonuniform temperature profile across the channel; and iii) use of a solder with poor wetting characteristics (e.g., a nonindium-based solder). Table 1 lists the compositions and physical properties of the twelve solder alloys that we tested (AIM Specialty Solders, Inc. In100, In97/Ag3, In80/Pb15/Ag5, In52/Sn48, In50/Pb50, In25/Sn75, Sn100, Sn63/Pb37 and Small Parts, Inc. LMA-117, LMA-158, LMA-255, LMA-288).

Cooling Solder into Microstructures: After filling the channels with solder, the device was removed from the hotplate and cooled to 25 °C; the solder cooled inside the microfluidic channels/chambers and solidified into metal structures in < 5 min. We peeled the polymer away from the silicon base to produce flexible, metallic structures embedded in PDMS (ca. 300 μm thick). In the electronic applications described in this paper, we inserted copper wires (Digikey Inc., 200 μm diameter) into the inlet holes of the solder channels when the solder was still liquid. The wires were fixed in place when the solder was cooled. We connected Nanograbber alligator clips (Pomona Inc.) to the copper wires in order to connect the external electrical wires and the network of solder structures embedded in the PDMS.

Injection of Solder into Multilayer Networks of Microfluidic Channels: We fabricated multilayer microsolidic structures using a procedure similar to that illustrated in Figure 1 (the Supporting Information contains a schematic diagram of the fabrication procedure). Masters for the upper and lower layers of a network of microfluidic channels were fabricated in photoresist on silicon wafers and silanized as described previously. PDMS (Sylgard 184, Dow Corning, Inc.) was poured on the masters, cured thermally, and peeled away. Vias and inlet holes were punched in the lower and upper layers of channels, respectively, using needles (20 Gauge = 0.90 mm diameter and 16 Gauge = 1.65 mm diameter, respectively). We aligned the top layer of channels to the lower layer of channels using a XYZ stage and the two layers of PDMS were plasma oxidized for 1 min; we bonded the two layers together to form a permanent seal. The two-layer device was treated with a second plasma oxidation and sealed to a third, unpatterned layer of PDMS that served as a substrate. Within 15 min of plasma oxidation, we placed a droplet of 3-mercaptopropyltrimethoxysilane in acetonitrile (0.1 M) at the inlets of each multilayer microfluidic channel; capillary action filled the channels with the solution completely. We stored the device at 22 °C until the solution had emptied the channels (ca. 1 h). We injected metal into the multilayer microfluidic network in the same manner as for the single-layer networks.

Release of Solder Microstructures from the PDMS Polymer: We released multilayer microsolidic devices from their PDMS molds by dissolving the PDMS in a solution of TBAF in DMF (1 M); the devices

were incubated in the solution at 25 °C for 48 h without agitation. After release, we removed the metallic structures from the solution with tweezers, mounted them on a glass slide using epoxy, and imaged them using light microscopy.

Electroplating Metal on Solder Microstructures: We electrolessly plated copper on the released microsolidic structures with Electroless Copper EC 50 solutions A and B (Technic, Inc., Cranston, RI) according to the instructions given by the manufacturer. After coating the solder with copper (about 1 h immersion, gentle agitation by an orbital shaker), we electroplated other metals, including 1 μm thick layers of gold (Technic Gold 25; Technic, Inc.; Cranston, RI) and 2 μm thick layers of nickel (Nickel Plating Solution SN10 Type; Transene; Danvers, MA)

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