Microfabrication of 3D Structures

Simple, Three-Dimensional Microfabrication of Electrodeposited Structures**

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Making three-dimensional (3D) micromachined objects is difficult using current techniques; there are few alternatives to using a large number of process steps and masks. We present a new approach to generate 3D microfabricated structures using very few steps and a single photolithographic mask. This new approach relies on a conductive template, which can be produced using conventional lift-off microfabrication, or by other means such as self-assembly or printing, and then an electrodeposition step to produce the full structure. The design of the conductive template determines the full 3D structure—gaps between regions of the template are intentionally introduced. As material is deposited, it expands both vertically and horizontally; the horizontal expansion bridges the spaces between the conductive regions. Once that space is bridged, the electrodeposited material forms an electrical connection with the new region and deposition continues on the existing structure, as well as initiating at the newly connected region. Figure 1 provides a schematic illustration of this process. If a small difference in height were desired between adjacent structures (regions), the gap would be small; a large difference in height is created with a larger gap. We have created a series of test structures, as well as a prototype master pattern to cast a soft microfluidic device.

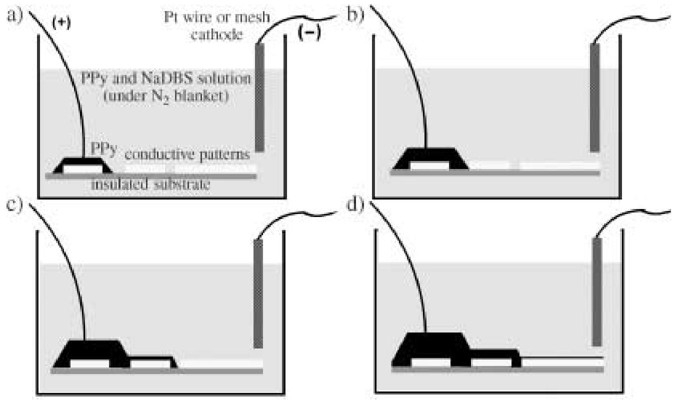

Figure 1. Schematic representation of the deposition technique for polypyrrole (the method is similar for metal films, but they are deposited on the cathode). a) Starting with isolated conductive patterns on a surface, the deposition initiates at region(s) connected to the anode, illustrated here with a wire; b) the deposited film grows horizontally and vertically from the initial region(s); c) the deposited film bridges to new regions, with deposition continuing over the larger surface; d) the deposited film bridges to another region; the relative heights of each region are determined by the spaces between them.

The formation of poly(dimethyl siloxane) (PDMS) replicas of micromachined master patterns for soft lithography[1] and for the creation of microfluidic devices is well known.[2,3] The fabrication of these microfluidic devices relies on bulk micromachining of silicon wafers or a thick layer of patterned photoresist to generate a master pattern—the reversed sense of the pattern is generated by casting a soft replica over this master. There is much interest in producing 3D structures using surface or bulk micromachining techniques[4–6] for the creation of more complex masters for microfluidic devices, as well as for other uses. Much of the published work that describes 3D microfluidic devices relies on the layer-by-layer construction of these structures, which requires a large number of masks and process steps, and the awkward alignment and assembly of the individual layers. The master pattern shown in Figure 2 demonstrates how easily a 3D microfluidic master can be formed. The technique can create

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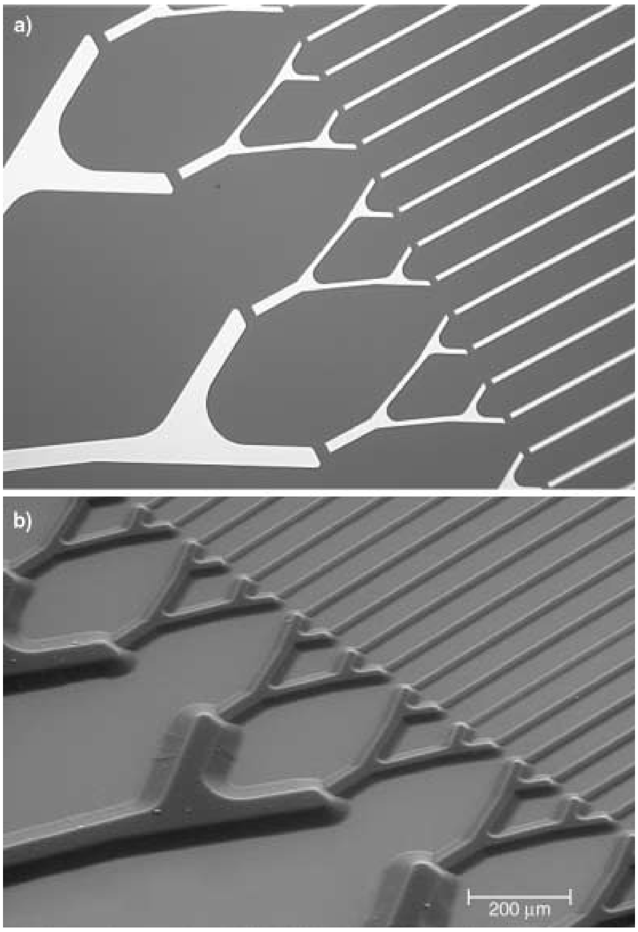

Figure 2. A 3D master pattern to cast a microfluidic mimic of a vascular network. The gaps in the original pattern determine the height of each section. a) The original two-dimensional conductive pattern—a gold film patterned onto a silicon nitride covered wafer; b) SEM image of the resulting 3D structure, the smallest lines are 10 µm high, the tallest are 80 µm. The deposition originated from the left side of the image.

devices with a large ratio between the thickest and thinnest structures (a ratio of 50:1 has been fabricated).

Pyrrole films have been extensively electrodeposited for more than twenty years,[7] and various dopants have been used;[8] of special interest for this technique are those that are highly chemically resistant, since microfabrication often involves aggressive cleaning and etching steps. For this reason, the sodium salt of dodecylbenzenesulfonic acid (NaDBS) was chosen here as the dopant.[9] Other dopants can create polymers that erode in water,[10] which may be of use for creating water-soluble sacrificial structures. Although the exact mechanism for electrodeposition of polypyrrole (PPy) is not fully understood, it involves the oxidation of the pyrrole monomer followed by several chemical and electron-transfer reactions.[8] Pyrrole electropolymerization propagates with a 3D nucleation/growth pattern under charge-transfer control. The film grows with different time constants in the upward and lateral directions.[11] The time constants vary as a function of current density, temperature, dopants, etc.

After studying the characteristics of a variety of PPy films, and observing the well-defined and adherent borders on the films, we believed that it would be possible to form stepped 3D structures by intentionally leaving spaces in the electrode pattern. The uncertainty was whether the film, as it grew, would bridge across the patterns and reliably make an electrical connection to each subsequent unattached pattern. A series of test structures were produced, which included some that were intended as a microfluidic mimic of a vascular network (Figure 2). The original experiments demonstrated that the lateral growth of the film would indeed bridge from the original anode to unattached conductive regions on the surface, and once the gap was bridged, the polymerization process would continue over the entire area.

Electroforming and molding (referred to by its German acronym, LIthography, Galvanoformung, Abformung, or LIGA)[12] of microelectromechanical systems (MEMS) using metal electroplated into an X-ray-defined poly(methyl methacrylate) (PMMA) mold provides a route to the preparation of planar microdevices with critical features of tens to thousands of micrometers. Since many LIGA MEMS are produced from nickel, experiments were also performed using nickel to address the question of whether the gap-bridging process could also be used to directly produce 3D electroplated structures from metals. The results were similar, except for significantly slower deposition rates and a radial expansion of the front, rather than a distinctly faceted surface. For the deposition conditions reported, the surface roughness of the nickel is significantly greater than that of PPy. Nickel LIGA wafers are routinely lapped to remove this roughness, however, this option is not available for the multilevel structures.

Comparing the two materials, there is a noticeable difference in the growth rates and growth behavior of PPy and nickel. The rate of electropolymerization for PPy is 780 $nm\,min^{-1}$ vertically and 1000 $nm\,min^{-1}$ horizontally, under the conditions described below. Nickel, under the conditions described below, had a deposition rate of 105 $nm\,min^{-1}$, both vertically and horizontally. The 4:3 lateral-to-vertical growth ratio for PPy creates a well-defined faceted profile with the polymer growing slightly faster outward than upward (Figure 3a). The nickel grows uniformly in all directions, which results in the edges of the pattern having a radius equal to the film thickness (Figure 3b). Depending on the application, one or the other of the materials may be more desirable. The PPy surface appears smoother than the nickel surface, and it deposits more rapidly. The sidewalls of the nickel structures, however, are closer to vertical than the corresponding PPy patterns. Vertical sidewalls, or a limit on horizontal expansion, could be obtained by introducing a sacrificial boundary, such as one made from photoresist, around the conductive patterns.

This approach has been demonstrated with a variety of test structures—we have been able to form tapered lines, branched structures, and concave and convex features. Very tall features such as mechanical barriers or sealing rings around a critical region of a device could also be produced. Concave and convex devices were created by a series of concentric patterns—the curvature is a function of the spacing

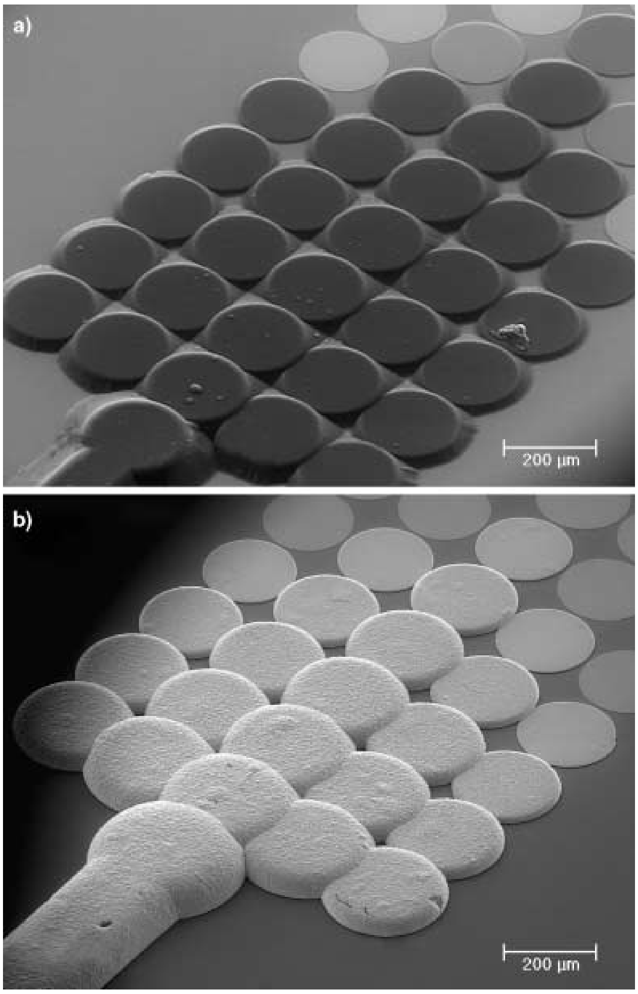

Figure 3. Test patterns in the form of an array of unattached circles. The original patterns are 200 µm in diameter, and 10 µm apart. In each case, deposition originated in the lower left corner of the image, from the circle attached to the anode. a) PPy pattern grown at 3 mA cm^{-2} for 48 min—the middle column has bridged eight gaps; b) nickel structure electroplated at 3 mA cm^{-2} for 14 h—the middle column has bridged six gaps.

of the pattern, and whether the deposition initiates from the inner or outer edge. It was observed that a series of finely spaced lines or arcs provides a more uniform deposition front than those with greater separation; each time the deposited material bridges from one conductive pattern to the next, the expanding front is smoothed. By varying the width of a line pattern, a 3D structure can be produced that varies in thickness and width, or the pattern can be designed so that the final structure maintains a constant width while varying only in thickness.

This technique opens the possibility of new methods to fabricate multilevel structures such as electrodes, interconnects, gratings, and photonic lattices. The next step is to develop approaches to augment these structures with additional films patterned over the first layer. An additional area to explore is the ability of this method to bridge gaps to form low-impedance connections between devices and substrates produced by self-assembly or fluidic self-assembly.[13,14] Lastly, this approach could be used to modify the LIGA process where regions of a microdevice are deposited to regulate the effect of current densities or to create composite or gradient materials from a single mold or pattern.

Experimental Methods

The layouts were generated with AutoCAD software, and DXF files were converted into a chrome-on-glass mask (International Phototool Company). The plating template was formed on 4-inch (10-cm) silicon wafers with a 3000-Å insulating layer of silicon nitride grown by low-pressure chemical vapor deposition (LPCVD). A standard lift-off process was used to pattern the gold electrodes: photoresist was patterned onto the wafer, 200 Å of titanium was deposited as an adhesion layer, after which 3000 Å of gold was deposited to form the conductive pattern. The photoresist was removed, which only left behind the gold in regions deposited directly onto the wafer. The wafers were cut into dies using a flood-cooled die saw. The patterns were protected using an additional layer of photoresist during die sawing; after sawing, the individual dies were cleaned in acetone, ethanol, and deionized water before use—it should be noted that greater adhesion could be achieved using more advanced cleaning procedures, or the addition of a titanium adhesion layer over the conductive layer.

The electrodeposition of PPy occurred at 25 °C using a constant-current power supply (HP 6614C). The current density was 3 mA cm^{-2}. The temperature and current density were varied to find the conditions that gave the smoothest deposited films. Other conditions can produce particularly rough surfaces. Solutions of 0.2 M pyrrole with 0.2 M NaDBS (both Aldrich) as a dopant were prepared more than 24 h in advance to ensure complete dissolution of the constituents. They were stored at 4 °C under nitrogen. Achieving uniform deposition over a large area was difficult, therefore, a platinum wire-mesh cathode was used with an area equal to that of the patterned area of the die, and stirring was adjusted so that the flow across the surface appeared uniform; deposition occurred under a nitrogen blanket. After deposition, the devices were ultrasonically cleaned in deionized water to remove loosely adherent deposits.

The nickel was electroplated using standard procedures.[15,16] The gold pattern acted as the cathode along with a pure nickel anode, and the plating bath was a commercially available nickel sulfamate solution (Mechanical Nickel Sulfamate, Technic Inc.). Current density was regulated to 3 mA cm^{-2}. These dies were also ultrasonically cleaned in deionized water after deposition.

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