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Communications

Microcontact Printing and Electroplating on Curved Substrates: Production of Free-Standing Three-Dimensional Metallic Microstructures**

By *John A. Rogers, Rebecca J. Jackman,* and *George M. Whitesides**

Microelectromechanical systems (MEMS) often require three-dimensional parts with micrometer-sized features. Currently, mechanical or laser micromachining tools,[1] or multistep planar lithographic schemes are used to construct these parts. In this communication, we describe a convenient means for fabricating three-dimensional microstructures. The method begins with the generation of thin patterns of metal produced by microcontact printing (μCP)[2] on curved substrates. Electrodeposition increases the thickness and rigidity of these structures,[3] and removal of the substrate results in free-standing, three-dimensional objects. We demonstrate this method through the fabrication of structures whose dimensions and mechanical properties are appropriate for micro-coil springs and medical devices known as coronary stents. Stents are small expandable tubular structures that are used to hold open anatomical structures and they are increasingly used to prevent blood vessels from collapsing after balloon angioplasty.[4]

Figure 1 summarizes the sequence of fabrication for microstructures with the geometries of micro-coil springs and coronary stents. We first coated all sides of glass cylinders (Kimble Products, KIMAX-51, outer diameter ~1.60 mm for the stents, and Polymicro Technologies, outer diameter ~134 μm for the micro-coil springs) with titanium (~25 Å) and silver (~500 Å) using an electron beam evaporator and a system of mechanical rotation stages.[5] μCP was then used to pattern the surface of these cylinders with a self-assembled monolayer of hexadecanethiolate.[6,7] In μCP, contact of an 'inked' elastomeric stamp with a substrate transfers ink from the stamp to the substrate. We printed the entire outer surface of our cylinders by rolling them over a stamp inked with a solution of hexadecanethiol. The stamping process was controlled with an arrangement of precision rotation and translation stages.[7]

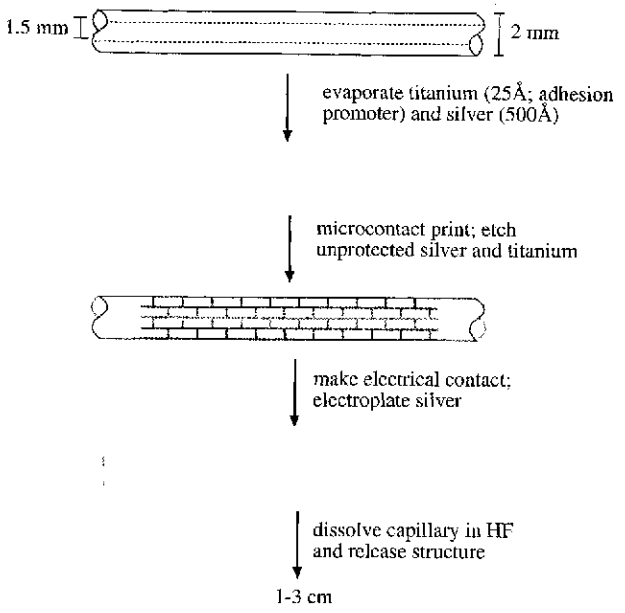

Fig. 1. Scheme for fabricating a stent using Microcontact Printing (μCP). Glass cylinders were coated with titanium (~25 Å) and silver (~500 Å) using an electron beam evaporator. μCP of hexadecanethiol onto the cylinder created a monolayer resist with the geometry of the stamp. A selective wet chemical etch removed silver not protected by the monolayer. Immersion of the patterned cylinder in 1 % HF removed exposed titanium. Electrodeposition of silver increased the thickness of the silver by a few hundred microns. Removal of the glass substrate using concentrated HF produced a rigid, free-standing structure made of silver.

For this work, stamps for μCP were formed by casting and curing PDMS against patterns in photoresist produced using photolithography. An amplitude mask designed using a personal computer, and printed with a commercially available high-resolution printer was used for the photolithography.[8] The mask for the coil springs consisted of 50 μm lines separated by a distance of 50 μm. During printing, we set the angle between these lines and the axis of the cylinder so that a single rotation of the cylinder over the stamp generated a continuous helical spiral on the cylinder. Figure 2 shows the design for the mask used for producing structures with the geometry of the Johnson and Johnson Palmaz–Schatz stent.

Placing the printed cylinders into a wet chemical etch (0.001 M $K_4Fe(CN)_6$, 0.01 M $K_3Fe(CN)_6$, 0.1 M $Na_2S_2O_3$) for ~20 s removed silver not protected by the hexadecanethiolate.[5] We used 1 % HF (~10 s) to remove titanium exposed by removing the silver. The result of these two etching steps were glass cylinders patterned with silver and titanium in a geometry determined by the computer-generated

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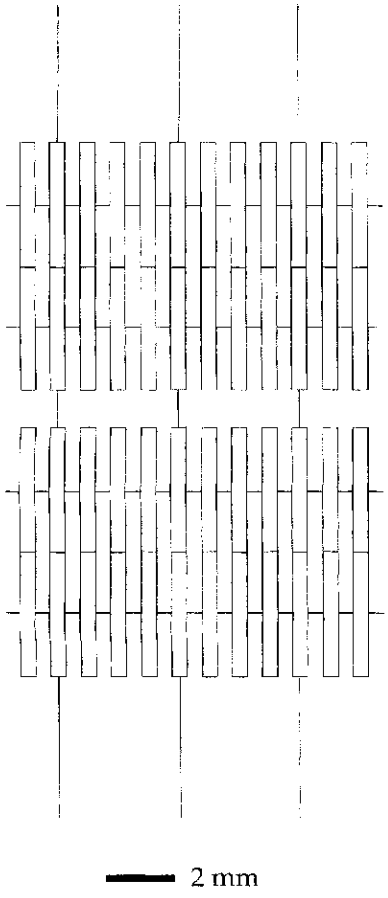

Fig. 2. Negative illustration of the amplitude photomask used to form the stamps for producing structures with the dimensions of a Palmaz Schatz coronary stent. The lines are 20 μm wide and correspond to raised regions of the stamp formed by this procedure. Lines extending from the top and the bottom parts of this pattern were used for electrical connection during the electrodeposition step, and were later removed with a razor blade.

by as much as a few hundred microns by electroplating silver, using a commercially available plating bath (Technic Inc., Techni-Silver E2), at a current density of ~20 mA/cm^2 for ~1 h. Placing the electroplated samples into concentrated HF removed the glass support, and yielded rigid, free-standing metallic microstructures.

Figure 3 shows a micro-coil spring formed using the procedure outlined in Figure 1 in undeformed and in elastically and inelastically deformed states. We could elastically stretch these springs by more than 100%. Figure 4 shows a structure with the dimensions of a coronary stent. The upper frame shows the unexpanded structure, and the lower frame shows the structure after ~250% expansion in diameter. The structure was expanded by inserting a balloon used for angioplasty into its center and inflating this balloon. The percentage change of the diameter of a stent with an inflated balloon in place and the diameter after the balloon is deflated is known as the recoil. The recoil of our structure was 3.5 ± 0.5 %.[9] Commercially available stents have recoils between 3 and 10%. The mechanical resistance to compression of our expanded structure is similar to that of the Johnson and Johnson Palmaz–Schatz coronary stent.[9]

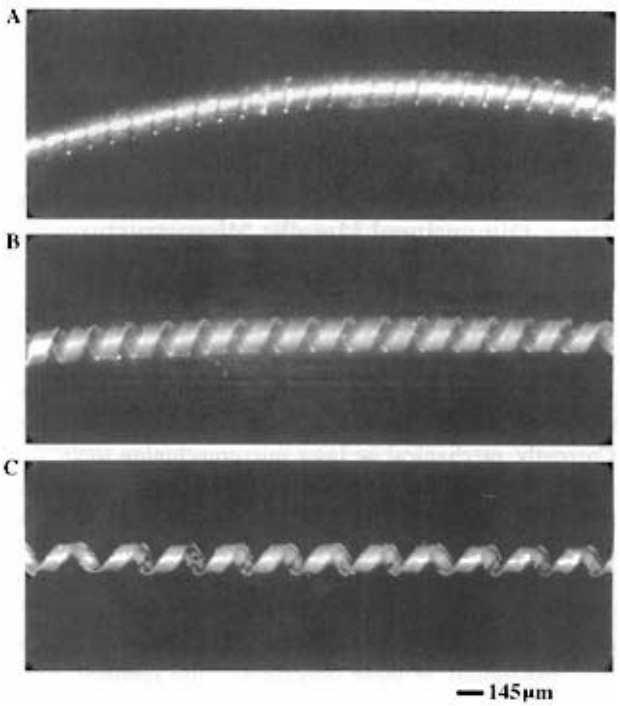

Fig. 3. Undeformed (A), elastically deformed (B), and inelastically deformed (C) micro-coil springs generated by electroplating silver onto silver micro-coils formed on glass capillaries with μCP. The glass was removed with concentrated HF after electrodeposition.

Although measurements on our structure show that its mechanical properties are suitable for applications as a stent, functional stents must be fabricated from a biocompatible metal. Most commercially available stents are made of stainless steel, nitinol, or tantalum. We believe that our fabrication process will be suitable for fabricating tantalum stents since tantalum can be electroplated using a fused-fluoride electrolyte.[10] We are currently exploring this possibility.

In this communication we have described a new procedure for forming free-standing metallic structures with micron dimensions. The minimum feature size of objects

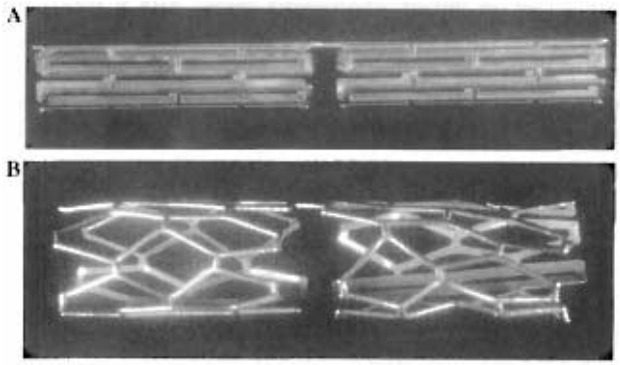

Fig. 4. Unexpanded (A) and expanded (B) structures with the dimensions of Palmaz Schatz coronary stents generated by electroplating silver onto silver structures formed on glass capillaries with μCP. The glass was removed with concentrated HF after electrodeposition.

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formed with this method is limited by the resolution of the microcontact printing (~0.2 μm),[2] by the ability to set the angle and position of the stamp relative to the object to be patterned (~0.01°, and ~2 μm for our apparatus),[8] and by uncertainties in the dimensions of the curved support. The composition of these parts is limited to materials that can be electrodeposited. We believe that our method offers a simple means for fabrication of complex three-dimensional microstructures that will be a valuable complement to other means for microfabrication. Many applications in biotechnology and MEMS should be found.

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Fabrication of Glassy Carbon Microstructures by Pyrolysis of Microfabricated Polymeric Precursors**

By *Olivier J. A. Schueller, Scott T. Brittain,* and *George M. Whitesides**

This paper describes a method of fabricating microstructures of glassy carbon and other high-carbon solids. This method uses micromolding of polymers to form precursors to these structures, and pyrolysis of these polymeric microstructures to form the carbon solids. These microstructures are stiff and can be either electrically insulating or conducting, depending on their thermal history. In addition, carbon structures can be very stable thermally, and the surface of carbon is readily functionalized.[1,2] We are developing carbon microstructures as components in microelectromechanical systems (MEMS), microreactors, and other systems in which thermal stability, chemical inertness, engineered surface properties, and electrical conductivity are useful characteristics.

The mechanical, electrical, and chemical properties of high-carbon solids can be controlled over wide ranges by the temperature at which these solids are prepared.[1,2] The range of electrical properties that can be achieved is especially interesting: the conductivity of a phenol-formaldehyde resin can be controlled over a range of ~$10^{19}\Omega^{-1}$ cm^{-1} by pyrolysis. Insulating, semiconducting, and semimetallic behaviors have been observed for pyrolyzed novolac photoresists, depending on the pyrolysis conditions.[4,5]

Glassy carbon is often produced by carbonization of organic polymeric precursors; resins of furfuryl alcohol, phenol-formaldehyde, acetone-furfural, or furfuryl alcohol-phenol copolymers are among those commonly used for this purpose.[2] In this work, copolymers of phenol-formaldehyde or furfuryl alcohol-phenol were formed in patterns on appropriate substrates (silica, Si/SiO_2, glassy carbon) using micro-molding in capillaries (MIMIC)[6–8] and microtransfer molding (μTM).[9] The resulting polymeric structures were carbonized at high temperatures in vacuum (600–1100 °C, 10^{-6}–10^{-7} torr) or in an inert atmosphere (argon), either on the substrate or after being lifted from the surface, to yield high-carbon structures having micron-scale dimensions.

Supported structures of a phenol-formaldehyde resin and of a furfuryl alcohol-modified phenolic resin were prepared by MIMIC, using a patterned poly(dimethylsiloxane)

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