Toward the Fabrication of Hybrid Polymer/Metal Three-Dimensional Microstructures

T. Baldacchini[1], C. N. LaFratta[1], R. A. Farrer[1], A. C. Pons[1], J. Pons[1], M. J. Naughton[2], B. E. A. Saleh[3], M. C. Teich[3], and J. T. Fourkas[1]

[1] Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts
E-mail: fourkas@bc.edu
[2] Department of Physics, Boston College, Chestnut Hill, Massachusetts
[3] Department of Electrical & Computer Engineering, Boston University, Boston, Massachusetts

Abstract. A method for coating three-dimensional microstructures fabricated by multiphoton absorption polymerization (MAP) with metallic patterns in a selective manner is introduced in this paper. We first use a small fraction of the output of a mode-locked Ti:sapphire laser to induce MAP in a homemade acrylic-based resin featuring a commercially-available photoinitiator. Then, through a novel multiphoton-induced process, we deposit metallic silver onto the surfaces of microstructures fabricated by MAP. In this paper we present preliminary results on the fabrication of hybrid polymer/metal microstructures.

1. Introduction

Different groups have used multiphoton absorption polymerization (MAP) for the fabrication of three-dimensional microstructures having complex topologies [1,2]. In MAP, excitation of the photoinitiator occurs only in the small volume of a tightly focused laser beam, the position of which can be controlled in three dimensions. For this reason, MAP presents unique advantages with respect to more traditional microfabrication techniques.

The properties of the materials used in MAP, which are generally acrylic or epoxy resins, pose the greatest limitations to the applications of this technique. Specifically, they lack electrical conductivity and are incompatible with most standard techniques for patterning electronic circuits. As a consequence, although MAP has been used for the fabrication of objects with complicated geometries with sub-micrometer resolution, few functional devices have been fabricated to date [3,4].

We introduce a direct laser writing method that allows for the deposition of metallic silver onto glass and polymer surfaces. In combination with MAP this technique permits the selective coating of three-dimensional microstructures with metals, and thus addresses some of the current limitations of this fabrication method.

2. Experimental Methods

The experimental apparatus used in MAP is also used in metal laser deposition and it has been described elsewhere [5]. A mode-locked Ti:sapphire laser at a repetition rate of 76 MHz is used as the light source. The composition of the resin for polymerization consists of a commercially available photoinitiator (Lucirin TPO-L) and two monomers, ethoxylated(6) trimethylolpropane triacrylate and tris(2-hydroxyethyl)isocyanurate triacrylate.

Laser deposition of metallic silver is achieved utilizing a solution of polyvinylpyrrolidone (PVP) and silver nitrate in ethanol. While mixing, the solution changes color from clear to yellow because of the formation of silver nanoparticles. Spin-coating or slow evaporation of the solvent then affords a thin film of PVP on top of glass or polymeric substrate.

3. Results

Figure 1 shows SEM images of microstructures fabricated by MAP. In Figure 1(a) a complex microstructure consisting of three bridges 12, 24 and 42 μm tall is represented. In this case a power of 7.2 mW was used in conjunction with a stage velocity of 20 μm/s. The micro-cup in Figure 1(b) was fabricated with a laser average power at the sample of 5.8 mW and a stage velocity of 10 μm/s. In both cases an objective with numerical aperture of 1.3 was used. Shrinkage upon polymerization is limited by the use of a monomer that presents stretchable moieties such as ethoxylated groups.

When the laser is focused onto a PVP film in which silver nanoparticles and silver nitrate are embedded, material is deposited. Energy dispersive spectroscopy analysis has shown this material to be silver. Deposition occurs only when the laser is mode-locked, demonstrating that a multiphoton process is responsible for the reduction of silver nitrate. Two-dimensional silver patterns fabricated with this method were not conductive. Gold enhancement by electroless deposition of a solution of $HAuCl_4 \cdot 3H_2O$ and $NH_2OH \cdot HCl$ can be used to grow a conductive film of gold on top the deposited silver patterns. Figure 2(a) illustrates a two dimensional Ag pattern deposited on a glass surface. An objective with NA = 0.5 was used with 35 mW of power at the sample and the stage was moved at 35 μm/s. Figure 2(b) shows a silver microstructure that has been coated with gold.

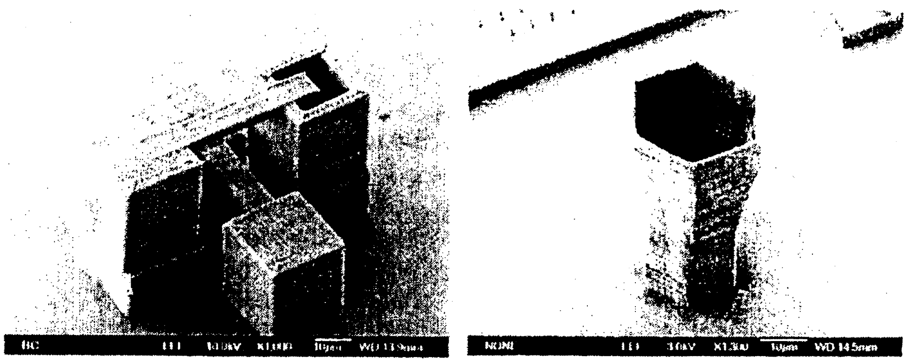

Fig.1. MAP-fabricated microstructures. (a) Interconnected micro-bridges (b) micro-cup.

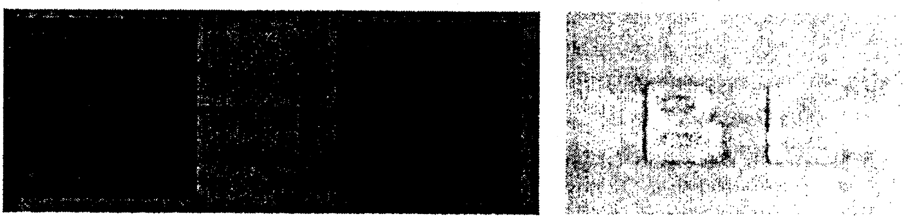

Fig. 2. Laser metal deposition (a) Optical micrograph in transmission mode of a silver pattern with line connecting squares being 200 μm long (b) gold coated silver microstructure; the length of the c is 70 μm.

4. Conclusion

We have fabricated three-dimensional polymer-based microstructures by MAP. We have introduced a novel method to deposit selectively metallic silver in two-dimensional patterns. The combination of the two techniques will facilitate the fabrication of hybrid polymer-metal microstructures.

References

1 S. Kawata, H.-B. Sun, T. Tanaka and K. Takada, *Nature* **412**, 697-698 (2001).

2 B. H. Cumpston, S. P. Ananthavel, S. Barlow, S. M. Kuebuler, D. M. Maugon, J. Qin, H. Rokel, M. Rumi, X.Wu, S. R. Marder and J. W. Perry, *Nature* **398**, 51-54 (1999).

3 S. Maruo, K. Ikuta and H. Korogi, *Appl. Phys.Lett.* **82**, 133-135 (2003).

4 K. Kaneko, H.-B. Sun, X.-M. Duan, S. Kawata, *Appl. Phys. Lett.* **83**, 1-4 (2003).

5 T. Baldacchini, R. A. Farrer, J. Moser, J. T. Fourkas and M. J. Naughton, *Synt. Met.* **135-136**, 11-12 (2003).