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Selective electroless plating to fabricate complex three-dimensional metallic micro/nanostructures

Florian Formanek,[a] Nobuyuki Takeyasu, and Takuo Tanaka
Nanophotonics Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa, Wako, Saitama, 351-0198, Japan

Kenta Chiyoda
Nanophotonics Laboratory, RIKEN, Hirosawa, Wako, Saitama, 351-0198, Japan, and Department of Physics, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171-8588, Japan

Atsushi Ishikawa and Satoshi Kawata
Nanophotonics Laboratory, RIKEN, Hirosawa, Wako, Saitama, 351-0198, Japan, and Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan

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We report on selective metal deposition over complex polymer structures formed by two-photon induced photopolymerization technique. Periodic three-dimensional micro/nanostructures are fabricated by means of a microlens array to produce multiple spots from a single-beam femtosecond laser. An electroless plating method is used to deposit a thin silver film onto the sample surface. The glass slide surface supporting the structures is chemically modified to avoid silver coating of the substrate. Our technique enables to produce complex metallic structures with arbitrary shapes under ambient conditions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2178261]

Fabrication of three-dimensional (3D) metallic micro/nanostructures has attracted considerable attention in nanotechnologies because of their interesting properties. Among several techniques, direct electron-beam writing[1] or focused-ion-beam chemical vapor deposition[2,3] have shown great capabilities for making various nanostructures and functional nanodevices. For the realization of 3D metallic periodic structure on a large scale, the self-organization of metal coated colloid[4] has also been successfully employed. Another promising method to realize 3D patterning is to take advantage of the 3D capability of multiphoton absorption.[5,6] Recent studies have shown the possibility to directly write metallic structures by irradiating a photoactive polymer matrix containing metal ions with a femtosecond laser source.[7,8]

We propose a new approach for 3D fabrication of metallic micro/nanostructures based on a two-photon photopolymerization (TPP) technique combined with selective metal deposition by electroless plating (EP). Selective coating is achieved by modifying the chemical property of the polymer and the substrate. We previously reported on the possibility to realize 3D polymer structures using multiple beam TPP technology.[9] This method is of great interest for applications such as microelectronics which require samples containing numerous structures spread out over a large area. While TPP enables arbitrary sculpturing below the micrometer scale, EP can provide uniform and thin coatings of various metals. In our experiments, the structures are fabricated by using a microlens array to generate multiple beam TPP inside a chemically modified resin matrix, lying on a beforehand deactivated glass substrate. Following this preparation, a selective silver coating only on the polymer structures is realized by EP. This is to our knowledge the first realization of 3D complex metallic samples obtained from TPP fabricated polymer structures, which opens the way to the fabrication of novel materials and metallic objects with complex features.

[a]Electronic mail: formanek@riken.jp

EP is a cost-effective technique in which metal deposition can be achieved in ambient conditions without the use of any electrical potential, making it suitable for insulating samples.[10] It allows uniform coating over large areas and even structures with complex shapes can be metalized.[11] However, the adhesion between metal films and most polymers is very weak.[12] For this reason, we chemically modified the photopolymerizable resin and applied a pretreatment before metal deposition to increase silver nucleation and adhesion on the polymer structure. Moreover, due to the presence of silanol groups, untreated glass surfaces are highly adsorptive and interact with many compounds. It is then necessary to modify the glass slides used as substrate during TPP fabrication to minimize silver adhesion during EP.

The fabrication process consists in different steps described in Fig. 1(a). (1) Hydrophobic coating of the glass slides to avoid metal deposition. (2) Modified photopolymerizable resin is dropped onto the substrate. (3) Microfabrication of the polymer structures by TPP. (4) Removal of unsolidified resin with acetone. (5) $SnCl_2$ surface pretreatment to improve metal deposition and adhesion. (6) Silver coating by EP. (7) Washing of the sample.

To produce a deactivated surface for EP, the glass slides were cleaned in a 0.1 mol/l sodium hydroxide solution for 15 min., washed with water and dried. The slides were then soaked into a 5 wt % solution of dimethyldichlorosilane (DMDCS) in toluene for 1 min., washed with methanol and dried. Two methyl groups coming from the DMDCS now align on the glass surface instead of the hydroxyl groups and behave as hydrophobic coating.[13]

The photopolymerizable material consists of a commercially available resin (Z7012C, JSR) mixed with styrene in a 1:1 volume ratio. In the case of two-photon absorption, the chemical reaction progresses by radical attacking[14] and thus is very effective for styrene which has a vinyl group. Moreover, we noticed that compounds containing benzene groups such as polycarbonate or polystyrene show a better affinity

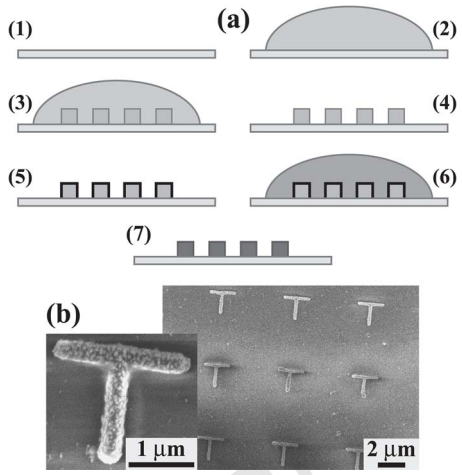

FIG. 1. (a) Fabrication process. (1) Hydrophobic coating of the glass surface to avoid metal deposition. (2) Modified photopolymerizable resin is dropped onto the substrate, (3) Microfabrication by TPP. (4) Removal of unsolidified resin, (5) $SnCl_2$ surface pretreatment to improve metal deposition. (6) Silver coating by EP. (7) Washing of the sample. (b) SEM images of 2D polymer structures selectively coated with small silver grains.

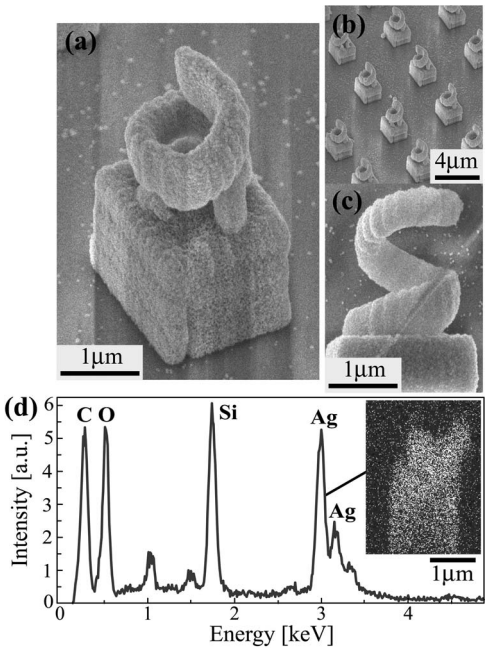

FIG. 2. (a) 45° tilted SEM image of a silver coated polymer structure composed of a cube (2 μm in size) holding up a spring (inner diameter 700 nm). (b) Large view of multiple structures written in parallel. (c) Side view of an individual structure. (d) Energy dispersive x-ray (EDX) spectrum and EDX image recorded at the main Ag peak energy.

towards silver adhesion compared to other compounds, such as polyethylene or polymethyl methacrylate. The addition of styrene also slightly reduces the minimum voxel size that can be produced via TPP.[15]

A drop of the modified resin, in which the polymer structures will be formed by TPP, is deposited on a hydrophobic coated glass slide. Details about the experimental setup for TPP fabrication can be found elsewhere.[9] The change lies in the use of a 50×50 microlens array, covering a range of 15×15 mm^2, to produce multiple focus spots. The lenses are 300 μm in diameter and are arranged in a square lattice with a lattice constant of 300 μm.

For a better silver deposition onto the polymer structures, a pretreatment is applied over the sample surface. After TPP fabrication, the sample is washed with acetone to remove the remaining unsolidified resin, then washed with water and methanol to remove any styrene trace. A sensitizing solution,[16] made of 1.5 g of stannous chloride ($SnCl_2$) dissolved in 84 ml of water and 6 ml of hydrochloric acid, is prepared. The sample is dipped into the solution for 1–2 min., then washed with water to remove the $SnCl_2$ from the glass surface. A thin $SnCl_2$ film is formed on the polymer and will act as a binder with the metallic film.

An uniform coating of the sample is realized by EP which involves the reduction of silver nitrate.[10] The solution used for silver deposition is made as follows: We prepared 0.15 mol/l silver nitrate ($AgNO_3$) in water as the silver ion solution, in which a 0.2 mol/l activating ammonia solution is added in drops until a brown Ag_2O precipitate is formed and then dissolved. The reductant is made of 1.9 mol/l glucose in a solution of 30 vol % methanol and 70 vol % water, and mixed with the silver nitrate solution to trigger the reduction of silver ions. The sample is dipped into the plating solution and the reaction stopped by washing the surface with acetone. The Sn^{2+} ions introduced by the pretreatment also works as reducing agents for the metal ions. If the reaction is realized over nonmodified polymer, the main metal deposition originates from silver grains formed inside the solution and falling on the structures.

At first, we realized two-dimensional (2D) metallic structures to optimize the different chemical parameters. Figure 1(b) shows a scanning electron microscopic (SEM) image of a periodic structure coated with silver, fabricated on a hydrophobic coated glass slide using the modified resin. EP was realized at room temperature and the reaction stopped after 6 min. As a result, small silver grains (~60 nm in diameter) were selectively deposited onto the polymer surface. The silver distribution is quite uniform and only a few grains are visible on the glass substrate. The diameter of the grains and the coating thickness can be tuned by changing the $AgNO_3$ and glucose concentrations or the plating reaction time.[11,17]

To fabricate fine 3D structures, silver deposition has to be optimized to control the film thickness on the polymer surface. The silver film also need to be smooth with regard to future experiments concerning the sample optical properties. For these reasons, we developed a new resin. 4-vinylbenzene sulfuric acid sodium salt is dissolved into a N,N-dimethyl acetic acid saturated solution. The new resin is obtained by mixing 20 vol % of this solution with 80 vol % of the Z7012C resin. Figures 2(a) and 2(b) show SEM images of 3D metalized structures composed of cubes (2 μm in size), holding self-standing springs (height 2.2 μm, inner diameter 700 nm). A side view of the spring [Fig. 2(c)] proves that the solidified resin is rigid enough to allow 3D fabrication. The plating solution was composed of a 0.3 mol/l $AgNO_3$ solution, mixed with a saturated solution of 2, 5-dihydroxybenzoic acid 300× diluted in water as reductant instead of glucose (to accelerate the plating process) in a volume ratio 1:1 volume ratio. The reaction was realized at 37 °C and stopped after 2 min. A second short plating (~10 s) was realized with the same $AgNO_3$ solution, mixed with ammonia and benzoic acid (10× diluted). This resulted in a very uniform coating of the polymer structures with

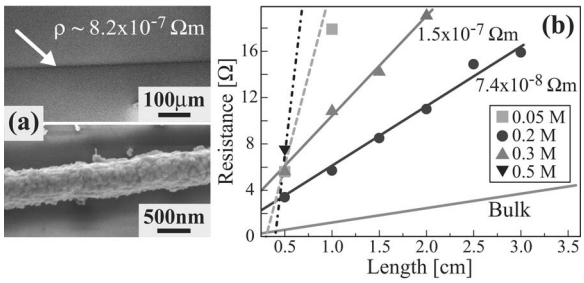

FIG. 3. (a) SEM images of long narrow coated lines used for resistivity measurements. (b) Resistance as a function of line length (with constant width ~1 mm) for different $AgNO_3$ concentrations and theoretical bulk silver curve.

small silver grains (~20 nm in diameter) and only little deposition on the substrate [Fig. 2(c)]. A more quantitative investigation was made by energy dispersive x-ray spectroscopy (EDX). Figure 2(d) shows a EDX spectrum recorded on the same area than on Fig. 2(a), which confirms the presence of silver (emission peak around 3 keV) on the sample. The inset is an EDX image recorded at the energy of the more intense silver peak. It reveals that only the polymer structure (bright central region) is coated and that only little silver deposition occurred on glass (the substrate remains purely insulating).

The conductivity of our structures was evaluated by making long narrow lines with similar dimensions (width $\leqslant 1$ μm, silver film thickness $\leqslant 100$ nm). Thick silver electrodes were formed at the extremities of the lines by EP. The silver film cross section was evaluated by assuming an ellipsoidal shape for the polymer lines formed by TPP.[18] Electrical measurements indicated that these lines [Fig. 3(a)] are highly conductive, with a resistivity $\rho \simeq 8.2 \times 10^{-8}$ Ω m (as compared to 1.6×10^{-8} Ω m for bulk silver). Since in the same time the glass substrate remained electrically insulating, this result confirms the possibility to realize isolated conducting structures with our technique. We have also studied macroscale lines coated by EP with different $AgNO_3$ concentrations (width ~1 mm, silver thickness ~100 nm). The dependence of the electrical resistance with respect to the lines length is shown in Fig. 3(b). A curve corresponding to a 100 nm thick line made of bulk silver is also plotted for comparison. The linear behavior of the curves indicates an uniform silver coating over long distances. The nonzero resistance value at origin is certainly due to a contact impedance effect at the electrode pad. The resistivity is typically 7.4×10^{-8} Ω m in the optimal conditions (0.2 M), but increases slightly to 1.5×10^{-7} Ω m in the case of 0.3 M. For higher $AgNO_3$ concentrations (0.5 M) the size of the silver grains because too large and the total contact surface between particles decreases, leading to higher resistivity. For low concentrations (0.05 M), the silver grains can hardly cover the entire polymer surface and discontinuities in the metal film reduce the conductivity of the line.

In conclusion, we achieved selective metal deposition over complex polymer structures fabricated by two-photon photopolymerization and electroless plating. 3D structures were coated with silver while letting the glass substrate apparent, leading to isolated and highly conductive structures. Where as all previous studies on TPP emphasize on polymer samples, our method is well suited for the fabrication of complex 3D metallic structures over large areas or periodic samples having arbitrary unit-cell shape such as metamaterials,[19] with a lateral resolution up to 100 nm.[15]

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