Direct Laser Patterning of Conductive Wires on Three-Dimensional Polymeric Microstructures

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We show that silver lines patterned on a substrate with multiphoton absorption can be rendered electrically conductive using electroless enhancement with copper. We demonstrate that this technique can be used to create metallic features on three-dimensional polymeric structures that have been fabricated with multiphoton absorption polymerization. This method makes it possible to use multiphoton absorption to create complete metal/polymer hybrid microstructures with a single fabrication setup.

I. Introduction

Over the past few decades, lithographic techniques have developed into tremendously powerful tools for creating devices with features of scales down to tens of nanometers. However, conventional lithographic techniques are best suited for the creation of structures that are essentially two-dimensional. While the lateral extent and complexity of structures fabricated with conventional lithography can be substantial, creating complex features with significant vertical dimensions is possible only through the sequential fabrication of many layers. As a result, there has been considerable interest in the development of nonconventional lithographic techniques that are better suited for the creation of truly three-dimensional (3-D) devices.

One promising class of techniques for 3-D lithography makes use of multiphoton absorption (MPA). MPA is a phenomenon wherein two or more photons, none of which is energetic enough to cause an electronic excitation on its own, are absorbed simultaneously to cause such an excitation. One particularly important facet of MPA is that the absorption probability is proportional to I^n, where I is the laser intensity and n is the number of photons absorbed.[1] Thus, for a focused laser beam efficient MPA occurs only in the focal spot, allowing photochemical or photophysical processes to be localized in three dimensions.[2,3]

The most common implementation of MPA in microfabrication is multiphoton absorption polymerization (MAP).[4−12] In MAP an ultrafast laser is focused tightly into a prepolymer resin through a high-numerical-aperture objective lens. At the focal point, MPA leads to electronic excitation of a photoinitiator, resulting in polymerization of a small point within the focal volume. The sample can be moved with respect to the focal point to produce 3-D shapes of arbitrary geometry. Voxels with submicrometer dimensions have been reported, and complex structures have been fabricated on the scale of micrometers to hundreds of micrometers. Because MAP is a truly 3-D fabrication technique, structures with free-moving parts and high aspect ratios can be created.

The concept of direct laser writing of metal via MPA has also been successfully demonstrated by a number of groups,[13−16] using one of two approaches. In the first approach, the metal is deposited in three dimensions inside of a matrix.[13,16] The matrix serves two purposes: to suspend the dissolved metal ions and to act as a support for the final structure. However, the resultant 3-D metallic structures are not self-supporting if the matrix is removed.[13] The second

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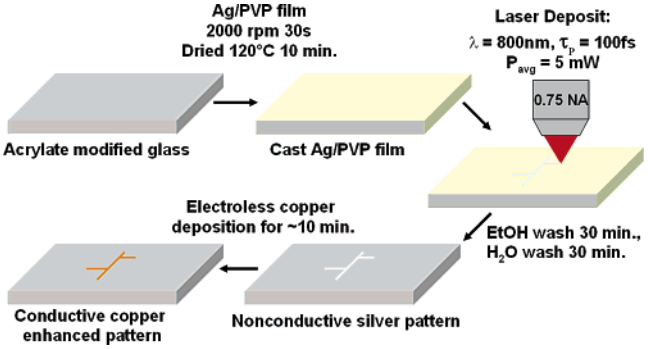

Figure 1. Schematic diagram for the direct laser writing of conductive wires onto glass substrates. A film of $AgNO_3$/PVP is cast onto an acrylate-modified glass substrate that is then exposed to focused, ultrafast, near-infrared radiation. The laser photoreduces Ag^+ onto existing Ag nanoparticles to form a nonconducting pattern of polydisperse Ag nanoparticles. This pattern is then electrolessly enhanced with copper to render it electrically conductive.

approach to multiphoton absorption metallization (MAM) is to form two-dimensional patterns on a substrate.[14,15] For instance, we have previously reported a technique for the direct laser writing of silver lines on glass from a poly(vinylpyrrolidone) (PVP) thin film.[15] These lines are deposited by focusing an ultrafast laser onto a film containing silver nanoparticles, silver cations, and PVP. The lines are composed of nanoparticle agglomerates in the range of tens to hundreds of nanometers in diameter and can be fabricated with a resolution of approximately 1 μm. However, because the lines are composed of agglomerated nanoparticles, they are not electrically conductive.[15]

Realization of many functional 3-D microdevice designs will require the ability to incorporate both metallic and dielectric components in the same structure. While this task is readily accomplished with conventional lithography, hybrid metallic/dielectric structures cannot yet routinely be created with emerging 3-D lithographic techniques, although two examples of techniques for creating hybrid structures have been reported recently.[17,18] Here we demonstrate that 3-D polymeric structures with conductive metallic features can be created with a single fabrication setup using MPA-based techniques. We accomplish this by fabricating 3-D polymeric structures with MAP, writing silver lines on the structures using MAM, and using electroless deposition to develop the metallic lines to render them electrically conductive.

II. Experimental Section

The procedure for fabricating wires on glass substrates is shown schematically in Figure 1 and consisted of the following steps:

Deposition of Silver Lines on Glass. Silver nitrate/PVP (MW 40 000) films were prepared by spin-casting on (3-acroxylpropyl)-trimethoxysilane-modified glass coverslips, as previously reported.[15] Silver lines in a shape suitable for four-point conductivity measurements were prepared using a 40×, 0.75-NA objective. The laser wavelength was 790 nm, and the pulse length was on the order of 100 fs. The power at the sample was 4 mW, and the writing speed was 20 μm/s. To create wires, several parallel lines, spaced 0.5 μm apart, were drawn to give the final line a width of approximately 10 μm. After fabrication, the films were washed twice in 30 mL of ethanol and then once in deionized water. All chemicals were reagent grade and were used as obtained from Aldrich except for the PVP, which was purchased from City Chemical.

Electroless Enhancement of Silver Lines. The silver pattern was enhanced electrolessly using a solution of 3 g of $CuSO_4$, 4 g of NaOH, and 14 g of sodium potassium tartrate (Rochelle salt) in 100 mL of deionized water. After fully dissolving the salts, 10 mL of an aqueous solution of formaldehyde (37 wt %) was added, and the solution was used within 30 min.[19] Coverslips containing silver patterns were immersed in the solution without stirring for 7 min, after which they were immersed in deionized water, dried, and inspected using two optical microscopes. A Zeiss Stemi DV4 microscope (working distance ~9 cm) was used for reflection imaging, and an American Optics 1000 microscope (working distance ~500 μm) was used for transmission imaging. Upon sufficient copper growth, the transmission image is opaque in the metallized regions and the reflection image shows shiny, copper-colored lines. Samples that did not meet these criteria were placed back into the enhancement solution for an additional 3 min. All enhancement times were within the range of 7−13 min.

Characterization of Copper Enhanced Silver Lines on Glass. To characterize the range of conductivities of the enhanced wires, 28 samples were prepared as described above. A gold wire with a diameter of 0.0005 in. (Sigmund Cohn) was glued to each lead in each four-point conductivity sample using Dupont 4929N silver paste. The gold microwires were connected to macroscopic wires using alligator clips. Conductivity measurements were made by using a Keithley 220 programmable current source to apply a current ranging from −100 μA to +100 μA through the sample via two leads. An Aglient HP 34401A digital multimeter was used to measure the voltage across the sample via the other two leads, and the resistance of the sample was determined from the slope of the resultant current−voltage ($I-V$) curve. The lateral dimensions of the samples were measured using an Amray 1000A scanning electron microscope and a Hitachi S-4700 field-emission scanning electron microscope. The thickness of the lines was measured using a Digital Instruments model MMAFM-2 atomic force microscope in tapping mode.

The procedure for fabricating wires on polymeric microstructures is shown schematically in Figure 2 and consisted of the following steps:

Preparation of Microstructures. To promote adhesion of the structures, microscope slides were treated with (3-acroxylpropyl)-trimethoxysilane.[10] A thin spacer with an open area in the center was placed on a slide, and a drop of prepolymer resin was placed in the resultant well. The formulation of the resin was 48 wt % ethoxylated(6) trimethylolpropane triacrylate (Sartomer), 49 wt % tris(2-hydroxyethyl)isocyanurate triacrylate (Sartomer), and 3 wt % Lucirin-TPOL (BASF). After addition of the resin, a coverslip was placed on top of the spacer and the entire assembly was placed on the stage of an upright microscope. Fabrication was accomplished with a commercial Ti:sapphire laser, as has been described previously.[10] Once fabrication was complete, the assembly was removed from the microscope stage, the coverslip was taken off, and the unexposed resin was washed away with ethanol. The structures fabricated for these experiments were bridges that were designed to allow one wire to pass over another without making electrical contact (Figure 2). The bridges were 60 μm long, 25 μm tall, and 10 μm wide and were supported by trusses that are sloped

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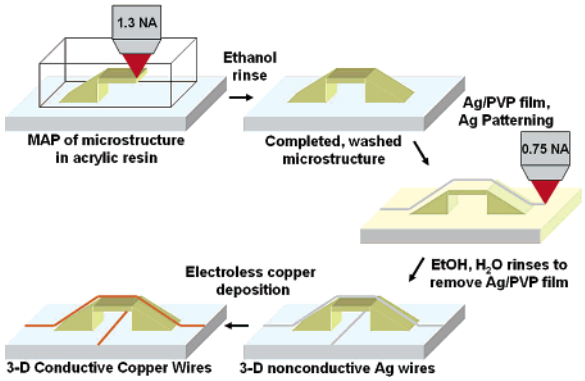

Figure 2. Schematic diagram for the direct laser writing of conductive wires onto polymeric microstructures. A microstructure is fabricated by MAP, using a tightly focused, ultrafast laser in the near-infrared. After the structure is complete, the unexposed resin is rinsed away and a film of $AgNO_3$/PVP is spin-coated onto the sample. Silver wires are deposited on the glass near the structure, after which a second $AgNO_3$/PVP film is drop-cast onto the sample. A nonconductive Ag pattern is then generated on the microstructure. After washing away the film, the silver pattern is made electrically conductive by electroless enhancement with copper.

to facilitate patterning of wires from the substrate up to the top of the bridge.

Patterning of Conductive Wires in 3-D. A film of $AgNO_3$/PVP was spin coated over a substrate with a bridge, and lead wires were patterned on the glass under the same conditions described above. The film was too thin to allow deposition onto the bridge itself, so after the lead wires were made a drop of the Ag/PVP solution was added and allowed to dry in an oven at 110 °C for 10 min. This drop-casting technique provides a thicker film than does spin-casting. A 40×, 0.75-NA objective was used to create a silver pattern on the bridge with a laser power of 3 mW at the sample. The silver was patterned on the bridge at a scan rate of about 1 μm/s. The scan speed was much slower on the bridge than on the substrate as a lower laser power was used to pattern silver on the bridge, both because it was necessary to prevent damage on the bridge and because there was some uncertainty in determining the height of the surface of the bridge. After deposition of the silver, the sample was washed in ethanol and water as above. The sample was processed in the copper solution as above, and the resistances of the wires above and below the bridge were measured by the four-point method.

III. Results and Discussion

We begin by discussing the characterization of the enhanced silver lines written directly on glass. Shown in Figure 3a is a reflection micrograph of a typical four-point conductivity structure after copper enhancement and attachment of the gold leads. The deposited wires are shiny and metallic in appearance. Peel tests of the enhanced structures with Scotch tape[19] demonstrate complete adhesion.

A representative $I-V$ curve for the enhanced structures is shown in Figure 3b. The plot is linear, and the slope yields a resistance of 2.35 Ω for the stretch of wire between the four leads. In total, 28 silver four-point patterns were enhanced with copper, and the resistance data from these samples are summarized in the histogram in Figure 3c. On the basis of the data in the histogram, the average resistance of the common stretch of wire is 2.4 ± 1.5 Ω.

To estimate the conductivity of the copper, it is necessary to determine the dimensions of the regions of the wires over which the resistance was measured. The lateral dimensions of the copper enhanced wires were measured via scanning electron microscopy (SEM). The average length was 90.6 ± 1.0 μm, and the average width was 9.5 ± 0.5 μm. Typical electron micrographs are shown in Figure 4a,b. The cross-sectional area of the wires was measured using atomic force microscopy (AFM). As shown in Figure 4c,d, the wires are approximately semicircular in cross section. In contrast, before enhancement the silver structures are higher at the edges than in the middle, which we believe is related to deformation of the polymer film during silver deposition, as discussed previously.[15] There is still evidence of residual ridges at the edges of the enhanced lines, but the fact that the center of the lines enhances more efficiently than the edges suggests that there is less silver present in the ridges initially. The average thickness of the enhanced wires is 575 ± 150 nm, and the average cross-sectional area as determined from analysis of 4 μm lengths of wire from a dozen samples is 3.75 ± 1 μm^2.

The conductivity ρ of a wire is given by the equation

$$\rho = \frac{L}{AR} \tag{1}$$

where A is the cross-sectional area, L is the length, and R is the resistance. On the basis of our data, the conductivity is found to be 1.0 ± 0.7 × 10^7 Ω^{-1} m^{-1}. This value is within a factor of 6 of the 5.96 × 10^7 Ω^{-1} m^{-1} conductivity of solid copper metal.[20] The lower conductivity of our wires is in line with previous measurements of electrolessly deposited copper[21] and is most likely due primarily to the porosity of the copper layer. In addition, it is known that the underlying silver seed layer is not conductive, and the ridges are most likely not conductive either. As a result, the conductive cross-sectional area is likely to be roughly a third smaller than we have measured, suggesting that the conductivity of the electrolessly deposited copper is within approximately a factor of 4 of that of the bulk metal.

The maximum current sustainable in these wires was approximately 100 mA. At high current, the wires exhibited localized melting at bottleneck points. Such bottlenecks arise from local inhomogeneities in the film that may be due to surface contaminants such as dust. Preparation and handling of samples under clean room conditions would presumably help to alleviate this problem.

Conductive lines with widths as small as 1.5 μm have been fabricated with this technique. The resistance of these lines was on the order of 200 Ω, due to the considerably smaller cross-sectional area in comparison with the lines discussed above. It may be possible to improve the conductivity by performing additional electrodeposition of copper after electroless deposition has been used to make the wires conductive, as electrodeposited wires tend to be less porous.

We now turn to the characterization of hybrid polymer/metal structures, in particular a bridge structure that demonstrates the ability to pattern wires in three dimensions that

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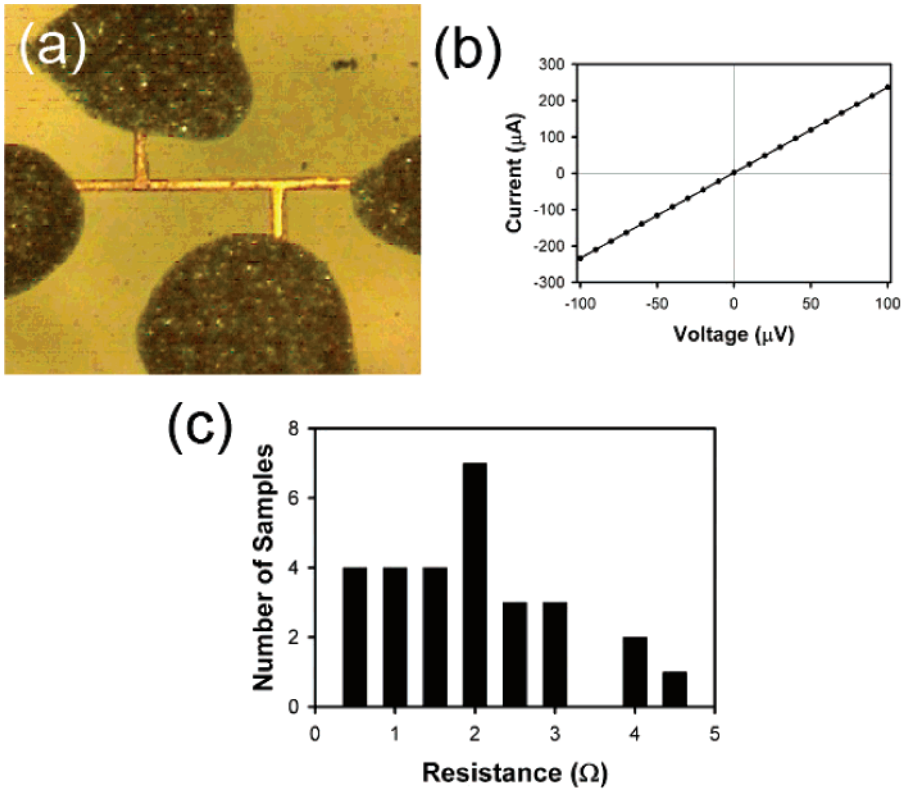

Figure 3. (a) Optical micrograph of a copper-enhanced silver pattern for four-point conductivity measurements. (b) A typical current−voltage curve for the stretch of wire between the four leads. The slope indicates a resistance of 2.35 Ω. (c) Histogram of the resistances measured for 28 identical structures. The average resistance for samples was 2.4 ± 1.5 Ω.

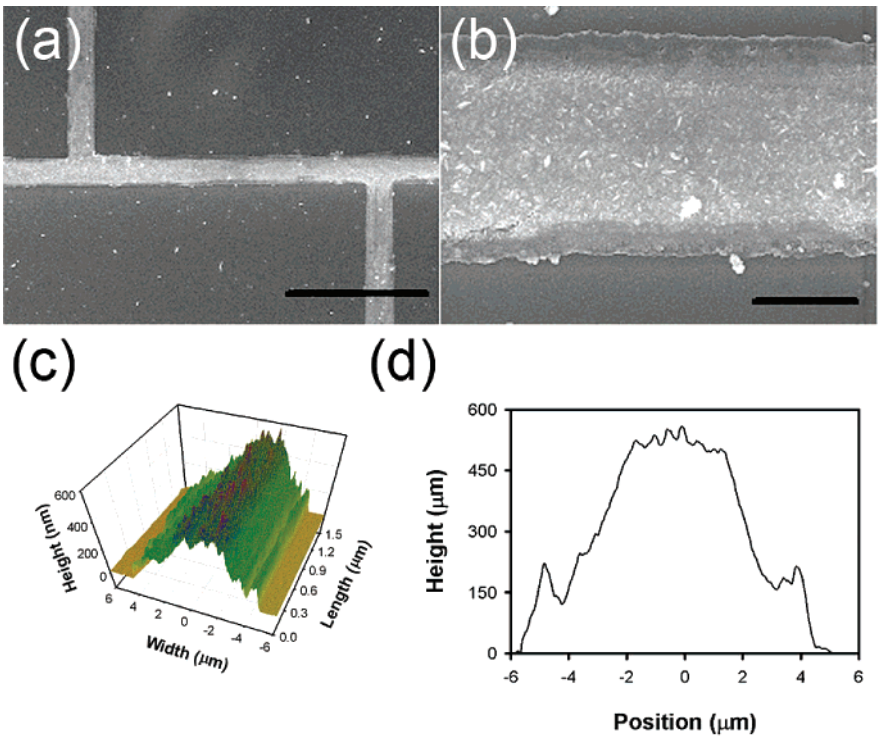

Figure 4. Characterization of the dimensions of the conductive lines using SEM and AFM. (a) Field emission SEM micrograph showing a wire that is 90 μm in length and 9 μm wide; the scale bar is 50 μm. (b) Close-up of the wire from part a; the scale bar is 5 μm. (c) AFM topological map of a section of the wire. (d) A typical cross-sectional profile of the sample from part c.

can cross one another without shorting. As alluded to above, it is necessary to perform two separate silver deposition steps to create wires both on the substrate and across the bridge. If the $AgNO_3$/PVP solution is spin-cast onto a polymer microstructure, a circular region forms around the structure that does not contain any film. This moat region, which extends for about 5 μm around the structure, makes formation of continuous silver lines emanating from the structure impossible. The reason for the formation of the moat is not entirely clear but probably has to do with the polymer

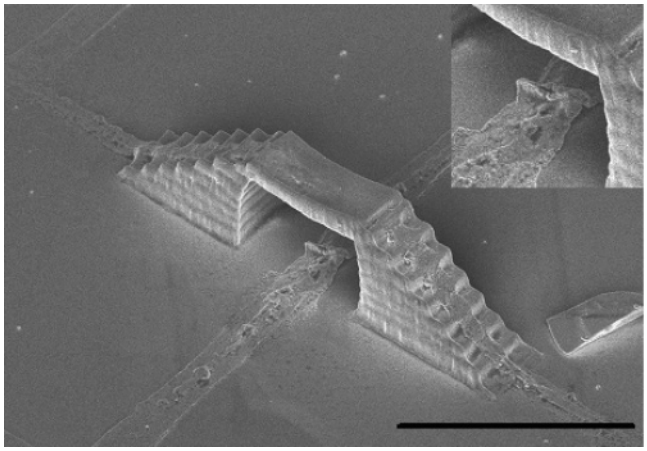

Figure 5. Field emission SEM images of a polymeric bridge with conducting copper wires patterned across and below it. The scale bar is 30 μm. The inset shows the buckling of the wire under the bridge.

solution wetting the acrylic microstructures poorly compared to the glass surface, which leaves the structure and the area immediately around it with little or no film. Thus, after initial patterning of silver wires on the substrate, a second film approximately 3 μm thick was made by drop-casting. This film made deposition of silver possible on and under the bridge, as well as in the moat region immediately adjacent to the structure. However, the thicker film inhibits deposition of lines of any significant length onto the glass, as the film depth prevents the lines from making contact with the substrate. While the second film does enable deposition in the moat region, the film atop the bridge is still quite thin.

Figure 5 shows a SEM image of a polymer bridge with a copper wire running above and below it. Both wires are approximately 100 μm long and 5 μm wide. While the wire is continuous as it crosses the bridge, it is apparent that less metal has been deposited on the segment of the wire on top of the bridge. As a result, the wire that passes over the bridge has a resistance of 178 Ω, whereas the wire going under the bridge has a resistance of 29 Ω. There was no observable electrical cross talk between the two wires.

For both wires, the conductivity is less than was observed for lines deposited on an open substrate. We did not attempt to measure the cross sections of these particular wires because they are not highly uniform, because the area under the bridge is not accessible, and because accurate AFM measurements cannot be made on top of the bridge. In the case of the wire passing over the bridge, the decreased conductivity is almost certainly due to the thinness of the initial silver layer. For the wire passing under the bridge, the decreased conductivity probably arises from the buckle in the wire shown in the inset of Figure 5. We have observed that thick films have a tendency to ablate if the focal point is positioned below the surface of the substrate. This effect likely stressed the silver pattern under the bridge causing it to buckle. It seems, therefore, that film thickness critically affects ability to pattern the silver using MAM. Once again, it is likely that additional electrodeposition of copper could be used to improve the conductivity of the deposited wires.

IV. Conclusions

We have demonstrated the fabrication of conductive metal wires using MAM followed by electroless deposition of copper. This technique was then combined with MAP to add conductive features to polymeric microstructures. These results demonstrate that 3-D metal/dielectric hybrid structures can be created using MPA-based techniques for all of the fabrication steps. This technique expands the capabilities of MPA-based fabrication by making it possible to add electrical and/or optical functionality to 3-D polymeric microstructures.

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